Supplementary Information for: Computational study and molecular orbital analysis of NMR shielding, spin-spin coupling, and electric field gradients of azido platinum complexes

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Table S1: ^{195}Pt and ^{15}N isotropic shielding calculated at different levels of theory.[a]

Complex	COSMO						No COSMO					
Theory	Pt	Npy	NH_3	N_α	N_β	N_γ	Pt	Npy	NH_3	N_α	N_β	N_γ
t-[$Pt(N_3)_2(py)_2$]												
QZ4P-SC	87.1	-6.2		155.3	-16.4	80.7	-80.9	-16.7		150.3	-16.4	68.2
QZ4P-SO	3699.8	17.9		165.5	-13.0	82.5	3579.4	8.3		156.0	-13.3	70.9
TZ2P-SC	259.4	-7.3		156.0	-16.6	81.3	90.9	-18.6		150.9	-16.8	69.1
TZ2P-SO	3297.4	17.6		167.3	-12.8	84.5	3163.8	5.8		156.4	-13.6	71.7
ctc-[$Pt(N_3)_2(OH)_2(NH_3)_2$]												
QZ4P-SC	-2162.3		229.6	145.5	-15.4	46.7	-1852.6		230.8	130.6	-13.6	13.6
QZ4P-SO	1370.6		242.4	150.6	-11.6	49.6	1693.6		238.4	127.6	-7.8	12.6
TZ2P-SC	-1892.7		231.8	145.3	-15.2	46.2	-1599.5		232.6	130.0	-13.6	13.1
TZ2P-SO	1152.7		246.6	147.9	-10.6	45.0	1431.8		241.4	126.7	-8.0	12.0
ttt-[$Pt(N_3)_2(OH)_2(NH_3)_2$]												
QZ4P-SC	-2032.7		227.0	141.7	-16.9	34.5	-1912.9		228.1	140.9	-12.2	18.7
QZ4P-SO	1432.1		237.2	142.9	-13.1	37.4	1652.4		232.6	137.7	-7.2	20.4
TZ2P-SC	-1772.5		229.1	141.4	-16.9	34.2	-1655.5		229.7	140.5	-12.4	19.0
TZ2P-SO	1455.6		237.2	141.7	-12.2	35.3	1385.8		234.2	137.0	-7.5	20.5
ttt-[$Pt(N_3)_2(OH)_2(Py)_2$]												
QZ4P-SC	-2083.3	-2.4		136.3	-17.1	31.0	-2003.4	-13.7		130.8	-15.8	17.7
QZ4P-SO	1471.4	14.8		130.9	-12.8	30.6	1568.9	3.7		124.3	-11.1	19.2
TZ2P-SC	-1835.6	-3.7		136.4	-17.4	31.0	-1759.7	-15.8		130.7	-16.3	18.2
TZ2P-SO	1445.3	17.1		132.9	-12.5	32.0	1568.9	3.7		124.3	-11.1	19.2
ttt-[$Pt(N_3)_2(OH)_2(NH_3)$(py)]												
QZ4P-SC	-2072.2	-4.7	230.2	138.5	-16.9	32.6	-1957.9	-13.7	229.5	134.1	-14.7	17.0
QZ4P-SO	1431.3	23.5	230.2	136.9	-12.8	33.8	1602.2	20.3	222.4	129.5	-9.9	18.5
TZ2P-SC	-1827.4	-6.0	232.2	138.4	-17.1	32.6	-1715.2	-15.7	231.1	133.9	-15.1	17.5
TZ2P-SO	1432.9	28.6	230.7	137.2	-12.2	33.5	1602.2	20.3	222.4	129.5	-9.9	18.5
t-[$PtCl_2(py)_2$]												
QZ4P-SC	64.7	-10.7					-83.6	-26.0				
QZ4P-SO	3501.8	17.0					3392.1	4.4				
TZ2P-SC	251.9	-10.9					120.2	-26.5				
TZ2P-SO	3142.2	18.0					3019.4	3.0				
Pyridine												
QZ4P-SC		-70.8						-92.8				
QZ4P-SO		-71.6						-92.8				
TZ2P-SC		-79.1						-103.0				
TZ2P-SO		-79.1						-103.0				
$PtCl_6^{2-}$												
QZ4P-SC	-1806.4						-2147.6					
QZ4P-SO	1777.8						1479.2					
TZ2P-SC	-1452.8						-1759.2					
TZ2P-SO	1459.3						1165.6					

[a] SC = Scalar ZORA, SO = spin–orbit ZORA. The computations where performed using the revised PBE functional and the QZ4P or TZ2P basis set for Pt.

Table S2: $J(^{195}\text{Pt-}^{15}\text{N})$ for various platinum azido complexes calculated at different levels of theory.

Complex	COSMO					No COSMO				
Theory	Npy	NH_3	N_α	N_β	N_γ	Npy	NH_3	N_α	N_β	N_γ
t-$[Pt(N_3)_2(py)_2]$										
QZ4P-SC	-422.7		-206.2	-1.6	-36.9	-464.7		-186.2	-4.5	-33.2
QZ4P-SO	-435.6		-185.9	-1.4	-37.0	-470.6		-169.6	-3.7	-34.8
TZ2P-SC	-370.3		-184.2	-0.5	-34.2	-407.5		-168.2	-3.0	-31.0
TZ2P-SO	-383.0		-175.1	-0.8	-34.7	-419.0		-158.9	-2.3	-32.7
ctc-$[Pt(N_3)_2(OH)_2(NH_3)_2]$										
QZ4P-SC		-248.1	-227.6	-3.5	-24.1		-207.7	-249.4	-1.1	-29.9
QZ4P-SO		-259.0	-216.4	-0.3	-22.5		-212.0	-240.9	3.1	-29.6
TZ2P-SC		-217.6	-203.5	-2.0	-22.8		-181.8	-224.3	0.1	-28.3
TZ2P-SO		-229.5	-203.6	1.2	-22.7		-188.9	-220.2	4.2	-28.5
ttt-$[Pt(N_3)_2(OH)_2(NH_3)_2]$										
QZ4P-SC		-267.4	-165.9	1.9	-25.7		-317.5	-164.4	0.2	-25.6
QZ4P-SO		-269.1	-158.3	5.3	-24.7		-335.0	-153.4	3.7	-26.3
TZ2P-SC		-235.6	-149.5	2.6	-24.4		-279.1	-149.3	1.1	-24.5
TZ2P-SO		-252.7	-145.3	5.6	-24.2		-299.3	-142.5	4.4	-25.4
ttt-$[Pt(N_3)_2(OH)_2(Py)_2]$										
QZ4P-SC	-356.9		-170.3	3.0	-26.8	-390.4		-165.8	1.1	-26.6
QZ4P-SO	-381.9		-159.8	5.7	-26.9					
TZ2P-SC	-313.2		-153.9	3.6	-25.5	-342.6		-151.3	1.9	-25.5
TZ2P-SO	-335.5		-148.9	6.6	-25.6	-366.7		-144.1	5.1	-26.6
ttt-$[Pt(N_3)_2(OH)_2(NH_3)(py)]$										
QZ4P-SC	-358.9	-266.6	-166.6	2.8	-26.1	-417.5	-295.5	-162.9	1.1	-25.8
QZ4P-SO	-355.7	-287.5	-156.8	5.9	-25.6	-439.4	-311.9	-151.6	4.5	-26.6
TZ2P-SC	-316.0	-234.8	-150.6	3.4	-24.8	-368.1	-259.0	-148.5	1.9	-24.8
TZ2P-SO	-337.9	-252.1	-145.9	6.3	-24.8	-393.6	-278.1	-141.5	5.1	-25.7
t-$[PtCl_2(py)_2]$										
QZ4P-SC	-373.2					-400.5				
QZ4P-SO	-389.7					-413.2				
TZ2P-SC	-327.7					-351.8				
TZ2P-SO	-345.6					-369.1				

Table S3: $J(^{195}\text{Pt-}^{15}\text{N})$ for various platinum-azido complexes calculated with the hybrid PBE0 functional (COSMO, spin-orbit ZORA).

