Synthesis, Reactions and Structure of a Highly Basic Platinum(II) Di(μ-oxo) Dimer with an Unusual Lithium Tetrafluoroborate Interaction[1]

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The reaction chemistry and X-ray crystal structure of the platinum(II) oxo complex $[PtL_2(\mu\text{-}O)]_2\cdot LiBF_4$ (L = PPh_3) reveal the presence of a highly basic oxo ligand and an unusual oxo–$LiBF_4$ interaction.

The oxo and imido ligands occupy an important position in the chemistry of the transition metals.[2] An extensive chemistry has been developed for groups 5–8 based on these ligands including applications in homogeneous and heterogeneous catalysis.[2a] In contrast, the chemistry of these ligands for groups 9–11[3] has only slowly developed despite indications that such complexes may be intermediates in reactions of complexes of these metals.[4] In addition, oxo and imido complexes should serve as homogeneous models[5] for oxygen adatoms and surface nitrenes. Such species are involved in several important reactions catalysed by 2nd and 3rd series group 9–11 metal surfaces.[6]

In this study a Pt^{II} oxo complex was prepared by treating white suspensions of the hydroxo complex[7] $[L_2Pt(\mu\text{-}OH)]_2(BF_4)_2$ (L = PPh_3) in tetrahydrofuran (THF) with slightly more than two equivalents of $LiN(SiMe_3)_2$ (Scheme 1). ^{31}P NMR spectra of the reaction mixture showed the presence of a single new phosphorus-containing product with a chemical shift of 7.80 ppm (H_3PO_4 ext. ref.) and J_{PPt} = 3286 Hz. White crystals were isolated by removing the volatile material, extracting the resulting solid with toluene and cooling the extract to −30 °C. An X-ray crystal structure determination shows the crystalline product to be $[L_2Pt(\mu\text{-}O)]_2\cdot LiBF_4$ **1**.† An ORTEP view of the structure (50% probability ellipsoids, phenyl rings omitted) is given in Scheme 1 and shows a Pt^{II} oxo bridged dimer [d(Pt–O) = 2.038(6) and 2.018(6) Å] consisting of two edge-shared

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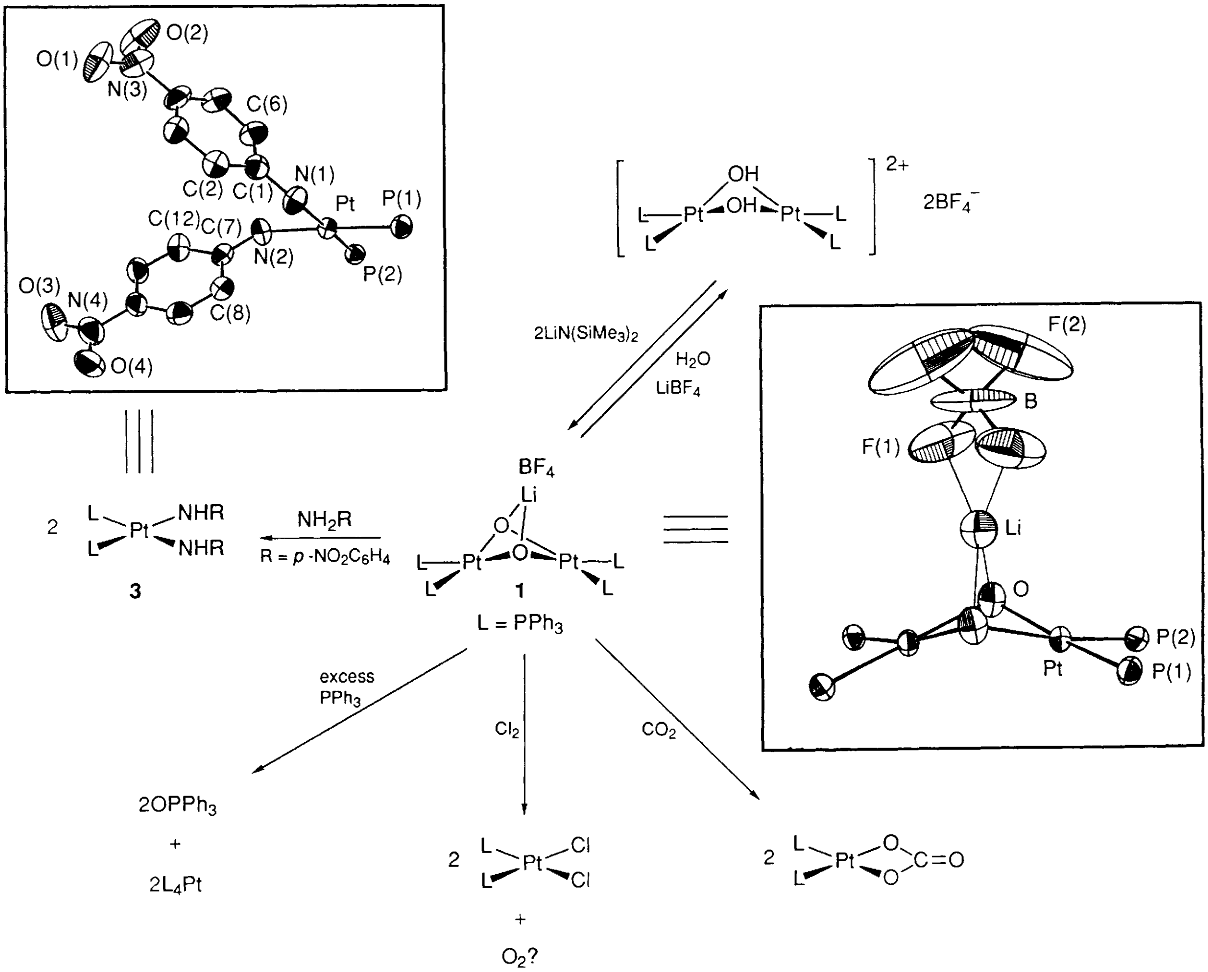
† *Crystal data* for **1**: $C_{72}H_{60}BF_4LiO_2P_4Pt_2\cdot 0.5C_7H_8$, M = 1611.2, monoclinic, space group $C2/c$ (183 K), a = 20.469(8), b = 18.085(9), c = 18.152(8) Å, β = 90.34(6)°, U = 6719.4 Å^3, Z = 4, D_c = 1.59 g cm^{-3}. Mo-Kα radiation, λ = 0.7107 Å, 2θ = 4–45°, μ = 43.5 cm^{-1} (empirical absorption correction), anisotropic thermal parameters for all non-hydrogen and non-solvent atoms, R = 0.048 for 403 parameters and 3524 observed reflections with $I > 3\sigma(I)$.

