Supplementary Material (ESI) for Chemical Communications

Unprecedented Intermolecular C-H Bond Activation of a Solvent Toluene Molecule Leading To a Seven-Membered Platinacycle

Alejandro Capapé, Margarita Crespo, Jaume Granell, Albert Vizcarro, Javier Zafrilla, Mercè Font-Bardía, Xavier Solans

SUPPORTING INFORMATION AVAILABLE:

Experimental procedures and characterization data for all new compounds

The solvents were purified and distilled by standard methods. Methanol (dry, max. 0.005 H_2O) was purchased from Panreac.

Mass spectra were performed by the Servei d'Espectrometria de Masses de la Universitat de Barcelona. NMR spectra were performed at the Unitat de NMR d'Alt Camp de la Universitat de Barcelona. Microanalyses were performed by the Servei de Recursos Científics i Tècnics de la Universitat Rovira i Virgili de Tarragona. FAB mass spectra were carried out in VG-Quattro (with a 3-nitrobenzyl alcohol matrix) and MALDI mass spectra in a Voyager DE-RP (with a dithranol matrix) spectrometers. ^{1}H-, ^{31}P- and ^{195}Pt-NMR spectra were recorded using Varian Gemini-200 (^{1}H, 200 MHz), Bruker DRX-250 (^{1}H, 250 MHz; ^{31}P, 101 MHz; ^{195}Pt, 54 MHz), Mercury-400 (^{1}H, 400 MHz; ^{1}H-^{1}H-NOESY, ^{1}H-^{13}C-gHSQC) and Bruker DMX-500 (^{1}H, 500 MHz; ^{1}H-^{1}H-COSY) spectrometers, and referenced to $SiMe_4$ (^{1}H), $P(OMe)_3$ in $(CD_3)_2CO$ (^{31}P) and H_2PtCl_6 in D_2O (^{195}Pt). δ values are given in ppm and J values in Hz.

cis-$[PtCl_2(dmso)_2]$ was prepared as reported[1] and $[Pt(OAc)_2(dmso)_2]$ was prepared from 200 mg (0.47 mmol) of *cis*-$[PtCl_2(dmso)_2]$ and 158 mg (0.95 mmol) of Ag(OAc), which were allowed to react protected from the light in a mixture of dicloromethane (20 mL) and methanol (20 mL) with vigorous stirring during 24 hours. The AgCl was filtered off and the solvent was removed in vacuo to yield a white solid. Yield 180 mg (81.6%). **^{1}H-NMR** (200 MHz, $CDCl_3$): δ = 3.41 [s, ^{3}J(Pt-H) = 15.0, 12H, $SOMe_2$], 2.02 [s, 6H, AcO]. **FAB-MS**, m/z: 409.0 $[M-AcO]^+$, 350.0 $[M-2AcO]^+$.

$[PtCl\{(2,6\text{-}Cl_2C_6H_3)CHNCH_2C_6H_4\}\{SOMe_2\}]$ (2a) was obtained from 0.215 g (0.51 mmol) of *cis*-$[PtCl_2(dmso)_2]$, 0.134 g (0.51 mmol) of imine **1a** and 42 mg (0.51 mmol) of sodium acetate which were allowed to react in refluxing methanol (30 mL) for 48 h. The solvent was filtered and removed in a rotary evaporator and the residue was treated with dicloromethane-methanol, yielding a solid which was filtered *in vacuo*. Yield 44 mg (15%). **^{1}H-NMR** (250 MHz, CDCl$_3$): δ = 9.64 [t, ^{4}J(H-H) = 2.4, ^{3}J(Pt-H) = 51.5, 1H, H^{c}], 8.14 [m, ^{3}J (Pt-H) = 44.0, 1H, H^{5}], 7.44 [m, 3H], 7.09 [m, 2H], 6.97 [m, 1H], 4.70 [d, ^{4}J(H-H) = 2.3, 2H, ^{3}J(Pt-H) = 32.6, H^{b}], 3.63 [s, ^{3}J(Pt-H) = 24.2, 6H, H^{a}]. **FAB-MS**, m/z: 686.8 [M-Cl-dmso]$^{+}$, 650.9 [M-dmso]$^{+}$. **Anal. Found (calc. for C$_{16}$H$_{16}$Cl$_3$NOPtS)**: C: 34.1 (33.61); H: 2.9 (2.82); N: 2.5 (2.45); S: 5.9 (5.61).

