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Platinum Bis(diphenylphosphino)methane and -methanide Oxo and Hydroxo Dimers[1]

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Oxo and imido complexes occupy an important position in the chemistry of transition metals.[2] They are frequently postulated in transition metal chemistry involving dioxygen, amines, and other oxygen- and nitrogen-containing small molecules. They may also serve as homogeneous models[3] for oxygen adatoms and surface nitrenes. Recently, considerable progress has been made in the chemistry of late transition metal oxo and imido complexes,[4] but there remain few examples of platinum oxo complexes.[5] In order to better understand the late transition metal oxygen and nitrogen interaction, we are preparing new oxo,[5] imido,[4] dioxygen,[6] hydrazido,[7] and nitroso[6] complexes. In this communication we report the synthesis of new platinum hydroxo and oxo complexes including the first example of an anionic platinum oxo complex.

The white hydroxo complex $[(\mathrm{dppm})\mathrm{Pt}(\mu\text{-OH})]_2(\mathrm{BF}_4)_2$ (**1**)[8] (dppm = bis(diphenylphosphino)methane) is prepared by treating $(\mathrm{dppm})\mathrm{PtCl}_2$[9] with AgBF_4 in 95% ethanol (eq 1)following a

$$2(\mathrm{dppm})\mathrm{PtCl}_2 + 4\mathrm{AgBF}_4 + 2\mathrm{H}_2\mathrm{O} \rightarrow [(\mathrm{dppm})\mathrm{Pt}(\mu\text{-OH})]_2(\mathrm{BF}_4)_2 + 4\mathrm{AgCl} + 2\mathrm{HBF}_4 \quad (1)$$

procedure developed for related complexes.[10] The IR spectra of **1** show an OH band at 3250 cm^{-1}, 300 cm^{-1} lower than those of related hydroxo complexes (3560 cm^{-1}).[11] The crystal structure of **1** was determined[12] and an ORTEP diagram is shown in Scheme 1. The hydroxo complex has a rather short O---O distance of 2.55 Å. This distance is similar to that in $[(\mathrm{PMe}_3)_2\mathrm{Pt}(\mu\text{-OH})]_2(\mathrm{NO}_3)_2$[13] and is much shorter than that in other hydroxo complexes (2.72 Å).[14,15]

Complex **2**[16] is obtained by dropwise addition of 2 equiv of $\mathrm{LiN}(\mathrm{SiMe}_3)_2$ or $\mathrm{NaN}(\mathrm{SiMe}_3)_2$ to **1** in THF under N_2 (Scheme 1). Workup gives a 75% yiel of highly air sensitive yellow solid **2**. Proton NMR spectra of **2** in $\mathrm{C}_6\mathrm{D}_6$ show phenyl groups at 7.0–7.9 ppm and two equal intensity singlets at 4.1 and –0.3 ppm. The singlet at 4.1 ppm is assigned to a bridging hydroxo group, and the one at –0.3 ppm, to a deprotonated dppm ligand. Thus, deprotonation occurs at the dppm ligand and not at the hydroxo ligand, giving $[(\mathrm{dppm\text{-}H})\mathrm{Pt}(\mu\text{-OH})]_2$ (**2**) (dppm-H = bis(diphenylphosphino)methanide) (Scheme 1).[17] Attempts at

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[8] Data for **1** are as follows. Anal. Calcd (found) for $\mathrm{Pt}_2\mathrm{P}_4\mathrm{N}_2\mathrm{O}_2\mathrm{B}_2\mathrm{F}_8\mathrm{C}_{54}\mathrm{H}_{60}$ $[(\mathrm{dppm})\mathrm{Pt}(\mu\text{-OH}))_2(\mathrm{BF}_4)_2\cdot 2\mathrm{DMF}]$: C, 44.16 (44.46); H, 3.99 (3.92); N, 1.85 (1.82). IR (cm^{-1}) (mineral oil): 3250 (m). ^{1}H NMR (500 MHz, DMSO-d_6, 22 °C): δ 7.2–7.8 (m, 40, phenyl), 5.2 (t, $J_{\mathrm{PH}} = 25$ Hz, 4, CH_2), 6.5 (s, 2, OH). $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR (121 MHz, DMSO, external $\mathrm{H}_3\mathrm{PO}_4$ reference, 22 °C): δ –64 ($J_{\mathrm{P-Pt}} = 3023$ Hz) ppm.

