

Paper: Platinum(II) mediated C^{sp3}-H activation of tetramethylthiourea
Serena Fantasia,^{a,b} *Alessandro Pasini*^{a*} and *Steven P. Nolan*^{b,c*}

^aDipartimento di Chimica Inorganica, Metallorganica e Analitica (CIMA), Università degli Studi di Milano, Via Venezian 21, 20133 Milan, Italy. ^bInstitute of Chemical Research of Catalonia (ICIQ), Av. Països Catalans 16, 43007 Tarragona, Spain. ^cSchool of Chemistry, University of St Andrews, St Andrews, KY16 9ST, UK.

Electronic supplementary information

Experimental: general.....	S2
Synthesis of [L ₂ Pt(NO ₃) ₂] complexes.....	S2
Synthesis of [L ₂ Pt(tmtu*)]NO ₃ complexes.....	S4
References and notes.....	S5

Experimental

General considerations: All manipulations unless otherwise noted were carried out in air. Solvents and reagents were used as received. *Cis*-[Pt(PPh₃)₂Cl₂], ¹ *cis*-[Pt(P(4-tol)₃)₂Cl₂], ² *cis*-[Pt(P(4-F-Ph)₃)₂Cl₂], ³ [Pt(dppp)Cl₂], ⁴ *cis*-[Pt(dmsO)₂Cl₂], ⁵ *cis*-[Pt(PPh₃)₂(NO₃)₂] **7a**, ⁶ [Pt(PPh₃)₂(tmtu*)](NO₃) **2**⁷ and the carbene ligand ICy **6**⁸ were synthesized according to literature procedures. Elemental analyses were performed at the Microanalytical Laboratory, the University of Milano. Mass spectra were recorded on a Water LCT Premier instrument. NMR spectra were recorded in CDCl₃ solution on a Bruker Avance DRX 300 MHz and 400 MHz. ¹⁹⁵Pt spectra were calibrated with Na₂[PtCl₆] in D₂O as 4522 ppm.

Synthesis of [PtL₂(NO₃)₂] Complexes

cis-[Pt(P(4-tol)₃)₂(NO₃)₂] **7b**. 132.0 mg of *cis*-[Pt(P(4-tol)₃)₂Cl₂] (0.150 mmol) are dissolved in 15 mL of CHCl₃ and 102.5 mg of AgNO₃ (0.6 mmol) are added. The suspension is refluxed for 8 h in the dark. The hot solution is filtered on a frit and the residue washed with hot CHCl₃ (3x20 mL). The solvent is collected in a flask and the volume reduced in vacuum to 4 mL. Addition of 15 mL of diisopropyl ether affords, after filtration, 132.0 mg of a white product (94% yield). ¹H NMR: δ (ppm) 7.37 (t, *J* = 8.3 Hz, 12 H, *CH* arom), 7.02 (d, *J* = 6.9 Hz, 12 H, *CH* arom), 2.36 (s, 18 H, *CH*₃). ³¹P NMR: δ (ppm) 2.2 (s, ¹*J*_{Pt-P} = 4028 Hz). Anal. Calcd for C₄₂H₄₂N₂O₆P₂Pt (927.82): C, 54.37; H, 4.56; N, 3.02. Found: C, 54.54; H 4.23; N, 2.95.

***cis*-[Pt(P(4-F-Ph)₃)₂(NO₃)₂] 7c.** 141.9 mg of *cis*-[Pt(P(4-F-Ph)₃)₂Cl₂] (0.158 mmol) are dissolved in 50 mL of CHCl₃ and 120.7 mg of AgNO₃ (0.71 mmol) are added. The suspension is refluxed for 8 h in the dark. The hot solution is filtered on a frit and the residue washed with hot CHCl₃ (3x20 mL). The solvent is collected in a flask and the volume reduced to 4 mL in vacuum. Addition of 15 mL of diisopropyl ether affords, after filtration, 105.4 mg of a white product (67% yield). ¹H NMR: δ (ppm) 7.46 (m, broad, 12 H, CH arom), 6.93 (m, broad, 12 H, CH arom). ³¹P NMR: δ (ppm) 1.8 (s, ¹J_{Pt-P} = 4021 Hz). Anal. Calcd for C₃₆H₂₄F₆N₂O₆P₂Pt (951.60): C, 45.44; H, 2.54; N, 2.94. Found: C, 45.63; H 2.36; N, 3.13.