	PBE0/SO with COSMO				
Complex	Npy	NH_3	N_α	N_β	N_γ
ctc-$[Pt(N_3)_2(OH)_2(NH_3)_2]$		-281.3	-231.8	14.2	-30.4
ttt-$[Pt(N_3)_2(OH)_2(NH_3)_2]$		-293.2	-179.7	19.7	-32.5
ttt-$[Pt(N_3)_2(OH)_2(Py)_2]$	-420.4		-179.3	20.4	-34.9
ttt-$[Pt(N_3)_2(OH)_2(NH_3)(py)]$	-387.6	-314.5	-177.5	20.5	-33.6
t-$[PtCl_2(py)_2]$	-389.7				

Table S4: Compositions of selected LMOs in the N_3 moiety in terms of atomic $s/p/d/f$ contributions. WBI = calculated Wiberg bond index.

	Azide, N_3^-		*t*-$[Pt(N_3)_2(py)_2]$		*ctc*-$[Pt(N_3)_2(OH)_2(NH_3)_2]$	
WBI(N_α–N_β)	1.93		1.69		1.63	
WBI(N_β–N_γ)	1.93		2.13		2.21	
σ(N_α–N_β)						
N_α	44	s[29]p[70]	44	s[29]p[71]	44	s[28]p[72]
N_β	56	s[49]p[51]	56	s[48]p[51]	56	s[48]p[52]
σ LP N_α						
N_α	98	s[71]p[29]	92	s[69]p[31]	93	s[67]p[33]
π_x LP N_α						
N_α	67	s[0]p[100]d[0]	71	s[0]p[100]d[0]	73	s[0]p[100]d[0]
N_β	17	s[0]p[99]d[1]	15	s[0]p[99]d[1]	14	s[1]p[98]d[1]
N_γ	16	s[0]p[100]d[0]	14	s[0]p[100]d[0]	13	s[0]p[100]d[0]
π_y LP N_α						
N_α	67	s[0]p[100]d[0]	64	s[3]p[97]d[0]	57	s[7]p[93]d[0]
N_β	17	s[0]p[99]d[1]	7	s[2]p[97]d[1]	4	s[1]p[97]d[2]
N_γ	16	s[0]p[100]d[0]	9	s[0]p[100]d[0]	6	s[0]p[100]d[0]
Pt			13	s[14]p[1]d[85]	31	s[13]p[0]d[87]
π_x (N_β–N_γ)						
N_β	47	s[0]p[100]d[0]	50	s[0]p[100]d[0]	50	s[0]p[100]d[0]
N_γ	52	s[0]p[100]d[0]	50	s[0]p[100]d[0]	49	s[0]p[100]d[0]
π_y (N_β–N_γ)						
N_α	0	s[0]p[99]d[1]	1	s[6]p[93]d[1]	1	s[4]p[95]d[1]
N_β	47	s[0]p[100]d[0]	54	s[1]p[99]d[0]	56	s[1]p[99]d[0]
N_γ	52	s[0]p[100]d[0]	44	s[1]p[99]d[0]	42	s[1]p[99]d[0]
Pt			0	s[17]p[0]d[82]	1	s[6]p[0]d[94]

All numerical values in %

Table S5: Compositions of selected LMOs in the N_3 moiety in terms of atomic $s/p/d/f$ contributions. WBI = calculated Wiberg bond index.

	ttt-[Pt(N_3)$_2$(OH)$_2$(NH_3)$_2$]		*ttt*-[Pt(N_3)$_2$(OH)$_2$(Py)$_2$]		*ttt*-[Pt(N_3)$_2$(OH)$_2$(NH_3)(py)]	
WBI(N_α–N_β)	1.64		1.66		1.65	
WBI(N_β-N_γ)	2.20		2.17		2.18	
σ(N_α–N_β)						
N_α	44	s[28]p[72]	44	s[28]p[71]	44	s[28]p[72]
N_β	56	s[49]p[51]	56	s[49]p[51]	56	s[48]p[52]
σ LP N_α						
N_α	93	s[68]p[32]	93	s[69]p[31]	93	s[69]p[31]
π_x LP N_α						
N_α	73	s[0]p[100]d[0]	71	s[0]p[100]d[0]	72	s[0]p[100]d[0]
N_β	13	s[0]p[99]d[1]	14	s[0]p[99]d[1]	14	s[1]p[98]d[1]
N_γ	14	s[0]p[100]d[0]	14	s[0]p[100]d[0]	14	s[0]p[100]d[0]
π_y LP N_α						
N_α	57	s[6]p[94]d[0]	62	s[4]p[96]d[0]	62	s[4]p[960]d[0]
N_β	5	s[1]p[97]d[2]	6	s[2]p[96]d[2]	6	s[2]p[96]d[2]
N_γ	6	s[0]p[100]d[0]	8	s[0]p[100]d[0]	8	s[0]p[100]d[0]
Pt	31	s[13]p[0]d[87]	15	s[10]p[1]d[89]	15	s[11]p[1]d[88]
π_x (N_β–N_γ)						
N_β	50	s[0]p[100]d[0]	50	s[0]p[100]d[0]	50	s[0]p[100]d[0]
N_γ	49	s[0]p[100]d[0]	50	s[0]p[100]d[0]	50	s[0]p[100]d[0]
π_y (N_β–N_γ)						
N_α	1	s[3]p[96]d[1]	1	s[7]p[92]d[1]	1	s[6]p[93]d[1]
N_β	56	s[1]p[99]d[0]	55	s[1]p[99]d[0]	56	s[1]p[99]d[0]
N_γ	42	s[1]p[99]d[0]	43	s[1]p[99]d[0]	43	s[1]p[99]d[0]
Pt	1	s[4]p[1]d[95]	1	s[3]p[1]d[96]	1	s[4]p[1]d[95]

All numerical values in %

Table S6: LMO Analysis of V_{33} at N_α in various platinum azido complexes, alongside data for azide (N_3) for comparison. All values in au.

