

Platinum-mediated aryl-aryl bond formation and sp^3 C-H bond activation

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SUPPORTING INFORMATION AVAILABLE:

Experimental procedures and characterization data for all new compounds

General

Microanalyses were performed at the *Serveis Científico-Tècnics (Universitat de Barcelona)*. Electrospray mass spectra were performed at the *Servei d'Espectrometria de Masses (Universitat de Barcelona)* in a LC/MSD-TOF spectrometer using H₂O-CH₃CN 1:1 to introduce the sample. NMR spectra were performed at the *Unitat de RMN d'Alt Camp de la Universitat de Barcelona* using Bruker DRX-250 (¹⁹⁵Pt, 54 MHz), Varian Unity 300 (¹H, 300 MHz; ³¹P-{¹H}, 121.4 MHz), Mercury-400 (¹H, 400 MHz; ¹H-¹H-NOESY, ¹H-¹H-COSY, ¹H-¹³C-gHSQC) and Varian Inova DMX-500 (¹³C) spectrometers, and referenced to SiMe₄ (¹H, ¹³C), H₃PO₄ (³¹P) and H₂PtCl₆ in D₂O (¹⁹⁵Pt). δ values are given in ppm and J values in Hz. Abbreviations used: s = singlet; d = doublet; t = triplet; m = multiplet; br = broad; NMR labelling as shown in the attached numbering scheme.

Preparation of the compounds

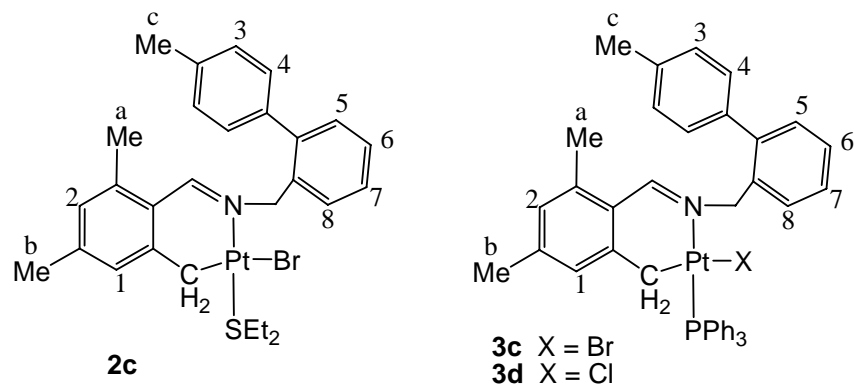
cis-[Pt₂(4-MeC₆H₄)₄(μ -SEt₂)₂]¹ and ligands **1c-1e**² were prepared as reported elsewhere.

Compound [PtBr{CH₂C₆H₂(CH₃)₂CHNCH₂C₆H₄(4-CH₃C₆H₄)}SEt₂] (**2c**) was obtained from 68 mg (0.21 mmol) of imine **1c** and 100 mg (0.11 mmol) of compound *cis*-[Pt(4-C₆H₄CH₃)₂(μ -SEt₂)₂] in 20 mL of toluene. The mixture was heated for 4 hours under refluxing conditions. The solvent was removed in a rotary evaporator to yield a yellow oil which could not be purified due to its low stability. ¹H NMR (400 MHz, CDCl₃): δ = 8.23 [br, 1H, CHN]; {7.39 [m, 3H]; 7.23 [m, 1H]; 7.14 [m, 4H]; 6.72 [s, 1H, H¹ or H²]; 6.57 [s, 1H, H¹ or H²], aromatics}; 5.56 [s, ³J(H-Pt) = 27.2, 2H, NCH₂]; 3.10 [m, 2H, SCH₂]; 2.70 [m, 2H, SCH₂]; 2.35 [s, 3H, CH₃^c]; 2.32 [m, 2H, CH₂Pt]; {2.18 [s, 3H]; 1.92 [s, 3H], CH₃^{ab}}; 1.24 [t, J(H-H) = 7.2, 6H, SCH₂CH₃].

