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To what extent can cyclometalation promote associative or dissociative ligand substitution at platinum(II) complexes? A combined kinetic and theoretical approach

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Supporting Information

(9 pages including this top sheet)

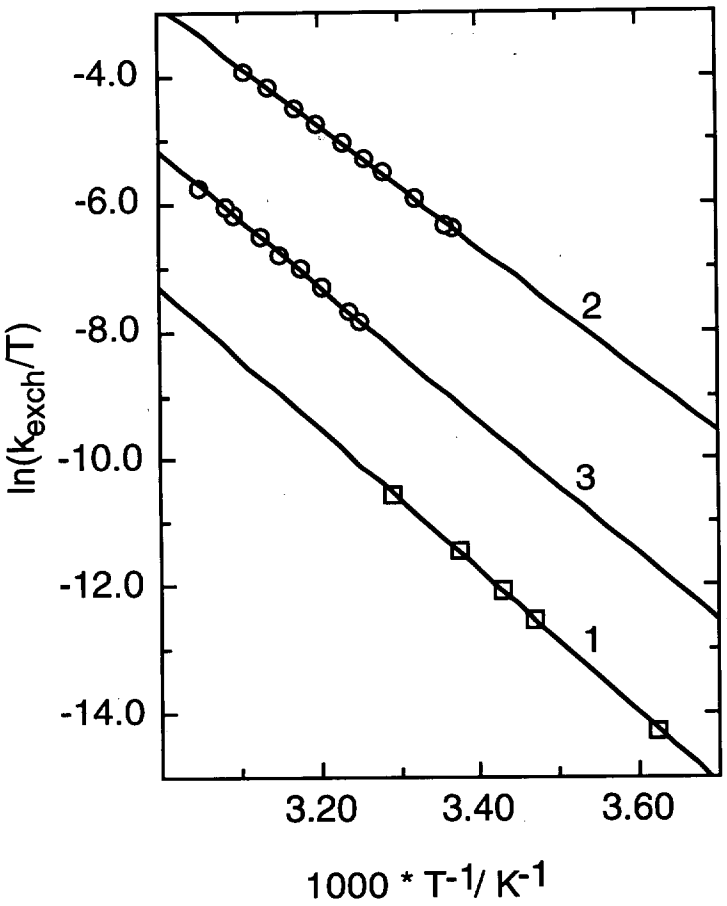

FIGURE S1

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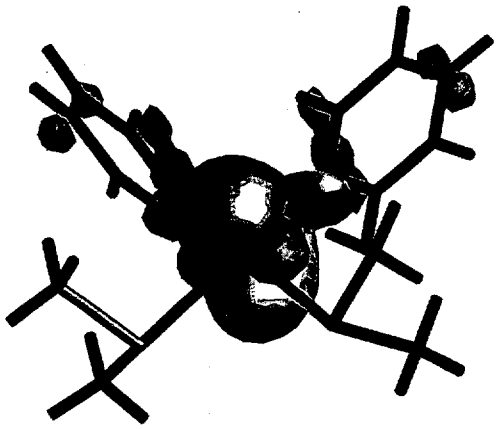
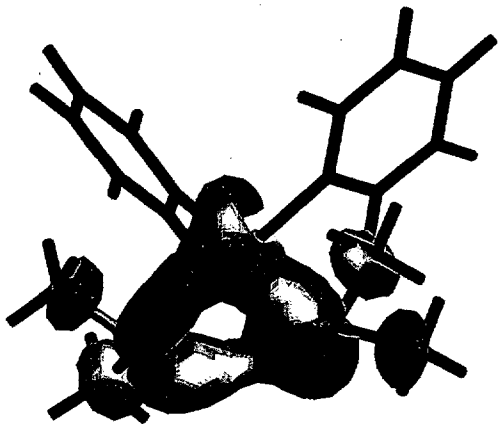
$PtPh_2(SMe_2)_2$

Energy a.u.