	Complexes					N_3^-
LMO type	1	2	3	4	5	N_α
Core N_α	0.04	0.05	0.05	0.04	0.04	0.14
Core N_β	-0.29	-0.24	-0.26	-0.26	-0.26	-0.22
Core N_γ	-0.02	-0.01	-0.01	-0.02	-0.02	0.08
$\pi_x(N_\beta–N_\gamma)$	-0.07	-0.06	-0.06	-0.07	-0.07	0.02
$\pi_y(N_\beta–N_\gamma)$	-0.09	-0.08	-0.08	-0.09	-0.09	0.02
π_x LP N_α	1.54	1.58	1.58	1.57	1.56	1.52
π_y LP N_α	0.60	0.08[a]	0.28[a]	0.28	0.32	1.52
σ LP N_α	-0.36	0.06	-0.09	-0.17	-0.18	-0.92
σ LP N_γ	-0.03	-0.01	-0.02	-0.02	-0.02	0.07
$\sigma(N_\alpha–N_\beta)$	-1.56	-1.34	-1.47	-1.38	-1.39	-1.79
$\sigma(N_\beta–N_\gamma)$	-0.11	-0.09	-0.09	-0.10	-0.10	-0.02
Core Pt	0.04	0.04	0.17	-0.13	0.00	
Pt LP	0.02	0.01	0.02	-0.01	0.01	
trans N_3	0.15	0.31	0.26	0.14	0.17	
others BD	0.55	0.23	0.20	0.56	0.40	
others LP	0.04	0.12	0.14	0.07	0.11	
others CR	0.24	0.08	0.09	0.25	0.18	
$\sum$ Analysis	0.68	0.74	0.70	0.69	0.69	0.44
Total calculated	0.68	0.73	0.71	0.69	0.70	0.44

1 = *t*-$[Pt(N_3)_2(py)_2]$, **2** = *ctc*-$[Pt(N_3)_2(OH)_2(NH_3)_2]$, **3** = *ttt*-$[Pt(N_3)_2(OH)_2(NH_3)_2]$, **4** = *ttt*-$[Pt(N_3)_2(OH)_2(Py)_2]$, **5** = *ttt*-$[Pt(N_3)_2(OH)_2(NH_3)(py)]$. BD = Other bonded nuclei (N-C, Pt-NPy etc.), LP = Other lone pairs from oxygen and other nitrogens, CR = other core nuclei contributions. [a] The π_y LP on N_α of complexes **2** and **3** form a dative bond ($N_\alpha \rightarrow Pt$) with platinum an example of which is shown in Figure S1 and S2 labeled as π_y LP N_α.

Table S7: NLMO Analysis of V_{33}(au) component of N_β in various platinum azido complexes alongside data for azide (N_3) for comparison. All values in au.

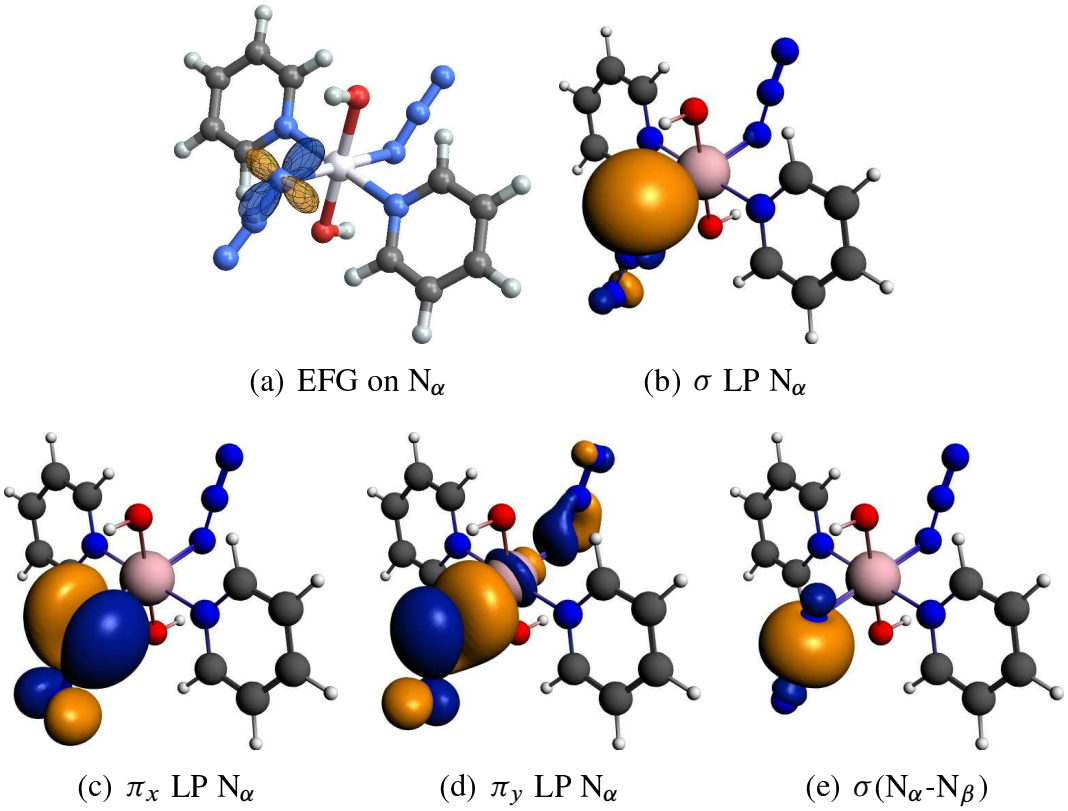
	Complexes					N_3^-
LMO type	1	2	3	4	5	N_β
Core N_α	-0.24	-0.22	-0.23	-0.24	-0.23	-0.13
Core N_β	0.07	0.08	0.08	0.07	0.08	0.27
Core N_γ	-0.30	-0.30	-0.30	-0.32	-0.31	-0.13
$\pi_x(N_\beta–N_\gamma)$	1.02	1.05	1.06	1.02	1.04	1.13
$\pi_y(N_\beta–N_\gamma)$	0.45	0.53	0.57	0.59	0.58	1.13
π_x LP N_α	0.22	0.19	0.19	0.20	0.19	0.43
π_y LP N_α	0.06	0.01[a]	0.01[a]	0.04	0.04	0.43
σ LP N_α	-0.14	-0.12	-0.12	-0.14	-0.13	0.02
σ LP N_γ	-0.15	-0.14	-0.14	-0.16	-0.15	0.02
$\sigma(N_\alpha–N_\beta)$	-1.62	-1.54	-1.58	-1.63	-1.61	-1.66
$\sigma(N_\beta–N_\gamma)$	-1.28	-1.34	-1.38	-1.41	-1.39	-1.66
Core Pt	0.25	0.57	0.58	0.21	0.37	
Pt LP	0.04	0.05	0.05	0.02	0.04	
trans N_3	0.27	0.37	0.40	0.25	0.29	
others BD	0.83	0.33	0.33	0.87	0.64	
others LP	0.04	0.23	0.21	0.13	0.17	
others CR	0.34	0.10	0.14	0.36	0.27	
$\sum$ Analysis	-0.14	-0.12	-0.12	-0.13	-0.12	-0.14
Total calculated	-0.13	-0.13	-0.12	-0.12	-0.12	-0.15

where; **1** = *t*-[$Pt(N_3)_2(py)_2$], **2** = *ctc*-[$Pt(N_3)_2(OH)_2(NH_3)_2$], **3** = *ttt*-[$Pt(N_3)_2(OH)_2(NH_3)_2$], **4** = *ttt*-[$Pt(N_3)_2(OH)_2(Py)_2$], **5** = *ttt*-[$Pt(N_3)_2(OH)_2(NH_3)(py)$]. See caption of table S6 for further details. [a] N_α forms a dative bond ($N_\alpha \rightarrow Pt$) with platinum of the kind shown in Figures S1 and S2.