Crystal data for **3**: $C_{48}H_{40}N_4O_2P_2Pt\cdot 2CH_2Cl_2$, M = 1163.78, monoclinic, space group $P2_1/c$, a = 12.758(3), b = 13.172(5), c = 28.675(6) Å, β = 94.77(3)°, U = 4802.3 Å^3, Z = 4, D_c = 1.61 g cm^{-3}. Mo-Kα radiation, λ = 0.7107 Å, 2θ = 4–45°, μ = 32.9 cm^{-1} (empirical absorption correction), anisotropic thermal parameters for all non-hydrogen and non-solvent atoms, R = 0.032 for 581 parameters and 4785 observed reflections with $I > 2\sigma(I)$.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

Spectral data for **3**: ^{31}P NMR (THF, d) 12.5 (s, J_{PtP} = 3070 Hz). IR (mineral oil mull) ν/cm^{-1} 3369 and 3342.



Scheme 1 ORTEP diagrams for the crystal structures of complexes **1** and **3** are included

square-planar fragments folded along the shared O–O edge [fold angle = 146.4(1)°]. Most interesting is the coordination of the bridging oxo groups to an Li atom [d(Li–O) = 2.08(2) Å] of an LiBF$_4$ contact ion pair. Two fluorine atoms of the tetrafluoroborate also interact closely with the Li [d(Li–F1) = 1.89(2) Å] resulting in a flattened tetrahedral geometry about the Li. The presence of the BF$_4$ moiety in toluene solutions is readily detected by ^{19}F NMR spectroscopy (δ −153.7 ppm, CFCl$_3$ ext. ref.). Similarly, IR spectra of the crystals from toluene show the expected B–F bands at 1054 cm^{-1}.

Substitution of NaN(SiMe$_3$)$_2$ for LiN(SiMe$_3$)$_2$ in the synthesis of the oxo complex **1** followed by the same work-up gives a similar product but with no evidence for the presence of BF$_4$. We formulate this product as the salt-free complex, [L$_2$Pt(μ-O)]$_2$ **2** (eqn. 1). Consistent with this formulation is the somewhat smaller P–Pt coupling constant [δ(^{31}P) 8.5 ppm, J_{PPt} = 3183 Hz] expected[8] for the stronger donor properties of the oxo ligand in the absence of the salt interaction.

$$[\mathrm{L_2Pt(\mu\text{-}OH)}]_2(\mathrm{BF_4})_2 + 2\mathrm{NaNR_2} \rightarrow \underset{\mathbf{2}}{[\mathrm{L_2Pt(\mu\text{-}O)}]_2} + 2\mathrm{NaBF_4} + 2\mathrm{HNR_2} \quad (1)$$

The reaction chemistry of **1** is illustrated in Scheme 1 and is dominated by the strong basicity of the oxo ligands. (Similar results are obtained with the salt-free complex **2**.) Thus, treating **1** with water in the presence of LiBF$_4$ regenerates the hydroxo complex. With amines, bis(amido) complexes are obtained, one of which, **3** (R = p-NO$_2$C$_6$H$_4$) was characterized by NMR spectroscopy and an X-ray crystal structure determination.† An ORTEP view of the structure (50% probability ellipsoids, phenyl rings omitted) is given in Scheme 1. Oxygen atom transfer is observed in reactions with CO$_2$ to give L$_2$Pt(CO$_3$)[9] and with PPh$_3$ to give L$_4$Pt[10] and OPPh$_3$. Surprisingly, **1** is inert to CO (3 atm; 25 °C). With two equivalents of Cl$_2$, L$_2$PtCl$_2$ is cleanly produced, presumably along with molecular oxygen.

The successful synthesis and properties of **1** and **2** suggest several areas for future exploration. The multiple coordination properties of the oxo ligands evidenced in **1** should make possible the synthesis of other mixed-metal μ_3-oxo complexes either by Li$^+$ displacement from **1** by other metal fragments or directly from **2**. The sulphur analogue[11] of **2** has already yielded a rich variety of complexes[12] based on similar considerations and one of the already known Pt$^{\mathrm{II}}$ oxo complexes[13] can be considered to have been derived in this way from a complex related to **2**. Another prospect is based on a retro-synthetic approach to **2**. Compound **2** can be considered to have been formed from dioxygen and two equivalents of 'L$_2$Pt'. We are currently exploring these areas.

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