Coordination Chemistry at the Turn of the Century
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WIRE-LIKE sp CARBON CHAINS THAT SPAN TWO PLATINUM ATOMS: SYNTHESIS AND CRYSTAL STRUCTURES OF BUILDING BLOCKS OF THE FORMULA *trans*-(p-tolyl)($Ph_3P)_2Pt(C{\equiv}C)_nSiMe_3$

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ABSTRACT

The elaboration of chloride complex *trans*-(p-tolyl)($Ph_3P)_2PtCl$ to *trans*-(p-tolyl)-($Ph_3P)_2Pt(C{\equiv}C)_nSiMe_3$ (n = 1,2) by copper mediated alkynylation reactions is described. These compounds or close relatives serve as intermediates in syntheses of complexes with $Pt(C{\equiv}C)_nPt$ linkages, and their crystal structures are reported.

INTRODUCTION

Complexes in which two metals are connected by an unsaturated bridging ligand represent an important frontier of coordination chemistry [1]. Bimetallic complexes of the formula $[L_nMC_xM'L'_{n'}]^{z+}$, where C_x is a sp hybridized carbon chain, feature the most fundamental class of organic unsaturated bridging ligand. Such compounds have recently attracted particular interest in numerous research groups [2-4]. They exhibit a variety of unusual chemical and physical properties [5], as well as an aesthetic appeal. As x becomes large, such assemblies become good models for the sp polymeric carbon allotrope, carbyne [6].

In previous papers, we have described the synthesis and properties of the twenty carbon dirhenium complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(C{\equiv}C)_{10}(Ph_3P)(ON)Re(\eta^5\text{-}C_5H_5)$ [2b,c]. However, we seek to investigate and compare a range of endgroups, and recently initiated work on a similar family of platinum capped complexes, as will be detailed in the accompanying oral presentation. In this note, we report representative syntheses and crystal structures of two monoplatinum building blocks. In order to carefully analyze and interpret the physical properties of the diplatinum complexes, good baseline data for a library of monoplatinum compounds are required.

EXPERIMENTAL

General. Reactions were conducted under N_2 atmospheres. Commercial chemicals were treated as follows: toluene, distilled from Na; $HNEt_2$, distilled from KOH; $HC{\equiv}CSiMe_3$ (Aldrich), CuI (Aldrich, 99.999%), and other materials, used as received. IR and NMR spectra were recorded on Mattson Polaris and Varian FT spectrometers. Mass spectra were recorded on a Finnigan MAT 95 high resolution instrument. Microanalyses were conducted by Atlantic Microlab.

***trans*-(*p*-tolyl)$(Ph_3P)_2PtC{\equiv}CSiMe_3$ (1)**. A Schlenk flask was charged with *trans*-(*p*-tolyl)$(Ph_3P)_2PtCl$ (**2** [7], 0.250 g, 0.296 mmol), CuI (0.020 g, 0.11 mmol), and $HNEt_2$ (30 mL). Then $HC{\equiv}CSiMe_3$ (0.064 mL, 0.45 mmol) was added with stirring. After 16 h, the solvent was evaporated under a N_2 stream. The residue was extracted with CH_2Cl_2 (5 mL). Water (10 mL) was added, and the CH_2Cl_2 layer was separated. The water layer was extracted with CH_2Cl_2 (2 x 10 mL). The combined CH_2Cl_2 extracts were dried ($MgSO_4$), filtered (2 cm celite), and taken to dryness (rotary evaporation). The residue was dissolved in CH_2Cl_2 (2 mL) and added dropwise to stirred EtOH (50 mL). The white precipitate was collected by filtration and dried by oil pump vacuum to give **1** (0.192 g, 0.212 mmol, 70%). Crystallization (benzene/EtOH layer-layer diffusion) gave large colorless prisms, dec pt 174 °C. Calcd for $C_{48}H_{46}P_2PtSi$: C, 63.57; H, 5.10. Found: C, 63.62; H, 5.13. IR (cm^{-1}, CH_2Cl_2) $\nu_{C\equiv C}$ 2037 (s). ^{1}H NMR (ppm, $CDCl_3$, 300 MHz) 7.16-7.58 (m, $6C_6H_5$), 6.08 (d, J_{HH} = 11 Hz, 2H of C_6H_4), 6.38 (d, J_{HH} = 12 Hz, 2H of C_6H_4), 1.94 (s, CCH_3), -0.50 (s, $Si(CH_3)_3$). $^{13}C\{^{1}H\}$ NMR (ppm, $CDCl_3$, 125 MHz) 152.0 (s, tol/*i* to Pt), 139.3 (s, tol/*o* to Pt), 135.2 (virtual t, J_{CP} = 6.4 Hz, *o*-Ph), 131.8 (virtual t, J_{CP} = 27.8 Hz, *i*-Ph), 129.7 (s, *p*-Ph), 128.6 (s, tol/*p* to Pt), 128.0 (s, tol/*m* to Pt), 127.5 (virtual t, J_{CP} = 5.2 Hz, *m*-Ph), 98.3 (s, $\underline{C}{\equiv}CSi$), 61.3 (s, $C{\equiv}\underline{C}Si$), 20.7 (s, $C\underline{C}H_3$), 0.8 (s, $Si\underline{C}H_3$). $^{31}P\{^{1}H\}$ NMR (ppm, $CDCl_3$, 121 MHz) 21.5 (s with satellites, J_{PtP} = 3007 Hz). MS [8] 907 (1^+, 30%), 810 ((tolyl)$(Ph_3P)_2Pt^+$, 80%), 719.4 ($(Ph_3P)_2Pt^+$, 100%); no other peaks above 400 of >3%.

