

# The Pt-catalyzed ethylene hydroamination by aniline: a Computational Investigation of the Catalytic Cycle.

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## SUPPORTING MATERIAL

**Full references with > 15 names.**

**Comparison of gas-phase and C-PCM optimized geometries and energies.**

**Figure S1.** Views of all optimized geometries.

**Table S1.** Energy results for all compounds optimized in this study.

**Figure S2.** Attempts to optimise 5-coordinated Pt-complexes.

**Figure S3.** Different pathways for the aniline addition to coordinated olefin in **II** and **IV**.

**Figure S4.** Different pathways for the aniline addition to coordinated olefin in **V**.

**Figure S5.** Intermolecular *anti* addition of aniline to coordinated olefin in **VII** and **VIII**.

**Structural description of the zwitterionic complexes IX-XIII.**

**Scheme S1.** Different geometrical arrangement found for the [Pt-CH<sub>2</sub>CH<sub>2</sub>NHPh] moiety.

**Table S2.** Relevant metric parameters for the zwitterionic compounds **IX-XIII**.

**Formation of Pt<sup>IV</sup>-H intermediates from the zwitterionic complexes X and XI**

**Formation of chelated aminoalkyl Pt<sup>II</sup> complexes**

**Formation of chelated aminoalkyl Pt<sup>IV</sup> complexes**

**Figure S6.** Reaction coordinate for the reductive elimination of PhNHEt from complex **XX**.

**Figure S7.** Comparison of the reductive eliminations from systems **XX** and **XXXVI**, with views of the relevant geometries and their relative  $\Delta G^{\text{CPCM}}$  in kcal mol<sup>-1</sup> at 298.15 K (and at 423.15 K in parentheses).

**Intermolecular proton transfer from the zwitterionic anilinium group to carbon.**

**Intramolecular proton transfer from the zwitterionic anilinium group to carbon with added aniline as proton shuttle.**

**Table S3.** Cartesian coordinates of all optimized geometries reported in this study.

**Full references with > 15 names.**

Reference 54

M. J. Frisch, G. W. T., H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. Montgomery, J. A., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople,, *Gaussian 03, Revision C.02, Gaussian, Inc., Wallingford CT* **2004**.

Reference 111

A. Albinati, V. I. Bakmutov, K. G. Caulton, E. Clot, J. Eckert, O. Eisenstein, D. G. Gusev, V. V. Grushin, B. E. Hauger, W. T. Klooster, T. F. Koetzle, R. K. McMullan, T. J. O'laughlin, M. Pélissier, J. S. Ricci, M. P. Sigalas, A. B. Vymenits, *J. Am. Chem. Soc.* **1993**, *115*, 7300-7312.

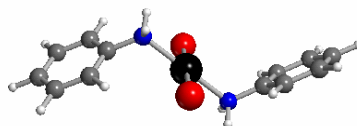
The geometries and energies obtained in two different approaches:

- were compared for two different molecules containing a weak H-bond:

- The relevant results are shown in the images below.

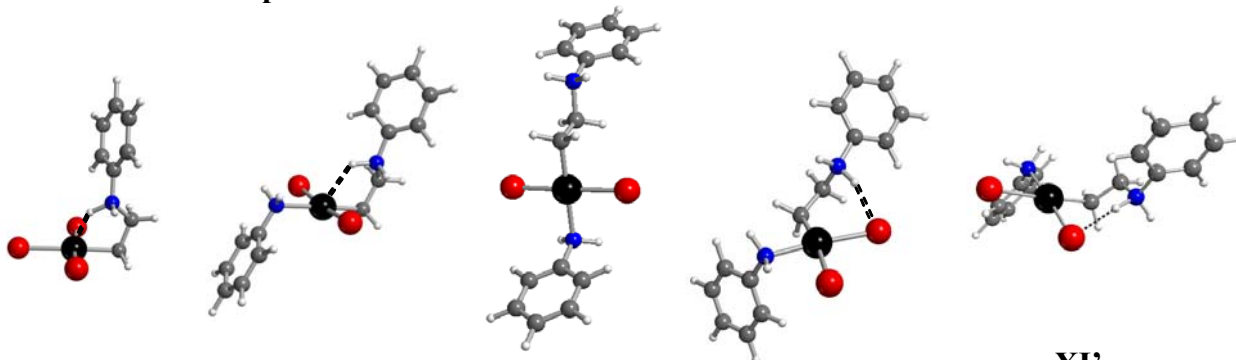
S3

**a. *trans*-PtBr<sub>2</sub>(PhNH<sub>2</sub>)<sub>2</sub> complex**



**VI'**  
-10.9 (-9.3)

**b. Zwitterionic complexes**



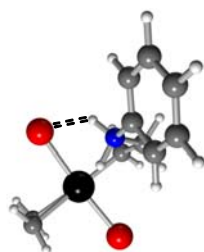
**IX**  
3.5 (5.6)

**X**  
1.4 (4.5)

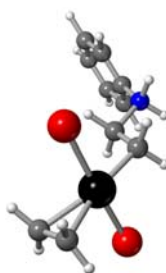
**Xanti**  
-1.9 (0.7)

**XI**  
1.9 (5.0)

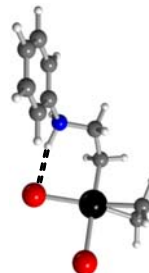
**XI'**  
2.9 (6.1)



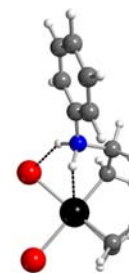
**XII**  
1.8 (4.0)



**XIIanti**  
-2.6 (-0.7)

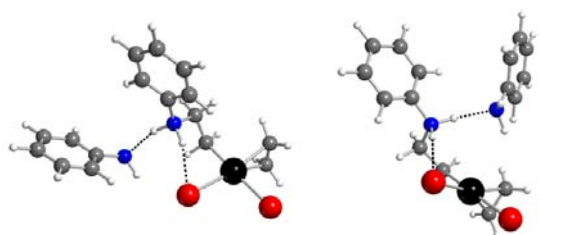


**XIII**  
-5.7 (-3.4)



**XIII'**  
-1.7 (0.7)

**c. H-bonded zwitterionic complexes with aniline**

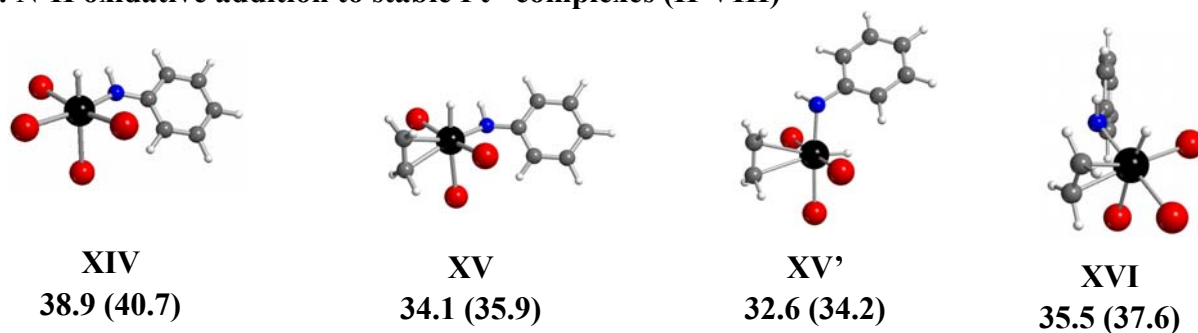


**XIII·PhNH<sub>2</sub> (a)**  
4.6 (9.3)

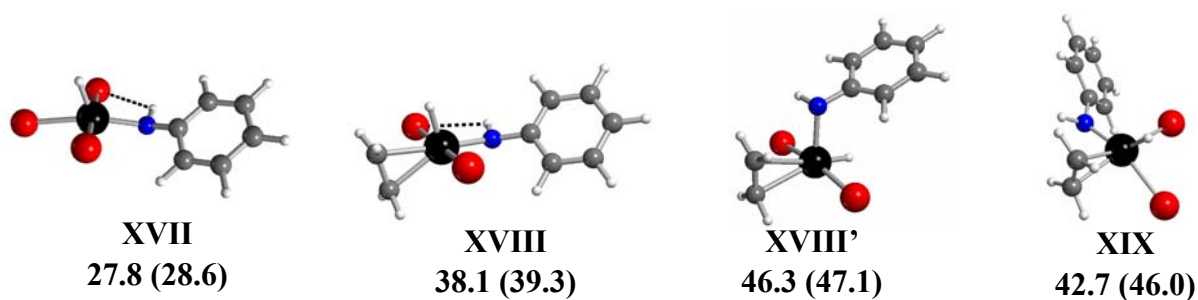
**XIII·PhNH<sub>2</sub> (b)**  
5.6 (10.3)

Figure S1. Views of optimized geometries and  $\Delta G^{\text{CPCM}}$  in kcal mol<sup>-1</sup> at 298.15 K (and at 423.15 K in parentheses) for all systems.

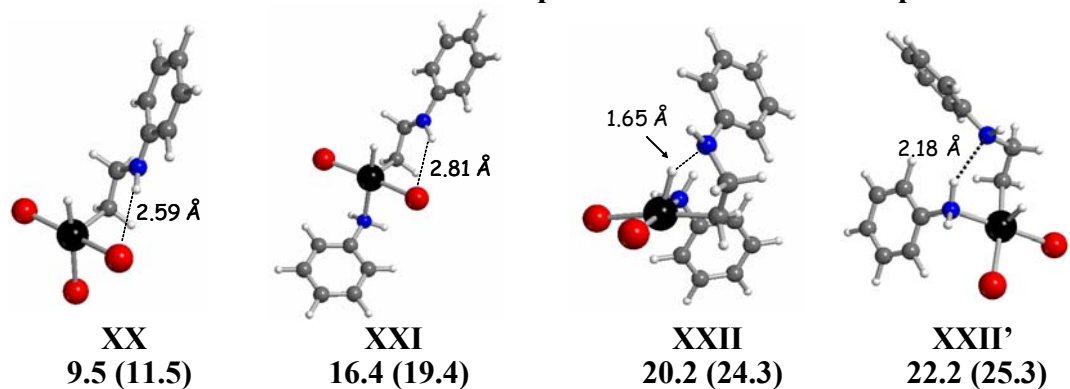
**d. N-H oxidative addition to stable Pt<sup>II</sup> complexes (II-VIII)**



**e. Bromide loss from XIV-XVI**



**f. Proton transfer to Pt from zwitterionic complexes: 16-electron Pt<sup>IV</sup>-H products**



**g. 18-electron Pt<sup>IV</sup>-H product derived from XX**

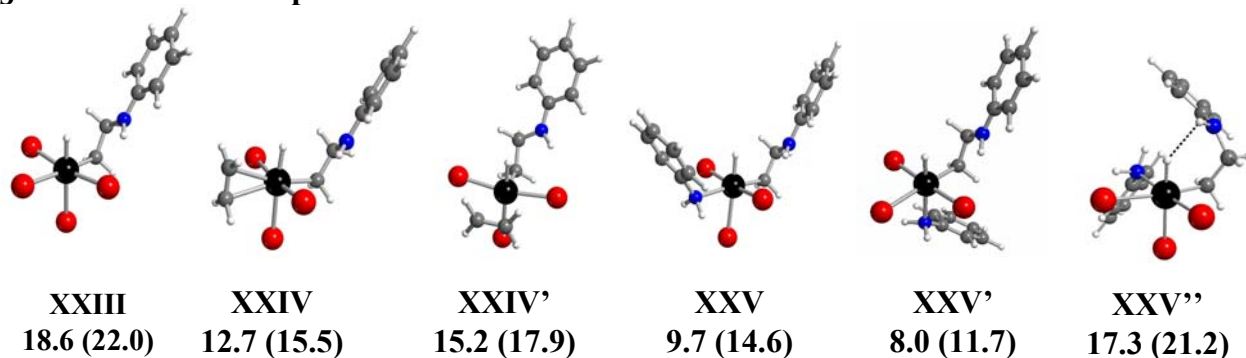
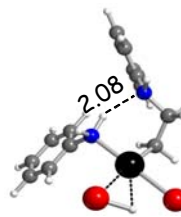


Figure S1. (contd.)

***h. Intramolecular proton transfer to Br: formation of Pt<sup>II</sup> σ-HBr intermediates***

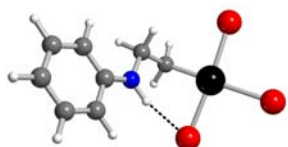


**XXVI**  
21.6 (23.7)

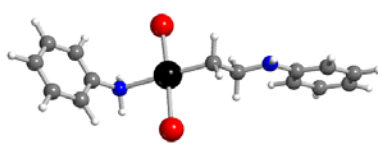


**XXVII**  
30.4 (33.6)

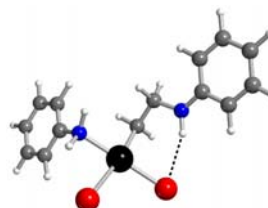
***i. Deprotonation of the zwitterionic complexes***



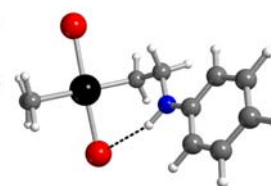
**XXVIII**  
29.8 (32.3)



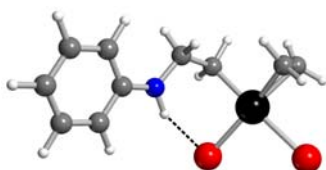
**XXIX**  
17.9 (21.0)



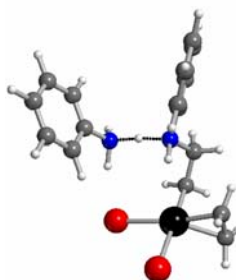
**XXX**  
22.0 (25.6)



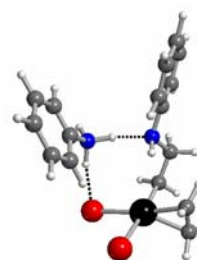
**XXXI**  
18.6 (21.3)



**XXXII**  
12.6 (15.4)

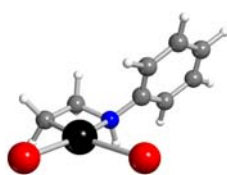


**TS(XXXI-XXXII)**  
8.1 (13.7)

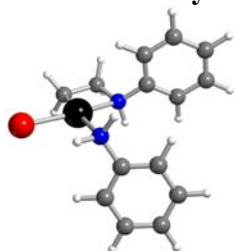


**XXXII·PhNH<sub>3</sub><sup>+</sup>**  
11.2 (15.8)

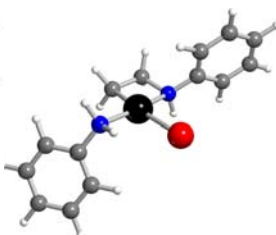
***j. Formation of chelated aminoalkyl Pt<sup>II</sup> complexes (platina(II)cycles)***



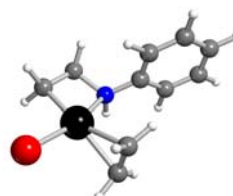
**XXXIII**  
18.4 (19.9)



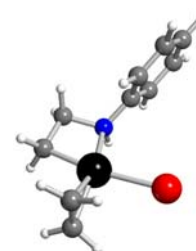
**XXXIV**  
22.4 (25.4)



**XXXIV'**  
19.7 (22.8)



**XXXV**  
18.6 (20.4)

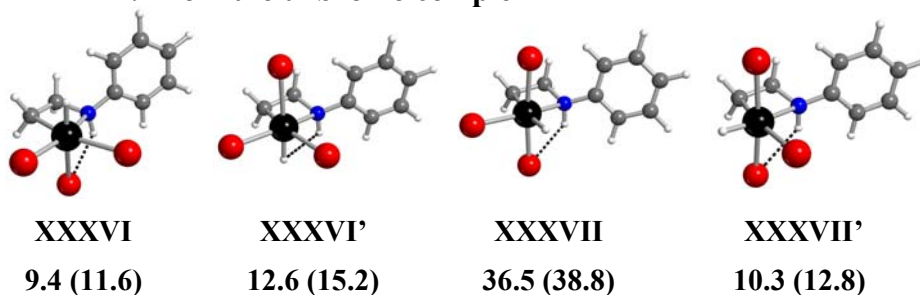


**XXXV'**  
14.9 (16.9)

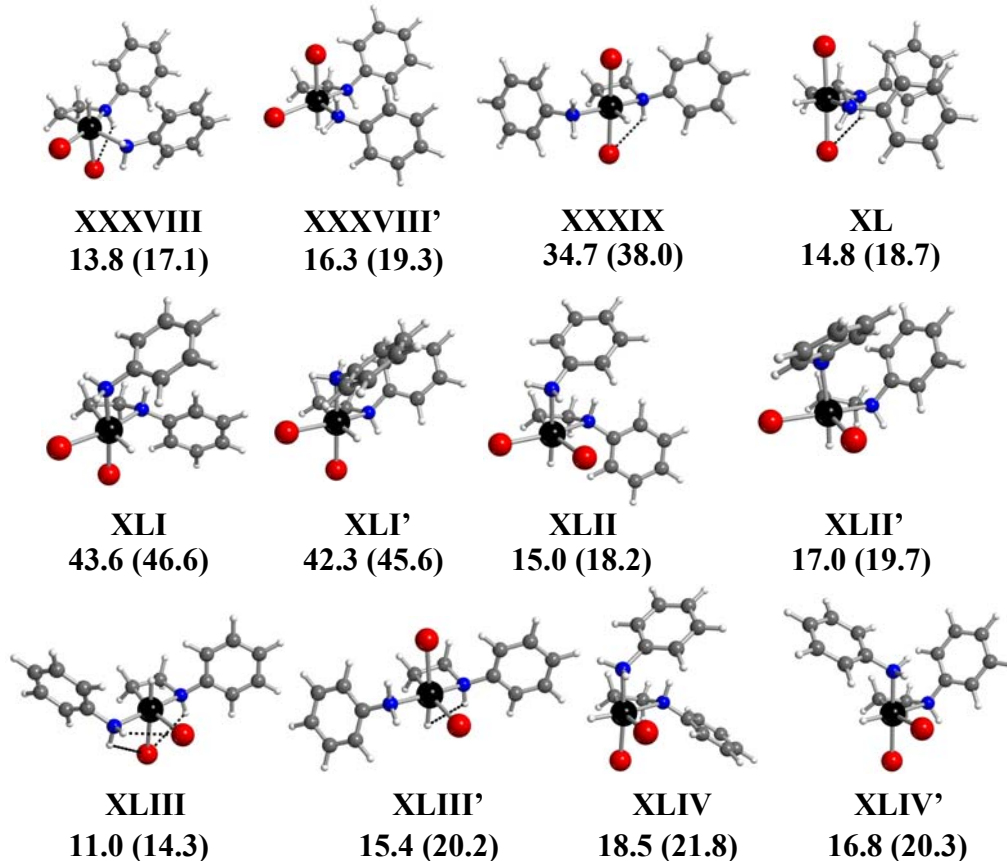
Figure S1. (contd.)

**k. Formation of chelated aminoalkyl Pt<sup>IV</sup> complexes (platina(IV)cycles)**

**k1. From the tribromo complex XX**



**k2. From the aniline-dibromo isomers XXI and XXII**



**k3. By formal HBr oxidative addition to XXXV and XXXV'**

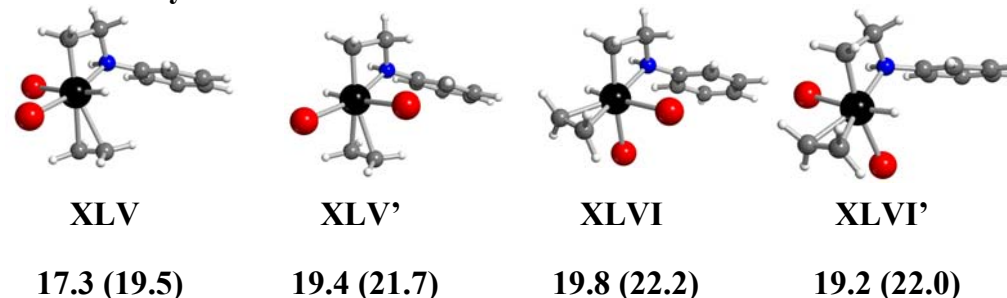
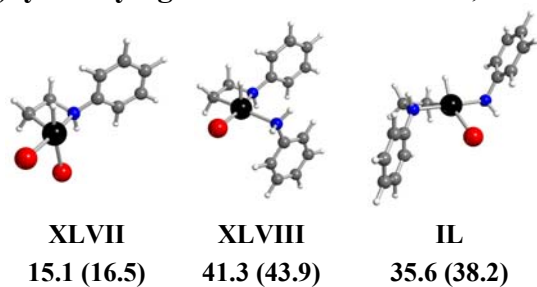
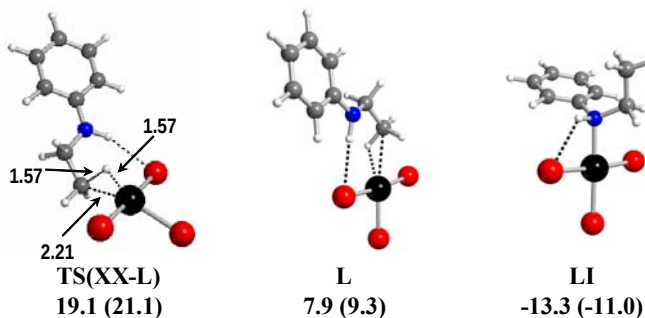


Figure S1. (contd.)

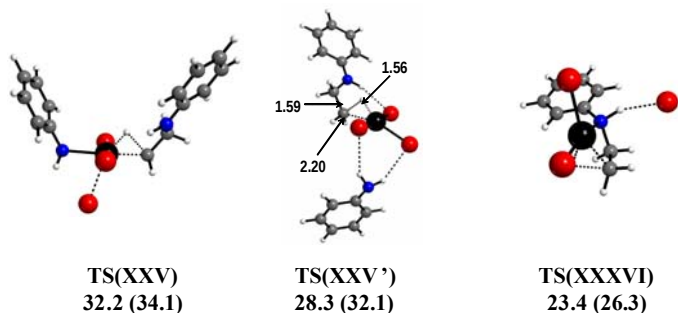
**l. 5-coordinate platina(IV)cycles by ligand loss from XXXVI, XLIII, and XXXVIII**



**m. Reductive elimination of PhNHEt from XX**



**n. Reductive eliminations from other Pt<sup>IV</sup>-H intermediates**



**o. Intermolecular proton transfer from the zwitterionic anilinium group to carbon**

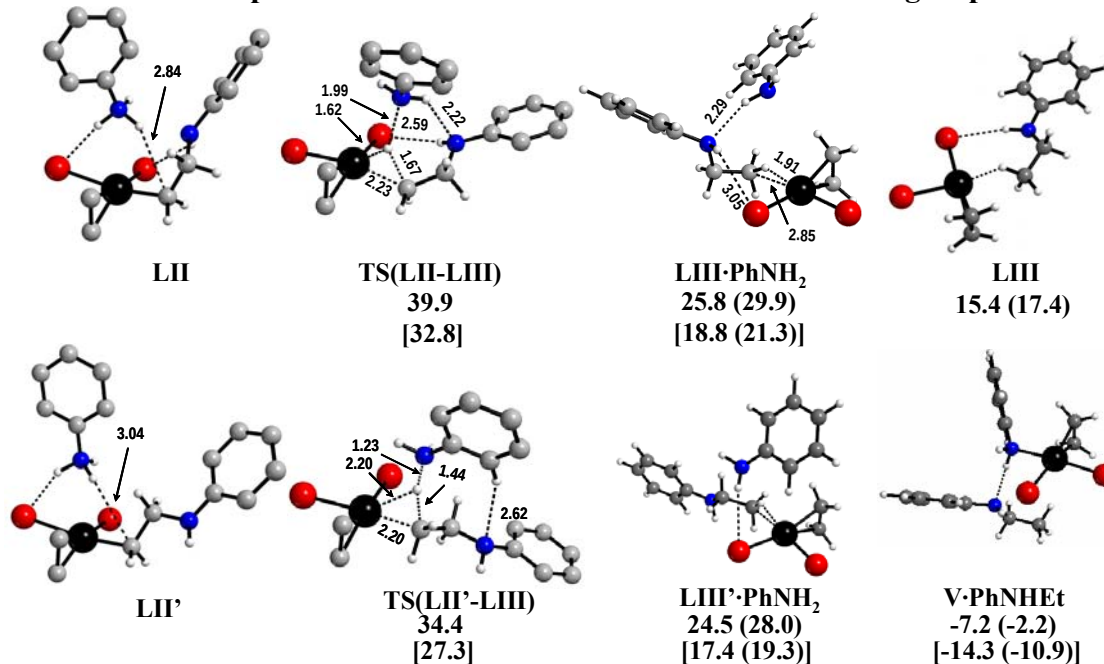
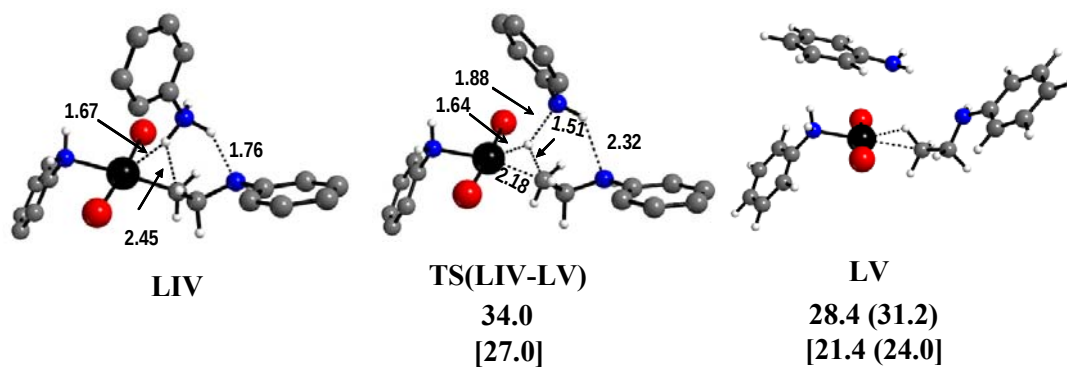


Figure S1. (contd.)