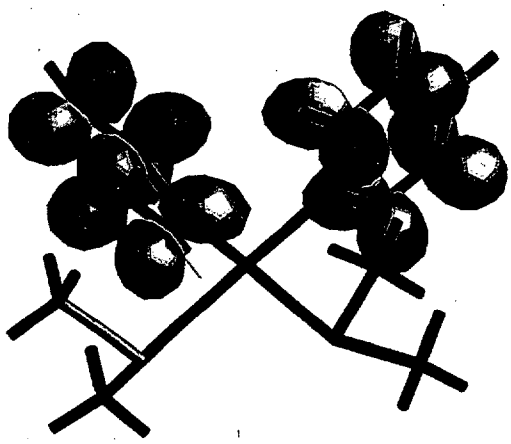
Occ. M.O. n.74 - **HOMO** **-0.2232**



Virt. M.O. n.75 - **LUMO** **-0.0302**



Virt. M.O. n.78
pure π(R1)+ π*(R2)* **-0.0152**



Virt. M.O. n.79
pure π(R1)+ π*(R2)* **-0.0054**

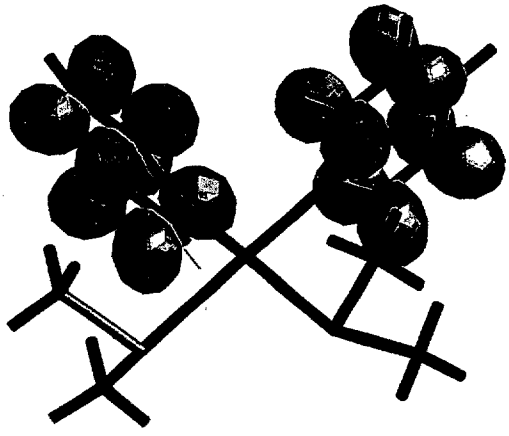
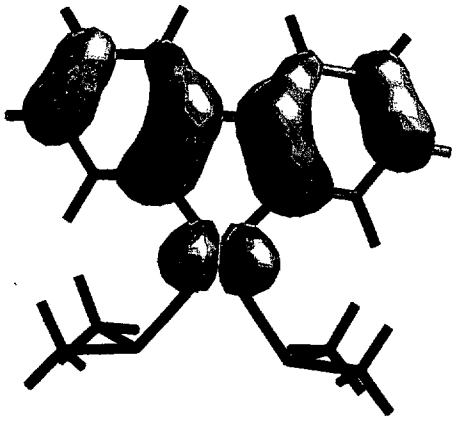


FIGURE S2

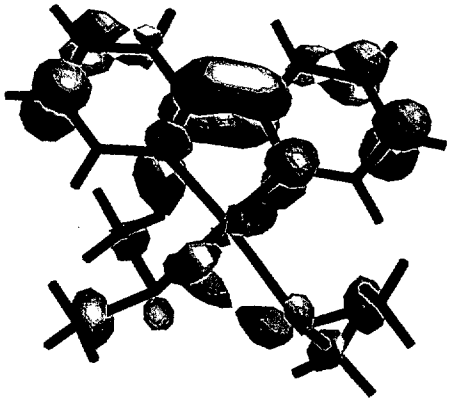
$Pt(bph)(SMe_2)_2$

Energy a.u.

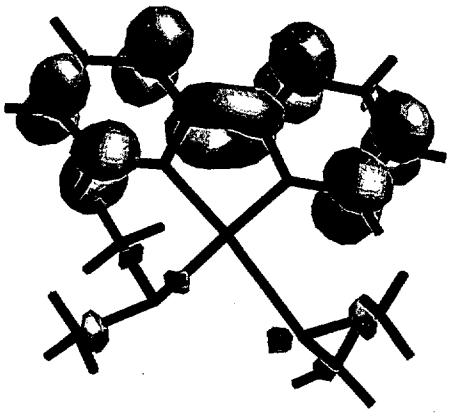
Occ. M.O. n.73 - **HOMO** **-0.2051**



Virt. M.O. n.74 - **LUMO** **-0.0513**



Virt. M.O. n.75 **-0.0309**



Virt. M.O. n.78 **-0.0067**

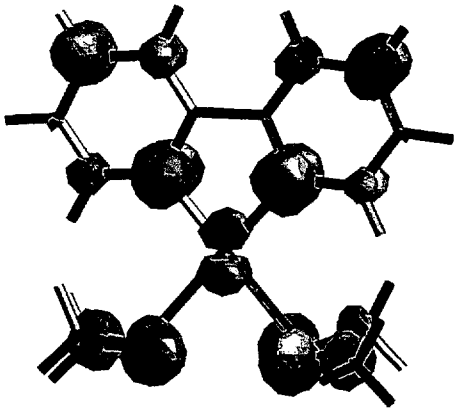


FIGURE S3

Table S1 - Pseudo-First-Order Rate Constants (k_{obsd}/s^{-1}) for the Reaction :