***trans*-(*p*-tolyl)$(Ph_3P)_2PtC{\equiv}CC{\equiv}CSiMe_3$ (3)**. A Schlenk flask was charged with **2** (0.252 g, 0.298 mmol), $Me_3SnC{\equiv}CC{\equiv}CSiMe_3$ [9] (0.085 g, 0.30 mmol), and toluene (25 mL). Then CuI (0.020 g, 0.11 mmol) was added with stirring. After 1 h, the solvent was removed by oil pump vacuum. The residue was extracted with CH_2Cl_2 (5 mL). Water (10 mL) was added, and the CH_2Cl_2 layer was separated. The water layer was extracted with CH_2Cl_2 (2 x 10 mL). The combined CH_2Cl_2 extracts were dried ($MgSO_4$), filtered (2 cm celite), and concentrated. Then EtOH (50 mL) was added. The white precipitate was collected by filtration and dried by oil pump vacuum to give **3** (0.215 g, 0.231 mmol, 75%). Crystallization (benzene/EtOH layer-layer diffusion) gave light yellow prisms, dec pt 187 °C. Calcd for $C_{50}H_{46}P_2PtSi$: C, 64.44; H, 4.94. Found: C, 64.42; H, 4.99. IR (cm^{-1}, CH_2Cl_2) $\nu_{C\equiv C}$ 2176 (m), 2126 (s). ^{1}H NMR (ppm, $CDCl_3$, 300 MHz) 7.20-7.60 (m, $6C_6H_5$), 6.35 (d, J_{HH} = 12 Hz, 2H of C_6H_4), 6.10 (d, J_{HH} = 11 Hz, 2H of C_6H_4), 1.95 (s, CCH_3), 0.10 (s, $Si(CH_3)_3$). $^{13}C\{^{1}H\}$ NMR (ppm, $CDCl_3$, 125 MHz) 149.2 (s, tol/*i* to Pt), 139.1 (s, tol/*o* to Pt), 135.0 (virtual t, J_{CP} = 7.2 Hz, *o*-Ph), 131.1 (virtual t, J_{CP} = 34.2 Hz, *i*-Ph), 130.0 (s, *p*-Ph), 129.8 (s, tol/*p* to Pt), 128.3 (s, tol/*m* to Pt), 127.9 (virtual t, J_{CP} = 6.0

Hz, *m*-Ph), 114.2 (s, $\underline{C}\equiv CC\equiv CSi$), 97.6, 93.4, 75.7 (3 s, $C\equiv \underline{CC}\equiv \underline{C}Si$), 20.6 (s, $C\underline{C}H_3$), 0.5 (s, $SiCH_3$). $^{31}P\{^1H\}$ NMR (ppm, $CDCl_3$, 121 MHz) 22.1 (s with satellites, J_{PtP} = 2966 Hz). MS [8] 932 ($\mathbf{3}^+$, 30%), 810 ((tolyl)$(Ph_3P)_2Pt^+$, (80%), 719 ($(Ph_3P)_2Pt^+$, 100%); no other peaks above 400 of >3%.