***p.* Intramolecular proton transfer from the zwitterionic anilinium group to carbon assisted by aniline**

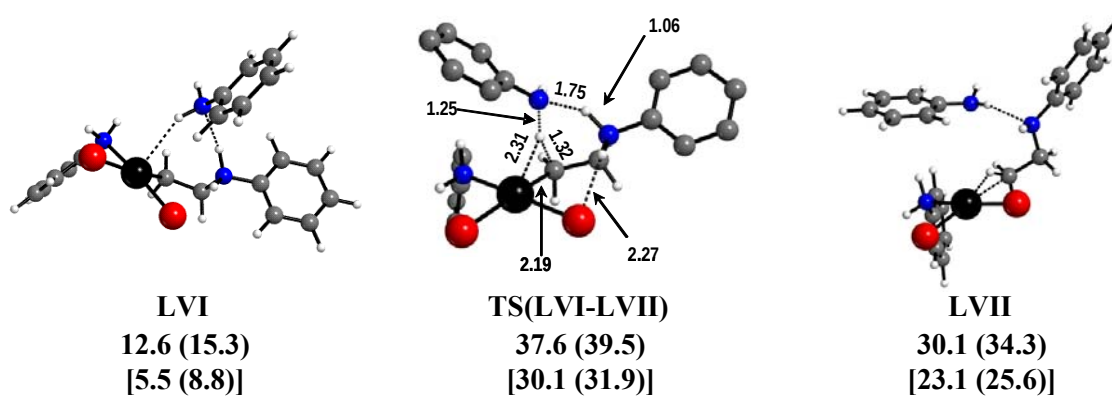


Figure S1. (contd.)

Table S1. Energy results for all compounds optimized in this study.

|                                                                                                                                                                            | E(gas)<br>(hartrees) | $\Delta E^{\text{gas}}$<br>(kcal/mol) | G(gas) <sub>298</sub><br>(hartrees) | G(gas) <sub>423</sub><br>(hartrees) | $\Delta G(\text{solv})_{298}$<br>(kcal/mol) | $\Delta G(\text{solv})_{423}$<br>(kcal/mol) | $\Delta G^{\text{CPCM}}_{,298}$<br>(kcal/mol) | $\Delta G^{\text{CPCM}}_{423}$<br>(kcal/mol) |
|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------|---------------------------------------|-------------------------------------|-------------------------------------|---------------------------------------------|---------------------------------------------|-----------------------------------------------|----------------------------------------------|
| <i>small molecules</i>                                                                                                                                                     |                      |                                       |                                     |                                     |                                             |                                             |                                               |                                              |
| C <sub>2</sub> H <sub>4</sub>                                                                                                                                              | -78.591691           |                                       | -78.561465                          | -78.572296                          | 7.5                                         | 13.2                                        |                                               |                                              |
| C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>                                                                                                                              | -287.610669          |                                       | -287.522715                         | -287.538839                         | 2.0                                         | 11.0                                        |                                               |                                              |
| C <sub>6</sub> H <sub>5</sub> NH <sub>3</sub> <sup>+</sup>                                                                                                                 | -287.957097          |                                       | -287.854428                         | -287.870219                         | -48.5                                       | -39.4                                       |                                               |                                              |
| Br <sup>-</sup>                                                                                                                                                            | -2571.496799         |                                       | -2571.512974                        | -2571.520929                        | -52.4                                       | -48.4                                       |                                               |                                              |
| aniline...aniline                                                                                                                                                          | -575.227504          |                                       | -575.037251                         | -575.064621                         | 6.0                                         | 22.4                                        |                                               |                                              |
| <i>Simple Pt complexes</i>                                                                                                                                                 |                      |                                       |                                     |                                     |                                             |                                             |                                               |                                              |
| [PtBr <sub>4</sub> ] <sup>2-</sup> , I                                                                                                                                     | -10405.053698        | 0.0                                   | -10405.089588                       | -10405.110844                       | -133.7                                      | -122.1                                      | 0.0                                           | 0.0                                          |
| [PtBr <sub>3</sub> (C <sub>2</sub> H <sub>4</sub> )] <sup>-</sup> , II                                                                                                     | -7912.253541         | -65.9                                 | -7912.234835                        | -7912.256582                        | -27.6                                       | -15.7                                       | -14.6                                         | -14.5                                        |
| [PtBr <sub>3</sub> (C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub> )] <sup>-</sup> , III                                                                                    | -8121.265677         | -61.6                                 | -8121.189991                        | -8121.216491                        | -33.0                                       | -17.2                                       | -10.7                                         | -9.6                                         |
| <i>trans</i> -[PtBr <sub>2</sub> (C <sub>2</sub> H <sub>4</sub> )(C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub> )], IV                                                     | -5628.340469         | -49.0                                 | -5628.208153                        | -5628.235760                        | 8.0                                         | 24.2                                        | -10.7                                         | -9.7                                         |
| <i>cis</i> -[PtBr <sub>2</sub> (C <sub>2</sub> H <sub>4</sub> )(C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub> )], V                                                        | -5628.329508         | -42.1                                 | -5628.197340                        | -5628.224833                        | 3.5                                         | 19.7                                        | -8.4                                          | -7.4                                         |
| <i>trans</i> -[PtBr <sub>2</sub> (C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub> ) <sub>2</sub> ], VI*                                                                      | -5837.364882         | -52.4                                 | -5837.173352                        | -5837.206074                        | 4.7                                         | 24.8                                        | -10.9                                         | -9.2                                         |
| <i>trans</i> -[PtBr <sub>2</sub> (C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub> ], VII                                                                                      | -5419.303111         | -37.4                                 | -5419.230821                        | -5419.253073                        | 10.8                                        | 23.4                                        | -3.2                                          | -2.6                                         |
| <i>cis</i> -[PtBr <sub>2</sub> (C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub> ], VIII                                                                                       | -5419.300633         | -35.9                                 | -5419.227055                        | -5419.249401                        | 6.4                                         | 18.7                                        | -5.3                                          | -5.0                                         |
| <i>Pt zwitterions</i>                                                                                                                                                      |                      |                                       |                                     |                                     |                                             |                                             |                                               |                                              |
| [PtBr <sub>3</sub> (CH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub> Ph)] <sup>-</sup> , IX                                                                                 | -8199.841449         | -51.6                                 | -8199.713776                        | -8199.743692                        | -34.9                                       | -17.1                                       | 3.5                                           | 5.6                                          |
| [PtBr <sub>3</sub> (C <sub>2</sub> H <sub>4</sub> )] <sup>-</sup> + PhNH <sub>2</sub> , TS(II-IX) anti                                                                     | -8199.823940         | -40.6                                 | -8199.696430                        | -8199.726146                        | -38.2                                       | -20.0                                       | 11.1                                          | 13.7                                         |
| <i>trans</i> -[PtBr <sub>2</sub> (CH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub> Ph)(PhNH <sub>2</sub> )], X                                                              | -5915.951868         | -49.4                                 | -5915.708167                        | -5915.743992                        | 7.8                                         | 30.2                                        | 1.4                                           | 4.4                                          |
| <i>trans</i> -[PtBr <sub>2</sub> (CH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub> Ph)(PhNH <sub>2</sub> )], X <sub>anti</sub>                                              | -5915.931298         | -36.5                                 | -5915.689732                        | -5915.726698                        | -7.0                                        | 15.6                                        | -1.8                                          | 0.7                                          |
| <i>trans</i> -[PtBr <sub>2</sub> (C <sub>2</sub> H <sub>4</sub> )(C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub> )] + PhNH <sub>2</sub> ,<br>TS(IV-X <sub>anti</sub> ) anti | -5915.935633         | -39.2                                 | -5915.695001                        | -5915.730528                        | 6.3                                         | 29.0                                        | 8.1                                           | 11.7                                         |
| <i>cis</i> -[PtBr <sub>2</sub> (CH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub> Ph)(PhNH <sub>2</sub> )], XI                                                               | -5915.935291         | -39.0                                 | -5915.690916                        | -5915.726425                        | -2.5                                        | 19.6                                        | 1.9                                           | 5.0                                          |
| <i>cis</i> -[PtBr <sub>2</sub> (CH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub> Ph)(PhNH <sub>2</sub> )], XI'                                                              | -5915.933742         | -38.0                                 | -5915.689384                        | -5915.724833                        | -2.5                                        | 19.8                                        | 2.8                                           | 6.1                                          |
| <i>cis</i> -[PtBr <sub>2</sub> (C <sub>2</sub> H <sub>4</sub> )(C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub> )], TS(V-XI) anti                                            | -5915.913164         | -25.1                                 | -5915.671154                        | -5915.706270                        | -2.9                                        | 19.7                                        | 13.9                                          | 17.7                                         |
| <i>trans</i> -[PtBr <sub>2</sub> (C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub> ], XII                                                                                      | -5706.925020         | -44.5                                 | -5706.740381                        | -5706.771310                        | 9.6                                         | 28.1                                        | 1.8                                           | 4.0                                          |

|                                                                                                                                                                                                                                   |               |       |               |               |        |       |      |      |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------|-------|---------------|---------------|--------|-------|------|------|
| <i>trans</i> -[PtBr <sub>2</sub> (C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub> ], <b>XII<sub>anti</sub></b>                                                                                                                       | -5706.907672  | -33.6 | -5706.724816  | -5706.756523  | -4.6   | 14.2  | -2.6 | -0.7 |
| [PtBr <sub>2</sub> (C <sub>2</sub> H <sub>4</sub> )(CH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub> Ph)], <b>TS(VII-XII<sub>anti</sub>)</b>                                                                                       | -5706.907510  | -33.5 | -5706.728589  | -5706.760528  | 8.0    | 26.9  | 7.6  | 9.5  |
| <i>cis</i> -[PtBr <sub>2</sub> (C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub> ] + PhNH <sub>2</sub> , <b>XIII</b>                                                                                                                  | -5706.920246  | -41.5 | -5706.734922  | -5706.765356  | -1.3   | 17.0  | -5.7 | -3.4 |
| <i>cis</i> -[PtBr <sub>2</sub> (C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub> ] + PhNH <sub>2</sub> , <b>XIII'</b>                                                                                                                 | -5706.919610  | -41.1 | -5706.733517  | -5706.763806  | 1.8    | 20.1  | -1.7 | 0.7  |
| [PtBr <sub>2</sub> (C <sub>2</sub> H <sub>4</sub> )(CH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub> Ph)], <b>TS(VIII-XIII)</b>                                                                                                    | -5706.898995  | -28.1 | -5706.717989  | -5706.749184  | 2.7    | 21.4  | 8.9  | 11.2 |
| <i>Pt...aniline adducts</i>                                                                                                                                                                                                       |               |       |               |               |        |       |      |      |
| <i>cis</i> -[PtBr <sub>2</sub> (C <sub>2</sub> H <sub>4</sub> )(C <sub>2</sub> H <sub>4</sub> NH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> )...NH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> ], <b>XIII-PhNH<sub>2</sub> (a)</b> | -5994.550328  | -53.7 | -5994.256667  | -5994.296120  | 10.4   | 35.6  | 4.6  | 9.3  |
| <i>cis</i> -[PtBr <sub>2</sub> (C <sub>2</sub> H <sub>4</sub> )(C <sub>2</sub> H <sub>4</sub> NH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> )...NH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> ], <b>XIII-PhNH<sub>2</sub> (b)</b> | -5994.548187  | -52.3 | -5994.255397  | -5994.295195  | 10.6   | 36.0  | 5.6  | 10.3 |
| <i>N-H activation complexes</i>                                                                                                                                                                                                   |               |       |               |               |        |       |      |      |
| [PtHBr <sub>4</sub> (NHPPh)] <sup>2-</sup> , <b>XIV</b>                                                                                                                                                                           | -10692.642830 | 13.5  | -10692.574862 | -10692.604793 | -116.2 | -98.5 | 38.9 | 40.7 |
| [PtH(C <sub>2</sub> H <sub>4</sub> )Br <sub>3</sub> (NHPPh)] <sup>2-</sup> , <b>XV</b>                                                                                                                                            | -8199.808599  | -31.0 | -8199.683695  | -8199.713562  | -23.2  | -5.6  | 34.8 | 35.9 |
| [PtH(C <sub>2</sub> H <sub>4</sub> )Br <sub>3</sub> (NHPPh)] <sup>2-</sup> , <b>XV'</b>                                                                                                                                           | -8199.814058  | -34.4 | -8199.691914  | -8199.719021  | -19.5  | -1.6  | 32.6 | 36.6 |
| [PtH(C <sub>2</sub> H <sub>4</sub> )Br <sub>3</sub> (NHPPh)] <sup>2-</sup> , <b>XVI</b>                                                                                                                                           | -8199.802308  | -27.0 | -8199.677684  | -8199.707271  | -25.6  | -7.9  | 35.5 | 37.6 |
| [PtHBr <sub>3</sub> (NHPPh)] <sup>-</sup> , <b>XVII</b>                                                                                                                                                                           | -8121.216016  | -30.4 | -8121.145201  | -8121.172641  | -22.6  | -6.5  | 27.8 | 28.6 |
| [PtH(C <sub>2</sub> H <sub>4</sub> )Br <sub>2</sub> (NHPPh)], <b>XVIII</b>                                                                                                                                                        | -5628.264662  | -1.4  | -5628.137703  | -5628.165300  | 12.5   | 29.0  | 38.1 | 39.3 |
| [PtH(C <sub>2</sub> H <sub>4</sub> )Br <sub>2</sub> (NHPPh)], <b>XVIII'</b>                                                                                                                                                       | -5628.249113  | 8.4   | -5628.124694  | -5628.153386  | 12.6   | 29.3  | 46.3 | 47.1 |
| [PtH(C <sub>2</sub> H <sub>4</sub> )Br <sub>2</sub> (NHPPh)], <b>XIX</b>                                                                                                                                                          | -5628.249722  | 8.0   | -5628.122917  | -5628.147113  | 7.9    | 24.3  | 42.7 | 46.0 |
| <i>Pt-hydrides (5-coordinate)</i>                                                                                                                                                                                                 |               |       |               |               |        |       |      |      |
| [PtHBr <sub>3</sub> (CH <sub>2</sub> CH <sub>2</sub> NHPPh)] <sup>-</sup> , <b>XX</b>                                                                                                                                             | -8199.849784  | -56.8 | -8199.724531  | -8199.754966  | -22.2  | -4.1  | 9.5  | 11.5 |
| [PtBr <sub>3</sub> H(CH <sub>2</sub> CH <sub>2</sub> NHPPh)] <sup>-</sup> , <b>TS(IX-XX)</b>                                                                                                                                      | -8199.839483  | -50.3 | -8199.714252  | -8199.743585  | -29.5  | -11.5 | 8.7  | 11.2 |
| <i>trans</i> -[PtHBr <sub>2</sub> (CH <sub>2</sub> CH <sub>2</sub> NHPPh)(PhNH <sub>2</sub> )], <b>XXI</b>                                                                                                                        | -5915.926622  | -33.6 | -5915.687950  | -5915.724095  | 10.2   | 32.6  | 16.4 | 19.4 |
| <i>cis</i> -[PtHBr <sub>2</sub> (CH <sub>2</sub> CH <sub>2</sub> NHPPh)(PhNH <sub>2</sub> )], <b>XXII</b>                                                                                                                         | -5915.919916  | -29.4 | -5915.676647  | -5915.710321  | 6.8    | 28.9  | 20.2 | 24.3 |
| <i>cis</i> -[PtHBr <sub>2</sub> (CH <sub>2</sub> CH <sub>2</sub> NHPPh)(PhNH <sub>2</sub> )], <b>XXII'</b>                                                                                                                        | -5915.916526  | -27.2 | -5915.674952  | -5915.709956  | 7.8    | 29.7  | 22.2 | 25.3 |
| <i>Pt-hydrides (6-coordinate)</i>                                                                                                                                                                                                 |               |       |               |               |        |       |      |      |
| [PtHBr <sub>4</sub> (CH <sub>2</sub> CH <sub>2</sub> NHPPh)] <sup>2-</sup> , <b>XXIII</b>                                                                                                                                         | -10771.284857 | -18.1 | -10771.162622 | -10771.195521 | -112.5 | -92.4 | 18.6 | 22.0 |
| [PtHBr <sub>3</sub> (CH <sub>2</sub> CH <sub>2</sub> NHPPh)(C <sub>2</sub> H <sub>4</sub> )] <sup>-</sup> (H trans to C <sub>2</sub> H <sub>4</sub> ), <b>XXIV</b>                                                                | -8278.454234  | -64.8 | -8278.277419  | -8278.311056  | -16.9  | 3.0   | 12.6 | 15.5 |

|                                                                                                                                                                            |              |       |              |              |        |       |      |      |
|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------|-------|--------------|--------------|--------|-------|------|------|
| [PtHBr <sub>3</sub> (CH <sub>2</sub> CH <sub>2</sub> NHPh)(C <sub>2</sub> H <sub>4</sub> )] <sup>-</sup> (H trans to C <sub>2</sub> H <sub>4</sub> , perp., <b>XXIV'</b> ) | -8278.449105 | -61.6 | -8278.273544 | -8278.307669 | -16.8  | 3.2   | 15.2 | 17.8 |
| [PtHBr <sub>3</sub> (CH <sub>2</sub> CH <sub>2</sub> NHPh)(PhNH <sub>2</sub> )] <sup>-</sup> (H trans to PhNH <sub>2</sub> ), <b>XXV</b>                                   | -8487.490672 | -75.8 | -8487.252790 | -8487.290029 | -16.4  | 7.6   | 9.7  | 14.6 |
| [PtHBr <sub>3</sub> (CH <sub>2</sub> CH <sub>2</sub> NHPh)(PhNH <sub>2</sub> )] <sup>-</sup> (H trans to Br <sup>-</sup> ), <b>XXV'</b>                                    | -8487.488780 | -74.6 | -8487.253124 | -8487.291824 | -17.9  | 5.9   | 8.0  | 11.7 |
| [PtHBr <sub>3</sub> (CH <sub>2</sub> CH <sub>2</sub> NHPh)(PhNH <sub>2</sub> )] <sup>-</sup> (H trans to Br <sup>-</sup> ), <b>XXV''</b>                                   | -8487.468452 | -61.8 | -8487.230198 | -8487.267910 | -23.0  | 0.4   | 17.3 | 21.2 |
| <i>σ-HBr complexes</i>                                                                                                                                                     |              |       |              |              |        |       |      |      |
| [PtBr(σ-HBr)(CH <sub>2</sub> CH <sub>2</sub> NHPh)(C <sub>2</sub> H <sub>4</sub> )], <b>XXVI</b>                                                                           | -5706.894136 | -25.1 | -5706.717420 | -5706.749080 | 15.0   | 33.8  | 21.6 | 23.6 |
| [PtBr(σ-HBr)(CH <sub>2</sub> CH <sub>2</sub> NHPh)(PhNH <sub>2</sub> )], <b>XXVII</b>                                                                                      | -5915.907910 | -21.8 | -5915.669787 | -5915.705545 | 12.8   | 35.1  | 30.4 | 33.6 |
| <i>Deprotonated zwitterions</i>                                                                                                                                            |              |       |              |              |        |       |      |      |
| [PtBr <sub>3</sub> (CH <sub>2</sub> CH <sub>2</sub> NHPh)] <sup>-2</sup> , <b>XXVIII</b>                                                                                   | -8199.242970 | 106.6 | -8199.127845 | -8199.158135 | -117.6 | -99.5 | 29.8 | 32.3 |
| [PtBr <sub>2</sub> (CH <sub>2</sub> CH <sub>2</sub> NHPh)(PhNH <sub>2</sub> )] <sup>-</sup> trans( <i>N,N</i> ), <b>XXIX</b>                                               | -5915.449898 | 48.2  | -5915.222974 | -5915.259700 | -21.4  | 1.1   | 17.9 | 21.0 |
| [PtBr <sub>2</sub> (CH <sub>2</sub> CH <sub>2</sub> NHPh)(PhNH <sub>2</sub> )] <sup>-</sup> cis( <i>N,N</i> ), <b>XXX</b>                                                  | -5915.442013 | 53.1  | -5915.212956 | -5915.248702 | -23.6  | -1.2  | 22.0 | 25.6 |
| [PtBr <sub>2</sub> (CH <sub>2</sub> CH <sub>2</sub> NHPh)(C <sub>2</sub> H <sub>4</sub> )] <sup>-</sup> (Br trans to C), <b>XXXI</b>                                       | -5706.432262 | 47.4  | -5706.261716 | -5706.292338 | -15.3  | 3.2   | 18.6 | 21.3 |
| [PtBr <sub>2</sub> (CH <sub>2</sub> CH <sub>2</sub> NHPh)(C <sub>2</sub> H <sub>4</sub> )] <sup>-</sup> (Br trans to C), <b>XXXII</b>                                      | -5706.434347 | 46.0  | -5706.262718 | -5706.292937 | -20.7  | -2.4  | 12.6 | 15.4 |
| <i>Proton transfer</i>                                                                                                                                                     |              |       |              |              |        |       |      |      |
| <b>TS (XIII-XXXII)</b>                                                                                                                                                     | -5994.527574 | -39.4 | -5994.247739 | -5994.277814 | 8.3    | 28.5  | 8.1  | 13.7 |
| cis-[PtBr <sub>2</sub> (CH <sub>2</sub> CH <sub>2</sub> NHPh)(PhNH <sub>3</sub> )] <sup>+</sup> , <b>XXXII·PhNH<sub>3</sub><sup>+</sup></b>                                | -5994.540600 | -47.6 | -5994.246390 | -5994.285252 | 10.6   | 35.2  | 11.2 | 15.8 |
| <i>Pt<sup>II</sup> azacyclobutane derivatives</i>                                                                                                                          |              |       |              |              |        |       |      |      |
| [PtBr <sub>2</sub> (CH <sub>2</sub> CH <sub>2</sub> NHPh)] <sup>-</sup> , <b>XXXIII</b>                                                                                    | -5627.798767 | 73.6  | -5627.678412 | -5627.705449 | -36.8  | -20.7 | 18.4 | 19.9 |
| PtBr(CH <sub>2</sub> CH <sub>2</sub> NHPh)(PhNH <sub>2</sub> ), <b>XXXIV</b>                                                                                               | -3343.902048 | 80.2  | -3343.666929 | -3343.699333 | 8.5    | 29.1  | 22.4 | 25.4 |
| PtBr(CH <sub>2</sub> CH <sub>2</sub> NHPh)(PhNH <sub>2</sub> ), <b>XXXIV'</b>                                                                                              | -3343.902468 | 80.8  | -3343.665744 | -3343.697667 | 5.0    | 25.6  | 19.7 | 22.8 |
| [PtBr <sub>2</sub> (CH <sub>2</sub> CH <sub>2</sub> NHPh)(C <sub>2</sub> H <sub>4</sub> )] <sup>-</sup> , <b>XXXV</b>                                                      | -3134.876271 | 84.5  | -3134.700401 | -3134.727786 | 6.8    | 23.3  | 18.6 | 20.4 |
| [PtBr <sub>2</sub> (CH <sub>2</sub> CH <sub>2</sub> NHPh)(C <sub>2</sub> H <sub>4</sub> )] <sup>-</sup> , <b>XXXV'</b>                                                     | -3134.881820 | 81.0  | -3134.705359 | -3134.732672 | 6.2    | 22.9  | 14.9 | 16.9 |

*Pt<sup>IV</sup>azacyclobutane derivatives (coord. VI)*

|                                                                                                                         |              |       |              |              |       |       |      |      |
|-------------------------------------------------------------------------------------------------------------------------|--------------|-------|--------------|--------------|-------|-------|------|------|
| [PtHBr <sub>3</sub> (CH <sub>2</sub> CH <sub>2</sub> NHPh)] <sup>-</sup> , <b>XXXVI</b>                                 | -8199.838468 | -49.7 | -8199.711708 | -8199.741744 | -30.3 | -12.3 | 9.4  | 11.6 |
| [PtHBr <sub>3</sub> (CH <sub>2</sub> CH <sub>2</sub> NHPh)] <sup>-</sup> , <b>XXXVI'</b>                                | -8199.831377 | -45.2 | -8199.702034 | -8199.731125 | -33.2 | -15.3 | 12.6 | 15.2 |
| [PtHBr <sub>3</sub> (CH <sub>2</sub> CH <sub>2</sub> NHPh)] <sup>-</sup> , <b>XXXVIII</b>                               | -8199.804139 | -28.2 | -8199.676176 | -8199.705226 | -25.6 | -8.0  | 36.4 | 38.8 |
| [PtHBr <sub>3</sub> (CH <sub>2</sub> CH <sub>2</sub> NHPh)] <sup>-</sup> , <b>XXXVII'</b>                               | -8199.848614 | -56.1 | -8199.720123 | -8199.749420 | -24.2 | -6.2  | 10.3 | 12.8 |
|                                                                                                                         |              |       |              |              |       |       |      |      |
| [PtHBr <sub>2</sub> (CH <sub>2</sub> CH <sub>2</sub> NHPh)(PhNH <sub>2</sub> )], <b>XXXVIII</b>                         | -5915.935584 | -39.2 | -5915.691809 | -5915.726347 | 9.9   | 31.8  | 13.8 | 17.1 |
| [PtHBr <sub>2</sub> (CH <sub>2</sub> CH <sub>2</sub> NHPh)(PhNH <sub>2</sub> )], <b>XXXVIII'</b>                        | -5915.927364 | -34.0 | -5915.684356 | -5915.719140 | 7.8   | 29.4  | 16.3 | 19.3 |
| [PtHBr <sub>2</sub> (CH <sub>2</sub> CH <sub>2</sub> NHPh)(PhNH <sub>2</sub> )], <b>XXXIX</b>                           | -5915.902038 | -18.1 | -5915.657946 | -5915.692086 | 9.6   | 31.1  | 34.7 | 38.0 |
| [PtHBr <sub>2</sub> (CH <sub>2</sub> CH <sub>2</sub> NHPh)(PhNH <sub>2</sub> )], <b>XL</b>                              | -5915.943538 | -44.2 | -5915.698533 | -5915.732560 | 15.1  | 37.2  | 14.8 | 18.7 |
| [PtHBr <sub>2</sub> (CH <sub>2</sub> CH <sub>2</sub> NHPh)(PhNH <sub>2</sub> )], <b>XLI</b>                             | -5915.881671 | -5.4  | -5915.637380 | -5915.671224 | 5.6   | 26.6  | 43.6 | 46.6 |
| [PtHBr <sub>2</sub> (CH <sub>2</sub> CH <sub>2</sub> NHPh)(PhNH <sub>2</sub> )], <b>XLI'</b>                            | -5915.883688 | -6.6  | -5915.638931 | -5915.672659 | 5.7   | 26.6  | 42.7 | 45.7 |
| [PtHBr <sub>2</sub> (CH <sub>2</sub> CH <sub>2</sub> NHPh)(PhNH <sub>2</sub> )], <b>XLII</b>                            | -5915.929388 | -35.3 | -5915.686966 | -5915.721934 | 8.1   | 30.1  | 15.0 | 18.2 |
| [PtHBr <sub>2</sub> (CH <sub>2</sub> CH <sub>2</sub> NHPh)(PhNH <sub>2</sub> )], <b>XLII'</b>                           | -5915.919646 | -29.2 | -5915.675586 | -5915.709911 | 3.0   | 24.0  | 17.0 | 19.7 |
| [PtHBr <sub>2</sub> (CH <sub>2</sub> CH <sub>2</sub> NHPh)(PhNH <sub>2</sub> )], <b>XLIII</b>                           | -5915.933630 | -38.0 | -5915.690237 | -5915.725138 | 6.2   | 28.2  | 11.0 | 14.3 |
| [PtHBr <sub>2</sub> (CH <sub>2</sub> CH <sub>2</sub> NHPh)(PhNH <sub>2</sub> )], <b>XLIII'</b>                          | -5915.929361 | -35.3 | -5915.682919 | -5915.716024 | 6.0   | 28.3  | 15.4 | 20.2 |
| [PtHBr <sub>2</sub> (CH <sub>2</sub> CH <sub>2</sub> NHPh)(PhNH <sub>2</sub> )], <b>XLIV</b>                            | -5915.923402 | -31.6 | -5915.679079 | -5915.713349 | 6.6   | 28.2  | 18.4 | 21.8 |
| [PtHBr <sub>2</sub> (CH <sub>2</sub> CH <sub>2</sub> NHPh)(PhNH <sub>2</sub> )], <b>XLIV'</b>                           | -5915.928818 | -35.0 | -5915.684461 | -5915.718630 | 8.3   | 30.1  | 16.8 | 20.3 |
|                                                                                                                         |              |       |              |              |       |       |      |      |
| [PtHBr <sub>3</sub> (CH <sub>2</sub> CH <sub>2</sub> NHPh)(C <sub>2</sub> H <sub>4</sub> )] <sup>-</sup> , <b>XLV</b>   | -5706.897672 | -27.3 | -5706.714338 | -5706.744433 | 8.7   | 26.7  | 17.3 | 19.5 |
| [PtHBr <sub>3</sub> (CH <sub>2</sub> CH <sub>2</sub> NHPh)(C <sub>2</sub> H <sub>4</sub> )] <sup>-</sup> , <b>XLV'</b>  | -5706.890638 | -22.9 | -5706.706225 | -5706.735931 | 5.8   | 23.6  | 19.4 | 21.7 |
| [PtHBr <sub>3</sub> (CH <sub>2</sub> CH <sub>2</sub> NHPh)(C <sub>2</sub> H <sub>4</sub> )] <sup>-</sup> , <b>XLVI</b>  | -5706.886714 | -20.4 | -5706.701104 | -5706.730415 | 2.9   | 20.6  | 19.8 | 22.2 |
| [PtHBr <sub>3</sub> (CH <sub>2</sub> CH <sub>2</sub> NHPh)(C <sub>2</sub> H <sub>4</sub> )] <sup>-</sup> , <b>XLVI'</b> | -5706.893620 | -24.8 | -5706.708830 | -5706.738443 | 7.2   | 25.5  | 19.2 | 22.0 |