Table S8: Supporting info: NLMO Analysis of V_{33}(au) component of N_γ in various platinum azido complexes alongside data for azide (N_3) for comparison. All values in au.

	Complexes					N_3^-
LMO type	1	2	3	4	5	N_γ
Core N_α	0.01	0.01	0.01	0.01	0.01	0.08
Core N_β	0.18	0.18	0.18	0.18	0.18	-0.22
Core N_γ	-0.02	-0.02	-0.02	-0.02	-0.02	0.14
$\pi_x(N_\beta–N_\gamma)$	1.11	1.25	1.24	1.09	1.24	1.13
$\pi_y(N_\beta–N_\gamma)$	-2.27	-1.87	-1.87	-2.29	-1.88	1.13
π_x LP N_α	0.21	0.33	0.33	0.19	0.34	0.42
π_y LP N_α	-0.65	-0.26[a]	-0.27[a]	-0.64	-0.35	0.42
σ LP N_α	0.06	-0.12	-0.11	0.06	-0.07	0.07
σ LP N_γ	0.56	0.57	0.57	0.58	0.57	-0.92
$\sigma(N_\alpha–N_\beta)$	0.06	0.06	0.06	0.06	0.06	-0.02
$\sigma(N_\beta–N_\gamma)$	1.01	0.97	0.95	1.02	0.96	-1.79
Core Pt	-0.14	-0.28	-0.27	-0.14	-0.21	
Pt LP	-0.02	-0.02	-0.02	-0.02	-0.02	
trans N_3	-0.08	-0.10	-0.18	-0.07	-0.09	
others BD	-0.27	-0.11	-0.09	-0.29	-0.17	
others LP	-0.01	-0.11	-0.08	-0.01	-0.07	
others CR	-0.11	-0.04	-0.04	-0.12	-0.08	
$\sum$ Analysis	-0.36	0.45	0.38	-0.41	0.39	0.44
Total calculated	-0.36	0.45	0.38	-0.40	0.39	0.44

where; **1** = *t*-[$Pt(N_3)_2(py)_2$], **2** = *ctc*-[$Pt(N_3)_2(OH)_2(NH_3)_2$], **3** = *ttt*-[$Pt(N_3)_2(OH)_2(NH_3)_2$], **4** = *ttt*-[$Pt(N_3)_2(OH)_2(Py)_2$], **5** = *ttt*-[$Pt(N_3)_2(OH)_2(NH_3)(py)$]. See caption of table S6 for further details. [a] N_α forms a dative bond (N_α→Pt) with platinum of the kind shown in Figures S1 and S2



(a) EFG on N_α (b) σ LP N_α

(c) π_x LP N_α (d) π_y LP N_α (e) $\sigma(N_\alpha\text{-}N_\beta)$

Figure S1: *ttt*-[$Pt(N_3)_2(OH)_2(Py)_2$] EFG tensor plot ($s = 200$ au/pm) and selected LMO isosurfaces ($\pm$ 0.03 au). The dative bond $N_\alpha \rightarrow Pt$ is depicted by the π_y LP N_α LMO.

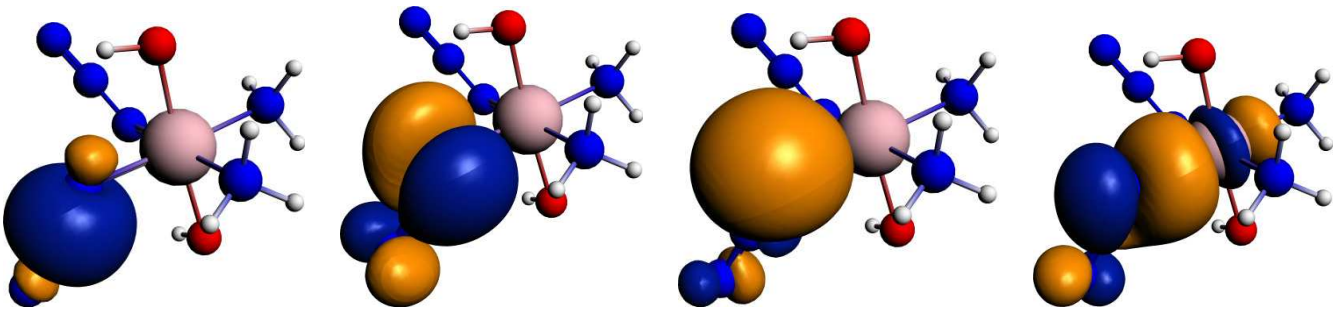


Figure S2: Selected LMO's of the complex *ctc*-$[Pt(N_3)_2(OH)_2(NH_3)_2]$. See also caption of Fig. S1.

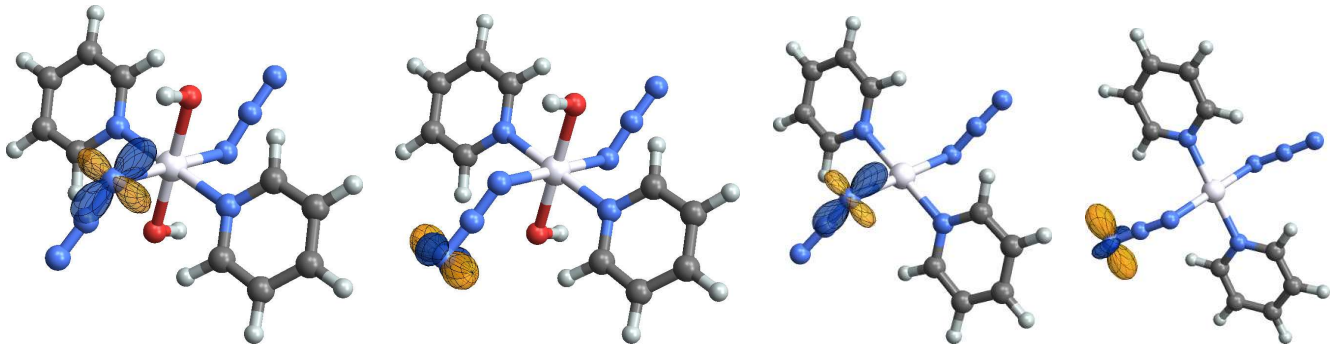
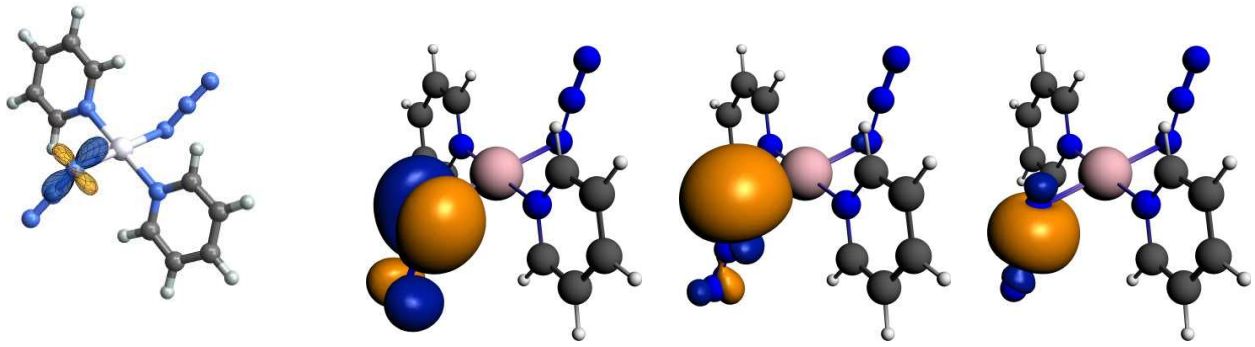