[PtCl{(2,6-Cl$_2$C$_6$H$_3$)CHNCH$_2$(4-ClC$_6$H$_3$)}{SOMe$_2$}] (2b) was obtained as a white solid from 0.218 g (0.52 mmol) of *cis*-[PtCl$_2$(dmso)$_2$], 0.150 g (0.52 mmol) of imine **1b** and 42 mg (0.52 mmol) of sodium acetate using the procedure reported for **2a**. Yield 57 mg (18%). **^{1}H-NMR** (250 MHz, CDCl$_3$): δ = 9.59 [t, ^{4}J(H-H) = 2.4, ^{3}J(Pt-H) = 50.0, 1H, H^{c}], 8.15 [d, ^{4}J(H-H) = 2.0, ^{3}J(Pt-H) = 51.8, 1H, H^{5}], 7.5-7.3 [m, 3H], 7.07 [dd, ^{3}J(H-H) = 2.2, ^{4}J(H-H) = 8.0, 1H], 6.88 [d, ^{3}J(H-H) = 8.0, 1H], 4.66 [d, ^{3}J(H-H) = 2.0, ^{3}J(Pt-H) = 32.8, 2H, H^{b}], 3.63 [s, ^{3}J(Pt-H) = 24.5, 6H, H^{a}]. **^{195}Pt-NMR** (54 MHz, CDCl$_3$): δ = -3584.54. **FAB-MS**, m/z: 607.0 [M^{+}], 570.0 [M-Cl]$^{+}$. **Anal. Found (calc. for C$_{16}$H$_{15}$Cl$_4$NOPtS)**: C: 32.6 (31.70); H: 2.2 (2.49); N: 2.4 (2.31); S: 4.8 (5.29).

[PtCl{(MeC$_6$H$_3$)ClC$_6$H$_3$CHNCH$_2$C$_6$H$_5$}{SOMe$_2$}] (3a) was obtained from 0.243 g (0.57 mmol) of *cis*-[PtCl$_2$(dmso)$_2$], 0.152 g (0.57 mmol) of imine **1a** and 47 mg (0.57 mmol) of sodium acetate (dissolved in 1 mL methanol) which were allowed to react in dry toluene (30 mL) at 90° for 48 h under N$_2$. The mixture was filtered, the solvent was removed in vacuum and the residue was eluted in a silica column chromatography using ethyl acetate: hexane = 100:20 as eluent. The first fractions collected contain aldehyde and **2a**; **3a** was obtained from a further fraction and crystallised in dichloromethane-methanol. Yield 54 mg (15%). **^{1}H-NMR** (250 MHz, CDCl$_3$): **major isomer** δ = 8.53 [s, ^{3}J(Pt-H) = 112.8, 1H, H^{d}], 7.47-7.31 [m, 4H], 7.27 [d, ^{3}J(H-H) = 7.2, 2H], 7.18 [d, ^{3}J(H-H) = 7.2, 2H], 6.85 [d, ^{3}J(H-H) = 8.0, 1H], 6.76 [dd, ^{3}J(H-H) = 7.6, ^{4}J(H-H) = 1.0, 1H], 6.63 [s, ^{3}J(Pt-H) = 52.4, 1H, H^{5}], 5.43 [dd, ^{2}J(H-H) = 13.2, ^{4}J(H-H) = 2.0, 1H, H^{c}], 5.04 [d, ^{2}J(H-H) = 13.2, 1H, H^{c}], 3.30 [s, ^{3}J(Pt-H) = 20.4, 3H, H^{b}], 2.83 [s, ^{3}J(Pt-H) = 31.2, 3H, H^{b}], 2.14 [s, 3H, Me^{a}], **minor isomer** δ = 8.47 [s, ^{3}J(Pt-H) = 109.6, 1H, H^{d}], 6.73 [dd, ^{3}J(H-H) = 8.0, ^{4}J(H-H) = 2.0, 1H], 5.35 [dd, ^{2}J(H-H) = 14.2, ^{4}J(H-H) = 2.0, 1H, H^{c}], 5.15 [d, ^{2}J(H-H) = 14.2, 1H, H^{c}], 3.31 [s, 3H, H^{b}], 2.86 [s, 3H, H^{b}], 2.24 [s, 3H, Me^{a}]. **ES-MS**, m/z: 592.0 [M-Cl]$^{+}$, 514.0 [M-Cl-dmso]$^{+}$. **Anal. Found (calc. for C$_{23}$H$_{23}$Cl$_2$NOPtS)**: C: 43.7 (44.02); H: 4.0 (3.69); N: 2.3 (2.23); S: 5.0 (5.11).