*Pt<sup>IV</sup>azacyclobutane derivatives (5-coord.)*

|                                                                                                |              |       |              |              |       |      |      |      |
|------------------------------------------------------------------------------------------------|--------------|-------|--------------|--------------|-------|------|------|------|
| [PtHBr <sub>2</sub> (CH <sub>2</sub> CH <sub>2</sub> NHPh)], <b>XLVII</b>                      | -5628.289597 | -17.0 | -5628.157886 | -5628.184789 | 2.2   | 18.4 | 15.1 | 16.5 |
| [PtHBr(CH <sub>2</sub> CH <sub>2</sub> NHPh)(PhNH <sub>2</sub> )] <sup>+</sup> , <b>XLVIII</b> | -3344.246871 | 81.2  | -3344.001905 | -3344.034231 | -21.2 | -0.5 | 41.3 | 43.9 |
| [PtHBr(CH <sub>2</sub> CH <sub>2</sub> NHPh)(PhNH <sub>2</sub> )] <sup>+</sup> , <b>IL</b>     | -3344.250014 | 79.3  | -3344.004108 | -3344.036506 | -25.4 | -4.8 | 35.6 | 38.1 |

# Hydroamination

|                                                                                                                  |              |       |              |              |       |      |       |       |
|------------------------------------------------------------------------------------------------------------------|--------------|-------|--------------|--------------|-------|------|-------|-------|
| [PtHBr <sub>3</sub> (CH <sub>2</sub> CH <sub>2</sub> NHPh)] <sup>-</sup> , <b>TS(XX-L)</b>                       | -8199.835563 | -47.9 | -8199.712556 | -8199.743030 | -20.0 | -2.0 | 19.1  | 21.1  |
| [PtBr <sub>3</sub> (H-CH <sub>2</sub> CH <sub>2</sub> NHPh)] <sup>-</sup> , <b>L</b>                             | -8199.854272 | -59.6 | -8199.730659 | -8199.762634 | -19.9 | -1.4 | 7.9   | 9.3   |
| [PtBr <sub>3</sub> (C <sub>6</sub> H <sub>5</sub> EtNH)] <sup>-</sup> , <b>LI</b>                                | -8199.884465 | -78.6 | -8199.754556 | -8199.784742 | -26.1 | -7.9 | -13.3 | -11.0 |
| [PtBr <sub>3</sub> (H-CH <sub>2</sub> CH <sub>2</sub> NHPh)(PhNH <sub>2</sub> )] <sup>-</sup> , <b>TS (XXV)</b>  | -8487.449690 | -50.0 | -8487.214783 | -8487.449690 | -17.8 | 2.7  | 32.2  | 34.1  |
| [PtBr <sub>3</sub> (H-CH <sub>2</sub> CH <sub>2</sub> NHPh)(PhNH <sub>2</sub> )] <sup>-</sup> , <b>TS (XXV')</b> | -8487.460639 | -56.9 | -8487.234948 | -8487.276350 | -9.0  | 16.5 | 28.3  | 32.0  |
| [PtBr <sub>3</sub> H(CH <sub>2</sub> CH <sub>2</sub> NHPh)] <sup>-</sup> , <b>TS(XXXVI)</b>                      | -8199.822164 | -39.5 | -8199.696673 | -8199.726494 | -25.6 | -7.2 | 23.6  | 26.3  |

# Supporting material

|                               |              |       |              |              |      |       |      |      |
|-------------------------------|--------------|-------|--------------|--------------|------|-------|------|------|
| <b>TS (XXXII-A) (a)</b>       | -5994.496442 | -19.8 | -5994.209545 | -5994.249010 | 16.1 | 38.2  | 39.9 | 41.4 |
| <b>TS (XXXII-A) (b)</b>       | -5994.490737 | -16.3 | -5994.203120 | -5994.490737 | 6.6  | 25.9  | 34.4 | 36.3 |
| <b>A·PhNH<sub>2</sub> (a)</b> | -5994.520749 | -35.1 | -5994.237191 | -5994.278435 | 19.4 | 45.1  | 25.8 | 29.9 |
| <b>A·PhNH<sub>2</sub> (b)</b> | -5994.518738 | -33.8 | -5994.234251 | -5994.276424 | 16.2 | 41.91 | 24.5 | 28.0 |
| <b>A</b>                      | -5706.902572 | -30.4 | -5706.723168 | -5706.755184 | 12.4 | 31.4  | 15.4 | 17.4 |
| <b>B</b>                      | -5994.577652 | -70.8 | -5994.284778 | -5994.324544 | 16.2 | 41.9  | -7.2 | -2.2 |
| <b>TS (XXIX-C)</b>            | -6203.534773 | -32.0 | -6203.188198 | -6203.534773 | 15.7 |       | 34.0 |      |
| <b>C·PhNH<sub>2</sub></b>     | -6203.547994 | -40.3 | -6203.202988 | -6203.547994 | 19.4 |       | 28.4 |      |
| <b>D</b>                      | -6203.565271 | -51.1 | -6203.213828 | -6203.258589 | 10.3 |       | 12.6 |      |
| <b>TS(D-E)</b>                | -6203.534566 | -31.9 | -6203.187219 | -6203.534566 | 18.7 |       | 37.6 |      |
| <b>E</b>                      | -6203.546149 | -39.1 | -6203.201389 | -6203.248228 | 20.1 | 49.2  | 30.1 | 34.3 |

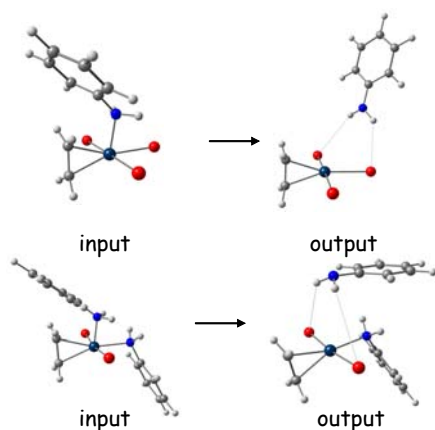


Figure S2. Attempts to optimise 5-coordinated Pt-complexes.

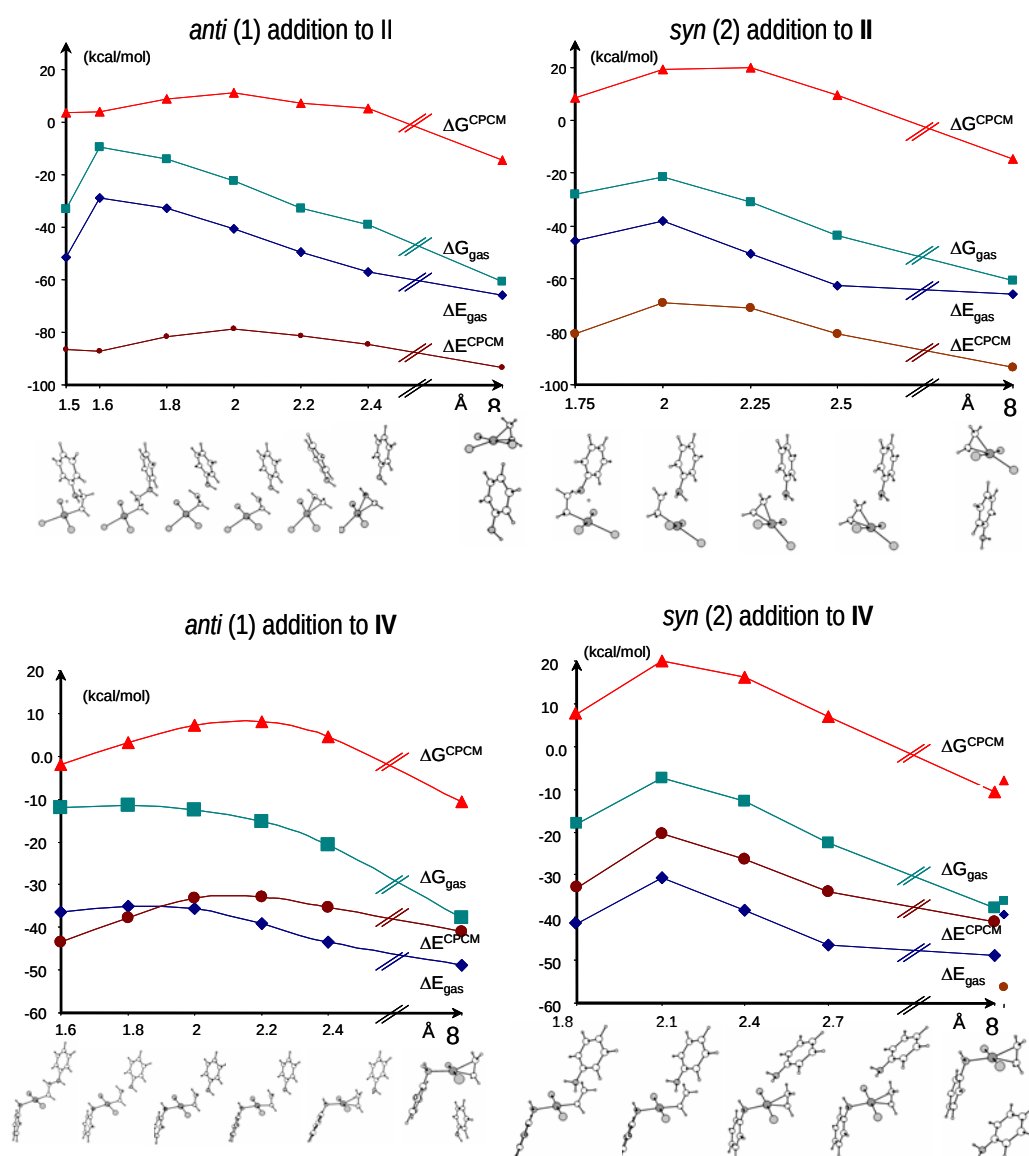


Figure S3. Different pathways for the aniline addition to coordinated olefin in **II** and **IV**.

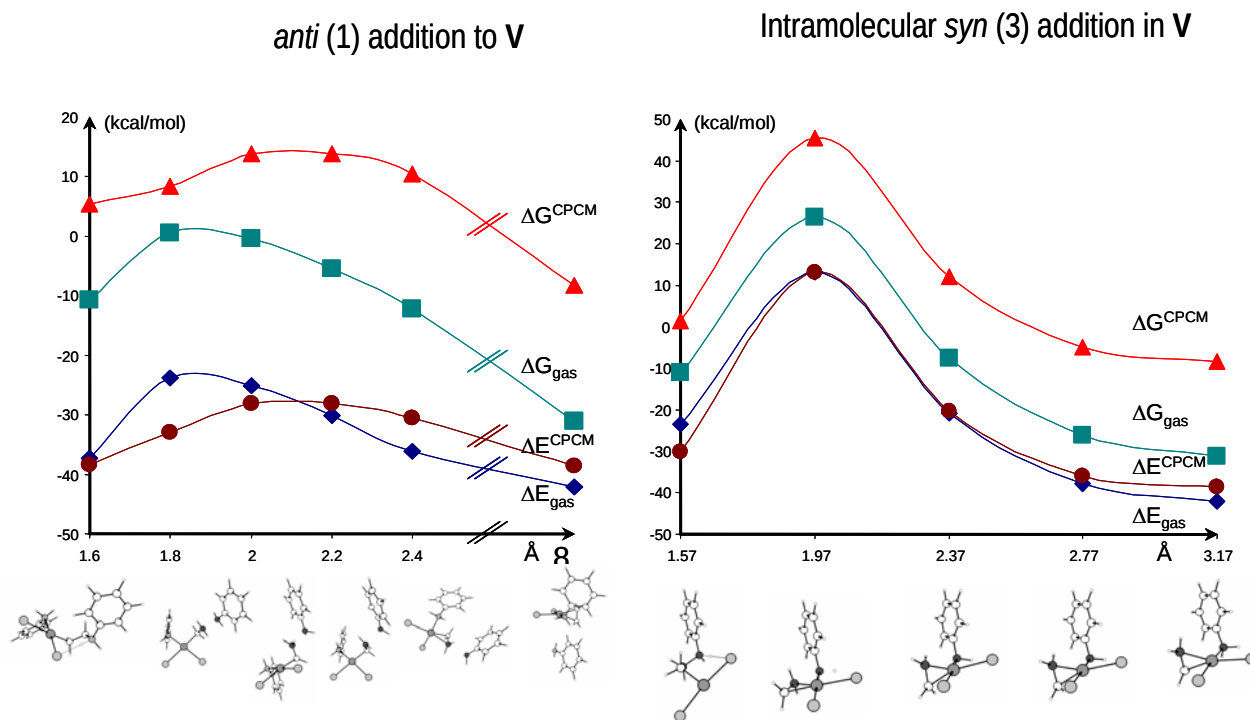


Figure S4. Different pathways for the aniline addition to coordinated olefin in **V**.

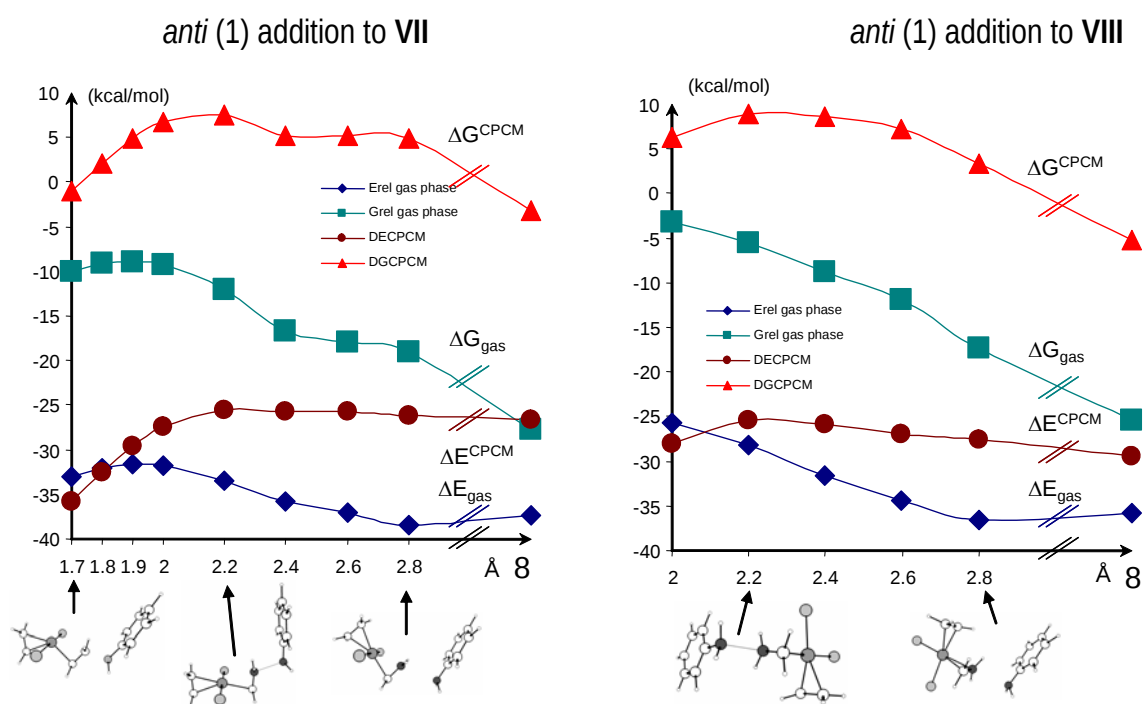
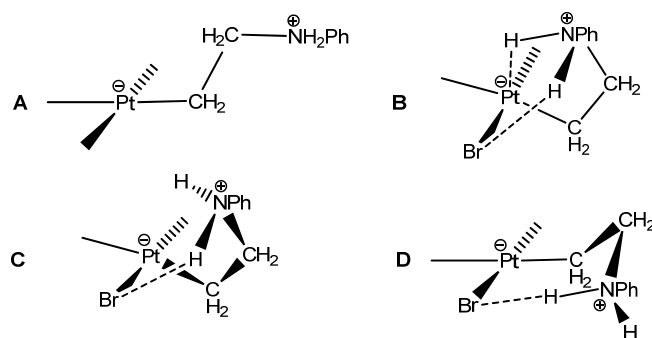


Figure S5. Intermolecular *anti* addition of aniline to coordinated olefin in **VII** and **VIII**.

### Structural description of the zwitterionic complexes IX-XIII.

The four types of structures observed in this study are summarized in the schematic drawings **A-D** in Scheme S1. The H $\cdots$ Pt interaction always brings about a secondary, sometimes weak, H $\cdots$ Br interaction in **B**, whereas the H $\cdots$ Br interaction in **C** and **D**, differing only in the stereochemistry at the N atom, does not entail any secondary H $\cdots$ Pt interaction. Thus, **II** led to product **IX** of type **B** (H $\cdots$ Pt = 1.97 Å;  $\angle$ N-H $\cdots$ Pt = 139.9°) where the H $\cdots$ Br interaction is very weak (H $\cdots$ Br = 2.89 Å;  $\angle$ N-H $\cdots$ Br = 114.8°), whereas system **IV** led to **X**, also of type **B** but with a less marked difference between the two interactions (H $\cdots$ Pt = 2.31 Å;  $\angle$ N-H $\cdots$ Pt = 125.6°; H $\cdots$ Br = 2.74 Å;  $\angle$ N-H $\cdots$ Br = 121.3°). A more stable structure of type **A**, labelled **Xanti**, could also be optimized for the zwitterions obtained from **IV** when a geometry with an *anti* arrangement of the Pt-CH<sub>2</sub>-CH<sub>2</sub>-NH<sub>2</sub>Ph moiety was used as input. The lower energy of **Xanti** relative to **X** suggests that the H-bond stabilization is not sufficient to compensate for the greater intramolecular repulsion of the less favourable conformation around the C-C bond.



Scheme S1. Different geometrical arrangement found for the [Pt-CH<sub>2</sub>CH<sub>2</sub>NHPh] moiety.

On the other hand, system **V** led to a zwitterion **XI** of type **C**. An isomer of type **D** was found at slightly higher energy. System **VII** led to **XII** of type **B** but a lower-energy isomer of type **A**, labelled **XIIanti** was again accessible, while **VIII** led to **XIII** of type **D** with a higher

energy isomer of type **B** but very close to **C** (stronger H $\cdots$ Br and weaker H $\cdots$ Pt interaction). Construction of input of type **A** did not yield stable local minima for the other zwitterionic products and no other minima could be obtained. For instance, a type **C** or **D** input geometry for **IX** or **X** reverted back to the **B** minimum, whereas a type **B** input geometry for **XI** reverted back to the **C** minimum and a type **A** input geometry for **IX** reverted back to the starting compounds.

Table S2. Relevant metric parameters for the zwitterionic compounds **IX-XIII**.

| complex        | type     | Pt $\cdots$ N, Å | H $\cdots$ Pt, Å | N-H $\cdots$ Pt, ° | Br $\cdots$ N, Å | H $\cdots$ Br, Å | N-H $\cdots$ Br, ° | Pt-C-C-N, ° |
|----------------|----------|------------------|------------------|--------------------|------------------|------------------|--------------------|-------------|
| <b>IX</b>      | <b>B</b> | 2.92             | 1.97             | 139.9              | 3.44             | 2.89             | 114.8              | 34.6        |
| <b>X</b>       | <b>B</b> | 3.04             | 2.31             | 125.6              | 3.40             | 2.74             | 121.3              | 39.7        |
| <b>Xanti</b>   | <b>A</b> |                  |                  |                    |                  |                  |                    | 178.4       |
| <b>XI</b>      | <b>C</b> |                  |                  |                    | 3.13             | 2.15             | 153.0              | 44.6        |
| <b>XI'</b>     | <b>D</b> |                  |                  |                    | 3.15             | 2.10             | 166.3              | 69.7        |
| <b>XII</b>     | <b>B</b> | 3.10             | 2.54             | 113.7              | 3.31             | 2.49             | 134.6              | 39.6        |
| <b>XIIanti</b> | <b>A</b> |                  |                  |                    |                  |                  |                    | 178.1       |
| <b>XIII</b>    | <b>D</b> |                  |                  |                    | 3.14             | 2.09             | 166.9              | 76.5        |
| <b>XIII'</b>   | <b>B</b> | 3.19             | 2.81             | 102.2              | 3.15             | 2.22             | 147.4              | 35.2        |

### Formation of Pt<sup>IV</sup>-H intermediates from the zwitterionic complexes **X** and **XI**

Starting from **X**, moving the proton from N-H...Pt to N...H-Pt followed by optimization leads again to the **X** minimum. However, moving the PhNH<sub>2</sub> ligand *trans* to the hydride ligand led to a new Pt<sup>IV</sup>-H system, **XXI**. The residual N-H bond in this system also establishes a new H...Br interaction, although weaker than in **XX** (H...Br = 2.81 Å). Transferring a proton to Pt in **XI** yielded **XXII** without any additional ligand rearrangement, though at a much higher  $\Delta G^{\text{CPCM}}$  (20.2 kcal mol<sup>-1</sup>, vs. 1.9 kcal mol<sup>-1</sup> for the **XI** precursor). Note the presence of a Pt-H...N interaction (H...N = 1.65 Å) in **XXII** and its absence in **XX** and **XXI**. This indicates residual acidic character ( $\delta^+$  polarization) for the hydrido ligand in **XXII**. Trying to force a Pt-H...N interaction for **XX** and **XXI** did not lead to new local minima. Moving a Br<sup>-</sup> ligand in **XXII** from *trans* relative to CH<sub>2</sub>CH<sub>2</sub>NHPh to *trans* relative to H also did not yield a stable minimum (the geometry reverted back to **XXII**). A new minimum (**XXII'**), though at higher  $\Delta G^{\text{CPCM}}$ , was obtained by moving the H bond from Pt-H...N to N-H...N. All attempts to transfer the ammonium proton to the Pt atom in complexes **XII** and **XIII'** were unsuccessful, leading back to the zwitterionic precursor during the optimization.

### Formation of chelated aminoalkyl Pt<sup>II</sup> complexes

Starting from the tribromo species **XXVIII**, only one anionic dibromo complex, **XXXIII**, can be obtained. For the two isomeric aniline-dibromido complexes **XXIX** and **XXX**, the *trans* isomer leads to a monobromido species with the PhNH<sub>2</sub> ligand *trans* to the C atom and the Br ligand *trans* to the N atom (**XXXIV**), whereas the *cis* isomer affords the stereoisomer where the PhNH<sub>2</sub> and Br ligands have exchanged position (**XXXIV'**). Analogously, the two isomeric ethylene-dibromido complexes **XXXI** and **XXXII** lead to the two isomeric complexes **XXXV** and **XXXV'**, respectively.