$[Pt(bph)(SMe_2)2] + N\text{-}N \text{ ---------> } [Pt(bph)(N\text{-}N)] + 2\ SMe_2$

carried out in the presence of different amounts of entering ligand and of free sulfide.[a] N-N are 2,2'-bipyridine (bpy) and 1,10-phenanthroline (phen).[a]

	$10^2 \times k_{obsd}$ [b]			
[phen][c]	$[SMe_2] = 1.7$[c]	$[SMe_2] = 4.5$[c]	$[SMe_2] = 10.8$[c]	$[SMe_2] = 17$[c]
2.5	5.53 (5.42)	2.96 (2.82)	1.49 (1.38)	0.97 (0.91)
3.7	6.36 (6.59)	3.74 (3.75)	1.98 (1.93)	1.24 (1.30)
5.0	7.16 (7.47)	5.00 (4.56)	2.51 (2.47)	1.65 (1.70)
10	8.91 (9.21)	6.48 (6.62)	3.88 (4.10)	3.03 (2.97)
15	10.0 (9.99)	7.98 (7.78)	5.47 (5.25)	3.74 (3.97)
20	10.0 (10.4)	8.85 (8.53)	5.92 (6.11)	4.79 (4.77)
25	11.0 (10.7)	9.44 (9.06)	6.91 (6.78)	5.11 (5.42)
[bpy][c]	$[SMe_2] = 1.7$[c]	$[SMe_2] = 4.5$[c]	$[SMe_2] = 10.8$[c]	$[SMe_2] = 17$[c]
16	5.39 (5.10)	2.97 (2.71)	1.55 (1.34)	1.22 (0.892)
29	5.90 (6.67)	3.50 (4.08)	2.68 (2.20)	1.32 (1.51)
40	7.02 (7.44)	4.39 (4.91)	3.34 (2.82)	2.01 (1.98)
72	8.18 (8.62)	6.53 (6.47)	4.74 (4.20)	3.46 (3.11)
100	9.10 (9.12)	7.13 (7.28)	5.26 (5.06)	3.93 (3.88)
200	10.0 (9.85)	8.61 (8.68)	6.76 (6.87)	5.86 (5.7)
400	10.8 (10.3)	9.92 (9.59)	8.33 (8.38)	7.33 (7.44)

[a] in toluene at T = 298.16K. [b] s^{-1}. Calculated values for k_{obsd} (see text) are given in parentheses. [c] mmol

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Table S2 - Pseudo-First-Order Rate Constants (k_{obs}/s^{-1}) for the Reaction :

$[Pt(bph)(SEt_2)2] + N\text{-}N \text{ ---------> } [Pt(bph)(N\text{-}N)] + 2\ SEt_2$

carried out in the presence of different amounts of entering ligand and of free sulfide.[a] N-N are 2,2'-bipyridine (bpy) and 1,10-phenanthroline (phen).[a]

	$10^2 \times k_{obsd}$ [b]			
[phen][c]	$[SEt_2]$ =12.5[c]	$[SEt_2]$ = 25.5[c]	$[SEt_2]$ = 39.0[c]	$[SEt_2]$ = 50.0[c]
2.5	0.711 (0.735)	0.431 (0.406)	0.280 (0.277)	0.238 (0.220)
3.7	0.978 (0.993)	0.571 (0.574)	0.419 (0.399)	0.330 (0.320)
5.0	1.17 (1.20)	0.769 (0.724)	0.536 (0.512)	0.429 (0.413)
10	1.75 (1.77)	1.25 (1.19)	0.850 (0.887)	0.764 (0.735)
20	2.31 (2.31)	1.88 (1.75)	1.33 (1.40)	1.11 (1.20)
25	2.43 (2.46)	1.95 (1.93)	1.60 (1.58)	1.35 (1.38)
[bpy][c]	$[SEt_2]$ =18.3 [c]	$[SEt_2]$ = 36.6 [c]	$[SEt_2]$ = 61.0[c]	$[SEt_2]$ = 73.2 [c]
16	0.785 (0.873)	0.468 (0.511)	0.358 (0.329)	0.268 (0.279)
29	1.21 (1.28)	0.766 (0.814)	0.610 (0.547)	0.486 (0.470)
40	1.49 (1.52)	1.01 (1.02)	0.756 (0.706)	0.631 (0.612)
72	1.98 (1.95)	1.49 (1.44)	1.15 (1.07)	0.992 (0.948)
100	2.13 (2.17)	1.72 (1.69)	1.41 (1.31)	1.22 (1.17)
200	2.61 (2.52)	2.08 (2.17)	1.87 (1.82)	1.61 (1.69)
400	2.85 (2.75)	2.50 (2.52)	2.20 (2.27)	2.05 (2.17)
[bpy][c,d]	$[SEt_2]$=2.5[c]	$[SEt_2]$=5[c]	$[SEt_2]$=10[c]	
12.0	2.03 (3.13)	1.10 (1.85)	0.72 (1.02)	
15.5	3.34 (3.71)	2.08 (2.27)	1.34 (1.28)	
31.0	5.33 (5.43)	3.62 (3.71)	2.16 (2.27)	
62.5	6.99 (7.09)	5.76 (5.45)	3.59 (3.73)	
500	9.93 (9.61)	9.00 (9.14)	8.53 (8.34)	