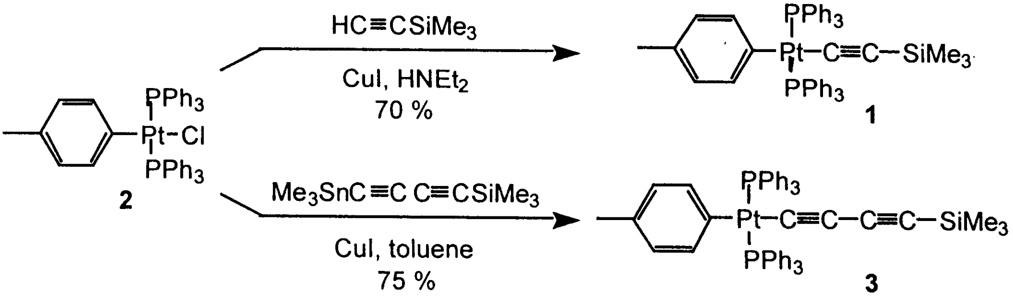
Crystallography. Data were collected with Nonius MACH3 (**1**) and Nonius Kappa CCD (**3**) diffractometers (0.71073 Å). Cell parameters were obtained from reflections with $5.0\_ < 2\Theta < 50.0\_$ (**1**, 293(2) K) or 10 frames using a 10° scan (**3**, 200.0(0.1) K). Space groups were determined from least-squares refinements. Lorentz, polarization, and absorption (ψ-scans) corrections were applied. The structures were solved by direct (**1**, SHELXS-86 [10]) or routine heavy atom methods (**3**). Complex **1** was refined with SHELXL-93 (497 parameters with all data by full matrix least squares on F^2; non-hydrogen atoms anisotropic; hydrogen atoms positions calculated and added to structure factor calculations using the riding model). Complex **3** was similarly refined with SHELXL-97. Scattering factors and $\Delta \underline{f}'$ and $\Delta \underline{f}''$ values were taken from literature [11,12]. Other data (**1**/**3**): crystal system, monoclinic/triclinic; space group, $\underline{C2/c}/\underline{P1\text{-bar}}$; $\underline{a}$, 26.846(2)/ 13.6700(5) Å; $\underline{b}$, 12.217(2)/13.7223(4) Å; $\underline{c}$, 29.689(3)/24.3745(9) Å; $\underline{\beta}$, 114.051(6)°/ 106.0977(11)°; $\underline{V}$, 8892(2)/4358.4(3) Å^3; $\underline{Z}$, 8/4; d(calc), 1.415/1.420 g/cm^3; reflections measured, 7987/8190; range/indices (h, k, l), $\underline{0, 31}/\underline{0, 13}$, $\underline{0, 14}/\underline{-13, 13}$, $\underline{-35, 32}/\underline{-24, 23}$; total unique data, 7807/8190; observed data ($I > 2\sigma(I)$), 5549/7925; absorption coefficient, 3.288/3.353 mm^{-1}; goodness of fit (all, observed) 1.060/1.304, 1.063/1.304; $\underline{R}$ (all, observed), 0.0697/0.0521, 0.0330/0.0502; weighted $\underline{R}$ (all, observed) 0.0791/0.1348, 0.0660/0.1328; Δ/σ (max), 0.004/0.000; $\Delta\rho$ (max) 0.931/0.786 e/Å^3.

Atomic coordinates and ORTEP diagrams have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC-115526 (**1**) and 115531 (**3**). Copies of the data can be obtained free of charge on request to: The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: Int. code +(1223) 336-033; e-mail: deposit@chemcrys.cam.ac.uk).

RESULTS AND DISCUSSION

The copper iodide catalyzed reaction of metal chlorides and terminal alkynes, often referred to as Hagihara coupling conditions, provides a versatile synthesis of alkynyl complexes [13,14]. A basic solvent such as $HNEt_2$ is employed, and absorbs the HCl that is formally evolved. As shown in Scheme 1, the readily available platinum chloride *trans*-(*p*-tolyl)$(Ph_3P)_2PtCl$ (**2**) [7] and trimethylsilyl ethyne gave the alkynyl complex *trans*-(*p*-tolyl)$(Ph_3P)_2PtC\equiv CSiMe_3$ (**1**) as a white powder in 70% yield after workup.