## Formation of chelated aminoalkyl Pt<sup>IV</sup> complexes

The tribromo complex **XX** (Figure S1 *f*) leads to an anionic complex of formula  $[\text{PtHBr}_3(\kappa^2\text{:C,N-CH}_2\text{CH}_2\text{NHPH})]^-$ , for which four stereoisomers can be conceived. These are shown in Figure S1 *k1*. Two of these are *fac*-PtBr<sub>3</sub> isomers, differing for the placement of the *trans* H and Br ligands relative to the NHPH substituents (**XXXVI** and **XXXVI'**). The other two display a *mer*-PtBr<sub>3</sub> geometry, with either H *trans* to the alkyl chain, **XXXVII**, or *trans* to the NHPH group, **XXXVII'**. Starting from the aniline-dibromo isomers **XXI** and **XXII** (or alternative by HBr oxidative addition to **XXXIV** or **XXXIV'**) the isomeric neutral dibromo species  $[\text{PtHBr}_2(\text{PhNH}_2)(\kappa^2\text{:C,N-CH}_2\text{CH}_2\text{NHPH})]$ , **XXXVIII-XLIV**, shown in Figure S1 *k2* may be obtained. Each pair of primed and unprimed isomers are diastereomeric pairs with different relative chirality at the metal atom and at the N donor atom that is part of the ring. Finally, additional systems may be derived by formal HBr oxidative addition to the ethylene-dibromo isomers **XXXV** and **XXXV'** of Figure S1 *j*. This led to the diastereomeric pairs **XLV/XLV'** and **XLVI/XLVI'**, respectively, shown in Figure S1 *k3*. Removal of the Br<sup>-</sup> ligand *trans* to H from **XXXVI** and optimization led to neutral  $[\text{PtHBr}_2(\kappa^2\text{:C,N-CH}_2\text{CH}_2\text{NHPH})]$  with structure **XLVII** where a geometry rearrangement has transferred the vacant site *trans* to the alkyl group, Figure S1 *l*. Analogously, the cationic complex  $[\text{PtHBr}(\text{PhNH}_2)(\kappa^2\text{:C,N-CH}_2\text{CH}_2\text{NHPH})]^+$  with the isomeric structures **XLVIII** and **IL** was obtained upon removing the Br<sup>-</sup> *trans* to H from **XXXVIII** and **XLIII**, in these cases without stereochemical rearrangement.

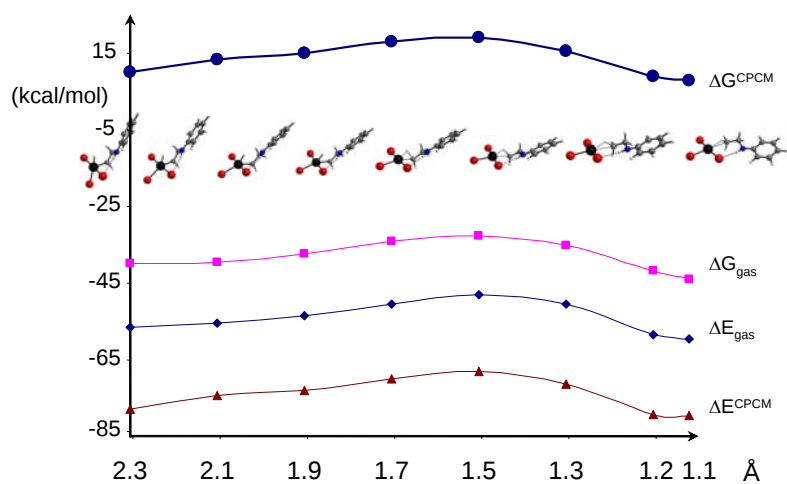


Figure S6. Reaction coordinate for the reductive elimination of PhNH-Et from complex **XX**.

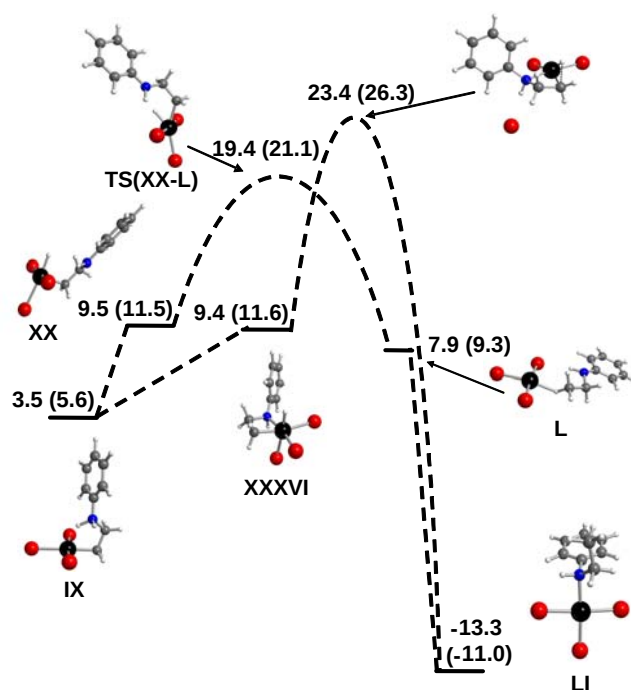


Figure S7. Comparison of the reductive eliminations from systems **XX** and **XXXVI**, with views of the relevant geometries and their relative  $\Delta G^{\text{CPCM}}$  in kcal mol<sup>-1</sup> at 298.15 K (and at 423.15 K in parentheses).

### Intermolecular proton transfer from the zwitterionic anilinium group to carbon.

The pathways starts with the intermolecular deprotonation of the zwitterionic complexes **IX-XIII** by aniline to afford the aminoalkyl complexes **XXVIII-XXXII** and an anilinium ion. We analyze here the intermolecular proton transfer from  $\text{PhNH}_3^+$  to the Pt-bonded C atom of the aminoalkyl ligand. Complex **XXXII** was chosen for the analysis of pathway (a1) because it has the lowest  $\Delta G^{\text{CPCM}}$  amongst all the deprotonated zwitterions **XXVIII-XXXII** (Figure 10). The second lowest  $\Delta G^{\text{CPCM}}$  derivative (**XXIX**), however, was also used for comparison. Starting from a partially optimized **XXXII**· $\text{PhNH}_3^+$  adduct, **LII**, where the C··H distance had been kept fixed at 2.84 Å, shown in Figure S1 o, a scan along the NH··C<sub>Pt</sub> coordinate led to the generation of **LIII** through the transition state **TS(LII-LIII)** and the adduct **LIII**· $\text{PhNH}_2$ , also shown in Figure S1 o. The transition state has the expected geometry, with the proton midway between the N and C atoms (N··H, 1.99 Å, H··C, 1.67 Å) but also showing a short contact to the Pt atom (H··Pt, 1.62 Å) suggesting significant metal assistance, and an imaginary frequency of 832i  $\text{cm}^{-1}$  along the expected motion of the proton from N to C. Starting from a second isomer **LII'** (differing from isomer **LII** by the relative position of the Ph group and a H atom on the aminoalkyl ligand), a related scan leads to **LIII** through the transition state **TS(LII'-LIII)** and the adduct **LIII'**· $\text{PhNH}_2$ . Starting from **LIII**· $\text{PhNH}_2$  or **LIII'**· $\text{PhNH}_2$ , aniline coordination displaces the  $\sigma$ -bonded  $\text{PhNHEt}$  product to yield a  $\text{PhNHEt}$  adduct of compound *cis*- $\text{PtBr}_2(\text{C}_2\text{H}_4)(\text{PhNH}_2)$ , **V**.

While the final isomeric adducts **LIII**· $\text{PhNH}_2$  and **LIII'**· $\text{PhNH}_2$  are very similar in geometry and energy, the transition states **TS(LII-LIII)** and **TS(LII'-LIII)** are significantly different: the former features the transferring proton much closer to the Pt atom (1.62 Å) and further away from the N atom (1.99 Å) and C atom (1.67 Å) relative to the latter (respectively, 2.20, 1.23 and 1.44 Å). In other words, isomer **TS(LII'-LIII)** seems more like a direct transfer of the proton from the N to the C atom with little metal assistance, whereas isomer **TS(LII-LIII)** shows a strong metal assistance. However, the energy of both transition states is too high to make these two pathways competitive relative to **TS(XX-L)**.

Starting from a partially optimized **XXIX**·PhNH<sub>3</sub><sup>+</sup> adduct, **LIV**, with the C··H distance kept fixed at 2.45 Å, the proton transfer pathway led to **LV** through transition state **TS(LIV-LV)**, which is geometrically similar to **TS(LII-LIII)**, also revealing the metal assistance, and also placed at quite high energy. The geometries of these two systems are featured in Figure S1 *o*. In conclusion, the intermolecular protonolysis pathway (1a) of Scheme 5 appears less favorable than the reductive elimination via the 5-coordinated Pt<sup>IV</sup> hydride.

### **Intramolecular proton transfer from the zwitterionic anilinium group to carbon with added aniline as proton shuttle.**

The concerted pathway (b2) of Scheme 5 was checked through a scan along the PtC··HN coordinate starting from the **XIII**·PhNH<sub>2</sub> (**b**) (Figure 3) and **LVI**, the latter being obtained by addition of an external aniline molecule to complex **XI**, see Figure S1 *p*. Complex **LVI** is 7 kcal/mol less stable than **XIII**·PhNH<sub>2</sub> (**b**) on both the  $\Delta G^{\text{CPCM}}$  and  $\Delta G^{\text{CPCM}}_{\text{cor}}$  scales, whereas the preference in favor of the latter is reduced to 1.2 kcal/mol on the  $\Delta E_{\text{gas}}$  scale. The  $\Delta G_{\text{solv}}$  term is almost equal for both complexes, the difference originating from  $\Delta G_{\text{solv}}$  of the free ligands (nearly 0 for PhNH<sub>2</sub>, ca. 5 kcal mol<sup>-1</sup> for C<sub>2</sub>H<sub>2</sub>). From the geometrical point of view, both complexes seem perfectly set up for a proton transfer through this mechanism. The proton transfer from **XIII**·PhNH<sub>2</sub> (**b**) leads to the final product **LIII**·PhNH<sub>2</sub>, already shown in Figure S1 *o*, through a transition state **TS(XIII-LIII)** which is identical to **TS(LII-LIII)** already discussed above (Figure S1 *o*). The proton transfer from **LVI** produces product **LVII** through **TS(LVI-LVII)**, shown in Figure S1 *p*. The geometry of **TS(LVI-LVII)** is very similar to that of **TS(LII'-LIII)**, shown in Figure S1 *o*, namely with little metal assistance to the proton transfer. The final product **LVII** is the aniline adduct of a  $\sigma$ -complex *cis*-PtBr<sub>2</sub>(PhNH<sub>2</sub>)( $\kappa^2$ :C,*H*-PhNH<sub>2</sub>Et), isomer of the previously analyzed complex **LV** (Figure S1 *o*), the latter being slightly more stable.

The energies of the transition states for these two (b2)-type pathways are quite high. One reason for these high barriers may be attributed to the unfavourable entropic component because

of the association of the additional aniline molecule. However, calculation of the  $\Delta G^{\text{CPCM}}_{\text{cor}}$  parameters by taking the H-bonded dimer aniline...aniline as a reference, as already detailed above in section (a), yields lower but still high values for the activation barriers, relative to that of the C-H reductive elimination from **XX**.

Table S3. Cartesian coordinates of all optimized geometries reported in this study.

(Note: the Cartesian coordinates of systems **I-VIII** have been reported in a previously published contribution: Dub, P. A.; Rodriguez-Zubiri, M.; Daran, J.-C.; Brunet, J.-J.; Poli, R. *Organometallics* **2009**, 28, 4764–4777).

| <i>trans</i> -PtBr <sub>2</sub> (PhNH <sub>2</sub> ) <b>VI*</b>                                         |              |              |              | [PtBr <sub>2</sub> (PhNH <sub>2</sub> )(CH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub> Ph)] <b>X</b>              |              |              |              |
|---------------------------------------------------------------------------------------------------------|--------------|--------------|--------------|--------------------------------------------------------------------------------------------------------------------|--------------|--------------|--------------|
| SCF Done: -5837.36488221                                                                                |              |              |              | SCF Done: -5915.951868                                                                                             |              |              |              |
| C                                                                                                       | -3.639261000 | -1.260291000 | -0.576909000 | 6                                                                                                                  | 3.986705000  | 0.989984000  | -0.718115000 |
| C                                                                                                       | -2.977256000 | -0.032208000 | -0.612242000 | 6                                                                                                                  | 3.218681000  | -0.125052000 | -1.070328000 |
| C                                                                                                       | -3.549750000 | 1.108878000  | -0.045429000 | 6                                                                                                                  | 3.790653000  | -1.400658000 | -1.082004000 |
| C                                                                                                       | -4.810679000 | 1.016106000  | 0.547080000  | 6                                                                                                                  | 5.138952000  | -1.556960000 | -0.751372000 |
| C                                                                                                       | -5.487446000 | -0.207383000 | 0.586290000  | 6                                                                                                                  | 5.917738000  | -0.447338000 | -0.410872000 |
| C                                                                                                       | -4.896807000 | -1.343536000 | 0.026761000  | 6                                                                                                                  | 5.335221000  | 0.824120000  | -0.395979000 |
| N                                                                                                       | -1.664995000 | 0.062073000  | -1.247923000 | 7                                                                                                                  | 1.816692000  | 0.040911000  | -1.383053000 |
| Pt                                                                                                      | -0.000015000 | 0.058020000  | -0.000048000 | 78                                                                                                                 | 0.427521000  | 0.106513000  | 0.348608000  |
| Br                                                                                                      | -0.000012000 | -2.424468000 | -0.000040000 | 6                                                                                                                  | -0.808111000 | 0.182005000  | 1.997647000  |
| Br                                                                                                      | 0.000004000  | 2.548677000  | -0.000053000 | 35                                                                                                                 | 0.202999000  | -2.388362000 | 0.285000000  |
| N                                                                                                       | 1.664944000  | 0.062051000  | 1.247881000  | 35                                                                                                                 | 0.420264000  | 2.578131000  | 0.171336000  |
| H                                                                                                       | -1.604854000 | 0.926436000  | -1.792213000 | 1                                                                                                                  | 1.490098000  | -0.715197000 | -1.983886000 |
| H                                                                                                       | -1.541388000 | -0.717766000 | -1.897346000 | 1                                                                                                                  | 1.654263000  | 0.926594000  | -1.863935000 |
| H                                                                                                       | -3.005542000 | 2.048836000  | -0.052719000 | 1                                                                                                                  | 3.180399000  | -2.265775000 | -1.327299000 |
| H                                                                                                       | -5.259732000 | 1.903254000  | 0.985324000  | 1                                                                                                                  | 5.577741000  | -2.551326000 | -0.759293000 |
| H                                                                                                       | -6.466868000 | -0.274696000 | 1.051905000  | 1                                                                                                                  | 6.966775000  | -0.572137000 | -0.156427000 |
| H                                                                                                       | -5.411283000 | -2.300053000 | 0.057775000  | 1                                                                                                                  | 5.928739000  | 1.693414000  | -0.124977000 |
| H                                                                                                       | -3.169806000 | -2.145885000 | -0.995954000 | 1                                                                                                                  | 3.525206000  | 1.973103000  | -0.680199000 |
| C                                                                                                       | 2.977246000  | -0.032217000 | 0.612298000  | 6                                                                                                                  | -2.267218000 | 0.400784000  | 1.614375000  |
| H                                                                                                       | 1.541263000  | -0.717811000 | 1.897262000  | 7                                                                                                                  | -2.567642000 | -0.426079000 | 0.361262000  |
| H                                                                                                       | 1.604761000  | 0.926404000  | 1.792174000  | 6                                                                                                                  | -3.892822000 | -0.271329000 | -0.236206000 |
| C                                                                                                       | 3.549834000  | 1.108882000  | 0.045608000  | 6                                                                                                                  | -4.175365000 | 0.892990000  | -0.952338000 |
| C                                                                                                       | 4.810823000  | 1.016103000  | -0.546771000 | 6                                                                                                                  | -5.446641000 | 1.051414000  | -1.507938000 |
| C                                                                                                       | 5.487552000  | -0.207408000 | -0.585986000 | 6                                                                                                                  | -6.416083000 | 0.055741000  | -1.347237000 |
| C                                                                                                       | 4.896813000  | -1.343576000 | -0.026599000 | 6                                                                                                                  | -6.115375000 | -1.105025000 | -0.629533000 |
| C                                                                                                       | 3.639208000  | -1.260324000 | 0.576944000  | 6                                                                                                                  | -4.845770000 | -1.275141000 | -0.069966000 |
| H                                                                                                       | 3.005655000  | 2.048857000  | 0.052903000  | 1                                                                                                                  | -3.415561000 | 1.660671000  | -1.074793000 |
| H                                                                                                       | 5.259954000  | 1.903262000  | -0.984910000 | 1                                                                                                                  | -5.676267000 | 1.952419000  | -2.069343000 |
| H                                                                                                       | 6.467023000  | -0.274727000 | -1.051497000 | 1                                                                                                                  | -7.403142000 | 0.184363000  | -1.782217000 |
| H                                                                                                       | 5.411261000  | -2.300109000 | -0.057619000 | 1                                                                                                                  | -6.864040000 | -1.882150000 | -0.505859000 |
| H                                                                                                       | 3.169677000  | -2.145923000 | 0.995891000  | 1                                                                                                                  | -4.604742000 | -2.178015000 | 0.486116000  |
| [PtBr <sub>3</sub> (CH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub> Ph)] <sup>-</sup> <b>IX</b>         |              |              |              | 1                                                                                                                  | -1.776173000 | -0.159291000 | -0.279181000 |
| SCF Done: -8199.841449                                                                                  |              |              |              | 1                                                                                                                  | -2.346944000 | -1.413730000 | 0.560285000  |
| Pt                                                                                                      | 0.962916000  | 0.003935000  | -0.353597000 | 1                                                                                                                  | -3.000064000 | 0.092833000  | 2.369207000  |
| Br                                                                                                      | 2.223586000  | -0.412838000 | 1.861610000  | 1                                                                                                                  | -2.458064000 | 1.437219000  | 1.327084000  |
| Br                                                                                                      | 1.068555000  | 2.510647000  | -0.080159000 | 1                                                                                                                  | -0.702252000 | -0.745978000 | 2.572783000  |
| C                                                                                                       | -0.033712000 | 0.348103000  | -2.155937000 | 1                                                                                                                  | -0.503487000 | 1.015973000  | 2.640484000  |
| H                                                                                                       | 0.262396000  | -0.398824000 | -2.902264000 | [PtBr <sub>2</sub> (PhNH <sub>2</sub> )(CH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub> Ph)] <b>Xanti</b>          |              |              |              |
| C                                                                                                       | 0.222678000  | 1.343980000  | -2.535343000 | SCF Done: -5915.931298                                                                                             |              |              |              |
| C                                                                                                       | -1.543472000 | 0.226823000  | -1.938102000 | Pt                                                                                                                 | -0.593421000 | 0.011760000  | 0.018391000  |
| H                                                                                                       | -1.850659000 | -0.821008000 | -1.923304000 | Br                                                                                                                 | -0.439764000 | -2.476329000 | -0.103699000 |
| H                                                                                                       | -2.178245000 | 0.783705000  | -2.639959000 | N                                                                                                                  | -2.343169000 | -0.051112000 | -1.301858000 |
| N                                                                                                       | -1.852509000 | 0.753544000  | -0.537601000 | Br                                                                                                                 | -0.637890000 | 2.497935000  | -0.071398000 |
| H                                                                                                       | -0.946494000 | 0.367856000  | -0.009114000 | H                                                                                                                  | -2.210657000 | -0.892705000 | -1.864063000 |
| H                                                                                                       | -1.678923000 | 1.766474000  | -0.508947000 | C                                                                                                                  | -2.248220000 | 0.760701000  | -1.912375000 |
| C                                                                                                       | -3.116312000 | 0.383524000  | 0.064973000  | H                                                                                                                  | -3.639432000 | -0.059928000 | -0.660834000 |
| C                                                                                                       | -3.289580000 | -0.940411000 | 0.482394000  | C                                                                                                                  | -4.163389000 | -1.263054000 | -0.176174000 |
| C                                                                                                       | -4.499953000 | -1.309988000 | 1.071151000  | C                                                                                                                  | -5.410173000 | -1.268506000 | 0.452169000  |
| C                                                                                                       | -5.522820000 | -0.370031000 | 1.246560000  | C                                                                                                                  | -6.130425000 | -0.079966000 | 0.611628000  |
| C                                                                                                       | -5.331390000 | 0.951572000  | 0.833766000  | C                                                                                                                  | -5.591714000 | 1.119396000  | 0.137219000  |
| C                                                                                                       | -4.123573000 | 1.333707000  | 0.242421000  | C                                                                                                                  | -4.347916000 | 1.134315000  | -0.499148000 |
| H                                                                                                       | -2.479000000 | -1.655858000 | 0.359202000  | H                                                                                                                  | -3.584975000 | -2.177802000 | -0.271780000 |
| H                                                                                                       | -4.637826000 | -2.334753000 | 1.405484000  | H                                                                                                                  | -5.814153000 | -2.206067000 | 0.825606000  |
| H                                                                                                       | -6.460422000 | -0.665327000 | 1.709649000  | H                                                                                                                  | -7.099445000 | -0.088330000 | 1.103651000  |
| H                                                                                                       | -6.117628000 | 1.689044000  | 0.973994000  | H                                                                                                                  | -6.137197000 | 2.051234000  | 0.262703000  |
| H                                                                                                       | -3.966222000 | 2.361895000  | -0.075347000 | H                                                                                                                  | -3.919045000 | 2.069610000  | -0.848659000 |
| Br                                                                                                      | 0.492205000  | -2.433773000 | -0.684127000 | C                                                                                                                  | 1.031231000  | 0.061291000  | 1.267138000  |
| [PtBr <sub>3</sub> (CH <sub>2</sub> CH <sub>2</sub> )NH <sub>2</sub> Ph)] <sup>-</sup> <b>TS(II-IX)</b> |              |              |              | C                                                                                                                  | 2.237281000  | 0.049547000  | 0.380518000  |
| SCF Done: -8199.823940                                                                                  |              |              |              | N                                                                                                                  | 3.569653000  | 0.043609000  | 1.271021000  |
| Pt                                                                                                      | -1.062701000 | 0.000961000  | -0.221000000 | C                                                                                                                  | 4.845910000  | 0.025587000  | 0.551301000  |
| C                                                                                                       | 1.296115000  | 0.022349000  | -0.588539000 | C                                                                                                                  | 5.373805000  | -1.198285000 | 0.140402000  |
| C                                                                                                       | 0.429043000  | 0.021794000  | -1.715445000 | C                                                                                                                  | 6.563659000  | -1.207896000 | -0.591141000 |
| Br                                                                                                      | -0.952895000 | -2.507969000 | -0.256994000 | C                                                                                                                  | 7.205477000  | -0.006493000 | -0.907031000 |
| Br                                                                                                      | -0.999683000 | 2.510940000  | -0.234502000 | C                                                                                                                  | 6.657341000  | 1.211213000  | -0.493544000 |
| H                                                                                                       | 1.490652000  | 0.944255000  | -0.053239000 | C                                                                                                                  | 5.467862000  | 1.233876000  | 0.238938000  |
| H                                                                                                       | 0.341163000  | 0.942845000  | -2.292102000 | H                                                                                                                  | 1.010313000  | -0.824436000 | 1.918320000  |
| H                                                                                                       | 0.353554000  | -0.894545000 | -2.301465000 | H                                                                                                                  | 0.997365000  | 0.973630000  | 1.878991000  |
| H                                                                                                       | 1.497871000  | -0.900477000 | -0.057845000 | H                                                                                                                  | 3.485710000  | -0.769689000 | 1.889076000  |
| N                                                                                                       | 3.159589000  | 0.023160000  | -1.314808000 | H                                                                                                                  | 3.504618000  | 0.864796000  | 1.880539000  |
| C                                                                                                       | 4.264151000  | 0.012605000  | -0.434544000 | H                                                                                                                  | 2.341560000  | 0.942437000  | -0.238810000 |
| C                                                                                                       | 4.789119000  | 1.220020000  | 0.056834000  | H                                                                                                                  | 2.329287000  | -0.852442000 | -0.227296000 |
| C                                                                                                       | 5.807610000  | 1.203827000  | 1.010291000  | H                                                                                                                  | 4.866191000  | -2.129759000 | 0.379678000  |
| C                                                                                                       | 6.314112000  | -0.008002000 | 1.492367000  | H                                                                                                                  | 6.985161000  | -2.155274000 | -0.913713000 |
| C                                                                                                       | 5.782160000  | -1.209371000 | 1.011393000  | H                                                                                                                  | 8.130296000  | -0.019322000 | -1.476308000 |
| C                                                                                                       | 4.763453000  | -1.205221000 | 0.058066000  | H                                                                                                                  | 7.151723000  | 2.146251000  | -0.739590000 |
| H                                                                                                       | 3.103490000  | 0.854605000  | -1.896535000 | H                                                                                                                  | 5.033730000  | 2.179609000  | 0.555079000  |
| H                                                                                                       | 3.093153000  | -0.802676000 | -1.903299000 | <i>cis</i> -[PtBr <sub>2</sub> (PhNH <sub>2</sub> )(CH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub> Ph)] <b>XI</b> |              |              |              |
| H                                                                                                       | 4.390929000  | 2.166428000  | -0.302672000 | SCF Done: -5915.93529122                                                                                           |              |              |              |
| H                                                                                                       | 6.203066000  | 2.146256000  | 1.381380000  | Pt                                                                                                                 | 0.607977000  | -0.323192000 | -0.145742000 |
| H                                                                                                       | 7.105215000  | -0.015994000 | 2.237238000  | Br                                                                                                                 | -1.098766000 | -1.654517000 | 1.100123000  |
| H                                                                                                       | 6.157447000  | -2.159530000 | 1.383661000  | C                                                                                                                  | -0.281952000 | 1.526706000  | 0.207526000  |
| H                                                                                                       | 4.344955000  | -2.143290000 | -0.300121000 | N                                                                                                                  | 2.148167000  | 0.648531000  | -1.188359000 |
| Br                                                                                                      | -3.132636000 | -0.023627000 | 1.211615000  | C                                                                                                                  | -1.761634000 | 1.598847000  | 0.558010000  |





SCF Done: -10692.64283

|    |              |              |              |
|----|--------------|--------------|--------------|
| Br | 0.218866000  | -0.085674000 | 2.413693000  |
| Pt | 0.474054000  | 0.069416000  | -0.319114000 |
| Br | 1.417617000  | 2.436455000  | -0.315402000 |
| Br | -0.456764000 | -2.240715000 | -0.772958000 |
| N  | -1.339944000 | 0.997309000  | -0.535113000 |
| H  | 0.631505000  | 0.142819000  | -1.853139000 |
| H  | -1.232386000 | 1.757689000  | -1.196572000 |
| C  | -2.634525000 | 0.639208000  | -0.344584000 |
| C  | -3.047841000 | -0.353851000 | 0.591238000  |
| C  | -4.394409000 | -0.626018000 | 0.794643000  |
| C  | -5.412535000 | 0.057937000  | 0.102568000  |
| C  | -5.024532000 | 1.043138000  | -0.816048000 |
| C  | -3.678248000 | 1.325752000  | -1.041361000 |
| H  | -2.286203000 | -0.871204000 | 1.161597000  |
| H  | -4.662210000 | -1.391520000 | 1.523876000  |
| H  | -6.463452000 | -0.170514000 | 0.274246000  |
| H  | -5.780934000 | 1.597515000  | -1.374958000 |
| H  | -3.401798000 | 2.090634000  | -1.768025000 |
| Br | 2.841750000  | -0.912010000 | -0.292450000 |