Compound [PtBr{CH₂C₆H₂(CH₃)₂CHNCH₂C₆H₄(4-CH₃C₆H₄)}PPh₃] (**3c**) was obtained from 68 mg (0.21 mmol) of imine **1c** and 100 mg (0.11 mmol) of compound *cis*-[Pt(4-C₆H₄CH₃)₂(μ-SEt₂)₂] in toluene. The mixture was heated for 4 hours under refluxing conditions. The solvent was removed in a rotary evaporator and a solution of 56 mg of PPh₃ (0.21 mmol) in 20 mL of acetone was added to the residue. After stirring at room temperature for 2 hours, the solvent was partially removed and yellow crystals were formed. Yield: 97 mg (54%). ¹H NMR (400 MHz, CDCl₃): δ = 8.30 [br. m, 1H, CHN]; 7.57-7.52 [m, 6H, PPh₃^{ortho}]; 7.49-7.47 [m, 2H]; 7.40-7.31 [m, 11H, PPh₃^{meta, para} + 2H]; 7.14 [dd, ³J(H-H) = 8.0, 4H, H^{3,4}]; 6.51 [s, 1H, H²]; 5.67 [d, ⁴J(H-H) = 2.0, ³J(H-Pt) = 32.0, CH₂N]; 5.62 [s, 1H, H¹]; 2.35 [s, 3H, Me^c]; 2.06 [d, ⁴J(H-P) = 4.0, ³J(H-Pt) = 96.0, CH₂Pt]; 2.02 [s, 3H, Me^b]; 1.92 [s, 3H, Me^a]. ¹³C NMR (125.9 MHz, CDCl₃): δ = 160.27 [s, CHN]; singlets at 145.10, 142.99, 141.63, 138.22, 137.84, 136.95, 133.11, 130.97, 130.49 [aromatic carbon atoms]; 134.86 [d, ²J(C-P) = 11.0, PPh₃, C^{ortho}]; 130.16 [d, ⁴J(C-P) = 2.0, PPh₃, C^{para}]; 129.15 [s, C^{3,4}]; 127.75 [d, ³J(C-P) = 11.0, PPh₃, C^{meta}]; singlets at 130.06; 129.95; 128.04; 127.42 [C^{5,6,7,8}]; 126.80 [s, C²]; 125.37 [s, C¹]; 63.77 [s, NCH₂]; 21.36 [s, CH₃^b]; 21.07 [s, CH₃^c]; 18.40 [CH₃^a]; 14.70 [d, ¹J(C-P) = 4.0, J(C-Pt) = 630.0, CH₂Pt]. ³¹P NMR (121.4 MHz, CDCl₃): δ = 19.09 [s, J(P-Pt) = 4484.5]. ¹⁹⁵Pt NMR (54 MHz, CDCl₃): δ = -4266.3 [d, J(P-Pt) = 4474.0]. **HR-ESI-MS**, m/z: 783.2458, calculated for C₄₂H₃₉NPt [M-Br] 783.2462; 824.2721, calculated for C₄₄H₄₂N₂PPt [M-Br+CH₃CN] 824.2727. **Anal. Found (calc. for C₄₂H₃₉BrNPt·CH₂Cl₂):** C: 54.2 (54.44); H: 4.2 (4.35); N: 1.6 (1.48).

Compound [PtCl{CH₂C₆H₂(CH₃)₂CHNCH₂C₆H₄(4-CH₃C₆H₄)}PPh₃] (**3d**) was obtained from 58 mg (0.21 mmol) of imine **1d** and 100 mg (0.11 mmol) of compound [Pt₂(4-MeC₆H₄)₂(μ-SEt₂)₂] in 20 mL of toluene. The mixture was heated for 4 hours under refluxing conditions. The solvent was removed in a rotary evaporator and a solution of 56 mg of PPh₃ (0.21 mmol) in 20 mL of acetone was added to the residue. After stirring at room temperature for 2 hours, the solvent was partially removed and yellow crystals were formed. Yield: 110 mg (63%). ¹H NMR (400 MHz, CDCl₃): δ = 8.26 [br. m, 1H, CHN]; 7.46 [m, 2H]; 7.40-7.30 [m, 11H]; 7.14 [m, 4H]; 6.52 [s, 1H, H²]; 5.71 [s, 1H, H¹]; 5.59 [d, ⁴J(H-H) = 2.0, 2H, CH₂N]; 2.35 [s, 3H, Me^c]; 2.05 [d, ⁴J(H-P) = 4.0, CH₂Pt]; 2.04 [s, 3H, Me^b]; 1.93 [s, 3H, Me^a]. ³¹P NMR (121.4 MHz, CDCl₃): δ = 18.54 [s, J(P-Pt) = 4482.1]. **ESI-MS**, m/z: 783.26 [M-Cl]⁺. **Anal. Found (calc. for C₄₂H₃₉CINPpt):** C: 61.3 (61.57); H: 5.3 (4.80); N: 2.0 (1.71).