[Pt(dppp)(NO₃)₂] 7d. 139.6 mg of [Pt(dppp)Cl₂] (0.206 mmol) are dissolved in 20 mL of CHCl₃ and 110.0 mg of AgNO₃ (0.62 mmol) are added. The suspension is refluxed for 10 h in the dark. The hot solution is filtered on a frit and the residue washed with hot CHCl₃ (3x20 mL). The solvent is collected in a flask and the volume reduced in vacuum to 4 mL. Addition of 15 mL of diisopropyl ether affords, after filtration, 102.5 mg of a white product (68% yield). ¹H NMR: δ (ppm) 7.77 (m, broad, 8 H, CH arom), 7.44 (m, broad, 12 H, CH arom), 2.52 (m, broad, 4 H, CH₂P), 2.05 (m, broad, 2H, CH₂). ³¹P NMR: δ (ppm) -13.4 (s, ¹J_{Pt-P} = 3664 Hz). Anal. Calcd for C₂₇H₂₆N₂O₆P₂Pt (731.09): C, 44.33; H, 3.58; N, 3.83. Found: C, 44.42; H 3.75; N, 3.42.

***cis*-[Pt(ICy)₂(NO₃)₂] 9.** 129.6 mg of *cis*-[Pt(ICy)₂Cl₂] (0.178 mmol) are dissolved in 30 mL of CH₂Cl₂ and 121.2 mg of AgNO₃ (0.713 mmol) are added. The suspension is refluxed overnight in the dark. The hot solution is filtered on a frit and the residue washed with hot

CH₂Cl₂ (3x20 mL). The solvent is collected in a flask and the volume reduced to 4 mL in vacuum. Addition of 15 mL of diethyl ether affords, after filtration, 120.4 mg of a white product (86% yield). ¹H NMR (CDCl₃, 400 MHz): δ 6.99 (s, 4H, CH imidazole), 4.89 (m, 4 H, CH cyclohexyl), 2.25 (d broad, *J* = 12 Hz, 4 H, CH₂ cyclohexyl), 1.84 (t broad, *J* = 14 Hz, 8 H, CH₂ cyclohexyl), 1.75 (t broad, *J* = 12 Hz, 8 H, CH₂ cyclohexyl), 1.53 (m, 8 H, CH₂ cyclohexyl), 1.40 (m, 8 H, CH₂ cyclohexyl), 1.21(m, 4 H, CH₂ cyclohexyl). ¹³C NMR (CDCl₃, 400 MHz): δ 133.7 (s, C carbene), 118.1 (s, CH imidazole), 59.4 (s, CH cyclohexyl), 34.9 (s, CH₂ cyclohexyl), 33.5 (s, CH₂ cyclohexyl), 25.2 (s, CH₂ cyclohexyl), 25.1 (s, CH₂ cyclohexyl), 25.0 (s, CH₂ cyclohexyl). ESI-MS (HRMS): calcd. For C₃₀H₄₈N₅O₃Pt [M-(NO₃)]⁺: 721.3405. Found: 721.3422.

Synthesis of [PtL₂(tmtu*)]NO₃ complexes

[Pt(P(4-tol)₃)₂(tmtu*)](NO₃) 7*b. 93.1 mg of *cis*-[Pt(P(4-tol)₃)₂(NO₃)₂] (0.1 mmol) are dissolved in 20 mL of CHCl₃ and 13.3 mg of tmtu (0.1 mmol) are added. The solution is stirred at room temperature for 5 h. The solvent volume is reduced to 4 mL in vacuum. Addition of 15 mL of *n*-hexane affords, after filtration, 73.0 mg of a white product (73% yield). ¹H NMR: δ(ppm) 7.10-7.30 (m, broad, 12 H, CH arom), 6.90-7.05 (m, broad, 12 H, CH arom), 3.44 (t, ³*J*_{P-H} = 5 Hz, ²*J*_{Pt-H} = 59 Hz, 2 H, CH₂Pt), 3.02 (s, 3 H CH₃N), 2.97 (s, 6 H, (CH₃)₂N), 2.18 (s, 18 H, CH₃). ³¹P NMR: δ(ppm) 20.2 (d, ²*J*_{P-P} = 23 Hz, ¹*J*_{Pt-P} = 3406 Hz, P *trans* S), 15.6 (d, ²*J*_{P-P} = 23 Hz, ¹*J*_{Pt-P} = 2037 Hz, P *trans* C). Anal. Calcd for C₄₇H₅₃N₃O₃P₂PtS (997.03): C, 56.62; H, 5.36; N, 4.21. Found: C, 57.01; H 5.57; N, 3.98.