*mer*-[PtH(C<sub>2</sub>H<sub>4</sub>)Br<sub>3</sub>NHPh]<sup>-</sup> **XV**

SCF Done: -8199.808599

|    |              |              |              |
|----|--------------|--------------|--------------|
| Br | 0.656846000  | -0.603110000 | 2.286200000  |
| Pt | 0.637628000  | -0.039122000 | -0.376227000 |
| Br | 2.163784000  | 1.978538000  | -0.177318000 |
| Br | -0.804815000 | -2.025012000 | -0.980450000 |
| N  | -0.887918000 | 1.281019000  | -0.041238000 |
| H  | 0.478117000  | 0.357925000  | -1.872466000 |
| H  | -0.690902000 | 2.092141000  | -0.621182000 |
| C  | -2.249967000 | 1.024877000  | -0.009112000 |
| C  | -2.798994000 | 0.039608000  | 0.846214000  |
| C  | -4.176988000 | -0.108152000 | 0.961906000  |
| C  | -5.063715000 | 0.716027000  | 0.250942000  |
| C  | -4.534190000 | 1.697808000  | -0.592537000 |
| C  | -3.152563000 | 1.841700000  | -0.733018000 |
| H  | -2.122391000 | -0.579682000 | 1.424183000  |
| H  | -4.569453000 | -0.874312000 | 1.628604000  |
| H  | -6.139765000 | 0.592809000  | 0.352893000  |
| H  | -5.198683000 | 2.348989000  | -1.159023000 |
| H  | -2.753238000 | 2.598341000  | -1.407705000 |
| C  | 2.347652000  | -1.136908000 | -1.448954000 |
| C  | 2.459860000  | -1.458108000 | -0.112073000 |
| H  | 3.121415000  | -0.905466000 | 0.545182000  |
| H  | 2.023872000  | -2.368129000 | 0.284062000  |
| H  | 1.848072000  | -1.808447000 | -2.140065000 |
| H  | 2.943280000  | -0.335484000 | -1.875414000 |

[PtHBr<sub>3</sub>NHPh]<sup>-</sup> **XV'**

SCF Done: -8199.814058

|    |              |              |              |
|----|--------------|--------------|--------------|
| 78 | -0.408031000 | 0.030337000  | 0.069288000  |
| 35 | -0.452953000 | 2.534307000  | -0.144870000 |
| 35 | -0.298123000 | -2.477020000 | 0.331857000  |
| 7  | 1.443165000  | 0.247364000  | 0.973707000  |
| 1  | 0.250340000  | -0.058528000 | -1.304684000 |
| 1  | 1.427073000  | 1.176184000  | 1.391539000  |
| 6  | 2.646142000  | 0.101656000  | 0.293928000  |
| 2  | 9.222148000  | -0.998175000 | -0.554514000 |
| 6  | 4.179516000  | -1.156780000 | -1.132973000 |
| 6  | 5.214736000  | -0.241174000 | -0.897632000 |
| 6  | 4.954935000  | 0.854594000  | -0.066288000 |
| 3  | 6.696920000  | 1.030822000  | 0.508157000  |
| 1  | 2.141779000  | -1.728716000 | -0.735289000 |
| 1  | 4.353932000  | -2.015674000 | -1.779299000 |
| 1  | 6.191980000  | -0.373972000 | -1.356034000 |
| 1  | 5.733579000  | 1.591760000  | 0.125003000  |
| 1  | 3.508201000  | 1.900797000  | 1.135455000  |
| 6  | -0.992682000 | 0.228006000  | 2.667289000  |
| 6  | -2.190184000 | 0.101158000  | 2.059990000  |
| 1  | -2.765110000 | 0.968257000  | 1.749559000  |
| 1  | -2.633697000 | -0.871911000 | 1.874469000  |
| 1  | -0.417495000 | -0.634606000 | 2.988716000  |
| 1  | -0.571300000 | 1.208399000  | 2.873169000  |
| 35 | -2.622758000 | -0.193872000 | -1.228437000 |

[PtHBr<sub>3</sub>NHPh]<sup>-</sup> **XVI**

SCF Done: -8199.802308

|    |              |              |              |
|----|--------------|--------------|--------------|
| 78 | -0.554024000 | -0.167256000 | 0.466589000  |
| 35 | -2.995996000 | -0.556979000 | -0.267653000 |
| 35 | 0.343736000  | -1.563704000 | -1.401495000 |
| 7  | 1.323301000  | 0.032491000  | 1.380185000  |
| 1  | -0.643894000 | -1.570682000 | 1.133970000  |
| 1  | 1.328215000  | -0.720569000 | 2.066962000  |
| 6  | 2.567858000  | 0.006001000  | 0.746154000  |
| 6  | 2.908792000  | 0.909468000  | -0.284992000 |
| 6  | 4.208301000  | 0.957707000  | -0.781757000 |
| 6  | 5.215513000  | 0.120175000  | -0.280025000 |
| 6  | 4.887477000  | -0.789407000 | 0.730070000  |
| 6  | 3.583331000  | -0.857342000 | 1.222158000  |
| 1  | 2.137197000  | 1.556799000  | -0.686328000 |
| 1  | 4.439050000  | 1.662716000  | -1.578548000 |
| 1  | 6.227393000  | 0.168550000  | -0.676399000 |
| 1  | 5.644021000  | -1.464901000 | 1.126752000  |
| 1  | 3.336939000  | -1.587913000 | 1.992549000  |
| 6  | -1.355287000 | 0.210132000  | 2.539465000  |
| 6  | -1.265774000 | 1.435522000  | 1.893598000  |
| 1  | -0.398310000 | 2.070591000  | 2.030339000  |

|    |              |              |              |
|----|--------------|--------------|--------------|
| 1  | -2.132908000 | 1.872367000  | 1.412156000  |
| 1  | -0.572699000 | -0.105306000 | 3.223353000  |
| 1  | -2.299809000 | -0.322454000 | 2.585930000  |
| 35 | -0.422474000 | 2.100848000  | -0.999253000 |

[PtHBr<sub>3</sub>NHPh]<sup>-</sup> **XVII**

SCF Done: -8121.216016

|    |              |              |              |
|----|--------------|--------------|--------------|
| Br | 2.852773000  | -0.918031000 | 0.028692000  |
| Pt | 0.498481000  | 0.059554000  | -0.004522000 |
| Br | 1.436186000  | 2.389576000  | 0.037456000  |
| Br | -0.420106000 | -2.254070000 | -0.192543000 |
| N  | -1.243643000 | 0.936449000  | 0.494166000  |
| H  | 0.829440000  | -0.035895000 | -1.492534000 |
| H  | -1.101347000 | 1.929726000  | 0.318263000  |
| C  | -2.581072000 | 0.614487000  | 0.243572000  |
| C  | -3.179369000 | -0.548884000 | 0.774434000  |
| C  | -4.537321000 | -0.799713000 | 0.587469000  |
| C  | -5.350446000 | 0.102990000  | -0.111065000 |
| C  | -4.775033000 | 1.269053000  | -0.627270000 |
| C  | -3.412385000 | 1.518373000  | -0.458090000 |
| H  | -2.563488000 | -1.243558000 | 1.331519000  |
| H  | -4.969855000 | -1.707601000 | 1.003925000  |
| H  | -6.410476000 | -0.098746000 | -0.248236000 |
| H  | -5.386712000 | 1.985856000  | -1.172542000 |
| H  | -2.969685000 | 2.420398000  | -0.877324000 |

[PtHBr<sub>2</sub>(C<sub>2</sub>H<sub>4</sub>)NHPh]<sup>-</sup> **XVIII**

SCF Done: -5628.264662

|    |              |              |              |
|----|--------------|--------------|--------------|
| Pt | -0.744401000 | 0.132023000  | -0.017656000 |
| Br | -2.155338000 | -1.933409000 | 0.059987000  |
| Br | 0.576442000  | 2.242372000  | -0.237065000 |
| N  | 0.786041000  | -1.032913000 | 0.370307000  |
| H  | -0.866276000 | 0.163578000  | -1.558101000 |
| H  | 0.502742000  | -1.998339000 | 0.203868000  |
| C  | 2.176095000  | -0.897090000 | 0.201946000  |
| C  | 2.899668000  | 0.081103000  | 0.908278000  |
| C  | 4.286376000  | 0.147541000  | 0.789842000  |
| C  | 4.977104000  | -0.763168000 | -0.018286000 |
| C  | 4.266467000  | -1.751590000 | -0.707895000 |
| C  | 2.878426000  | -1.820795000 | -0.598492000 |
| H  | 2.367911000  | 0.768909000  | 1.554629000  |
| H  | 4.833223000  | 0.907355000  | 1.342104000  |
| H  | 6.058954000  | -0.707398000 | -0.103862000 |
| H  | 4.792758000  | -2.468085000 | -1.333246000 |
| H  | 2.324742000  | -2.582822000 | -1.142930000 |
| C  | -2.613465000 | 1.361448000  | -0.531744000 |
| C  | -2.472482000 | 1.361070000  | 0.846110000  |
| H  | -3.023548000 | 0.653761000  | 1.459492000  |
| H  | -1.992542000 | 2.192616000  | 1.353557000  |
| H  | -2.265154000 | 2.206377000  | -1.117495000 |
| H  | -3.299626000 | 0.671864000  | -1.013802000 |

[PtHBr<sub>2</sub>(C<sub>2</sub>H<sub>4</sub>)NHPh]<sup>-</sup> **XVIII'**

SCF Done: -5628.249113

|    |              |              |              |
|----|--------------|--------------|--------------|
| Pt | 0.708789000  | 0.048710000  | -0.172261000 |
| Br | 1.157671000  | -2.377720000 | -0.425226000 |
| Br | 0.587615000  | 2.509334000  | -0.363235000 |
| N  | -0.890183000 | -0.460838000 | 1.055543000  |
| H  | -0.194879000 | -0.039785000 | -1.413976000 |
| H  | -0.719460000 | -1.457505000 | 1.223353000  |
| C  | -2.185304000 | -0.336174000 | 0.555669000  |
| C  | -2.734922000 | 0.950224000  | 0.345195000  |
| C  | -4.073953000 | 1.086696000  | 0.002404000  |
| C  | -4.889895000 | -0.046534000 | -0.139862000 |
| C  | -4.353532000 | -1.325279000 | 0.053854000  |
| C  | -3.007601000 | -1.474133000 | 0.377411000  |
| H  | -2.090610000 | 1.817359000  | 0.447158000  |
| H  | -4.490207000 | 2.077792000  | -0.155807000 |
| H  | -5.936166000 | 0.068071000  | -0.410087000 |
| H  | -4.981184000 | -2.204286000 | -0.064627000 |
| H  | -2.579331000 | -2.465684000 | 0.504072000  |
| C  | 1.906829000  | 0.199569000  | 2.113300000  |
| C  | 2.869698000  | 0.285751000  | 1.164235000  |
| H  | 3.407798000  | -0.595708000 | 0.826681000  |
| H  | 3.197909000  | 1.249529000  | 0.783818000  |
| H  | 1.418312000  | 1.084109000  | 2.510794000  |
| H  | 1.640641000  | -0.754591000 | 2.559102000  |

[PtHBr<sub>2</sub>(C<sub>2</sub>H<sub>4</sub>)NHPh]<sup>-</sup> **XIX**

SCF Done: -5628.249722

|    |              |              |              |
|----|--------------|--------------|--------------|
| Pt | 0.619821000  | 0.380108000  | -0.086404000 |
| Br | 2.975545000  | -0.573620000 | 0.294097000  |
| Br | -0.298421000 | -1.876112000 | -0.427197000 |
| N  | -1.153592000 | 1.196802000  | 0.300706000  |
| H  | 1.304787000  | 0.033559000  | -1.430520000 |
| H  | -1.174628000 | 2.159985000  | -0.032676000 |
| C  | -2.457728000 | 0.667237000  | 0.238482000  |
| C  | -2.857113000 | -0.342138000 | 1.133304000  |
| C  | -4.170166000 | -0.806099000 | 1.124593000  |
| C  | -5.108760000 | -0.271463000 | 0.233265000  |
| C  | -4.722153000 | 0.739867000  | -0.651909000 |
| C  | -3.406821000 | 1.204106000  | -0.652328000 |
| H  | -2.133178000 | -0.742666000 | 1.834544000  |
| H  | -4.465788000 | -1.585426000 | 1.822044000  |
| H  | -6.132010000 | -0.637047000 | 0.232320000  |
| H  | -5.442286000 | 1.163382000  | -1.347256000 |
| H  | -3.103448000 | 1.978784000  | -1.354279000 |

|   |             |             |              |
|---|-------------|-------------|--------------|
| C | 1.429338000 | 2.416059000 | -0.628928000 |
| C | 1.482237000 | 2.300760000 | 0.752598000  |
| H | 0.701181000 | 2.716025000 | 1.382448000  |
| H | 2.400478000 | 1.998596000 | 1.245236000  |
| H | 0.626376000 | 2.954465000 | -1.126197000 |
| H | 2.315261000 | 2.224918000 | -1.227032000 |

[PtHBr<sub>3</sub>(C<sub>2</sub>H<sub>4</sub>NHPh)]<sup>-</sup> **XX**

SCF Done: -8199.849784

|    |              |              |              |
|----|--------------|--------------|--------------|
| Pt | 0.950370000  | 0.026620000  | -0.312664000 |
| Br | 0.093089000  | -2.318160000 | -0.467543000 |
| Br | 3.139236000  | -0.683944000 | 0.922221000  |
| Br | 1.680539000  | 2.382971000  | -0.613370000 |
| C  | -0.133327000 | 0.473111000  | 1.387606000  |
| H  | -0.288375000 | 0.426812000  | -1.168826000 |
| C  | -1.563768000 | 0.934059000  | 1.182465000  |
| N  | -2.425998000 | -0.121546000 | 0.685844000  |
| C  | -3.758558000 | 0.061636000  | 0.398276000  |
| C  | -4.469494000 | 1.218037000  | 0.794844000  |
| C  | -5.833356000 | 1.343532000  | 0.516230000  |
| C  | -6.530519000 | 0.341888000  | -0.163834000 |
| C  | -5.828235000 | -0.803840000 | -0.568150000 |
| C  | -4.471950000 | -0.946313000 | -0.297536000 |
| H  | -0.076799000 | -0.444383000 | 1.978289000  |
| H  | 0.455146000  | 1.260165000  | 1.861715000  |
| H  | -1.925895000 | 1.254650000  | 2.176731000  |
| H  | -1.589113000 | 1.822485000  | 0.533069000  |
| H  | -1.952565000 | -0.886146000 | 0.211728000  |
| H  | -3.956509000 | 2.017812000  | 1.319259000  |
| H  | -6.352727000 | 2.245518000  | 0.835261000  |
| H  | -7.590465000 | 0.449254000  | -0.379652000 |
| H  | -6.345141000 | -1.596076000 | -1.106624000 |
| H  | -3.939420000 | -1.838679000 | -0.619260000 |

trans-[PtHBr(C<sub>2</sub>H<sub>4</sub>NHPh)(PhNH<sub>2</sub>)] **XXI**

SCF Done: -5915.926622

|    |              |              |              |
|----|--------------|--------------|--------------|
| Pt | 0.445551000  | 0.288825000  | -0.102851000 |
| Br | 0.926143000  | 2.695817000  | -0.379800000 |
| C  | -0.849331000 | 0.624165000  | 1.491920000  |
| Br | 0.111695000  | -2.156946000 | -0.096365000 |
| H  | -0.736505000 | 0.420561000  | -1.090974000 |
| H  | -0.439917000 | 1.516768000  | 1.968944000  |
| H  | -0.725058000 | -0.257117000 | 2.127165000  |
| C  | -2.298514000 | 0.844113000  | 1.114712000  |
| H  | -2.385126000 | 1.671885000  | 0.393137000  |
| H  | -2.787224000 | 1.190667000  | 2.043600000  |
| N  | -2.950747000 | -0.365566000 | 0.662117000  |
| H  | -2.340753000 | -1.048554000 | 0.225877000  |
| C  | -4.266733000 | -0.363431000 | 0.207273000  |
| C  | -5.142579000 | 0.715078000  | 0.440362000  |
| C  | -6.470021000 | 0.653616000  | 0.003865000  |
| C  | -6.954245000 | -0.465867000 | -0.674471000 |
| C  | -6.083290000 | -1.537508000 | -0.914185000 |
| C  | -4.761055000 | -1.491500000 | -0.483049000 |
| H  | -4.796672000 | 1.602055000  | 0.961875000  |
| H  | -7.126730000 | 1.498829000  | 0.197008000  |
| H  | -7.985723000 | -0.505114000 | -1.013077000 |
| H  | -6.437374000 | -2.418455000 | -1.444568000 |
| H  | -4.096021000 | -2.331798000 | -0.671885000 |
| N  | 2.266769000  | 0.118869000  | 1.273081000  |
| C  | 3.461929000  | -0.369977000 | 0.617443000  |
| C  | 3.846376000  | -1.705517000 | 0.766219000  |
| C  | 4.976211000  | -2.176243000 | 0.093119000  |
| C  | 5.722675000  | -1.319818000 | -0.721086000 |
| C  | 5.328606000  | 0.013911000  | -0.865452000 |
| C  | 4.195366000  | 0.492922000  | -0.204526000 |
| C  | 2.019236000  | -0.480838000 | 2.059462000  |
| H  | 2.408468000  | 1.066376000  | 1.626395000  |
| H  | 3.260037000  | -2.376602000 | 1.388272000  |
| H  | 5.270245000  | -3.215902000 | 0.207919000  |
| H  | 6.602570000  | -1.688976000 | -1.240346000 |
| H  | 5.899376000  | 0.686952000  | -1.499361000 |
| H  | 3.875312000  | 1.523636000  | -0.330546000 |

cis-[PtHBr(C<sub>2</sub>H<sub>4</sub>NHPh)(PhNH<sub>2</sub>)] **XXII**

SCF Done: -5915.919916

|    |              |              |              |
|----|--------------|--------------|--------------|
| Pt | -0.691672635 | -0.379556270 | -0.097434730 |
| Br | -1.760137952 | -2.346176000 | -1.100123000 |
| C  | 0.483684317  | -0.197643952 | -1.822604095 |
| N  | 0.159884000  | 1.348154095  | 0.815722222  |
| H  | 0.668442143  | -1.217117635 | 0.105983175  |
| C  | 1.479759952  | -1.361058317 | -1.937187365 |
| N  | 2.006310444  | -1.748406317 | -0.600174587 |
| C  | 3.163078175  | -1.147526095 | -0.041706222 |
| C  | 3.673041952  | 0.074270540  | -0.511308857 |
| C  | 4.784142317  | 0.654257762  | 0.110413508  |
| C  | 5.395256905  | 0.039478032  | 1.203353508  |
| C  | 4.885658127  | -1.177865603 | 1.673455825  |
| C  | 3.781598762  | -1.765299825 | 1.059804778  |
| H  | -0.175488683 | -0.186888317 | -2.698326778 |
| H  | 0.993180000  | 0.771612365  | -1.779141825 |
| H  | 0.956607635  | -2.238543635 | -2.318658730 |
| H  | 2.312837730  | -1.137315365 | -2.616893905 |
| H  | 1.985547032  | -2.752872317 | -0.450006587 |
| H  | 3.224796000  | 0.563399587  | -1.369694857 |
| H  | 5.173931730  | 1.594239079  | -0.275210809 |
| H  | 6.257944270  | 0.495320619  | 1.681748873  |
| H  | 5.350683397  | -1.673278651 | 2.520903825  |

|    |              |              |              |
|----|--------------|--------------|--------------|
| H  | 3.388263666  | -2.709026143 | 1.436532095  |
| C  | -0.122514095 | 2.629249413  | 0.189309905  |
| C  | 0.898692492  | 3.344253143  | -0.439934825 |
| C  | 0.609546397  | 4.567869460  | -1.051968143 |
| C  | -0.693164968 | 5.073241730  | -1.029418048 |
| C  | -1.707613556 | 4.348823000  | -0.394220000 |
| C  | -1.432285460 | 3.123019683  | 0.212771317  |
| H  | 1.914365175  | 2.955878191  | -0.444879556 |
| H  | 1.404526666  | 5.124983508  | -1.539840191 |
| H  | -0.916821381 | 6.024304048  | -1.503329365 |
| H  | -2.721974238 | 4.737045952  | -0.372776270 |
| H  | -2.215135730 | 2.549075635  | 0.701168365  |
| Br | -2.274573762 | -0.294719413 | 1.929877778  |
| H  | 1.166934683  | 1.225581825  | 0.933606492  |
| H  | -0.276180270 | 1.296880730  | 1.743910905  |

cis-[PtHBr(C<sub>2</sub>H<sub>4</sub>NHPh)(PhNH<sub>2</sub>)] **XXII'**

SCF Done: -5915.916526

|    |              |              |              |
|----|--------------|--------------|--------------|
| C  | 3.998980000  | -1.071983000 | -0.756835000 |
| C  | 3.454803000  | -1.365927000 | 0.505950000  |
| C  | 4.300222000  | -0.131190000 | 1.631632000  |
| C  | 5.646550000  | -0.979009000 | 1.496801000  |
| C  | 6.186902000  | -0.692658000 | 0.237481000  |
| C  | 5.353762000  | -0.744923000 | -0.881321000 |
| N  | 2.084620000  | -1.659849000 | 0.688114000  |
| C  | 1.288303000  | -2.248240000 | -0.413002000 |
| C  | 0.396811000  | -1.250557000 | -1.157303000 |
| Pt | -1.096450000 | -0.344588000 | -0.008642000 |
| Br | -2.779250000 | -1.714510000 | -1.125111000 |
| N  | 0.370864000  | 0.902944000  | 0.872441000  |
| C  | 0.759841000  | 2.061112000  | 0.079798000  |
| C  | 2.043226000  | 2.128943000  | -0.469394000 |
| C  | 2.403593000  | 3.241859000  | -1.234179000 |
| C  | 1.488936000  | 4.275981000  | -1.450405000 |
| C  | 0.207567000  | 4.196080000  | -0.895365000 |
| C  | -0.168319000 | 3.086953000  | -0.135132000 |
| Br | -2.773254000 | 0.944080000  | 1.490016000  |
| H  | -0.095315000 | -1.768859000 | -1.985226000 |
| H  | 0.994783000  | -0.427724000 | -1.573868000 |
| H  | 0.669273000  | -3.045544000 | 0.011199000  |
| H  | 1.967149000  | -2.736388000 | -1.128692000 |
| H  | 1.937336000  | -2.149773000 | 1.564285000  |
| H  | 3.895478000  | -1.539520000 | 2.616621000  |
| H  | 6.278164000  | -0.950525000 | 2.381125000  |
| H  | 7.237374000  | -0.437381000 | 0.132923000  |
| H  | 5.754327000  | -0.528999000 | -1.868803000 |
| H  | 3.374972000  | -1.095895000 | -1.644460000 |
| H  | -0.061012000 | 1.198271000  | 1.753559000  |
| H  | 1.174299000  | 0.288938000  | 1.065035000  |
| H  | -1.164263000 | 3.011880000  | 0.292079000  |
| H  | -0.509000000 | 4.996384000  | -1.057786000 |
| H  | 1.773483000  | 5.140184000  | -2.044218000 |
| H  | 3.403596000  | 3.297096000  | -1.655452000 |
| H  | 2.761463000  | 1.332585000  | -0.294501000 |
| H  | -0.886791000 | -1.397845000 | 1.062303000  |

[PtHBr<sub>3</sub>(C<sub>2</sub>H<sub>4</sub>NHPh)] **TS(IX-XX)**

SCF Done: -8199.839483

|    |              |              |              |
|----|--------------|--------------|--------------|
| Pt | 0.916236000  | -0.012627000 | -0.327931000 |
| Br | 1.304957000  | 2.457356000  | -0.119643000 |
| Br | 2.229678000  | -0.500814000 | 1.839308000  |
| Br | 0.362870000  | -2.431293000 | -0.655792000 |
| C  | -0.033195000 | 0.357541000  | -2.157974000 |
| H  | -0.695398000 | 0.373575000  | -0.033669000 |
| C  | -1.549467000 | 0.257090000  | -1.961384000 |
| N  | -1.886599000 | 0.817408000  | -0.609854000 |
| C  | -3.128089000 | 0.477639000  | 0.005963000  |
| C  | -3.429558000 | -0.869895000 | 0.258400000  |
| C  | -4.627439000 | -1.200343000 | 0.892352000  |
| C  | -5.524630000 | -0.203182000 | 1.294063000  |
| C  | -5.210647000 | 1.138198000  | 1.058922000  |
| C  | -4.018296000 | 1.479657000  | 0.415147000  |
| H  | 0.254016000  | 1.355071000  | -2.508533000 |
| H  | 0.283259000  | -0.382166000 | -2.901753000 |
| H  | -2.138885000 | 0.786718000  | -2.724393000 |
| H  | -1.855742000 | -0.790388000 | -1.945506000 |
| H  | -1.709157000 | 1.823458000  | -0.589071000 |
| H  | -2.711634000 | -1.640540000 | -0.009688000 |
| H  | -4.850584000 | -2.245523000 | 1.092148000  |
| H  | -6.452425000 | -0.469469000 | 1.794291000  |
| H  | -5.893072000 | 1.924110000  | 1.374172000  |
| H  | -3.775350000 | 2.524196000  | 0.231090000  |

[PtHBr<sub>4</sub>(C<sub>2</sub>H<sub>4</sub>NHPh)]<sup>2-</sup> **XXIII**

SCF Done: -10771.28486

|    |              |              |              |
|----|--------------|--------------|--------------|
| C  | 6.027248000  | -1.070435000 | 0.620740000  |
| C  | 4.685736000  | -1.082785000 | 0.261918000  |
| C  | 4.037299000  | 0.096911000  | -0.204997000 |
| C  | 4.819402000  | 1.282298000  | -0.274501000 |
| C  | 6.166938000  | 1.271345000  | 0.090469000  |
| C  | 6.795653000  | 0.104365000  | 0.539316000  |
| N  | 2.731884000  | 0.057852000  | -0.574577000 |
| C  | 1.942794000  | 1.207300000  | -1.001017000 |
| C  | 0.535371000  | 0.805269000  | -1.433996000 |
| Pt | -0.729428000 | 0.066214000  | 0.048619000  |
| Br | -2.278434000 | -0.864685000 | 2.053169000  |
| Br | -1.259135000 | 2.462448000  | 0.642360000  |
| Br | 0.176472000  | -2.271760000 | -0.404441000 |