Numbering scheme:



X-Ray Structure Analysis of 3c

A prismatic crystal was selected and mounted on a MAR345 diffractometer with an image plate detector. Intensities were collected with graphite monochromatized Mo K α radiation. The structure was solved by direct methods using SHELXS computer program³ and refined by the full-matrix least-squares method, with the SHELXL97 computer program using 16366 reflections (very negative intensities were not assumed). All hydrogen atoms were computed and refined, using a riding model, with an isotropic temperature factor equal to 1.2 time the equivalent temperature factor of the atom to which they are linked. Further details are given in Table 1.

References

- 1.- Steele, B.R.; Vrieze, K., *Trans. Met. Chem.* **1977**, 2, 140.
- 2.- a) Crespo, M.; Martinez, M.; Sales, J.; Solans, X.; Font-Bardia, M. *Organometallics* **1992**, 11, 1288. b) Capapé, A.; Crespo, M.; Granell, J.; Font-Bardía, M.; Solans, X. *Dalton Trans.* **2007**, 2030.
- 3.- Sheldrick, G.M. SHELXS97, A Computer Program for Crystal Structure Determination, University of Göttingen: Germany, 1997.

Table 1.- Crystallographic and refinement data for compound 3c.

Formula	C ₄₂ H ₃₉ BrNPt, H ₂ O
Fw	881.73
temp, K	293(2)
wavelength, Å	0.71073
crystal system	Triclinic
space group	P-1
a, Å	12.032(5)
b, Å	12.230(4)
c, Å	12.715(3)
α, deg	81.08(2)
β, deg	72.52(2)
γ, deg	79.01(2)
V, Å ³ ; Z	17742.3(10); 2
d (calcd), Mg/m ³	1.681
abs coeff, mm ⁻¹	5.254
F(000)	872
rlns coll. / unique	16366 / 8758 [R(int) = 0.0627]
Data/restraint/parameters	8758 / 2 / 435
GOF on F ²	1.087
R ₁ (I>2σ(I))	0.0550
wR ₂ (all data)	0.1579
peak and hole, e.Å ⁻³	1.802 and -2.558

Table 2.- Selected bond lengths (Å) and angles (deg.) for compound 3c with estimated standard deviations.

Pt-C(22)	1.988(6)
Pt-N	2.055(4)
Pt-P	2.1801(16)
Pt-Br	2.4417(10)
N-C(15)	1.204(7)
N-C(1)	1.487(7)
C(1)-C(2)	1.547(8)
C(2)-C(3)	1.349(9)
C(2)-C(7)	1.362(8)
C(3)-C(4)	1.381(10)
C(4)-C(5)	1.339(10)
C(5)-C(6)	1.360(9)
C(6)-C(7)	1.384(9)
C(7)-C(8)	1.350(8)
C(8)-C(9)	1.359(10)
C(8)-C(13)	1.392(9)
C(9)-C(10)	1.346(10)
C(10)-C(11)	1.383(13)
C(11)-C(12)	1.370(13)
C(11)-C(14)	1.412(13)
C(12)-C(13)	1.353(10)
C(15)-C(16)	1.414(9)
C(16)-C(17)	1.373(9)
C(16)-C(21)	1.398(9)
C(17)-C(18)	1.386(10)
C(17)-C(23)	1.543(10)
C(18)-C(19)	1.385(10)
C(19)-C(20)	1.374(9)
C(19)-C(24)	1.459(11)
C(20)-C(21)	1.383(9)
C(21)-C(22)	1.443(8)
C(22)-Pt-N	86.8(2)
C(22)-Pt-P	90.32(17)
N-Pt-P	176.63(12)
C(22)-Pt-Br	174.40(17)
N-Pt-Br	87.73(13)
P-Pt-Br	95.11(5)
C(15)-N-C(1)	117.3(5)
C(15)-N-Pt	122.5(4)
C(1)-N-Pt	119.8(3)
N-C(15)-C(16)	123.3(6)
C(21)-C(16)-C(15)	120.7(6)
C(16)-C(21)-C(22)	124.5(6)
C(21)-C(22)-Pt	104.0(4)