Scheme 1



In contrast, an analogous reaction of **2** and trimethylsilyl butadiyne ($HC{\equiv}CC{\equiv}C\text{-}SiMe_3$) gave a mixture of the target complex *trans*-(*p*-tolyl)$(Ph_3P)_2PtC{\equiv}CC{\equiv}CSiMe_3$ (**3**) and the redistribution product *trans*-$(Ph_3P)_2Pt(C{\equiv}CC{\equiv}CSiMe_3)_2$. The latter has been independently prepared and characterized [15]. Hence, recourse was made to the copper catalyzed coupling of platinum chlorides and stannyl alkynes, which has seen use in several laboratories [16] and is reminiscent of copper promoted Stille reactions [17]. Accordingly, **2** and the trimethylstannyl butadiyne $Me_3SnC{\equiv}CC{\equiv}CSiMe_3$ [9] were combined in toluene in the presence of CuI. After 1 h, workup gave **3** in 75% yield.

Complexes **1** and **3** were air stable, easily crystallized, and decomposed in the solid state only at 174-187 °C. FAB mass spectra exhibited strong molecular ions, and IR $\nu_{C\equiv C}$ bands were easily detected (2176-2037 cm^{-1}). The methyl ^1H and ^{13}C NMR signals of the tolyl ligands provide convenient probes for monitoring reactions. The $Pt\underline{C}{\equiv}C$ ^{13}C NMR signals (98.3-114.2 ppm) were downfield of the other sp carbons (61.3-97.6 ppm).

The X-ray crystal structures of **1** and **3** were determined as described in the experimental section. The resulting ORTEPS and key metrical parameters are given in Figure 1. Most features are routine, resembling those of other square planar platinum(II) and metal alkynyl complexes [16c,d,18]. The C≡C bond lengths fall into the narrow range 1.186(7)-1.196(18) Å, and the $\equiv\underline{C\text{-}C}\equiv$ bond of **3** is as expected much shorter than that of ethane (1.37(2) vs 1.53 Å). The bond angles that involve two sp carbons or trans ligands on platinum range from 172.3(6)° to 178.1(14)°.

The preceding syntheses have been extended to homologs with $P(p\text{-tolyl})_3$ and C_6F_5 ligands, and butadiyne itself has been used as a coupling partner [15]. This has allowed the synthesis of a large family of $Pt(C{\equiv}C)_nPt$ complexes, as will be detailed in the companion lecture.

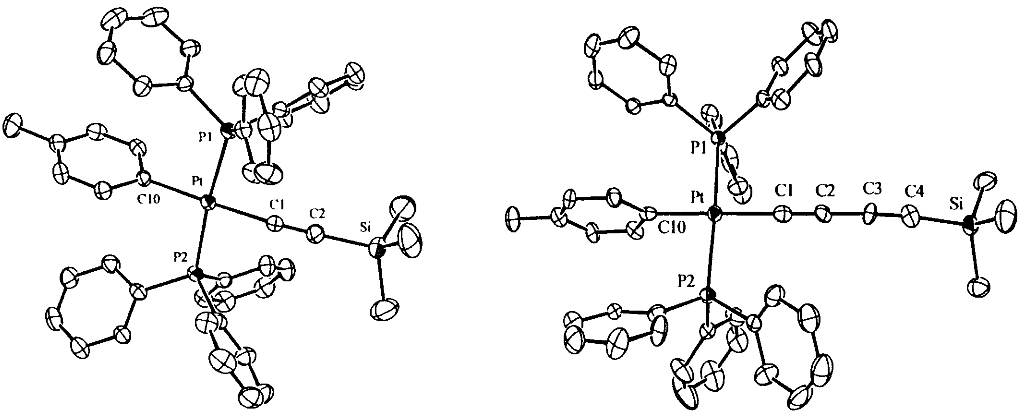


Figure 1. Molecular structures of **1** (left) and **3** (right). Key bond lengths (**1**/**3**): Pt-C1, 2.035(5)/2.039(15); Pt-C10, 2.057(4)/2.080(13); Pt-P1, 2.2916(13)/2.302(3); Pt-P2, 2.2998(13)/2.311(3); C1-C2, 1.186(7)/1.196(18); C2-C3, -/1.37(2); C3-C4, -/1.196(18). Key bond angles (**1**/**3**): C1-Pt-C10, 176.8(2)/175.2(5); P1-Pt-P2, 174.43(4)/172.45(12); Pt-C1-C2, 174.2(5)/175.0(11); C1-C2-Si, 172.3(6)/-; C1-C2-C3, -/178.1(14); C2-C3-C4, -/176.8(15); C3-C4-Si, -/174.0(13).

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