H 0.255884000 0.991392000 1.852165000  
Br -1.666305000 1.528541000 -1.544168000

[Pt( $\sigma$ -HBr)Br(C<sub>2</sub>H<sub>4</sub>NHPh)(C<sub>2</sub>H<sub>4</sub>)] XXVI

SCF Done: -5706.894136

|    |              |              |              |
|----|--------------|--------------|--------------|
| C  | 2.117206000  | 2.403581000  | 0.082630000  |
| C  | 1.185077000  | 2.238124000  | 1.125693000  |
| H  | 0.253368000  | 2.799081000  | 1.125517000  |
| H  | 1.501528000  | 1.882426000  | 2.104107000  |
| H  | 3.169834000  | 2.172960000  | 0.235023000  |
| H  | 1.919836000  | 3.094140000  | -0.734373000 |
| Pt | 1.066383000  | 0.571872000  | -0.209178000 |
| Br | 3.074735000  | -0.996241000 | 1.290505000  |
| Br | 0.565186000  | -1.665684000 | -1.184340000 |
| H  | 2.345291000  | -1.918843000 | 0.419331000  |
| C  | -0.405864000 | 1.491454000  | -1.311327000 |
| C  | -1.795822000 | 1.494265000  | -0.676274000 |
| N  | -2.410624000 | 0.184253000  | -0.643551000 |
| C  | -3.635953000 | -0.044002000 | -0.031660000 |
| C  | -4.051227000 | -1.372139000 | 0.214498000  |
| C  | -5.289530000 | -1.635340000 | 0.791328000  |
| C  | -6.154400000 | -0.590289000 | 1.145358000  |
| C  | -5.748861000 | 0.724060000  | 0.908720000  |
| C  | -4.505930000 | 1.004387000  | 0.331399000  |
| H  | -0.088351000 | 2.528641000  | -1.466168000 |
| H  | -0.420647000 | 0.983467000  | -2.280787000 |
| H  | -1.764982000 | 1.953024000  | 0.327324000  |
| H  | -2.414829000 | 2.164009000  | -1.297725000 |
| H  | -1.769428000 | -0.600424000 | -0.648426000 |
| H  | -4.222519000 | 2.037964000  | 0.159137000  |
| H  | -6.402746000 | 1.551232000  | 1.176124000  |
| H  | -7.120663000 | -0.799937000 | 1.595445000  |
| H  | -5.582838000 | -2.667669000 | 0.968071000  |
| H  | -3.391764000 | -2.193047000 | -0.059817000 |

[Pt( $\sigma$ -HBr)Br(C<sub>2</sub>H<sub>4</sub>NHPh)(PhNH<sub>2</sub>)] XXVII

SCF Done: -5915.90791

|    |              |              |              |
|----|--------------|--------------|--------------|
| C  | 2.152884000  | 2.225416000  | -0.432453000 |
| C  | 0.871353000  | 2.120016000  | 0.112254000  |
| C  | -0.040013000 | 3.173779000  | -0.009172000 |
| C  | 0.343146000  | 4.343302000  | -0.666647000 |
| C  | 1.623940000  | 4.458156000  | -1.219027000 |
| C  | 2.523525000  | 3.396648000  | -1.101508000 |
| N  | 0.474877000  | 0.904246000  | 0.809934000  |
| Pt | -0.982380000 | -0.322335000 | -0.074504000 |
| Br | -3.280863000 | 0.832780000  | 1.294148000  |
| Br | -2.763832000 | -1.758963000 | -1.013091000 |
| C  | 0.498378000  | -1.281013000 | -1.091995000 |
| C  | 1.317526000  | -2.250740000 | -0.233818000 |
| N  | 2.155713000  | -1.597931000 | 0.798168000  |
| C  | 3.529985000  | -1.369845000 | 0.574760000  |
| C  | 4.398075000  | -1.258789000 | 1.679213000  |
| C  | 5.751683000  | -0.981910000 | 1.497828000  |
| C  | 6.277453000  | -0.809942000 | 0.211806000  |
| C  | 5.421985000  | -0.919277000 | -0.886204000 |
| C  | 4.060498000  | -1.191481000 | -0.715751000 |
| H  | 0.027473000  | -1.842945000 | -1.906030000 |
| H  | 1.142739000  | -0.513417000 | -1.543172000 |
| H  | 0.644585000  | -2.945071000 | 0.277604000  |
| H  | 1.961905000  | -2.860743000 | -0.887260000 |
| H  | 1.994910000  | -1.990447000 | 1.719646000  |
| H  | 4.003987000  | -1.397043000 | 2.684951000  |
| H  | 6.400380000  | -0.907317000 | 2.367109000  |
| H  | 7.333471000  | -0.598350000 | 0.070924000  |
| H  | 5.810647000  | -0.791426000 | -1.893651000 |
| H  | 3.418825000  | -1.262041000 | -1.587897000 |
| H  | 0.131010000  | 1.140089000  | 1.742627000  |
| H  | 1.278592000  | 0.268640000  | 0.941408000  |
| H  | -1.044663000 | 3.070766000  | 0.391185000  |
| H  | -0.366120000 | 5.161437000  | -0.758298000 |
| H  | 1.915946000  | 5.367762000  | -1.736493000 |
| H  | 3.521457000  | 3.474828000  | -1.524447000 |
| H  | 2.861033000  | 1.406548000  | -0.334146000 |
| H  | -3.642836000 | -0.292837000 | 0.377808000  |

[PtBr<sub>3</sub>(C<sub>2</sub>H<sub>4</sub>NHPh)]<sup>2-</sup> XXVIII

SCF Done: -8199.242970

|    |              |              |              |
|----|--------------|--------------|--------------|
| Pt | 1.006690000  | 0.061333000  | -0.306539000 |
| Br | 2.883117000  | -0.972123000 | 1.328490000  |
| Br | 1.782242000  | 2.412101000  | 0.156409000  |
| C  | -0.383548000 | 0.869447000  | -1.588310000 |
| H  | -0.594730000 | 0.156791000  | -2.400923000 |
| H  | 0.051147000  | 1.771732000  | -2.039955000 |
| C  | -1.714813000 | 1.287229000  | -0.947892000 |
| H  | -2.359559000 | 1.783664000  | -1.699842000 |
| H  | -1.531261000 | 2.017234000  | -0.144399000 |
| N  | -2.439541000 | 0.130338000  | -0.430043000 |
| H  | -1.883130000 | -0.721405000 | -0.351381000 |
| C  | -3.695024000 | 0.140669000  | 0.074125000  |
| C  | -4.275341000 | -1.060176000 | 0.582076000  |
| C  | -5.571716000 | -1.078779000 | 1.178135000  |
| C  | -6.364983000 | 0.083181000  | 1.102653000  |
| C  | -5.803024000 | 1.270398000  | 0.617472000  |
| C  | -4.501231000 | 1.314090000  | 0.115702000  |
| H  | -3.673999000 | -1.966497000 | 0.575313000  |
| H  | -5.974983000 | -2.017380000 | 1.458569000  |
| H  | -7.379469000 | 0.061284000  | 1.495715000  |

H -6.386737000 2.191305000 0.634997000  
H -4.090361000 2.254816000 -0.236134000  
Br 0.084243000 -2.245242000 -0.815625000

trans-[PtBr<sub>2</sub>(C<sub>2</sub>H<sub>4</sub>NHPh)(PhNH<sub>2</sub>)]<sup>-</sup> XXIX

SCF Done: -5915.449898

|    |              |              |              |
|----|--------------|--------------|--------------|
| C  | -5.173190000 | -0.300071000 | -0.918886000 |
| C  | -4.905205000 | -0.028178000 | 0.444874000  |
| C  | -6.011984000 | 0.252461000  | 1.287049000  |
| C  | -7.312101000 | 0.248883000  | 0.791770000  |
| C  | -7.569619000 | -0.030593000 | -0.558349000 |
| C  | -6.484308000 | -0.302685000 | -1.398000000 |
| N  | -3.632589000 | -0.058736000 | 0.956977000  |
| C  | -2.402714000 | -0.101235000 | 0.147086000  |
| C  | -1.167307000 | 0.013576000  | 1.040899000  |
| Pt | 0.578432000  | 0.006106000  | -0.017322000 |
| Br | 0.666161000  | -2.488766000 | -0.031718000 |
| Br | 0.576295000  | 2.499823000  | -0.217868000 |
| N  | 2.487497000  | 0.004695000  | -1.242817000 |
| C  | 3.739412000  | 0.013973000  | -0.551255000 |
| C  | 4.273747000  | 1.224674000  | -0.088618000 |
| C  | 5.487384000  | 1.229908000  | 0.600759000  |
| C  | 6.172591000  | 0.035087000  | 0.849145000  |
| C  | 5.623374000  | -1.171405000 | 0.403524000  |
| C  | 4.412474000  | -1.187179000 | -0.292426000 |
| H  | 2.356572000  | 0.840607000  | -1.810729000 |
| H  | 2.376341000  | -0.826412000 | -1.820813000 |
| H  | 3.717354000  | 2.144718000  | -0.245601000 |
| H  | 5.891806000  | 2.174803000  | 0.956989000  |
| H  | 7.115580000  | 0.043670000  | 1.390684000  |
| H  | 6.133988000  | -2.110875000 | 0.603396000  |
| H  | 3.969197000  | -2.127190000 | -0.609604000 |
| H  | -1.219983000 | 0.952444000  | 1.613878000  |
| H  | -1.156883000 | -0.824930000 | 1.751961000  |
| H  | -3.514270000 | 0.326930000  | 1.884984000  |
| H  | -2.375628000 | -1.050054000 | -0.402146000 |
| H  | -2.415825000 | 0.714900000  | -0.590623000 |
| H  | -5.831515000 | 0.468170000  | 2.339277000  |
| H  | -8.136384000 | 0.468914000  | 1.468391000  |
| H  | -8.586594000 | -0.032410000 | -0.942439000 |
| H  | -6.655609000 | -0.518571000 | -2.451281000 |
| H  | -4.351478000 | -0.512974000 | -1.594236000 |

cis-[PtBr<sub>2</sub>(C<sub>2</sub>H<sub>4</sub>NHPh)(PhNH<sub>2</sub>)]<sup>-</sup> XXX

SCF Done: -5915.449898

|    |              |              |              |
|----|--------------|--------------|--------------|
| C  | 4.380385000  | 2.187263000  | 0.370024000  |
| C  | 3.936731000  | 0.895415000  | -0.007319000 |
| C  | 4.844459000  | -0.184353000 | 0.157184000  |
| C  | 6.123419000  | 0.026273000  | 0.657640000  |
| C  | 6.559533000  | 1.311071000  | 1.020828000  |
| C  | 5.671360000  | 2.379313000  | 0.870000000  |
| N  | 2.693713000  | 0.667819000  | -0.530593000 |
| C  | 1.634866000  | 1.656933000  | -0.596012000 |
| C  | 0.352692000  | 1.072666000  | -1.206095000 |
| Pt | -0.546075000 | -0.430028000 | -0.124801000 |
| Br | 0.697057000  | -2.125086000 | -1.416643000 |
| N  | -1.590183000 | 0.972383000  | 1.076394000  |
| C  | -2.682664000 | 1.706099000  | 0.486247000  |
| C  | -2.565128000 | 3.075347000  | 0.231002000  |
| C  | -3.627711000 | 3.769497000  | -0.358260000 |
| C  | -4.810328000 | 3.101953000  | -0.682982000 |
| C  | -4.920794000 | 1.730063000  | -0.418909000 |
| C  | -3.863232000 | 1.027002000  | 0.156198000  |
| Br | -1.911277000 | -2.114594000 | 1.461803000  |
| H  | 0.575931000  | 0.713596000  | -2.219007000 |
| H  | 1.980958000  | 2.508052000  | -1.211053000 |
| H  | 1.433512000  | 2.069704000  | 0.411994000  |
| H  | 2.390283000  | -0.296506000 | -0.643368000 |
| H  | 4.519746000  | -1.185622000 | -0.117099000 |
| H  | 6.791887000  | -0.825589000 | 0.770961000  |
| H  | 7.561254000  | 1.469057000  | 1.412737000  |
| H  | 5.981415000  | 3.385597000  | 1.148331000  |
| H  | 3.714396000  | 3.038130000  | 0.266597000  |
| H  | -1.931351000 | 0.315676000  | 1.793799000  |
| H  | -0.917776000 | 1.605269000  | 1.509426000  |
| H  | -3.924874000 | -0.042374000 | 0.339780000  |
| H  | -5.834709000 | 1.199077000  | -0.674308000 |
| H  | -5.636199000 | 3.640867000  | -1.140912000 |
| H  | -3.524588000 | 4.832877000  | -0.561664000 |
| H  | -1.644222000 | 3.597245000  | 0.482356000  |
| H  | -0.370309000 | 1.897261000  | -1.312617000 |

trans-[PtBr<sub>2</sub>(C<sub>2</sub>H<sub>4</sub>NHPh)(C<sub>2</sub>H<sub>4</sub>)]<sup>-</sup> XXXI

SCF Done: -5706.432262

|    |              |              |              |
|----|--------------|--------------|--------------|
| C  | -4.125204000 | -1.399258000 | -0.317586000 |
| C  | -3.417627000 | -0.181066000 | -0.159108000 |
| C  | -4.083710000 | 0.881530000  | 0.508839000  |
| C  | -5.382592000 | 0.730229000  | 0.979490000  |
| C  | -6.079279000 | -0.477563000 | 0.812911000  |
| C  | -5.430455000 | -1.531405000 | 0.162073000  |
| N  | -2.149499000 | -0.002177000 | -0.633883000 |
| C  | -1.327628000 | -1.044611000 | -1.234334000 |
| C  | 0.048937000  | -0.510104000 | -1.646787000 |
| Pt | 1.255377000  | 0.102790000  | -0.066255000 |
| Br | 2.019048000  | -2.265524000 | 0.192315000  |
| C  | 2.004421000  | 0.602566000  | 2.024077000  |
| C  | 3.039403000  | 0.846891000  | 1.143637000  |



H -0.937216000 4.856967000 1.448192000  
H -1.775538000 2.816758000 0.305161000

[PtBr(PhNH<sub>2</sub>)(κ<sup>2</sup>:C,N-CH<sub>2</sub>CH<sub>2</sub>NHPh)] XXXIV'

SCF Done: -3343.902468

Pt -0.126486000 -0.242871000 -0.207574000  
Br 0.305927000 2.298788000 0.007594000  
N 1.544824000 -1.076814000 0.698005000  
H 1.376406000 -1.009980000 1.702790000  
C 2.906334000 -0.638587000 0.439613000  
C 1.186941000 -2.493316000 0.231765000  
C -0.251180000 -2.298621000 -0.254016000  
N -1.905442000 0.348259000 -1.130183000  
C 3.839560000 -0.646601000 1.479366000  
C 5.160535000 -0.260596000 1.232653000  
C 5.549890000 0.119141000 -0.053727000  
C 4.609855000 0.122559000 -1.089996000  
C 3.287282000 -0.250667000 -0.847267000  
H 3.537762000 -0.943902000 2.481919000  
H 5.880120000 -0.258056000 2.046945000  
H 6.575444000 0.422348000 -0.246116000  
H 4.901143000 0.436061000 -2.088806000  
H 2.540028000 -0.209417000 -1.633659000  
H -0.421630000 -2.730051000 -1.247587000  
H 1.346344000 -3.203903000 1.053940000  
H -1.001431000 -2.692232000 0.442387000  
H 1.877188000 -2.739998000 -0.577507000  
C -3.139494000 0.090791000 -0.405790000  
H -1.765099000 1.359668000 -1.250468000  
H -1.951872000 -0.065735000 -2.061799000  
C -3.985261000 -0.943833000 -0.808099000  
C -5.164381000 -1.188077000 -0.096894000  
C -5.497183000 -0.397038000 1.005307000  
C -4.641535000 0.638891000 1.397777000  
C -3.457824000 0.884355000 0.700491000  
H -3.726056000 -1.560171000 -1.666468000  
H -5.821859000 -1.994420000 -0.410902000  
H -6.415932000 -0.584391000 -1.554281000  
H -4.892885000 1.257837000 2.254944000  
H -2.776079000 1.672214000 1.009246000

[PtBr(C<sub>2</sub>H<sub>4</sub>)(κ<sup>2</sup>:C,N-CH<sub>2</sub>CH<sub>2</sub>NHPh)] XXXV

SCF Done: -3134.87627129

C -0.686438000 2.129921000 0.145228000  
C -0.200469000 -2.130959000 0.104262000  
C -0.526093000 -1.932199000 -1.219944000  
Pt -0.675006000 0.096590000 -0.163720000  
N 1.234211000 0.938865000 -0.613266000  
H 1.267642000 1.019321000 -1.629235000  
C 0.820700000 2.299407000 -0.032807000  
H 1.155156000 3.094364000 -0.712317000  
H 1.350182000 2.414830000 0.914706000  
H -1.048428000 2.403157000 1.140170000  
H -1.285195000 2.647838000 -0.611178000  
Br -3.025607000 -0.290371000 0.421398000  
C 2.480644000 0.363576000 -0.162053000  
C 3.486834000 0.078073000 -1.090639000  
C 4.693940000 -0.484985000 -0.664638000  
C 4.903505000 -0.755088000 0.689163000  
C 3.893686000 -0.467768000 1.614807000  
C 2.681865000 0.082385000 1.195176000  
H 3.332060000 0.296079000 -2.145814000  
H 5.468771000 -0.704999000 -1.393992000  
H 5.841962000 -1.189774000 1.021468000  
H 4.043765000 -0.683801000 2.669145000  
H 1.887677000 0.275333000 1.910738000  
H -0.946889000 -2.474705000 0.814166000  
H 0.837064000 -2.186196000 0.425253000  
H 0.247678000 -1.832148000 -1.978320000  
H -1.533288000 -2.116536000 -1.582034000

[PtBr(C<sub>2</sub>H<sub>4</sub>)(κ<sup>2</sup>:C,N-CH<sub>2</sub>CH<sub>2</sub>NHPh)] XXXV'

SCF Done: -3134.881820

H -1.546202000 -0.162678000 1.806986000  
C -2.375941000 -0.107266000 1.108214000  
C -3.615328000 0.389021000 1.513524000  
H -3.753760000 0.701882000 2.544750000  
C -4.664599000 0.510289000 0.596087000  
H -5.623961000 0.908956000 0.914095000  
C -4.468772000 0.130943000 -0.733552000  
C -5.274053000 0.229291000 -1.456417000  
H -3.083380000 -0.677583000 -2.178193000  
C -3.233265000 -0.379821000 -1.142218000  
C -2.189602000 -0.496637000 -0.220826000  
H -0.880902000 -1.027367000 -1.662071000  
H -0.968546000 -3.204566000 -0.902099000  
H -1.134711000 -2.620013000 0.765776000  
C -0.595550000 -2.473656000 -0.172293000  
C 0.921645000 -2.409798000 0.032786000  
H 1.486632000 -2.874060000 -0.785061000  
H 1.240200000 -2.851810000 0.983116000  
Br 0.615924000 2.172826000 -0.260502000  
N -0.919412000 -1.055491000 -0.642442000  
Pt 1.004143000 -0.345697000 -0.022732000  
C 2.712188000 -0.048238000 1.246118000  
C 3.136282000 -0.102523000 -0.087467000  
H 2.824166000 -0.910282000 1.899973000  
H 2.584353000 0.912171000 1.738771000

H 3.341353000 0.815201000 -0.633020000  
H 3.581881000 -1.009169000 -0.491049000

[PtBr<sub>3</sub>H(κ<sup>2</sup>:C,N-CH<sub>2</sub>CH<sub>2</sub>NHPh)] XXXVI

SCF Done: -8199.83846808

C -3.080964000 -0.299699000 -1.409741000  
C -2.592363000 0.497307000 -0.367907000  
C -3.389257000 0.733314000 0.757796000  
C -4.672360000 0.187649000 0.833841000  
C -5.171290000 -0.592057000 -0.212677000  
C -4.366968000 -0.835238000 -1.331249000  
N -1.279310000 1.073061000 -0.421381000  
C -0.842607000 1.824952000 -1.671466000  
C 0.589570000 1.326616000 -1.902425000  
Pt 0.529342000 -0.061431000 -0.368518000  
Br 2.789625000 -1.007619000 -0.740343000  
Br -0.182673000 -1.739995000 1.526031000  
H -1.106564000 1.664101000 0.400964000  
H -2.993801000 1.323787000 1.580061000  
H -5.277424000 0.368998000 1.718729000  
H -6.168909000 -1.019868000 -0.151526000  
H -4.733862000 -1.461110000 -2.141241000  
H -2.445439000 -0.530846000 -2.259053000  
H 0.741692000 0.864718000 -2.880837000  
H -0.929476000 2.899796000 -1.476514000  
H 1.356836000 2.075491000 -1.703179000  
H -1.529590000 1.560383000 -2.478822000  
H 0.051191000 -1.136015000 -1.373580000  
Br 1.160455000 1.993720000 1.336657000

[PtBr<sub>3</sub>H(κ<sup>2</sup>:C,N-CH<sub>2</sub>CH<sub>2</sub>NHPh)] XXXVI'

SCF Done: -8199.83137652

H 6.134606000 0.281650000 -0.893241000  
H 4.502351000 -1.312585000 -1.896780000  
H 2.227331000 -1.555358000 -0.932496000  
H 3.217796000 1.337192000 2.092184000  
H 5.470038000 1.622479000 1.104186000  
C 3.509865000 0.742123000 1.228604000  
C 4.778606000 0.905414000 0.667903000  
C 5.149130000 0.155338000 -0.451047000  
C 4.234648000 -0.744713000 -1.009024000  
C 2.961771000 -0.908965000 -0.460567000  
C 2.603938000 -0.167671000 0.670464000  
N 1.312598000 -0.321683000 1.294583000  
H 1.287923000 0.303959000 2.096713000  
H 1.359522000 -1.962342000 2.697939000  
C 0.867366000 -1.700708000 1.748504000  
H 1.178370000 -2.400605000 0.973021000  
H -1.179987000 -2.411576000 1.328832000  
C -0.657687000 -1.557474000 1.761162000  
H -1.073312000 -1.303723000 2.741052000  
H -0.891705000 1.033042000 1.647721000  
Br -0.027985000 2.214698000 -0.909251000  
Br -0.324184000 -1.734246000 -1.538798000  
Pt -0.655361000 0.059147000 0.461084000  
Br -3.104652000 0.195723000 0.136000000

[PtBr<sub>3</sub>H(κ<sup>2</sup>:C,N-CH<sub>2</sub>CH<sub>2</sub>NHPh)] XXXVII

SCF Done: -8199.80413862

C 2.637446000 0.416819000 0.251343000  
C 3.225898000 1.471904000 -0.461979000  
C 4.486583000 1.315670000 -1.039063000  
C 5.174295000 0.104545000 -0.911394000  
C 4.579996000 -0.948292000 -0.209434000  
C 3.315684000 -0.802960000 0.366472000  
N 1.339855000 0.627401000 0.827308000  
Pt -0.543276000 0.012076000 -0.032693000  
Br -2.911315000 -0.586305000 -0.533187000  
C 0.989557000 0.079271000 2.207842000  
C -0.532086000 -0.018063000 2.157070000  
H -0.288064000 0.085555000 -1.638956000  
Br 0.125721000 -2.416697000 -0.094751000  
H 6.157088000 -0.019452000 -1.360002000  
H 5.095222000 -1.901734000 -0.119181000  
H 2.846685000 -1.639866000 0.868493000  
H 2.682644000 2.407120000 -0.576308000  
H 4.927938000 2.141877000 -1.591638000  
H 1.147254000 1.632684000 0.830064000  
H 1.452444000 0.732274000 2.965564000  
H 1.443317000 -0.909305000 2.279936000  
H -0.912720000 -0.946236000 2.590679000  
H -1.040404000 0.850140000 2.587598000  
Br -1.036665000 2.503569000 -0.064705000

[PtBr<sub>3</sub>H(κ<sup>2</sup>:C,N-CH<sub>2</sub>CH<sub>2</sub>NHPh)] XXXVII'

SCF Done: -8199.84861445

C 2.480541000 -0.725138000 -0.423364000  
C 3.078072000 -1.878988000 0.109118000  
C 4.352891000 -1.821720000 0.675591000  
C 5.056266000 -0.614371000 0.712525000  
C 4.456757000 0.537794000 0.191615000  
C 3.177790000 0.492738000 -0.364416000  
N 1.170063000 -0.800272000 -0.967073000



|   |              |              |              |
|---|--------------|--------------|--------------|
| C | 1.958072000  | -2.480083000 | -1.254103000 |
| H | -0.588742000 | -2.653985000 | -0.577068000 |
| H | -0.399335000 | -2.547089000 | 1.042251000  |
| H | 1.694197000  | -2.713680000 | 2.142762000  |
| H | 4.129168000  | -3.131366000 | 1.904806000  |
| H | 5.176427000  | -3.160139000 | -0.354245000 |
| H | 3.746207000  | -2.745560000 | -2.370366000 |
| H | 1.344417000  | -2.268891000 | -2.126881000 |
| H | 1.577279000  | -0.144139000 | 1.015778000  |
| C | 2.988297000  | 1.302025000  | -0.337588000 |
| C | 3.829153000  | 2.248815000  | -0.923059000 |
| C | 3.506763000  | 3.607343000  | -0.858765000 |
| C | 2.336750000  | 4.005756000  | -0.207531000 |
| C | 1.485591000  | 3.064365000  | 0.376412000  |
| H | 3.240320000  | 0.245412000  | -0.394770000 |
| H | 4.735556000  | 1.922336000  | -1.425872000 |
| H | 4.159985000  | 4.347510000  | -1.312590000 |
| H | 2.072097000  | 5.058422000  | -0.158244000 |
| H | 0.568940000  | 3.390097000  | 0.850431000  |

[PtBr<sub>2</sub>H(PhNH<sub>2</sub>)] (κ<sup>2</sup>:C,N-CH<sub>2</sub>CH<sub>2</sub>NHPh) ] **XLII'**