[a] in toluene at T = 298.16K. [b] s^{-1}. Calculated values for k_{obsd} (see text) are given in parentheses. [c] mmol [d] in dichloromethane at T=298.16K.

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Table S3- Temperature Dependence of Observed Rate Constants (k_{obs}/s^{-1}) for the isotopic exchange of $S(CD_3)_2$ with *cis*-$[PtPh_2(SMe_2)_2]$ in $CDCl_3$.[a]

T, K[a]	$10^3 k_{obsd}$, s^{-1}[b]
303.8	15.0± 0.2
296.4	6.22± 0.1
291.7	3.24± 0.01
288.2	1.97 ± 0.01
275.9	0.338± 0.001

[a] [complex] = 10. 4 mM ; $[S(CD_3)_2]$ = 283 mM ($\Delta H^{\ddagger}$ = +93 ± 1 kJ mol^{-1} ; $\Delta S^{\ddagger}$ = +26 ± 3 J K^{-1} mol^{-1}).

Table S4 - Temperature Dependence (Upper Set of Data) and Ligand Concentration Dependence (Lower Set of Data) of the Rate Constants (k_{exch} /s^{-1}) for ligand (SMe_2) exchange reaction on the complex $[Pt(bph)(SMe_2)_2]$ in $CDCl_3$.[a]

T, K	k_{exc} /s^{-1}
296.8	0.986 ± 0.008
297.5	1.06 ± 0.01
301.0	1.63 ± 0.04
304.5	2.46 ± 0.06
306.9	3.02 ± 0.05
308.9	3.96 ± 0.04
312.6	5.42 ± 0.04
315.1	6.84 ± 0.08
317.8	9.92 ± 0.06
322.1	13.0 ± 0.1

[a] from ^1H NMR magnetic transfer experiments; [complex] = 22 mM ; $[SMe_2]$ = 33.3 mM ($\Delta H^{\ddagger}$ = +80 ± 1 kJ mol^{-1} ; $\Delta S^{\ddagger}$ = +24 ± 4 J K^{-1} mol^{-1}).

$[SMe_2]$[b]	k_{exc} , s^{-1}[c]
15.9	1.08 ± 0.02
28.2	1.08 ± 0.02
46.0	1.05 ± 0.04
56.3	1.10 ± 0.04

[b] mM [c] at T=298 K, [complex] = 13.5 mM

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Table S5 - Temperature Dependence (Upper Set of Data) and Ligand Concentration Dependence (Lower Set of Data) of the Rate Constants (k_{exch} /s^{-1}) for ligand (SEt_2) exchange reaction on the complex $[Pt(bph)(SEt_2)_2]$ in $CDCl_3$.[a]

T, K	k_{exc} /s^{-1}
307.5	0.240 ± 0.002
309.0	0.284 ± 0.003
312.6	0.422 ± 0.004
313.8	0.562 ± 0.006
317.1	0.714 ± 0.005
319.5	0.962 ± 0.002
322.9	1.33 ± 0.01
324.2	1.50 ± 0.02
328.4	2.10 ± 0.03

[a] from ^1H NMR magnetic transfer experiments; [complex] = 8.7 mM ; $[SEt_2]$ = 35.9 mM ($\Delta H^{\ddagger}$ = +86 ± 2 kJ mol^{-1} ; $\Delta S^{\ddagger}$ = +23 ± 8 J K^{-1} mol^{-1}).

$[SEt_2]$[b]	k_{exc} , s^{-1}[c]
12.1	0.652 ± 0.004
20.4	0.618 ± 0.006
30.5	0.662 ± 0.002
35.9	0.592 ± 0.003

[b] mM [c] [complex] = 4.6 mM, at T=315.3K.