[PtCl{(MeC$_6$H$_3$)ClC$_6$H$_3$CHNCH$_2$(4-ClC$_6$H$_4$)}{SOMe$_2$}] (3b) was obtained from 0.142 g (0.34 mmol) of *cis*-[PtCl$_2$(dmso)$_2$], 0.100 g (0.34 mmol) of imine **1b** and 28 mg (0.34 mmol) of sodium acetate (dissolved in 1 mL methanol) which were allowed to react in dry toluene (30 mL) at 90° for 48 h under N$_2$. The mixture was filtered, the solvent was removed in vacuum and the residue was recrystallised in dicloromethane-methanol, yielding a light yellow solid which was filtered *in vacuo*. Yield 67.5 mg (30%). **^{1}H-NMR** (250 MHz, CDCl$_3$): **major isomer** δ= 8.59 [s, ^3J(Pt-H) = 116.0, 1H, H^d], 7.46-7.34 [m, 3H], {7.24 [d, ^3J(H-H) = 8.0, 2H], 7.12 [d, ^3J(H-H) = 8.0, 2H], H$^{2'}$, H$^{3'}$}, {6.84 [d, ^3J(H-H) = 7.6, 1H], 6.77 [d, ^3J(H-H) = 7.0, 1H], H^3, H^4}, 6.56 [s, ^3J(Pt-H) = 48.0, 1H, H^5], 5.48 [dd, ^2J(H-H) = 13.0, ^4J(H-H) = 1.6, 1H, H^c], 4.90 [d, ^2J(H-H) = 13.0, 1H, H^c], 3.29 [s, ^3J(Pt-H) = 21.6, 3H, H^b], 2.82 [s, ^3J(Pt-H) = 30.0, 3H, H^b], 2.17 [s, 3H, Me^a], **minor isomer** δ = 8.52 [s, ^3J(Pt-H) = 104.0, 1H, H^d], {7.24 [d, ^3J(H-H) = 8.0, 2H], 7.13[d, ^3J(H-H) = 8.0, 2H], H$^{2'}$, H$^{3'}$}, 5.40 [dd, ^2J(H-H) = 13.6, ^4J(H-H) = 1.7, 1H, H^c], 5.03 [d, ^2J(H-H) = 14.2, 1H, H^c], 3.30 [s, 3H, H^b], 2.85 [s, ^3J(Pt-H) = 30.0, 3H, H^b], 2.24 [s, 3H, Me^a]. **^{195}Pt-NMR** (54 MHz, CDCl$_3$): δ = -3802.06 (major isomer). **FAB-MS**, m/z: 626.0 [M-Cl]$^+$, 548.0 [M-Cl-dmso]$^+$, 510 [M-2Cl-dmso]$^+$. **Anal. Found (calc. for C$_{23}$H$_{22}$Cl$_3$NOPtS)**: C: 42.0 (41.73); H: 3.2 (3.35); N: 2.1 (2.12); S: 5.0 (4.84).