SCF Done: -5915.88368790

|    |              |              |              |
|----|--------------|--------------|--------------|
| C  | -2.328338000 | -2.174567000 | 1.189112000  |
| C  | -1.631157000 | -2.078102000 | -0.022574000 |
| C  | -2.338003000 | -2.062556000 | -1.232960000 |
| C  | -3.728125000 | -2.166993000 | -1.231281000 |
| C  | -4.428580000 | -2.279918000 | -0.024827000 |
| C  | -3.723971000 | -2.280017000 | 1.180563000  |
| N  | -0.194541000 | -1.987965000 | -0.065270000 |
| C  | 0.622064000  | -2.551543000 | 1.110452000  |
| C  | 1.155089000  | -1.306036000 | 1.807245000  |
| Pt | 0.780878000  | -0.071642000 | 0.048869000  |
| Br | 2.609332000  | -1.190047000 | -1.222795000 |
| N  | -0.761609000 | 0.984329000  | 1.084814000  |
| C  | -1.717549000 | 1.812228000  | 0.355256000  |
| C  | -1.271100000 | 2.961675000  | -0.303561000 |
| C  | -2.195133000 | 3.764434000  | -0.971523000 |
| C  | -3.551384000 | 3.418008000  | -1.000470000 |
| C  | -3.982425000 | 2.261068000  | -0.349463000 |
| C  | -3.065783000 | 1.454718000  | 0.333757000  |
| Br | 2.191316000  | 1.909884000  | 0.616559000  |
| H  | 0.149232000  | -2.372635000 | -0.947283000 |
| H  | -1.796287000 | -1.962588000 | -2.170465000 |
| H  | -4.264669000 | -2.161457000 | -2.175957000 |
| H  | -5.511182000 | -2.369814000 | -0.026476000 |
| H  | -4.255273000 | -2.370640000 | 2.124333000  |
| H  | -1.797092000 | -2.192544000 | 2.135551000  |
| H  | 2.206819000  | -1.386047000 | 2.087604000  |
| H  | 1.432475000  | -3.118568000 | 0.650179000  |
| H  | 0.565038000  | -1.014627000 | 2.688299000  |
| H  | -0.002806000 | -3.247896000 | 1.680567000  |
| H  | -0.192242000 | 1.574622000  | 1.700341000  |
| H  | -1.263642000 | 0.323538000  | 1.679235000  |
| H  | -3.404158000 | 0.553333000  | 0.837311000  |
| H  | -5.032052000 | 1.980174000  | -0.365944000 |
| H  | -4.264250000 | 4.045948000  | -1.527873000 |
| H  | -1.850359000 | 4.660137000  | -1.480798000 |
| H  | -0.214341000 | 3.208872000  | -0.298772000 |
| H  | 0.363010000  | 0.635051000  | -1.358520000 |

[PtBr<sub>2</sub>H(PhNH<sub>2</sub>)] (κ<sup>2</sup>:C,N-CH<sub>2</sub>CH<sub>2</sub>NHPh) ] **XLIII**

SCF Done: -5915.92938770

|    |              |              |              |
|----|--------------|--------------|--------------|
| Br | -3.185850000 | -0.813098000 | -0.222020000 |
| Pt | -0.743138000 | -0.451768000 | -0.342023000 |
| Br | -0.226921000 | -1.234169000 | 2.095769000  |
| N  | 1.256768000  | 0.023652000  | -0.925032000 |
| C  | -0.675929000 | 0.261442000  | -2.288455000 |
| C  | 0.847620000  | 0.149648000  | -2.390219000 |
| H  | 1.376537000  | 0.990514000  | -2.856226000 |
| H  | -1.219560000 | -0.358960000 | -3.001971000 |
| H  | -1.044653000 | 1.290665000  | -2.334963000 |
| H  | -1.186014000 | 1.205306000  | 1.644748000  |
| N  | -1.158303000 | 1.572790000  | 0.689208000  |
| H  | -2.111998000 | 1.798994000  | 0.406709000  |
| H  | 1.091101000  | 1.918999000  | 2.064554000  |
| C  | 0.917216000  | 2.700920000  | 1.328723000  |
| C  | -0.250815000 | 2.669474000  | 0.551365000  |
| H  | 2.724813000  | 3.773174000  | 1.782491000  |
| C  | 1.831522000  | 3.745381000  | 1.163786000  |
| C  | -0.485659000 | 3.674387000  | -0.396820000 |
| C  | 0.437684000  | 4.711228000  | -0.556108000 |
| C  | 1.599429000  | 4.752174000  | 0.220896000  |
| H  | 2.310783000  | 5.564098000  | 0.099314000  |
| H  | 0.241966000  | 5.491784000  | -1.286542000 |
| H  | -1.393422000 | 3.653416000  | -0.995541000 |
| H  | 1.420359000  | 0.959570000  | -0.547439000 |
| H  | 1.522655000  | -2.657859000 | -1.185924000 |
| C  | 2.427209000  | -0.781405000 | -0.627117000 |
| H  | 3.569079000  | 0.926694000  | 0.034389000  |
| C  | 3.572879000  | -0.147276000 | -0.138937000 |
| C  | 4.722155000  | -0.895279000 | 0.131046000  |
| C  | 4.729532000  | -2.273069000 | -0.094287000 |
| C  | 3.578757000  | -2.900800000 | -0.582948000 |
| C  | 2.425453000  | -2.161380000 | -0.846114000 |
| H  | 3.569967000  | -3.975323000 | -0.742773000 |
| H  | 5.620534000  | -2.856891000 | 0.119104000  |
| H  | 5.607478000  | -0.397217000 | 0.516727000  |
| H  | -0.597049000 | -1.869791000 | -0.934146000 |
| H  | 1.157586000  | -0.772670000 | -2.884092000 |

[PtBr<sub>2</sub>H(PhNH<sub>2</sub>)] (κ<sup>2</sup>:C,N-CH<sub>2</sub>CH<sub>2</sub>NHPh) ] **XLII'**

SCF Done: -5915.91964562

|    |              |              |              |
|----|--------------|--------------|--------------|
| C  | 1.977316000  | 2.168968000  | -0.821044000 |
| C  | 0.622280000  | 1.947216000  | -1.075296000 |
| C  | -0.299351000 | 2.990528000  | -0.951102000 |
| C  | 0.146412000  | 4.262006000  | -0.588008000 |
| C  | 1.501825000  | 4.495463000  | -0.336520000 |
| C  | 2.413919000  | 3.443834000  | -0.452305000 |
| N  | 0.164692000  | 0.624070000  | -1.449156000 |
| Pt | -0.871361000 | -0.767200000 | 0.076171000  |
| Br | -2.997707000 | 0.245499000  | -0.681093000 |
| N  | 0.778902000  | -2.099595000 | 0.464140000  |
| C  | 0.123789000  | -3.183301000 | -0.379670000 |
| C  | -0.874015000 | -2.388228000 | -1.227705000 |
| C  | 2.125071000  | -1.683246000 | 0.149866000  |
| C  | 2.663479000  | -1.834895000 | -1.134330000 |
| C  | 3.973079000  | -1.412614000 | -1.389516000 |
| C  | 4.741330000  | -0.833783000 | -0.376975000 |
| C  | 4.189993000  | -0.671636000 | 0.898888000  |
| C  | 2.886172000  | -1.088251000 | 1.164823000  |
| H  | -1.695807000 | -1.644316000 | 1.048532000  |
| H  | 0.719061000  | -2.303639000 | 1.460118000  |
| H  | 2.446033000  | -0.929602000 | 2.145180000  |
| H  | 4.772879000  | -0.212216000 | 1.692230000  |
| H  | 5.758508000  | -0.510565000 | -0.579239000 |
| H  | 4.388776000  | -1.542586000 | -2.385068000 |
| H  | 2.084779000  | -2.288031000 | -1.933283000 |
| H  | -1.847901000 | -2.866825000 | -1.335923000 |
| H  | -0.393722000 | -3.846671000 | 0.317669000  |
| H  | -0.488766000 | -2.112166000 | -2.216574000 |
| H  | 0.882367000  | -3.768792000 | -0.901095000 |
| H  | -0.594322000 | 0.697006000  | -2.128524000 |
| H  | 0.926474000  | 0.109480000  | -1.891076000 |
| H  | 2.689242000  | 1.351330000  | -0.900337000 |
| H  | 3.469523000  | 3.610550000  | -0.253823000 |
| H  | 1.842384000  | 5.486452000  | -0.048994000 |
| H  | -0.574122000 | 5.069395000  | -0.489095000 |
| H  | -1.355951000 | 2.801699000  | -1.115337000 |
| Br | -0.397043000 | 0.777285000  | 2.097971000  |

[PtBr<sub>2</sub>H(PhNH<sub>2</sub>)] (κ<sup>2</sup>:C,N-CH<sub>2</sub>CH<sub>2</sub>NHPh) ] **XLIII**

SCF Done: -5915.93362966

|    |              |              |              |
|----|--------------|--------------|--------------|
| C  | -2.761307000 | -2.046852000 | -0.826284000 |
| C  | -2.807826000 | -0.650410000 | -0.824032000 |
| C  | -3.986098000 | 0.017592000  | -0.484554000 |
| C  | -5.126885000 | -0.716017000 | -0.148669000 |
| C  | -5.091628000 | -2.111749000 | -0.157389000 |
| C  | -3.906078000 | -2.772721000 | -0.496122000 |
| N  | -1.642368000 | 0.137629000  | -1.181543000 |
| C  | -0.936314000 | -0.161742000 | -2.502389000 |
| C  | 0.541555000  | -0.134292000 | -2.093491000 |
| Pt | 0.117595000  | 0.127678000  | -0.071453000 |
| H  | 0.098540000  | -1.426010000 | 0.083852000  |
| N  | 2.001355000  | 0.263835000  | 0.837095000  |
| C  | 3.099271000  | -0.556670000 | 0.367831000  |
| C  | 3.945792000  | -0.071095000 | -0.631166000 |
| C  | 4.999024000  | -0.869437000 | -1.085012000 |
| C  | 5.201290000  | -2.143597000 | -0.546838000 |
| C  | 4.344000000  | -2.620176000 | 0.450523000  |
| C  | 3.288733000  | -1.829855000 | 0.910534000  |
| Br | -0.754676000 | 0.211222000  | 2.396778000  |
| H  | -1.893241000 | 1.129859000  | -1.158587000 |
| H  | -4.011497000 | 1.104659000  | -0.467456000 |
| H  | -6.038909000 | -0.191495000 | 0.121831000  |
| H  | -5.977689000 | -2.682301000 | 0.106386000  |
| H  | -3.866468000 | -3.858505000 | -0.491472000 |
| H  | -1.834996000 | -2.564926000 | -1.054734000 |
| H  | 1.069871000  | -1.068492000 | -2.293782000 |
| H  | -1.227424000 | 0.595549000  | -3.236609000 |
| H  | 1.090927000  | 0.720096000  | -2.490120000 |
| H  | -1.276389000 | -1.138131000 | -2.851357000 |
| H  | 2.217233000  | 1.262648000  | 0.751329000  |
| H  | 1.784597000  | 0.094013000  | 1.826934000  |
| H  | 2.615802000  | -2.198424000 | 1.680767000  |
| H  | 4.496538000  | -3.608476000 | 0.875477000  |
| H  | 6.022730000  | -2.760600000 | -0.900161000 |
| H  | 5.661806000  | -0.491068000 | -1.858400000 |
| H  | 3.783311000  | 0.919568000  | -1.048580000 |
| Br | 0.205498000  | 2.742923000  | -0.431306000 |

[PtBr<sub>2</sub>H(PhNH<sub>2</sub>)] (κ<sup>2</sup>:C,N-CH<sub>2</sub>CH<sub>2</sub>NHPh) ] **XLIII'**

SCF Done: -5915.92936147

|    |              |              |              |
|----|--------------|--------------|--------------|
| C  | 3.852996000  | 1.218077000  | -0.664896000 |
| C  | 3.262255000  | 0.203826000  | 0.092445000  |
| C  | 3.863391000  | -1.052079000 | 0.200339000  |
| C  | 5.074053000  | -1.290173000 | -0.455404000 |
| C  | 5.676409000  | -0.282081000 | -1.213962000 |
| C  | 5.063374000  | 0.971006000  | -1.316014000 |
| N  | 2.005232000  | 0.456014000  | 0.768462000  |
| Pt | 0.198149000  | 0.059540000  | -0.207117000 |
| C  | 0.527418000  | -1.738513000 | -1.222312000 |
| C  | -0.967340000 | -1.952183000 | -1.471704000 |
| N  | -1.479542000 | -0.522560000 | -1.330996000 |
| C  | -2.887452000 | -0.332773000 | -0.992379000 |
| C  | -3.770366000 | -0.024920000 | -2.032398000 |
| C  | -5.132607000 | 0.130459000  | -1.764269000 |
| C  | -5.607754000 | -0.027293000 | -0.460078000 |



Br 0.328763000 -1.494692000 1.628300000  
H 1.170500000 0.835065000 -1.752792000

H -2.402753000 4.187950000 1.263030000  
H -2.507310000 2.083062000 -0.046799000  
H -0.170871000 -1.841324000 -0.779231000

[PtBr<sub>2</sub>H(C<sub>2</sub>H<sub>4</sub>)(κ<sup>2</sup>:C,N-CH<sub>2</sub>CH<sub>2</sub>NHPh)] **XLVI'**

SCF Done: -5706.89362017

C 2.333361000 -0.696791000 0.082099000  
C 3.003991000 -0.422355000 -1.112829000  
C 4.325071000 0.024478000 -1.073106000  
C 4.975337000 0.205566000 0.152143000  
C 4.294438000 -0.060085000 1.341914000  
C 2.973854000 -0.514195000 1.310040000  
N 0.966404000 -1.178073000 0.084644000  
Pt -0.685996000 -0.013187000 -0.535298000  
C -2.789386000 0.685434000 -0.828356000  
C -2.054438000 1.082224000 -1.938513000  
C 0.592063000 -2.353079000 -0.813410000  
C -0.738200000 -1.901518000 -1.430207000  
Br -0.095898000 2.242485000 0.616527000  
H 4.496948000 -0.528530000 -2.067316000  
H 2.842779000 0.242915000 -2.003031000  
H 6.001659000 0.560715000 0.177217000  
H 4.785107000 0.087243000 2.299788000  
H 2.439859000 -0.708787000 2.236824000  
H 0.684949000 -1.394940000 1.046106000  
H 0.527646000 -3.255850000 -0.199300000  
H 1.388362000 -2.484937000 -1.547519000  
H -1.600599000 -2.470410000 -1.081577000  
H -0.715156000 -1.852466000 -2.521209000  
H -2.092799000 0.512483000 -2.862469000  
H -1.654567000 2.089834000 -1.997015000  
H -2.963322000 1.373142000 -0.007015000  
H -3.403760000 -0.208627000 -0.854656000  
H 0.164967000 0.505386000 -1.740927000  
Br -1.779980000 -1.085061000 1.616163000

[PtBr<sub>2</sub>H(κ<sup>2</sup>:C,N-CH<sub>2</sub>CH<sub>2</sub>NHPh)] **XLVIII**

SCF Done: -5628.28959672

C 3.031580000 -1.288781000 0.159482000  
C 2.601151000 0.041530000 0.194299000  
C 3.389473000 1.054793000 -0.359211000  
C 4.619395000 0.735942000 -0.940969000  
C 5.062776000 -0.588104000 -0.966874000  
C 4.264972000 -1.596874000 -0.416170000  
N 1.327938000 0.402422000 0.785424000  
C 1.031586000 -0.035783000 2.202065000  
C -0.460361000 -0.359172000 2.111362000  
Pt -0.540635000 -0.306359000 0.062428000  
Br -2.704983000 -1.164987000 -0.632806000  
Br -1.060133000 2.213406000 -0.234407000  
H 1.185931000 1.415547000 0.700587000  
H 3.042991000 2.085404000 -0.342165000  
H 5.227178000 1.526607000 -1.371703000  
H 6.018791000 -0.835435000 -1.419439000  
H 4.595927000 -2.631249000 -0.445397000  
H 2.400750000 -2.081271000 0.550699000  
H -0.755754000 -1.335764000 2.492382000  
H 1.294096000 0.755682000 2.913056000  
H -1.127685000 0.430849000 2.458404000  
H 1.632678000 -0.919828000 2.417091000  
H -0.105280000 -1.807488000 0.127646000

[PtBr<sub>2</sub>H(κ<sup>2</sup>:C,N-CH<sub>2</sub>CH<sub>2</sub>NHPh)] **XLVIII**

SCF Done: -3344.24687145

C -1.582626000 2.652577000 0.000607000  
C -0.450223000 2.221489000 -0.704411000  
C 0.737306000 2.959601000 -0.669673000  
C 0.787045000 4.144268000 0.070038000  
C -0.338490000 4.587282000 0.772820000  
C -1.520729000 3.842682000 0.731706000  
N -0.507067000 0.961852000 -1.425333000  
Pt -0.611878000 -0.682053000 0.102803000  
Br -2.911784000 -1.046352000 -0.599626000  
N 1.285377000 -0.588507000 1.069438000  
C 0.966711000 -1.804172000 1.947705000  
C -0.536067000 -1.966670000 1.710042000  
C 2.551823000 -0.582903000 0.344461000  
C 4.458263000 0.452989000 0.585029000  
C 4.683597000 0.469760000 -0.088771000  
C 5.000455000 -0.545190000 -0.994003000  
C 4.087347000 -1.579678000 -1.227190000  
C 2.859442000 -1.601154000 -0.563484000  
H 1.265455000 0.251391000 1.652154000  
H 3.220872000 1.238968000 1.299185000  
H 5.389253000 1.272285000 0.104564000  
H 5.953395000 -0.533709000 -1.514239000  
H 4.328493000 -2.372511000 -1.929033000  
H 2.157077000 -2.407879000 -0.755555000  
H -0.856132000 -2.985003000 1.484529000  
H 1.278095000 -1.610467000 2.979285000  
H -1.168127000 -1.553996000 2.504659000  
H 1.546227000 -2.643756000 1.562908000  
H -1.362916000 0.883478000 -1.980997000  
H 0.283552000 0.865129000 -2.063167000  
H 1.607785000 2.627883000 -1.231496000  
H 1.702847000 4.728360000 0.083118000  
H -0.297322000 5.513856000 1.337398000

[PtBr<sub>2</sub>H(κ<sup>2</sup>:C,N-CH<sub>2</sub>CH<sub>2</sub>NHPh)] **IL**

SCF Done: -3344.25001393

C 3.396709000 -1.287315000 0.449869000  
C 3.180465000 -0.172914000 -0.363136000  
C 4.108785000 0.865742000 -0.438959000  
C 5.284848000 0.781964000 0.311369000  
C 5.520184000 -0.329353000 1.125896000  
C 4.578461000 -1.361593000 1.190602000  
N 1.944301000 -0.092433000 -1.148748000  
Pt 0.188354000 0.413784000 -0.107183000  
C -0.217878000 2.391479000 -0.664011000  
C -1.351061000 2.557095000 0.347418000  
N -1.544756000 1.129613000 0.849264000  
C -2.842395000 0.500350000 0.609080000  
C -3.461829000 -0.165548000 1.667466000  
C -4.707513000 -0.764484000 1.465044000  
C -5.324002000 -0.694068000 0.213666000  
C -4.691154000 -0.026519000 -0.840043000  
C -3.445033000 0.571675000 -0.648701000  
Br -0.544316000 -1.922664000 -0.542834000  
H -1.368942000 1.098003000 1.854366000  
H -2.981435000 -0.225266000 2.642035000  
H -5.192136000 -1.281972000 2.287355000  
H -6.292556000 -1.159347000 0.057698000  
H -5.163962000 0.024602000 -1.816202000  
H -2.951730000 1.068487000 -1.479420000  
H -0.546438000 2.301255000 -1.704011000  
H -1.062523000 3.179209000 1.198098000  
H 0.589164000 3.117791000 -0.573734000  
H -2.288083000 2.935848000 -0.066369000  
H 1.736505000 -1.006553000 -1.568010000  
H 2.073630000 0.562435000 -1.923368000  
H 3.930775000 1.725555000 -1.081842000  
H 6.017202000 1.581426000 0.250626000  
H 6.437372000 -0.394063000 1.703484000  
H 4.761416000 -2.229178000 1.817489000  
H 2.660604000 -2.085254000 0.498963000  
H 1.032252000 1.345814000 0.805354000

[PtBr<sub>3</sub>(η<sup>2</sup>-H-CH<sub>2</sub>CH<sub>2</sub>NHPh)]<sup>-</sup> **TS(XX-L)**

SCF Done: -8199.83556270

C -4.023628000 0.171410000 0.026929000  
C -4.631205000 -1.029479000 -0.419509000  
C -5.976471000 -1.061090000 -0.767857000  
C -6.772859000 0.092114000 -0.690773000  
C -6.181468000 1.280128000 -0.254497000  
C -4.830661000 1.331151000 0.100642000  
H -4.025399000 -1.930291000 -0.487566000  
H -6.410947000 -1.999328000 -1.107906000  
H -7.823975000 0.061228000 -0.965909000  
H -6.775361000 2.190123000 -0.188695000  
H -4.402037000 2.271313000 0.433058000  
N -2.696797000 0.177408000 0.374532000  
C -1.979600000 1.346873000 0.835497000  
C -0.531576000 1.026390000 1.229932000  
H -0.299964000 0.725396000 -0.324340000  
H -2.169295000 -0.689697000 0.301548000  
H -2.467662000 1.761775000 1.735880000  
H -2.001755000 2.142339000 0.072983000  
H -0.037316000 1.952423000 1.521754000  
H -0.527294000 0.306008000 2.050862000  
Pt 1.058892000 0.068747000 0.072253000  
Br 2.112255000 2.307321000 -0.259104000  
Br 3.211239000 -1.082106000 -0.424078000  
Br -0.100929000 -2.149226000 0.350003000

[PtBr<sub>3</sub>(η<sup>2</sup>-H-CH<sub>2</sub>CH<sub>2</sub>NHPh)]<sup>-</sup> **L**

SCF Done: -8199.85427241

C -4.298119000 0.337546000 0.121857000  
C -4.754806000 -0.994789000 0.277023000  
C -6.105006000 -1.303505000 0.158585000  
C -7.054068000 -0.307612000 -0.120264000  
C -6.611387000 1.006826000 -0.282331000  
C -5.256681000 1.334770000 -0.168621000  
H -4.029466000 -1.775481000 0.493451000  
H -6.422921000 -2.336925000 0.282886000  
H -8.108541000 -0.555193000 -0.212247000  
H -7.325836000 1.797248000 -0.505907000  
H -4.946084000 2.365521000 -0.307220000  
N -2.958317000 0.619317000 0.287339000  
C -2.375682000 1.897743000 -0.074154000  
C -0.874094000 1.923916000 0.207665000  
H -0.364058000 1.218527000 -0.502428000  
H -2.323184000 -0.177205000 0.245631000  
H -2.848466000 2.693434000 0.521174000  
H -2.563087000 2.141996000 -1.135116000  
H -0.433756000 2.901020000 -0.003846000  
H -0.660407000 1.663217000 1.247131000  
Pt 1.238473000 0.049921000 -0.019103000  
Br 2.641649000 2.082222000 0.024201000  
Br 3.130084000 -1.437491000 -0.027521000  
Br -0.397099000 -1.831434000 -0.035634000

[PtBr<sub>3</sub>(CH<sub>3</sub>CH<sub>2</sub>NHPh)]<sup>-</sup> **LI**

SCF Done: -8199.88446487

|    |              |              |              |
|----|--------------|--------------|--------------|
| C  | 3.054295000  | -0.953116000 | -0.258775000 |
| C  | 2.387337000  | 0.268846000  | -0.112131000 |
| C  | 2.729052000  | 1.350168000  | -0.935491000 |
| C  | 3.739529000  | 1.213794000  | -1.888554000 |
| C  | 4.418690000  | -0.000484000 | -2.030357000 |
| C  | 4.067369000  | -1.078463000 | -1.212268000 |
| N  | 1.329213000  | 0.448085000  | 0.862405000  |
| Pt | -0.630836000 | -0.005361000 | 0.097723000  |
| Br | -2.909966000 | -0.382639000 | -0.750693000 |
| Br | -0.906111000 | 2.499485000  | 0.136549000  |
| Br | -0.192385000 | -2.462279000 | 0.215785000  |
| H  | 1.177917000  | 1.457183000  | 0.970967000  |
| C  | 1.572960000  | -0.121084000 | 2.222319000  |
| H  | 2.177911000  | 2.282552000  | -0.844918000 |
| H  | 3.988399000  | 2.058970000  | -2.526161000 |
| H  | 5.204370000  | -0.108081000 | -2.774494000 |
| H  | 4.572386000  | -2.035152000 | -1.324452000 |
| C  | 2.761238000  | -1.808691000 | 0.337965000  |
| H  | 2.808456000  | 0.457420000  | 2.916608000  |
| C  | 0.668226000  | 0.100716000  | 2.793865000  |
| H  | 1.621682000  | -1.206488000 | 2.126195000  |
| H  | 2.898193000  | 0.026035000  | 3.921662000  |
| H  | 3.730421000  | 0.235337000  | 2.368431000  |
| H  | 2.730009000  | 1.546890000  | 3.026219000  |

[PtHBr<sub>3</sub>(CH<sub>3</sub>CH<sub>2</sub>NHPh)(PhNH<sub>2</sub>)]<sup>-</sup> **TS(xxv)**

SCF Done: -8487.44969025

|    |              |              |              |
|----|--------------|--------------|--------------|
| C  | -4.318864000 | -0.234602000 | 0.034052000  |
| C  | -5.163653000 | -0.694526000 | 1.071733000  |
| C  | -6.468462000 | -0.208476000 | 1.192269000  |
| C  | -6.978702000 | 0.733469000  | 0.295342000  |
| C  | -6.145965000 | 1.190680000  | -0.737891000 |
| C  | -4.843727000 | 0.722921000  | -0.870609000 |
| H  | -4.797861000 | -1.425327000 | 1.786019000  |
| H  | -7.092613000 | -0.578583000 | 2.003874000  |
| H  | -7.995063000 | 1.105447000  | 0.396290000  |
| H  | -6.516797000 | 1.927011000  | -1.448633000 |
| H  | -4.207789000 | 1.091018000  | -1.672720000 |
| N  | -3.035636000 | -0.692395000 | -0.124594000 |
| H  | -2.466214000 | -0.277666000 | -0.857124000 |
| C  | -2.362225000 | -1.576742000 | 0.806033000  |
| H  | -2.896945000 | -2.540520000 | 0.860092000  |
| H  | -2.375199000 | -1.151663000 | 1.823769000  |
| C  | -0.918393000 | -1.902536000 | 0.373676000  |
| H  | -0.511941000 | -2.589606000 | 1.119209000  |
| H  | -0.958358000 | -2.419164000 | -0.591200000 |
| H  | -0.718656000 | -0.352338000 | 0.715715000  |
| Pt | 0.653050000  | -0.552881000 | 0.059648000  |
| Br | -0.319803000 | 0.188294000  | -2.144093000 |
| Br | 2.769748000  | -1.933219000 | -1.207161000 |
| Br | 1.533311000  | -0.983861000 | 2.373092000  |
| N  | 2.321110000  | 0.976279000  | -0.167268000 |
| H  | 2.640181000  | 0.787638000  | -1.118150000 |
| H  | 3.015037000  | 0.571809000  | 0.461391000  |
| C  | 2.067869000  | 2.358881000  | 0.095025000  |
| C  | 1.750326000  | 3.228661000  | -0.955992000 |
| C  | 1.474948000  | 4.571487000  | -0.689301000 |
| C  | 1.513667000  | 5.058631000  | 0.620997000  |
| C  | 1.825448000  | 4.183530000  | 1.667412000  |
| C  | 2.094270000  | 2.837951000  | 1.411814000  |
| H  | 1.697998000  | 2.845341000  | -1.970943000 |
| H  | 1.223698000  | 5.236813000  | -1.512120000 |
| H  | 1.298529000  | 6.104760000  | 0.824932000  |
| H  | 1.849221000  | 4.545191000  | 2.692859000  |
| H  | 2.303397000  | 2.148905000  | 2.225540000  |