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[12] Crystals of **2** from DMF/Et_2O are monoclinic, $P2_1/n$, with $a = 17.193(6)$ Å, $b = 9.341(5)$ Å, $c = 18.666(7)$ Å, $\beta = 98.73(2)°$, and $Z = 4$. Selected bond distances (Å) and angles (deg): Pt–P(1), 2.22(2); Pt–P(2), 2.21(2); Pt–O(1), 2.06(1); Pt–O(1)′, 2.05(1); O(1)–H, 0.76(10); P(1)–C(1)–P(2), 92.6(3); P(1)–Pt–P(2), 73.55(1); Pt–P(1)–C(1), 96.6(2); Pt–P(2)–C(1), 96.9(2); O(1)–Pt–O(1)′, 74.7(2); Pt–O(1)–Pt′, 105.3(2); Pt–O(1)–H, 1 40(7); Pt′–O(1)–H, 111(8). (Primed atoms indicate inversion related atoms.)

[13] Trovó, G.; Bandoli, G.; Casellato, U.; Corain, B.; Nicolini, M.; Longato, B. *Inorg. Chem.*, **1990**, *29*, 4616–4621.

[14] The O---O distance and the low ν(OH) may be related to the P–Pt–P angle; the PMe_3 complex and **1** have the smallest P–Pt–P angles.

[15] Bushnell, G. W. *Can. J. Chem.* **1978**, *56*, 1773.

[16] Data for **2** are as follows. Anal. Calcd (found) for $\mathrm{Pt}_2\mathrm{P}_4\mathrm{O}_2\mathrm{C}_{50}\mathrm{H}_{44}$: C, 50.42(50.12); H, 3.73(3.75). IR (mineral oil): no OH stretch detected. ^{1}H NMR (300 MHz, $\mathrm{C}_6\mathrm{D}_6$, 22 °C): δ 7.0–7.9 (m, 40, phenyl), 4.1 (s, 2, OH), –0.3 (s, 2, CH). $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR (121 MHz, THF, external $\mathrm{H}_3\mathrm{PO}_4$ reference, 22 °C): δ –69 ($J_{\mathrm{P-Pt}} = 2830$ Hz) ppm.

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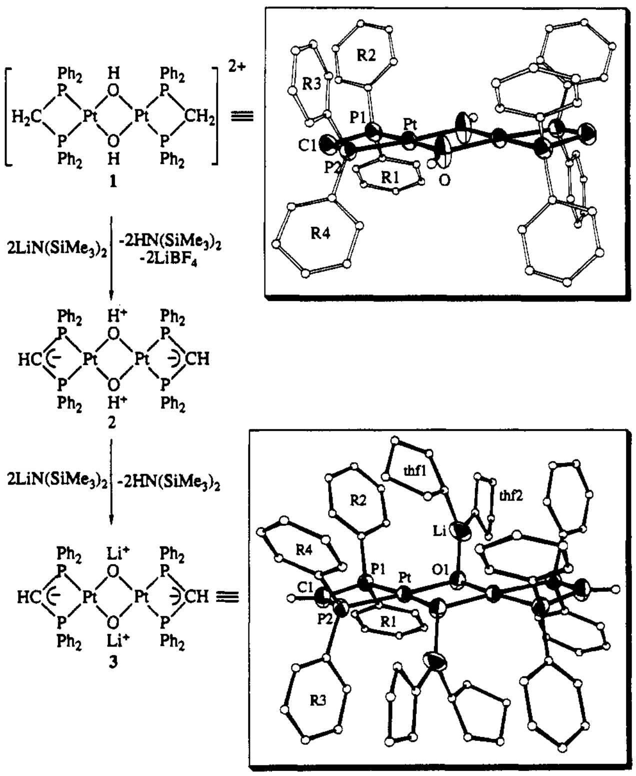
Scheme 1



obtaining ^{13}C NMR data on **2** were thwarted by its poor solubility in C_6D_6 and its rapid decomposition in solvents in which it is more soluble. Attempts to grow crystals have also been fruitless. However, further deprotonation of **2** is possible.