[PtCl{(CD$_3$C$_6$D$_3$)ClC$_6$H$_3$CHNCH$_2$(4-ClC$_6$H$_4$)}{SOMe$_2$}] (3b-d^6) was obtained from 0.150 g (0.32 mmol) of [Pt(OAc)$_2$(dmso)$_2$] and 0.095 g (0.32 mmol) of imine **1b** which were allowed to react in deuterated toluene (5 mL) at 90° for 48 h under N$_2$. The mixture was filtered, the solvent was removed in vacuum and the residue was eluted in a silica column chromatography using ethyl acetate: hexane = 100:80 as eluent; **3b** was obtained from the last fractions. Yield 42 mg (30%). **^{1}H-NMR** (250 MHz, CDCl$_3$): **major isomer** δ= 8.59 [s, ^3J(Pt-H) = 116.0, 1H, H^d], 7.46-7.34 [m, 3H], {7.24 [d, ^3J(H-H) = 8.0, 2H], 7.12 [d, ^3J(H-H) = 8.0, 2H], H$^{2'}$, H$^{3'}$}, 5.48 [dd, ^2J(H-H) = 13.0, ^4J(H-H) = 1.6, 1H, H^c], 4.90 [d, ^2J(H-H) = 13.0, 1H, H^c], 3.29 [s, ^3J(Pt-H) = 21.6, 3H, H^b], 2.82 [s, ^3J(Pt-H) = 30.0, 3H, H^b], **minor isomer** δ = 8.52 [s, ^3J(Pt-H) = 104.0, 1H, H^d], {7.24 [d, ^3J(H-H) = 8.0, 2H], 7.13[d, ^3J(H-H) = 8.0, 2H], H$^{2'}$, H$^{3'}$}, 5.40 [dd, ^2J(H-H) = 13.6, ^4J(H-H) = 1.7, 1H, H^c], 5.03 [d, ^2J(H-H) = 14.2, 1H, H^c], 3.30 [s, 3H, H^b], 2.85 [s, ^3J(Pt-H) = 30.0, 3H, H^b]. **Maldi-MS**, m/z: 632.0 [M-Cl]$^+$, 554.0 [M-Cl-dmso]$^+$, 359.0 [M-Cl-dmso-Pt]$^+$.

[PtCl{(4-ClC$_6$H$_3$)CHNCH$_2$C$_6$H$_5$}{SOMe$_2$}] (4c) was obtained from 0.187 g (0.44 mmol) of *cis*-[PtCl$_2$(dmso)$_2$], 0.102 g (0.44 mmol) of imine **1c** and 36 mg (0.44 mmol) of sodium acetate (in 1 mL methanol) which were allowed to react in dry toluene (30 mL) at 90° for 48 h. The solvent was filtered and removed in a rotary evaporator and the residue was treated with dicloromethane-methanol, yielding a deep yellow solid which was filtered *in vacuo*. Yield 125 mg (53%). **IR**: ν(CH=N) = 1608.5 cm^{-1}; **^{1}H-NMR** (250 MHz, CDCl$_3$): δ = 8.25 [d, ^{4}J(H-H) = 1.8, ^{3}J(Pt-H) = 48.5, 1H, H^{5}], 7.79 [s, 1H, ^{3}J(Pt-H) = 116.8, 1H, H^{c}], 7.50-7.30 [m, 5H, H$^{2',3',4'}$], 7.15 [d, ^{3}J(H-H) = 7.9, 1H, H^{2}], 7.08 [dd, ^{3}J(H-H) = 8.2 , ^{4}J(H-H) = 1.8, H^{3}], 5.18 [s, ^{3}J(Pt-H) = 20.0, 2H, H^{b}], 3.57 [s, ^{3}J(Pt-H) = 23.78, 6H, H^{a}]. **FAB-MS**, m/z: 502.3 [M-Cl]$^{+}$, 461.2 [M-Cl-dmso]$^{+}$, 423.28 [M-2Cl-dmso]$^{+}$. **Anal. Found (calc. for C$_{16}$H$_{17}$Cl$_2$NOPtS)**: C: 35.4 (35.76); H: 3.0 (3.19); N: 2.7 (2.60); S: 5.7 (5.97).