Figure S3: EFG tensor for the platinum diazo complexes **4.**[(a) and (b)] and **1.**[(c) and (d)]. The scaling factor,*s*, for (a)-(d) is 200, 300, 200 and 300 au / pm respectively was used to generate the EFG tensor plot. Blue color indicate a positive EFG while orange indicate a negative EFG.



(a) EFG tensor on N_α (b) π LP on N_α (c) σ LP on N_α (d) $\sigma(N_\alpha\text{-}N_\beta)$

Figure S4: *t*-[$Pt(N_3)_2(py)_2$] EFG tensor plot ($s = 200$ au/pm and selected LMOs.

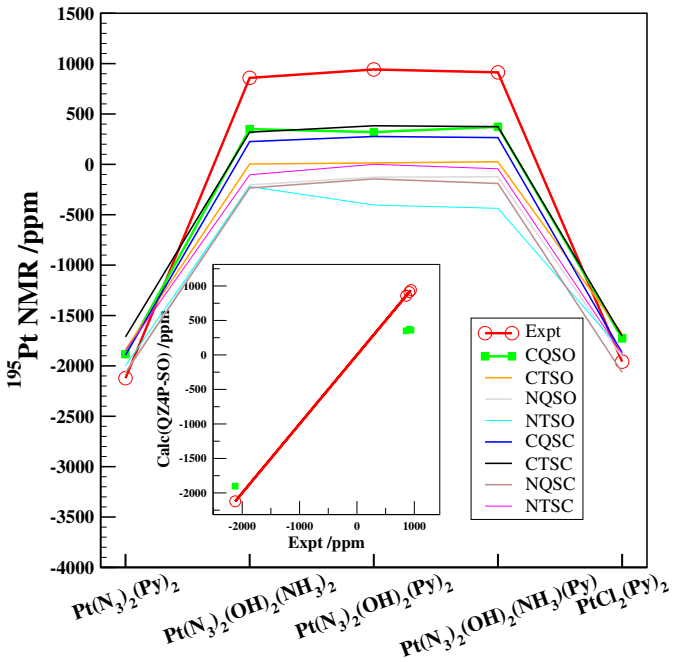
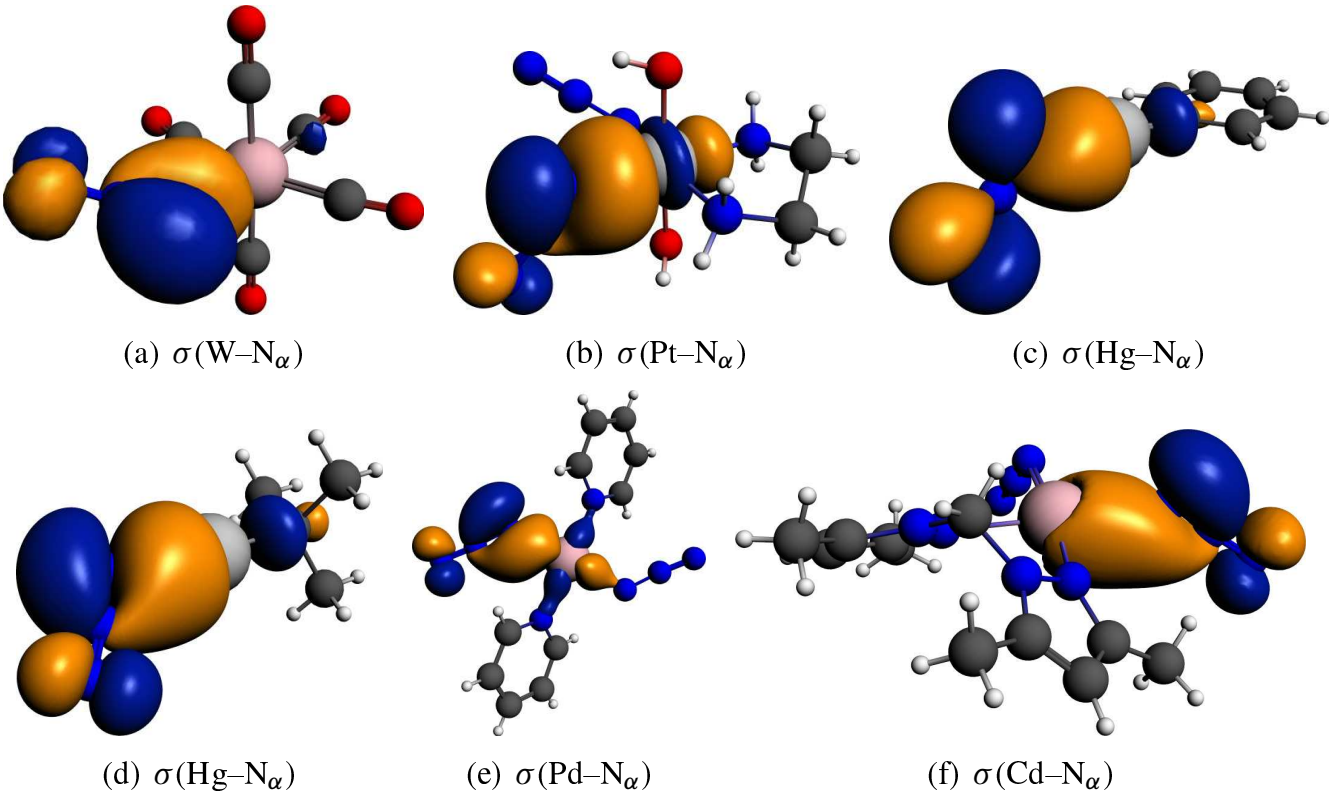


Figure S5: Calculated versus experimental ^{195}Pt NMR chemical shifts for various platinum complexes. Best agreement with experimental values is obtained with COSMO (C), the QZ4P (Q) basis on Pt, and with spin-orbit (SO) effects included in the calculations [green line labeled CQSO]. Results from other calculations (N = No COSMO, T = TZ2P basis for Pt, SC = scalar ZORA) are also shown. The inset shows CQSO versus experiment.