[Pt(P(4-F-Ph)₃)(tmtu*)](NO₃) 7*c. 50.0 mg of *cis*-[Pt(P(4-F-Ph)₃)(NO₃)₂] (0.053 mmol) are dissolved in 20 mL of CHCl₃ and 7.0 mg of tmtu (0.053 mmol) are added. The solution is stirred at room temperature for 5 h. The solvent is reduced to 4 mL in vacuum. Addition of 15 mL of diisopropyl ether affords, after filtration, 33.0 mg of a white product (61% yield). ¹H NMR: δ (ppm) 7.20-7.50 (m, broad, 12 H, CH arom), 6.90-7.10 (m, broad, 12 H, CH arom), 3.48 (t, ³J_{P-H} = 5 Hz, ²J_{Pt-H} = 73 Hz, 2 H, CH₂Pt), 3.06 (s, 3 H CH₃N), 2.99 (s, 6 H, (CH₃)₂N). ³¹P NMR: δ (ppm) 20.7 (d, ²J_{P-P} = 23 Hz, ¹J_{Pt-P} = 3483 Hz, P *trans* S), 15.6 (d, ²J_{P-P} = 23 Hz, ¹J_{Pt-P} = 2010 Hz, P *trans* C). Anal. Calcd for C₄₁H₃₅F₆N₃O₃P₂PtS (1020.82): C, 48.24; H, 3.46; N, 4.12. Found: C, 47.95; H 3.21; N, 4.21.

[Pt(dppp)(tmtu*)](NO₃) 7*d. 51.1 mg of [Pt(dppp)(NO₃)₂] (0.07 mmol) are dissolved in 25 mL of CH₂Cl₂ and 9.2 mg of tmtu (0.07 mmol) are added. The solution is stirred at room temperature for 2 days. The solvent is reduced in vacuum to 4 mL. Addition of 15 mL of *n*-hexane affords, after filtration, 40.0 mg of a white product (71% yield). ¹H NMR: δ (ppm) 7.20-7.50 (m, broad, 20 H, CH arom), 3.38 (t, ³J_{P-H} = 6 Hz, ²J_{Pt-H} = 56 Hz, 2 H, CH₂Pt), 3.06 (s, 3 H CH₃N), 2.96 (s, 6 H, (CH₃)₂N), 2.30 (m, broad, 4 H, CH₂P), 1.93 (m, broad, 2H, CH₂). ³¹P NMR: δ (ppm) 0.7 (d, ²J_{P-P} = 34 Hz, ¹J_{Pt-P} = 3189 Hz, P *trans* S), -5.4 (d, ²J_{P-P} = 34 Hz, ¹J_{Pt-P} = 1877 Hz, P *trans* C). Anal. Calcd for C₃₂H₃₇N₃O₃P₂PtS (800.75): C, 48.00; H, 4.66; N, 5.25. Found: C, 48.26; H 4.35; N, 5.23.

References and Notes

- ¹ L. Malatesta, C. Cariello, *J. Chem. Soc.* 1958, 2323.
- ² Prepared accordingly to ref. 1. For spectroscopic data, see: C. J. Cobley, P. G. Pringle, *Inorg. Chim. Acta* **1997**, 265, 107.

- ³ Prepared according to ref. 1. For spectroscopic data, see: A. R. Siedle, R. A. Newmark, W. B. Gleason, *J. Am. Chem. Soc.* 1986, **108**, 767.
- ⁴ Prepared accordingly to: M. P. Brown, R. J. Puddephatt, M. Rashidi, K. R. Seddon, *J. Chem. Soc., Dalton Trans.* 1977, 951. For spectroscopic data, see: T. G. Appleton, M. A. Bennett; I. B. Tomkins, *J. Chem. Soc., Dalton Trans.* 1976, 439.
- ⁵ R. Romeo, L. M. Scolaro, *Inorg. Synt.* 1998, **32**, 153.
- ⁶ A. Pasini, S. Rizzato, D. De Cillis, *Inorg. Chim. Acta* 2001, **315**, 196.
- ⁷ S. Fantasia, M. Manassero, A. Pasini, *Inorg. Chem. Commun.* 2004, 7, 97.
- ⁸ N. Kuhn, T. Kratz, *Synthesis* 1993, 561.