The anionic oxo complex [(dppm-H)Pt(μ-O)]$_2$[Li]$_2$ (**3**)[18] is obtained by dropwise addition of 2 equiv of LiN(SiMe$_3$)$_2$ to isolated **2** in THF at -20 °C (Scheme 1). Workup gives a 90% yield of air sensitive light yellow solid **3**. The crystal structure[19] of **3** (Scheme 1) shows coordination of the bridging oxo ligand to the Li ion (d(Li–O) = 1.75(7) Å). Two THF molecules also interact closely with the Li ion (d(Li–O) = 1.93 Å), resulting in a trigonal planar geometry about the Li ion.

Substitution of NaN(SiMe$_3$)$_2$ for LiN(SiMe$_3$)$_2$ in the synthesis of **3** gives a similar product, but with a smaller P–Pt coupling constant (^{31}P{^{1}H} NMR(THF): δ = −54.4 ppm (J_{P-Pt} = 2360 Hz)). This is consistent with a more electron rich oxo ligand as a result of the weaker Na–O interaction.

Both **2** and **3** react rapidly with CO (1 atm, 25 °C) to give complex mixtures. In contrast, [(PPh$_3$)$_2$Pt(μ-O)]$_2$[5a] is inert to CO (3 atm, 25 °C). This indicates significant ligand effects on the reactivity of this class of oxo complexes. Further reactivity studies of **2** and **3** are in progress.

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Supplementary Material Available: Tables of atom coordinates and thermal parameters for **1** and **3** (5 pages). Ordering information is given on any current masthead page.

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(17) The dppm-H ligand has been observed in many complexes: Usón, R.; Laguna, A.; Laguna, M.; Gimeno, M. C.; Jones, P. G.; Fittschen, C.; Sheldrick, G. M. *J. Chem. Soc., Chem. Commun.* **1986**, 509–510. El-Amouri, H.; Bahsoun, A. A.; Osborn, J. A.; Youinou, M. T.; Fischer, J. *Polyhedron*, **1989**, *8*, 2119–2124. Chebi, D. E.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1990**, *9*, 2948–2952. Rubio González, J. M.; Ruiz, Z.; García Granda, S.; Fayos, J. *Acta Crystallogr.* **1991**, *C47*, 706–708.

(18) Data for **3** are as follows. ^{1}H NMR (300 MHz, C_6D_6, 22 °C): δ 7.1–8.0 (m, 40, phenyl), −0.4 (s, 2CH). ^{31}P{^{1}H} NMR (121 MHz, THF, external H_3PO_4 reference, 22 °C): δ −54.4 (J_{P-Pt} = 2430 Hz) ppm.

(19) Crystals of **3**·4THF (M = Li) from THF are monoclinic, $P2_1/c$, with a = 10.534(2) Å, b = 21.016(2) Å, c = 18.402(4) Å, β = 103.41(1)°, and Z = 4. Selected bond distances (Å) and angles (deg): P(1)–C(1), 1.72(9); P(2)–C(1), 1.71(7); C(1)–H(1), 1.10(10); Pt–P(1), 2.22(1); Pt–P(2), 2.23(1); Pt–O(1), 2.05(1); Pt–O(1)′, 2.03(1); O(1)–Li, 1.75(3); Li–O(2), 1.92(3); Li–O(3), 1.94(3); P(1)–C(1)–P(2), 96.0(6); P(1)–C(1)–H(1), 142(5); P(2)–C(1)–H(1), 120(5); P(1)–Pt–P(2), 70.1(1); Pt–P(1)–C(1), 96.8(4); Pt–P(2)–C(1), 97.0(4); O(1)–Pt–O(1)′, 81.0(3); Pt–O(1)–Pt′, 99.0(3); Pt–O(1)–Li, 108(1); Pt′–O(1)–Li, 105.4(9); O(1)–Li–O(2), 129(1); O(1)–Li–O(3), 120(2); O(2)–Li–O(3), 111(1). (Primed atoms indicate inversion center related atoms.)