(a) σ(W–N_α) (b) σ(Pt–N_α) (c) σ(Hg–N_α)

(d) σ(Hg–N_α) (e) σ(Pd–N_α) (f) σ(Cd–N_α)

Figure S6: Metal–N_α bonding LMOs in (a) $W(N_3)(CO)_5$, Ref. 1. (b) tetrakis(axido-N)-(1,2-diaminoethane-N,N')-platinum ($Pt(N_3)_2(OH)_2N_2C_2H_8$), Ref. 2. (c) Phenymercury(II) Azide ($Hg(N_3)(C_6H_5)$), Ref. 3. (d) *tert*-Butylmercury(II) Azide ($Hg(N_3)C(CH_3)_2$), Ref. 4. (e) bis(azido)bis(pyridine)palladium(II) ($Pd((N_3)_2(Py)_2$), Ref. 5. (f) Cadmium bis(3,5-dimethylpyrazol-1-yl)methane ($Cd(N_3)_2$(bdmpzm)), Ref. 3

Table S9: Calculated J(M-N_α) and K(M–N_α) coupling values for various metal complexes containing azido group(s).

Complex	M–N_α–N_β(deg)	J(M–N_α)(Hz)	K(M–N_α)	$\%s$ at N_α
ttt-[Pt$(N_3)_2(OH)_2(NH_3)_2$] (**3**) (OPT)	118.0	-269.1	1024.7	6.0
ttt-[Pt$(N_3)_2(OH)_2(NH_3)_2$] (**3**)	140.0	-281.0	1069.8	6.6
ttt-[Pt$(N_3)_2(OH)_2(NH_3)_2$] (**3**)	150.0	-386.6	1472.1	7.4
Pt$(N_3)_2(OH)_2N_2C_2H_8$ (XRD)	118.4	-232.9	886.9	6.2
Pt$(N_3)_2(OH)_2N_2C_2H_8$	150.0	-429.8	1636.5	9.6
Cd$(N_3)_2$(bdmpzm) (XRD)	132.0	65.3	240.7	0.3
Cd$(N_3)_2$(bdmpzm)	150.0	167.1	616.2	0.5
Pd$((N_3)_2(Py)_2$(XRD)	116.8	32.0	571.6	3.8
Pd$((N_3)_2(Py)_2$	150.0	273.3	4879.9	8.2
W$(N_3)(CO)_5$ (XRD)	124.9	-20.8	408.2	1.4
W$(N_3)(CO)_5$	150.0	-30.5	597.7	2.1
Hg$(N_3)(C_6H_5)$(XRD)	119.9	272.8	-1236.4	0.7
Hg$(N_3)(C_6H_5)$	150.0	175.2	-794.2	0.1
Hg$(N_3)C(CH_3)_3$ (XRD)	116.0	552.4	-2504.0	0.4
Hg$(N_3)C(CH_3)_3$	150.0	785.1	-3558.6	0.4

XRD = XRay diffraction geometries obtained from the references listed in the caption of Figure S6. Calculations carried out using the same computational settings as described in the main article for the Pt azide complexes. J-coupling calculated for the isotopes ^{15}N, ^{105}Pd, ^{113}Cd, ^{183}W, ^{195}Pt, and ^{199}Hg. Reduced coupling constants K in units of 10^{19} T^2 / J. Structures not labeled by 'XRD' have the M–N_α–N_β angle modified as indicated, without further geometry optimization. $\%s$ character at N_α refers to the s character of the nitrogen hybrids forming the bonding LMOs with the metal (Figure S6).

Below are optimized coordinates for the Pt azide complexes, and additional geometries used for calculations reported in the SI. The energies (Hartree atomic units) are relative to isolated spherical atoms calculated with the same functional and basis set (see the ADF manual at www.scm.com for details). XRD is given instead of an energy value for geometries taken from single-crystal X-Ray diffraction studies.

1. *t*-[Pt(N_3)$_2$(py)$_2$]

```
29
Energy:  -6.91851230
  C       0.000622     -0.043990      0.024195
  N      -0.005257      0.026308      1.381682
  C       1.183264      0.062706      2.041134
  C       2.403263      0.035623      1.366820
  C       2.411585     -0.032738     -0.032092
  C       1.186363     -0.072927     -0.709094
 Pt      -1.771668      0.078526      2.418881
  N      -1.325103     -1.751961      3.271600
  N      -0.710493     -1.815336      4.321003
  N      -0.129026     -1.985046      5.321642
  N      -3.537916      0.133390      3.457416
  C      -4.729192      0.108259      2.803269
  C      -5.946855      0.153162      3.481049
  C      -5.950128      0.222516      4.879612
  C      -4.721895      0.244087      5.552579
  C      -3.539485      0.197821      4.815502
  N      -2.217565      1.907142      1.563704
  N      -2.837016      1.970234      0.516923
  N      -3.424673      2.140588     -0.480062
  H      -2.564871      0.219420      5.301291
  H      -6.889910      0.259289      5.433921
  H      -6.873992      0.133021      2.907131
  H      -4.684624      0.046940      1.716807
  H      -0.972261     -0.080229     -0.463939
  H       1.135886     -0.125985     -1.797155
  H       3.353913     -0.052269     -0.583001
  H       3.328573      0.070243      1.942920
  H       1.133573      0.122124      3.127430
  H      -4.666439      0.298465      6.640310
```

2. *ctc*-[Pt(N_3)$_2$(OH)$_2$(NH_3)$_2$]

```
19
```

```
Energy:  -3.97819856
  N      3.390228      5.558924     20.947344
 Pt      3.480249      5.980033     18.901460
  O      3.403320      3.971690     18.505373
  N      1.428287      6.217674     18.948517
  N      0.741393      5.413504     18.334522
  N     -0.005008      4.709683     17.787755
  N      3.568984      6.306739     16.863946
  N      3.347056      7.435840     16.449792
  N      3.152757      8.466155     15.947999
  N      5.565591      5.829791     18.898196
  O      3.656143      7.957924     19.404789
  H      2.740972      8.303777     19.346511
  H      3.338236      3.920985     17.528871
  H      6.009742      6.407826     19.616815
  H      5.930295      6.126682     17.988080
  H      5.844133      4.853525     19.039585
  H      4.024636      4.812148     21.242595
  H      3.619172      6.410959     21.469411
  H      2.438884      5.280204     21.203432
```

3. *ttt*-[$Pt(N_3)_2(OH)_2(NH_3)_2$]

```
19
Energy:  -3.98872083
 Pt      3.375460      6.021444     18.832464
  N      3.375278      5.513565     20.835722
  N      1.303945      6.253532     18.908886
  N      0.602512      5.344217     18.490361
  N     -0.153038      4.541376     18.118884
  N      5.447189      5.790345     18.754621
  N      6.148806      6.696398     19.179994
  N      6.904545      7.496199     19.557603
  N      3.376361      6.525733     16.828749
  O      3.520382      7.979827     19.383848
  O      3.230064      4.063592     18.280964
  H      2.587794      8.282824     19.448170
  H      4.162687      3.763855     18.202920
  H      4.303852      6.838009     16.526754
  H      2.708147      7.272826     16.618992
  H      3.128667      5.698101     16.275364
  H      4.050260      4.772018     21.043483
  H      3.614241      6.340510     21.393854
  H      2.450864      5.189885     21.134895
```