[PtHBr<sub>3</sub>(CH<sub>3</sub>CH<sub>2</sub>NHPh)(PhNH<sub>2</sub>)]<sup>-</sup> **TS(xxv')**

SCF Done: -8487.460639

|    |              |              |              |
|----|--------------|--------------|--------------|
| C  | -4.699863000 | 2.570335000  | 0.293697000  |
| C  | -4.591717000 | 1.259243000  | -0.220838000 |
| C  | -5.055072000 | 1.024800000  | -1.534345000 |
| C  | -5.606925000 | 2.057417000  | -2.291085000 |
| C  | -5.715319000 | 3.354116000  | -1.772796000 |
| C  | -5.253436000 | 3.595187000  | -0.473114000 |
| N  | -4.104689000 | 0.225051000  | 0.558724000  |
| Pt | -0.018612000 | -0.677521000 | 0.293161000  |
| Br | -1.736688000 | -2.442766000 | -0.120617000 |
| C  | 0.945592000  | 1.295160000  | 0.248351000  |
| C  | 2.395674000  | 1.689971000  | 0.555323000  |
| N  | 3.349399000  | 0.906007000  | -0.199353000 |
| C  | 4.703596000  | 1.137664000  | -0.209036000 |
| C  | 5.543892000  | 0.356810000  | -1.041033000 |
| C  | 6.917910000  | 0.566797000  | -1.063291000 |
| C  | 7.512084000  | 1.556150000  | -0.264868000 |
| C  | 6.690428000  | 2.329867000  | 0.558141000  |
| C  | 5.306733000  | 2.134109000  | 0.592468000  |
| Br | -1.037692000 | -0.090086000 | 2.5004468000 |
| Br | 1.137080000  | -1.262585000 | -1.854886000 |
| H  | 1.332341000  | -0.121965000 | 0.852883000  |
| H  | 0.281519000  | 1.851478000  | 0.908458000  |
| H  | 0.719837000  | 1.498717000  | -0.799852000 |
| C  | 2.594980000  | 1.602216000  | 1.634811000  |
| H  | 2.488388000  | 2.762216000  | 0.303204000  |
| H  | 2.971398000  | 0.226469000  | -0.854658000 |
| H  | 4.696503000  | 2.750141000  | 1.245420000  |

|   |              |              |              |
|---|--------------|--------------|--------------|
| H | 7.126422000  | 3.102849000  | 1.188415000  |
| H | 8.587094000  | 1.715124000  | -0.285547000 |
| H | 7.535580000  | -0.050944000 | -1.712365000 |
| H | 5.096871000  | -0.416404000 | -1.661873000 |
| H | -3.478862000 | 0.477006000  | 1.318008000  |
| H | -3.738076000 | -0.588831000 | 0.072235000  |
| H | -4.345676000 | 2.772874000  | 1.302503000  |
| H | -5.320499000 | 4.595838000  | -0.049617000 |
| H | -6.143439000 | 4.156520000  | -2.368355000 |
| H | -5.950311000 | 1.846258000  | -3.302192000 |
| H | -4.971259000 | 0.024224000  | -1.952836000 |

[PtHBr<sub>3</sub>(CH<sub>3</sub>CH<sub>2</sub>NHPh)(PhNH<sub>2</sub>)]<sup>-</sup> **TS(XXXVI)**

SCF Done: -8199.82216394

|    |              |              |              |
|----|--------------|--------------|--------------|
| C  | 1.468366000  | 2.351191000  | -0.897415000 |
| C  | 2.292910000  | 3.477002000  | -0.847786000 |
| C  | 3.599529000  | 3.372888000  | -0.359099000 |
| C  | 4.075796000  | 2.134013000  | 0.079272000  |
| C  | 3.262351000  | 0.998454000  | 0.024404000  |
| C  | 1.955925000  | 1.114634000  | -0.463411000 |
| H  | 0.438561000  | 2.433784000  | -1.232220000 |
| H  | 1.905000000  | 4.439292000  | -1.173466000 |
| H  | 4.236142000  | 4.253462000  | -0.310524000 |
| H  | 5.087531000  | 2.043438000  | 0.467423000  |
| H  | 3.620196000  | 0.025425000  | 0.354609000  |
| N  | 1.125777000  | -0.075332000 | -0.538347000 |
| C  | 1.057319000  | -0.749436000 | -1.894342000 |
| C  | -0.386330000 | -1.249761000 | -1.909706000 |
| H  | -1.157279000 | 0.262342000  | -1.813882000 |
| H  | 1.523928000  | -0.804131000 | 0.102355000  |
| H  | 1.818708000  | -1.535300000 | -1.942890000 |
| H  | -0.520721000 | -2.237909000 | -1.458941000 |
| H  | -0.867951000 | -1.237368000 | -2.890988000 |
| Pt | -0.975058000 | -0.013178000 | -0.296507000 |
| Br | 2.843133000  | -2.675312000 | 0.478113000  |
| Br | -3.442629000 | -0.257958000 | -0.329824000 |
| Br | -0.917705000 | 0.796379000  | 2.053521000  |
| H  | 1.236832000  | 0.009399000  | -2.660295000 |

[PtBr<sub>2</sub>(CH<sub>2</sub>CH<sub>2</sub>NHPh)(C<sub>2</sub>H<sub>4</sub>)(PhNH<sub>3</sub>)]<sup>+</sup> **TS (XXXII-A) (a)**

SCF Done: -5994.496442

|    |              |              |              |
|----|--------------|--------------|--------------|
| C  | 4.515453000  | -0.955997000 | 1.026872000  |
| C  | 3.512713000  | -1.529958000 | 0.222863000  |
| C  | 3.894803000  | -2.440497000 | -0.784513000 |
| C  | 5.235600000  | -2.759073000 | -0.980003000 |
| C  | 6.232879000  | -2.183375000 | -0.181391000 |
| C  | 5.859780000  | -1.284199000 | 0.818104000  |
| N  | 2.161123000  | -1.192160000 | 0.361360000  |
| C  | 1.666392000  | -0.569122000 | 1.577666000  |
| C  | 0.150774000  | -0.690418000 | 1.773349000  |
| Pt | -1.581925000 | -0.246857000 | 0.444183000  |
| Br | -3.814828000 | -0.224001000 | -0.650006000 |
| Br | -0.858671000 | -2.065664000 | -1.085591000 |
| C  | -1.967383000 | 1.760350000  | 1.271613000  |
| C  | -2.536160000 | 0.818493000  | 2.129012000  |
| H  | -2.042628000 | 0.529229000  | 3.052430000  |
| H  | -3.594453000 | 0.586885000  | 2.062261000  |
| H  | -2.581717000 | 2.268671000  | 0.534076000  |
| H  | -1.013218000 | 2.226156000  | 1.502848000  |
| H  | -0.100607000 | -0.135513000 | 2.677881000  |
| H  | -0.127422000 | -1.740146000 | 1.893476000  |
| H  | 2.114005000  | -1.040118000 | 2.471512000  |
| H  | 1.966194000  | 0.487879000  | 1.602331000  |
| H  | 1.510029000  | -1.841574000 | -0.072738000 |
| H  | 4.256879000  | -0.253366000 | 1.813249000  |
| H  | 6.617752000  | -0.828768000 | 1.451087000  |
| H  | 7.278005000  | -2.435428000 | -0.336502000 |
| H  | 5.504233000  | -3.465722000 | -1.761471000 |
| H  | 3.129155000  | -2.892367000 | -1.411673000 |
| H  | -0.060449000 | 0.295084000  | 0.445285000  |
| N  | 0.999147000  | 1.307242000  | -0.916641000 |
| H  | 0.354387000  | 1.166897000  | -1.688773000 |
| H  | 1.704401000  | 0.569545000  | -0.908471000 |
| C  | 1.485776000  | 2.624360000  | -0.789242000 |
| C  | 0.681450000  | 3.716257000  | -1.158456000 |
| C  | 1.139910000  | 5.022038000  | -0.977053000 |
| C  | 2.400483000  | 5.264010000  | -0.420948000 |
| C  | 3.202596000  | 4.178303000  | -0.055406000 |
| C  | 2.754504000  | 2.868419000  | -0.236480000 |
| H  | -0.299473000 | 3.537496000  | -1.594372000 |
| H  | 0.507144000  | 5.854306000  | -1.275238000 |
| H  | 2.754977000  | 6.281522000  | -0.283074000 |
| H  | 4.190695000  | 4.348121000  | 0.365125000  |
| H  | 3.395410000  | 2.031171000  | 0.031394000  |

[PtBr<sub>2</sub>(CH<sub>2</sub>CH<sub>2</sub>NHPh)(C<sub>2</sub>H<sub>4</sub>)(PhNH<sub>3</sub>)]<sup>+</sup> **TS (XXXII-A) (b)**

SCF Done: -5994.490737

|    |              |              |              |
|----|--------------|--------------|--------------|
| C  | 4.089615000  | -2.006570000 | -0.705020000 |
| C  | 3.993143000  | -1.419085000 | 0.570417000  |
| C  | 5.118751000  | -1.468367000 | 1.419411000  |
| C  | 6.298884000  | -2.079197000 | 1.003814000  |
| C  | 6.395212000  | -2.654019000 | -0.270097000 |
| C  | 5.128345000  | -2.611258000 | -1.112846000 |
| N  | 2.839722000  | -0.749084000 | 1.003896000  |
| C  | 1.563224000  | -0.908008000 | 0.307058000  |
| C  | 0.459204000  | -0.124440000 | 1.036472000  |
| Pt | -1.646336000 | -0.315682000 | 0.418200000  |



H 2.508424000 4.302824000 1.899000000  
H 1.826803000 1.925363000 1.701581000

[PtBr<sub>2</sub>(CH<sub>2</sub>CH<sub>2</sub>NHPh) (PhNH<sub>3</sub>) (PhNH<sub>2</sub>) ] **TS(XXXIX-C)**

SCF Done: -6203.53477258

C -4.634538000 -1.782119000 -0.699822000  
C -4.304379000 -1.779514000 0.667473000  
C -5.330072000 -2.006421000 1.607679000  
C -6.642218000 -2.220264000 1.193357000  
C -6.970070000 -2.212947000 -0.168292000  
C -5.957437000 -1.994069000 -1.103289000  
N -3.002529000 -1.506827000 1.131220000  
C -1.852383000 -1.652367000 0.231174000  
C -0.548258000 -1.308856000 0.977447000  
Pt 1.032179000 -0.077787000 0.120375000  
Br 0.466806000 -0.759299000 -2.203418000  
Br 1.669187000 0.793463000 2.363515000  
N 2.857399000 0.701600000 -0.666407000  
C 4.034655000 -0.152817000 -0.556413000  
C 4.974044000 0.088918000 0.447896000  
C 6.095410000 -0.738422000 0.551383000  
C 6.278178000 -1.795350000 -0.344276000  
C 5.328114000 -2.028097000 -1.344059000  
C 4.198848000 -1.214065000 -1.450880000  
H 3.020955000 1.586152000 -0.183333000  
H 2.657761000 0.908911000 -1.648020000  
H 4.823463000 0.902089000 1.152496000  
H 6.824898000 -0.552101000 1.334762000  
H 7.153172000 -2.434306000 -0.263074000  
H 5.459334000 -2.850782000 -2.041672000  
H 3.444013000 -1.405191000 -2.208121000  
H -0.734716000 -1.044712000 2.022511000  
H 0.135008000 -2.164477000 0.981762000  
H -2.833792000 -1.922981000 2.042324000  
H -1.788354000 -2.669882000 -0.184727000  
H -1.995399000 -0.982530000 -0.619152000  
H -5.089790000 -2.005459000 2.669659000  
H -7.139545000 -2.393745000 1.939440000  
H -7.993873000 -2.380211000 -0.490531000  
H -6.188717000 -1.993042000 -2.165795000  
H -3.870101000 -1.627788000 -1.453778000  
N -1.847956000 1.409498000 1.078249000  
H -1.373739000 1.700669000 1.929212000  
H -2.620871000 0.777700000 1.289003000  
C -2.162291000 2.473867000 0.203541000  
C -1.352181000 3.619909000 0.167668000  
C -1.632892000 4.649214000 -0.732400000  
C -2.714450000 4.550215000 -1.613759000  
C -3.516880000 3.405359000 -1.580758000  
C -3.246717000 2.372265000 -0.681688000  
H -0.505389000 3.698525000 0.845846000  
H -1.000440000 5.533730000 -0.743715000  
H -2.930013000 5.353373000 -2.312948000  
H -4.363251000 3.313059000 -2.256881000  
H -3.878755000 1.486958000 -0.661499000  
H -0.522459000 0.161139000 0.600210000

[PtBr<sub>2</sub>(CH<sub>2</sub>CH<sub>2</sub>NHPh) (PhNH<sub>3</sub>) (PhNH<sub>2</sub>) ] **C·PhNH<sub>2</sub>**

SCF Done: -6203.547994

C -5.287596000 -1.087705000 -0.879135000  
C -4.931382000 -0.536386000 0.364145000  
C -5.901751000 0.194898000 1.078931000  
C -7.182378000 0.376820000 0.561890000  
C -7.532522000 -0.168311000 -0.679433000  
C -6.575982000 -0.897896000 -1.388466000  
N -3.632778000 -0.648278000 0.889633000  
C -2.776933000 -1.768408000 0.500321000  
C -1.432653000 -1.686991000 1.213439000  
Pt 0.633063000 -0.518927000 0.274703000  
Br -0.138704000 -0.957225000 -2.052056000  
Br 1.420771000 -0.051124000 2.580724000  
N 2.285344000 0.395258000 -0.477928000  
C 3.533242000 -0.359528000 -0.546426000  
C 4.521717000 -0.141802000 0.413571000  
C 5.725181000 -0.846189000 0.323635000  
C 5.933661000 -1.755391000 -0.717074000  
C 4.929843000 -1.965587000 -1.668836000  
C 3.721075000 -1.272969000 -1.585607000  
H 2.407463000 1.240683000 0.088126000  
H 2.003555000 0.707081000 -1.412960000  
H 4.346764000 0.555149000 1.227867000  
H 6.497190000 -0.680870000 1.069912000  
H 6.870114000 -2.302352000 -0.783418000  
H 5.083281000 -2.675690000 -2.476758000  
H 2.926529000 -1.445811000 -2.305601000  
H -1.490986000 -1.725080000 2.306654000  
H -0.773889000 -2.498422000 0.888925000  
H -3.622046000 -0.489944000 1.892780000  
H -3.243635000 -2.742305000 0.730739000  
H -2.600703000 -1.729971000 -0.578037000  
H -5.641139000 0.625481000 2.044757000  
H -7.911974000 0.943870000 1.135030000  
H -8.532244000 -0.030364000 -1.081305000  
H -6.828886000 -1.333200000 -2.352296000  
H -4.566067000 -1.657252000 -1.455949000  
N -1.468604000 2.156089000 0.637073000  
H -1.678509000 2.430461000 1.586602000  
H -2.265108000 1.800601000 0.123694000  
C -0.486667000 2.864588000 -0.040038000  
C 0.531673000 3.533228000 0.672433000  
C 1.565771000 4.177713000 -0.006788000  
C 1.620481000 4.170395000 -1.407620000

C 0.606706000 3.514107000 -2.116193000  
C -0.437839000 2.873753000 -1.446846000  
H 0.516517000 3.522974000 1.759252000  
H 2.333401000 4.693977000 0.565500000  
H 2.423119000 4.679987000 -1.933496000  
H 0.621028000 3.502992000 -3.203660000  
H -1.208832000 2.356319000 -2.010974000  
H -1.065835000 -0.611303000 1.027508000

[PtBr<sub>2</sub>(CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>Ph) (PhNH<sub>2</sub>) (PhNH<sub>2</sub>) ] **D**

SCF Done: -6203.565271

Pt 1.135569000 0.087881000 -0.217350000  
Br -0.359366000 0.024529000 -2.211082000  
C 0.571898000 -1.767488000 0.537982000  
N 2.534145000 0.242923000 1.343162000  
C -0.734365000 -2.431838000 0.114480000  
N -1.902027000 -1.453288000 0.107795000  
H 1.370889000 -2.479168000 0.282109000  
H 0.568939000 -1.695801000 1.640315000  
H -0.680877000 -2.816455000 -0.906902000  
H -1.028112000 -3.251562000 0.780733000  
H -1.869855000 -0.824399000 0.946280000  
H -1.687558000 -0.813262000 -0.696783000  
C -3.219673000 -2.063902000 -0.059728000  
C -3.672347000 -2.353007000 -1.347704000  
C -4.919794000 -2.961416000 -1.506561000  
C -5.700308000 -3.272565000 -0.388909000  
C -5.234303000 -2.973369000 0.894759000  
C -3.986994000 -2.366978000 1.064872000  
H -3.061939000 -2.098177000 -2.209879000  
H -5.282424000 -3.185679000 -2.505936000  
H -6.671300000 -3.742446000 -0.518120000  
H -5.841266000 -3.206036000 1.765165000  
H -3.621369000 -2.124931000 2.059509000  
Br 2.001080000 2.454586000 -0.795811000  
C 3.739433000 -0.561994000 1.216240000  
H 2.764328000 1.244409000 1.285219000  
H 2.099724000 0.074280000 2.250936000  
C 4.672520000 -0.240452000 0.224828000  
C 5.829501000 -1.010356000 0.103606000  
C 6.052671000 -2.101664000 0.951815000  
C 5.110809000 -2.417642000 1.933172000  
C 3.952487000 -1.645388000 2.070509000  
H 4.479057000 0.595182000 -0.441944000  
H 6.556802000 -0.759391000 -0.663746000  
H 6.953966000 -2.699476000 0.847535000  
H 5.273895000 -3.261791000 2.597967000  
C 3.221370000 -1.890679000 2.838076000  
N -1.640069000 0.841537000 1.898014000  
H -0.771174000 1.027182000 1.382722000  
H -1.436853000 0.816075000 2.894404000  
C -2.679142000 1.764248000 1.579861000  
C -2.697261000 2.397818000 0.328102000  
C -3.753591000 3.249698000 -0.001938000  
C -4.797190000 3.480505000 0.900018000  
C -4.774006000 2.848939000 2.147274000  
C -3.723703000 1.993450000 2.487431000  
H -1.883489000 2.234272000 -0.374226000  
H -3.751432000 3.741138000 -0.971394000  
H -5.613224000 4.148179000 0.637872000  
H -5.573989000 3.023037000 2.862792000  
H -3.712719000 1.503942000 3.460075000

[PtBr<sub>2</sub>(CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>Ph) (PhNH<sub>2</sub>) (PhNH<sub>2</sub>) ] **TS (D-E)**

SCF Done: -6203.534566

Pt 1.320204000 -0.287194000 -0.206885000  
Br 2.576640000 -1.780039000 -1.710875000  
C 0.390041000 -2.046418000 0.755507000  
N 0.218288000 1.063163000 1.015319000  
C -0.175671000 -3.242580000 -0.022964000  
N -1.270207000 -2.882674000 -0.914136000  
H 1.312617000 -2.336707000 1.267748000  
H -0.319732000 -1.656259000 1.486985000  
H 0.618721000 -3.667156000 -0.639154000  
H -0.488199000 -4.013881000 0.698071000  
H -1.903315000 0.394881000 -1.296980000  
H -1.121003000 -3.108452000 -1.888566000  
C -2.602296000 -2.754718000 -0.530434000  
C -3.592315000 -2.589284000 -1.524404000  
C -4.930925000 -2.421381000 -1.178628000  
C -5.328165000 -2.411715000 0.165035000  
C -4.355355000 -2.583343000 1.152538000  
C -3.007461000 -2.751382000 0.819386000  
H -3.300173000 -2.596997000 -2.573104000  
H -5.670378000 -2.300857000 -1.966588000  
H -6.373170000 -2.284627000 0.432212000  
H -4.642089000 -2.593321000 2.01605000  
H -2.279473000 -2.888631000 1.612100000  
Br 2.796939000 1.655737000 -0.656935000  
C 0.276081000 0.898645000 2.455386000  
H 0.627268000 1.964972000 0.748859000  
H -0.757654000 1.050606000 0.667962000  
C 1.482731000 1.129005000 3.125131000  
C 1.537990000 0.972788000 4.510468000  
C 0.401560000 0.579010000 5.226850000  
C -0.797394000 0.347294000 4.549048000  
C -0.865173000 0.508628000 3.161135000  
H 2.363666000 1.420519000 2.559869000  
H 2.474022000 1.155535000 5.031137000  
H 0.451519000 0.456426000 6.305217000  
H -1.686675000 0.047284000 5.096996000

|   |              |              |              |
|---|--------------|--------------|--------------|
| H | -1.801607000 | 0.343815000  | 2.633951000  |
| N | -2.348726000 | 0.958314000  | -0.576683000 |
| H | 0.026607000  | -1.170647000 | -0.459078000 |
| H | -3.199717000 | 0.484274000  | -0.283699000 |
| C | -2.564228000 | 2.302991000  | -0.984789000 |
| C | -1.627170000 | 2.940813000  | -1.812998000 |
| C | -1.798013000 | 4.282670000  | -2.158970000 |
| C | -2.895561000 | 5.007338000  | -1.683534000 |
| C | -3.825233000 | 4.371845000  | -0.854873000 |
| C | -3.664209000 | 3.029128000  | -0.505065000 |
| H | -0.764951000 | 2.388635000  | -2.181418000 |
| H | -1.064443000 | 4.761452000  | -2.802377000 |
| H | -3.024521000 | 6.051170000  | -1.955200000 |
| H | -4.685213000 | 4.920470000  | -0.478902000 |
| H | -4.394187000 | 2.541550000  | 0.138332000  |

[PtBr<sub>2</sub>(CH<sub>3</sub>CH<sub>2</sub>NHPh)(PhNH<sub>2</sub>)(PhNH<sub>2</sub>)] **E**

SCF Done: -6203.546149

|    |              |              |              |
|----|--------------|--------------|--------------|
| Pt | 1.056401000  | -0.968611000 | -0.042652000 |
| Br | -0.297236000 | -3.002300000 | 0.031216000  |
| C  | -0.807514000 | 0.144386000  | 1.659426000  |
| N  | 2.161581000  | 0.833920000  | -0.148448000 |
| C  | -2.215045000 | -0.442576000 | 1.733712000  |
| N  | -2.948493000 | -0.184974000 | 0.482699000  |
| H  | -0.142217000 | -0.278151000 | 2.414261000  |
| H  | -0.795042000 | 1.236173000  | 1.713015000  |
| H  | -2.167807000 | -1.519294000 | 1.941320000  |
| H  | -2.738582000 | 0.033191000  | 2.566824000  |
| H  | -2.441525000 | 1.912266000  | -0.198323000 |
| H  | -2.576011000 | -0.798615000 | -0.240869000 |
| C  | -4.364118000 | -0.222739000 | 0.472267000  |
| C  | -5.030394000 | -0.820691000 | -0.613172000 |
| C  | -6.422472000 | -0.797467000 | -0.696949000 |
| C  | -7.185318000 | -0.189375000 | 0.305078000  |
| C  | -6.529412000 | 0.400714000  | 1.388835000  |
| C  | -5.135063000 | 0.391377000  | 1.475524000  |
| H  | -4.449107000 | -1.309116000 | -1.392992000 |
| H  | -6.911606000 | -1.268175000 | -1.546137000 |

|    |              |              |              |
|----|--------------|--------------|--------------|
| H  | -8.269821000 | -0.178127000 | 0.243544000  |
| H  | -7.104667000 | 0.879345000  | 2.177775000  |
| H  | -4.654262000 | 0.874839000  | 2.320968000  |
| Br | 2.824156000  | -1.945988000 | -1.362047000 |
| C  | 2.547479000  | 1.466332000  | 1.102219000  |
| H  | 2.991443000  | 0.570315000  | -0.690485000 |
| H  | 1.625420000  | 1.485566000  | -0.731781000 |
| C  | 3.010619000  | 0.852324000  | 1.909649000  |
| C  | 3.879410000  | 1.455525000  | 3.112598000  |
| C  | 3.285031000  | 2.657622000  | 3.514155000  |
| C  | 2.321578000  | 3.259505000  | 2.701262000  |
| C  | 1.948822000  | 2.666951000  | 1.490488000  |
| H  | 3.955239000  | -0.089800000 | 1.600680000  |
| H  | 4.629666000  | 0.981703000  | 3.739609000  |
| H  | 3.573887000  | 3.121481000  | 4.453159000  |
| H  | 1.858271000  | 4.195204000  | 3.002152000  |
| H  | 1.205719000  | 3.140698000  | 0.853160000  |
| N  | -2.036446000 | 2.848848000  | -0.193331000 |
| H  | -0.442338000 | -0.050520000 | 0.597341000  |
| H  | -2.715981000 | 3.567655000  | 0.024106000  |
| C  | -1.126681000 | 3.157237000  | -1.203200000 |
| C  | -0.533822000 | 2.142655000  | -1.983235000 |
| C  | 0.431728000  | 2.456756000  | -2.944959000 |
| C  | 0.831789000  | 3.780911000  | -3.154044000 |
| C  | 0.239797000  | 4.791961000  | -2.387604000 |
| C  | -0.722284000 | 4.489746000  | -1.423829000 |
| H  | -0.849462000 | 1.110219000  | -1.852910000 |
| H  | 0.857494000  | 1.655975000  | -3.545647000 |
| H  | 1.576748000  | 4.021503000  | -3.906887000 |
| H  | 0.529549000  | 5.828930000  | -2.539997000 |
| H  | -1.167751000 | 5.287010000  | -0.831735000 |