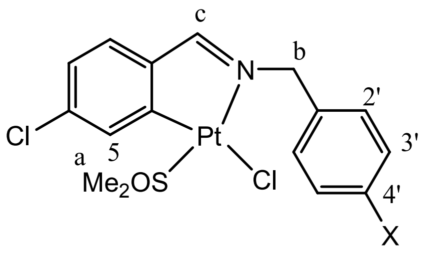
[PtCl{(4-ClC$_6$H$_3$)CHNCH$_2$(4-ClC$_6$H$_4$)}{SOMe$_2$}] (4d) was obtained from 0.160 g (0.38 mmol) of *cis*-[PtCl$_2$(dmso)$_2$], 0.100 g (0.38 mmol) of imine **1d** and 31 mg (0.38 mmol) of sodium acetate, using the procedure reported for **4c**. Yield 119 mg (55%). **IR**: ν(CH=N) = 1624.6 cm^{-1}; **^{1}H-NMR** (250 MHz, CDCl$_3$): δ = 8.24 [d, ^{4}J(H-H) = 2.0, ^{3}J(Pt-H) = 48.3, 1H, H^{5}], 7.86 [s, ^{3}J(Pt-H) = 114.0, 1H, H^{c}], 7.36 [d, ^{3}J(H-H) = 8.7, 2H, H$^{2'}$], 7.30 [d, ^{3}J(H-H) = 8.5, 2H, H$^{3'}$], 7.19 [s, ^{3}J(H-H) = 8.0, 1H, H^{2}], 7.11 [dd, ^{3}J(H-H) = 8.0, ^{4}J(H-H) = 1.7, 1H, H^{3}], 5.15 [s, ^{3}J(Pt-H) = 13.0, 2H, H^{b}], 3.55 [s, ^{4}J(Pt-H) = 24.0 , 6H, H^{a}]. **^{195}Pt-RMN** (54 MHz, CDCl$_3$): δ = -3833.96 [s]. **FAB-MS**, m/z: 536.3 [M-Cl]$^{+}$, 459.3 [M-Cl-dmso]$^{+}$. **Anal. Found (calc. for C$_{16}$H$_{16}$Cl$_3$NOPtS)**: C: 34.2 (33.61); H: 3.2 (2.82); N: 2.4 (2.45); S: 5.6 (5.61).

PtCl{(2,4,6-(CH$_3$)$_3$C$_6$H$_2$)CHNCH$_2$(4-ClC$_6$H$_3$)}{SO(CH$_3$)$_2$}] (2e) was obtained as a pale brown solid from 0.160 g (0.38 mmol) of [PtCl$_2$(dmso)$_2$], 0.100 g (0. 38 mmol) of imine **1e** and 0.031 g (0.38 mmol) of sodium acetate using the procedure reported for **4c**. Yield 33 mg (15%). **IR**: ν(CH=N) = 1634.9 cm^{-1}. **^{1}H-NMR** (250 MHz, CDCl$_3$): δ = 9.61 [s, ^{3}J(Pt-H) = 52.7, 1H, H^{c}], 8.13 [d, ^{4}J(H-H) = 1.7, ^{3}J(Pt-H) = 51.4, 1H, H^{5}], 7.04 [dd, ^{3}J(H-H) = 8.0, ^{4}J(H-H) = 1.6, 1H, H^{3}], 6.93 [s, 2H, H$^{3',5'}$], 6.85 [d, ^{3}J(H-H) = 7.9, 1H, H^{2}], 4.50 [s, ^{3}J(Pt-H) = 33.4, 2H, H^{b}], 3.61 [s, ^{3}J(Pt-H) = 23.4, 6H, H^{a}], 2.33 [s, 3H, H$^{4'}$], 2.17 [s, 6H, H$^{2',6'}$]; **FAB-MS**, m/z: 578.93 [M]$^{+}$, 543.9 [M-Cl]$^{+}$, 462.9 [M-Cl-dmso]$^{+}$; **Anal. Found (calc. for C$_{19}$H$_{23}$Cl$_2$NOPtS)**: C: 39.0 (39.38); H: 4.2 (4.00); N: 2.4 (2.42); S: 6.5 (5.53).

References

[1] J. H. Price, A. N. Williamson, R. F. Schramm, B.B. Wayland, Inorg. Chem. 11 (1972) 1280.

Numbering scheme:



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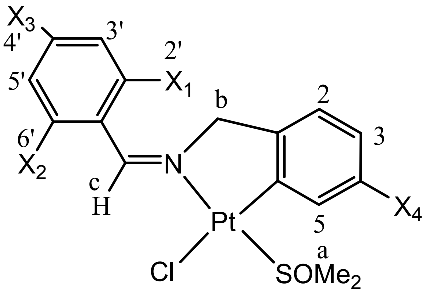

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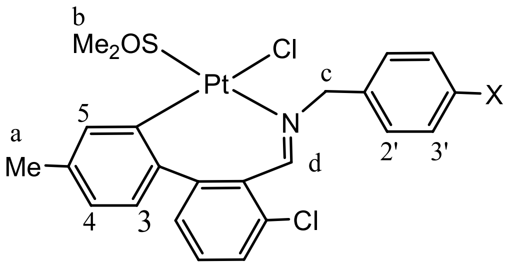

3a, X = H
3b, X = Cl