4. *ttt*-[Pt(N$_3$)$_2$(OH)$_2$(Py)$_2$]

```
33
Energy:  -7.63673609
 Pt      3.298228      6.053541     18.892959
  O      3.496877      8.038805     19.302237
  H      2.574013      8.364481     19.385631
  O      3.099578      4.066448     18.487127
  H      4.022607      3.734548     18.434063
  N      1.227192      6.352790     18.947278
  N      0.504498      5.397854     18.707614
  N      5.369313      5.754211     18.841252
  N      6.093612      6.723977     19.004648
  N      6.863808      7.584403     19.152138
  N      3.306385      6.472960     16.858206
  C      3.942584      7.577893     16.395264
  H      4.400770      8.216692     17.147718
  C      3.972878      7.881624     15.034878
  H      4.500710      8.777000     14.705050
  C      3.324549      7.034489     14.128008
  H      3.331651      7.254393     13.058677
  C      2.667098      5.900137     14.618409
  H      2.145858      5.208928     13.955386
  C      2.678476      5.642704     15.988565
  H      2.210348      4.760750     16.420957
  N      3.290998      5.635887     20.924058
  C      3.982677      6.424103     21.784192
  H      4.500195      7.275295     21.346601
  C      3.997673      6.165000     23.154083
  H      4.571189      6.820981     23.809710
  C      3.275816      5.074382     23.653770
  H      3.269911      4.854416     24.723115
  C      2.561910      4.270892     22.756629
  H      1.983031      3.410604     23.094020
  C      2.592444      4.573282     21.395962
  H      2.082604      3.964717     20.652077
  N     -0.263719      4.549403     18.495793
```

5. *ttt*-[Pt(N$_3$)$_2$(OH)$_2$(NH$_3$)(py)]

```
26
Energy:  -5.81303336
 Pt      3.383067      6.074116     18.894592
  O      3.471834      8.073308     19.280932
  H      2.534920      8.338978     19.410269
  O      3.301304      4.095023     18.418609
```

H	4.226219	3.780048	18.521138
N	1.303410	6.273334	18.835464
N	0.643266	5.301721	18.498887
N	5.465639	5.890279	18.893028
N	6.133803	6.895653	19.081967
N	6.857332	7.790794	19.252309
N	3.444888	6.469403	16.866767
N	-0.072718	4.437293	18.192515
H	2.209772	3.917898	20.585734
C	2.658503	4.544431	21.354557
H	4.412785	7.348414	21.394368
H	2.053392	3.333381	23.020505
C	3.908280	6.194708	23.176040
C	2.595280	4.227360	22.710624
H	4.420219	6.874515	23.857675
H	3.198937	4.829610	24.706314
C	3.230699	5.060422	23.639740
N	3.313441	5.649055	20.917988
C	3.928188	6.466052	21.808537
H	3.322584	5.587154	16.356601
H	4.344545	6.872336	16.589195
H	2.705621	7.119765	16.583951

6. *t*-[$PtCl_2(py)_2$]

25
Energy: -5.52200579

Pt	0.000000	0.000000	0.000000
Cl	-1.218567	1.982482	0.289713
Cl	1.218567	-1.982482	-0.289713
N	-1.195460	-0.934835	1.366683
N	1.195460	0.934835	-1.366683
C	-2.535096	-1.028708	1.162162
C	-0.664363	-1.473749	2.494814
C	2.535096	1.028708	-1.162162
C	0.664363	1.473749	-2.494814
C	-3.377669	-1.662771	2.073714
H	-2.915528	-0.580604	0.248508
C	-1.453390	-2.117407	3.446706
H	0.411151	-1.377611	2.614853
C	3.377669	1.662771	-2.073714
H	2.915528	0.580604	-0.248508
C	1.453390	2.117407	-3.446706
H	-0.411151	1.377611	-2.614853
C	-2.833843	-2.217790	3.237968
H	-4.444435	-1.712579	1.862850

H	-0.979582	-2.531464	4.334961
C	2.833843	2.217790	-3.237968
H	4.444435	1.712579	-1.862850
H	0.979582	2.531464	-4.334961
H	-3.471666	-2.717482	3.966624
H	3.471666	2.717482	-3.966624

$W(N_3)(CO)_5$

14
XRD

W	3.700649245	4.740749464	1.256562433
N	2.422214557	3.591782212	-0.167226730
N	1.311803232	3.310100234	0.017006108
N	0.169258365	3.006156216	0.109594919
C	4.029111543	6.086549404	-0.255091622
C	3.273883724	3.324461360	2.651063297
C	4.774360423	5.703216177	2.537689243
C	5.433232545	3.805754933	0.825741027
C	2.204654143	5.924097350	1.974598108
O	4.222131109	6.839050093	-1.091225270
O	3.029329038	2.513066603	3.425786000
O	5.433923644	6.265608724	3.319025433
O	6.490927595	3.382864452	0.711422189
O	1.520317852	6.676445415	2.488560487

$Cd(N_3)_2$(bdmpzm)

38
XRD

Cd	5.225211684	12.363452418	5.640598277
N	6.244582287	14.483452963	5.442248635
N	5.951808274	15.480743689	5.998015604
N	5.680501623	16.409672920	6.622647242
N	6.544554466	11.765956159	7.541166126
N	4.484418052	10.138372897	6.018384027
N	7.019222223	10.486762801	7.697324036
N	5.314529874	9.210647428	6.602278819
N	4.007320306	12.545515287	3.606180792
N	2.920894812	12.846402863	3.298714597
N	1.842093916	13.111049993	2.909774711
H	8.009975988	11.802304602	10.293813003
H	6.634158358	14.075698448	9.749685132
H	8.884999738	9.248543380	10.059091176
C	6.714608756	9.506416595	6.694421685

H	7.196536719	8.689101127	6.895196140
H	7.025315837	9.829686022	5.834098296
H	5.544175977	7.255439055	8.630391793
C	6.920807772	12.424528028	8.625542169
C	4.608217814	8.144451564	7.058143524
C	7.633632670	11.575024363	9.474226459
C	7.675616127	10.351948023	8.880632418
C	6.614589313	13.864321393	8.813707600
H	5.742441132	14.054745007	8.460654935
H	7.269160864	14.393449601	8.352023346
C	8.303290518	9.080526982	9.314188850
H	7.619901688	8.459509328	9.576068574
H	8.811318842	8.710248681	8.588685022
C	2.055997088	10.326087096	5.613925343
H	1.794536624	11.011356946	6.233707356
H	2.264117461	10.725599805	4.765241052
H	1.335408856	9.701836430	5.504323828
C	3.255323089	9.616106264	6.134775016
C	3.315914684	8.365321826	6.762316429
H	2.600576335	7.797050185	6.939812686
C	5.243876356	6.979311644	7.761339079
H	5.992735726	6.666076984	7.248248805
H	4.601912460	6.272243824	7.853481945

$Hg(N_3)C(CH_3)_3$

17
XRD

Hg	1.308777254	0.452685180	5.284303925
N	0.139507517	1.021215500	6.998895924
N	-1.740206067	-0.251921300	7.528281961
N	-0.821491812	0.350499200	7.223483940
C	2.635398767	0.108242400	3.673618260
C	3.662205487	-0.915550300	4.090710289
H	4.166408394	-0.577292800	4.858434629
H	4.274393401	-1.084356900	3.345903094
H	3.210082659	-1.749274500	4.338215450
C	1.834741190	-0.360808000	2.481926747
H	1.180245148	0.327304400	2.236713301
H	1.367650750	-1.190666400	2.708806477
H	2.437716733	-0.519950100	1.725660979
C	3.357196892	1.441299100	3.357361666
H	3.866855320	1.730589800	4.143419722
H	2.694607641	2.126190000	3.128190221
H	3.967666205	1.311150500	2.603387613

$Hg(N_3)(C_6H_5)$

```
15
XRD
Hg             0.434670640     6.088667904     1.555711924
N              0.993827650     5.654558910    -0.402007800
N             -0.135490690     4.059683320    -1.686684900
N              0.412662000     4.826766340    -1.010845700
C              0.894101000     6.527347970     5.779590400
H              1.497963060     6.190945640     6.432124800
C             -0.856273650     7.515128060     3.886075400
H             -1.464262330     7.853673080     3.239367200
C             -0.094224490     7.415135860     6.149554100
H             -0.176069120     7.686543260     7.055528200
C              0.132051840     6.628768630     3.501546200
C             -0.967004620     7.910097250     5.196970400
H             -1.645145840     8.525763510     5.450410100
C              1.008270820     6.127379170     4.465782300
H              1.685036500     5.509570220     4.215255700
```

$Pd((N_3)_2(Py)_2$

```
29
XRD
Pd             2.016760787     2.891250000     9.958108959
N              3.591430994     2.218938000    11.060670783
N              3.520531350     1.754410500    12.167813337
N              3.548066957     1.301833500    13.224966184
N              0.442090580     3.563562000     8.855547135
N              0.512990224     4.028089500     7.748404581
N              0.485454617     4.480666500     6.691251734
N              0.652409095     2.592873000    11.447443735
N              3.381112479     3.189627000     8.468774183
C              0.863921863     3.063183000    12.701767139
H              1.617480891     3.496485000    12.828035961
C             -0.092059273     2.929800000    13.698175522
H              0.067617899     3.288315000    14.510956375
C             -1.290945006     2.313000000    13.410983659
H             -1.870168766     2.220480000    14.030975523
C             -1.506488034     1.839606000    12.128777550
H             -2.240315592     1.476465000    11.884007232
C             -0.506835226     1.991107500    11.178375631
H             -0.586655749     1.700055000    10.382324401
C              3.169599711     2.719317000     7.214450779
H              2.416040683     2.286015000     7.088181957
C              4.125580847     2.852700000     6.218042396
```

H	3.965903675	2.494185000	5.405261543
C	5.324466580	3.469500000	6.505234259
H	5.903690340	3.562020000	5.885242395
C	5.540009608	3.942894000	7.787440368
H	6.273837166	4.306035000	8.032210686
C	4.540356800	3.791392500	8.737842287
H	4.620177322	4.082445000	9.533893517

$Pt(N_3)_2(OH)_2N_2C_2H_8$

23
XRD

Pt	2.928709745	1.313845936	2.227366458
N	1.146447370	2.281640920	2.373129741
N	0.616350107	2.307214260	3.457744272
N	0.020534793	2.395785340	4.434411386
N	2.075758832	-0.539535100	2.261755421
N	0.990488965	-0.706697420	1.752860451
N	-0.022826562	-0.970539440	1.300509367
N	4.767925748	0.474666140	1.960188031
N	3.987001223	3.062563400	2.304591698
O	3.153534512	1.128345660	4.199668588
H	3.118175937	1.887437240	4.557779863
O	2.764930330	1.488867380	0.240568531
H	1.967478304	1.663514580	0.039409375
H	5.021918076	0.026820820	2.722673760
H	4.738730965	-0.129114180	1.266240345
C	5.743037720	1.541885280	1.656907191
H	5.666587275	1.818202100	0.709368746
H	6.666780480	1.220659180	1.816258141
C	5.427928603	2.700170460	2.566749712
H	6.019124339	3.468618140	2.367989388
H	5.553905304	2.440694620	3.512574707
H	3.911237965	3.516646120	1.509550398
H	3.665007826	3.599603540	2.979691422

Complete reference [32]:

E. J. Baerends, T. Ziegler, J. Autschbach, D. Bashford, A. Bérces, F. M. Bickelhaupt, C. Bo, P. M. Boerrigter, L. Cavallo, D. P. Chong, L. Deng, R. M. Dickson, D. E. Ellis, M. van Faassen, L. Fan, T. H. Fischer, C. Fonseca Guerra, A. Ghysels, A. Giammona, S. J. A. van Gisbergen, A. W. Götz, J. A. Groeneveld, O. V. Gritsenko, M. Grüning, S. Gusarov, F. E. Harris, P. van den Hoek, C. R. Jacob, H. Jacobsen, L. Jensen, J. W. Kaminski, G. van Kessel, F. Kootstra, A. Kovalenko, M. V. Krykunov, E. van Lenthe, D. A. McCormack, A. Michalak, M. Mitoraj, J. Neugebauer, V. P. Nicu, L. Noodleman, V. P. Osinga, S. Patchkovskii, P. H. T. Philipsen, D. Post, C. C. Pye, W. Ravenek, J. I. Rodríguez, P. Ros, P. R. T. Schipper, G. Schreckenbach, J. S. Seldenthuis, M. Seth, J. G. Snijders, M. Solà, M. Swart, D. Swerhone, G. te Velde, P. Vernooijs, L. Versluis, L. Visscher, O. Visser, F. Wang, T. A. Wesolowski, E. M. van Wezenbeek, G. Wiesenekker, S. K. Wolff, T. K. Woo, A. L. Yakovlev, *Amsterdam Density Functional (ADF)*, 2012 Developer's version, SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands. URL http://www.scm.com.

References

[1] Sellmann, D.; Weber, W.; Liehr, G.; Beck, H. P. *J. Organomet. Chem.* **1984,** *269,* 155-170.

[2] Parsons, S.; Mueller, P.; Sadler, P.; Johnstone, R., Private communication to CSD, CCDC 611051.

[3] Klapötke, T. M.; Krumm, B.; Moll, R. *Z. Anorg. Allg. Chem.* **2011,** *637,* 507-514.

[4] Chand, B.; Ray, U.; Mostafa, G.; Cheng, J.; Lu, T.; Sinha, C. *Inorg. Chim. Acta* **2005,** *358,* 1927-1933.

[5] Beck, W.; Klapötke, T. M.; Knizek, J.; Nöth, H.; Schütt, T. *Eur. J. Inorg. Chem.* **1999,** *1999,* 523-526.