# Formation of an unusual tetralithium diplatinum complex $[Pt(C{\equiv}CBu^t)_2(PPh_2O)_2Li_2(\mu\text{-}H_2O)(Me_2CO)_2]_2$ containing $\mu_3\text{-}PPh_2O^-$ Ligands

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**The very unusual complex $[Pt(C{\equiv}CBu^t)_2(PPh_2O)_2Li_2(\mu\text{-}H_2O)(Me_2CO)_2]_2$ 2 is obtained by the reaction of '$Li_2[Pt(C{\equiv}CBu^t)_4]$' with an excess of $PPh_2H$ in acetone–ethanol and possesses an unusual linear chain of four Li atoms sandwiched between two square planar dianionic units *trans*-$^-OPPh_2\{Pt(C{\equiv}CBu^t)_2\}PPh_2O^-$, to which it is bound through $\mu_3\text{-}PPh_2O^-$ bridging ligands.**

Platinum–alkynyl chemistry has long been the subject of intensive study[1] and recently there has been a growing interest in the synthesis of polymetallic species derived from dianionic ($C_2^{2-}$, $C_2RC_2^{2-}$, *etc.*) or substituted (pyridyl, bipyridyl, ruthenocenyl, ferrocenyl, *etc.*) building blocks due to their increasing importance in materials science.[1,2] The family of alkynyl Pt complexes, particularly that of mononuclear heteroleptic derivatives which are stabilised by tertiary phosphine ligands is now quite large.[1,2*d*,*e*,3] The chemistry of monomeric derivatives containing other types of ligands is comparatively less developed[1,3*a*,4] and analogous complexes containing secondary phosphines as additional ligands have not been explored. The presence of acidic protons in this type of ligand ($PR_2H$) probably prevents the use of the most general synthetic routes such as the reaction of halides with alk-1-ynes (base, CuI-catalysed)[1,2*d*,*e*,3*b*,4*d*] or with metal acetylide reagents.[1,4] Recently, we have reported the preparation of *trans*-$[Pt(C{\equiv}CBu^t)_2(PPh_3)_2]$[5] in high yield by partial displacement of the alkynyl groups with $PPh_3$ from the reactive species $Li_2[Pt(C{\equiv}CBu^t)_4]$, prepared '*in situ*'. We report here the application of this method to the diphenylphosphine ligand, which allows not only the preparation of the homologous complex *trans*-$[Pt(C{\equiv}CBu^t)_2(PPh_2H)_2]$ **1** but also the synthesis of an unexpected tetralithium diplatinum compound **2**, which contains lithium atoms in the form of an unusual linear chain of four Li atoms stabilised by $\mu_3\text{-}PPh_2O^-$ and $\mu\text{-}OH_2$ bridging ligands. Complex **2** represents the second alkynyl–platinum lithium complex crystallographically characterised,[6] and also the second example reported containing one small chain of four sandwiched Li ions.[7]

The tetraalkynylplatinatelithium species '$Li_2[Pt(C{\equiv}CBu^t)_4]$' was initially formed by addition of $LiC{\equiv}CBu^t$ to $[PtCl_2(tht)_2]$ (molar ratio 5.5 : 1) as previously reported.[5,8] Treatment of the colourless solution obtained by dissolving $Li_2[Pt(C{\equiv}CBu^t)_4]$ in acetone–ethanol with an excess of $PPh_2H$ (1 : 3, $N_2$ atmosphere) causes the slow precipitatiion (7 h of stirring) of *trans*-$[Pt(C{\equiv}CBu^t)_2(PPh_2H)_2]$ **1** as a white microcrystalline solid (25% yield on the Pt starting material). Prolonged stirring (7 h) of the resulting filtrate under aerobic conditions produces the separation of a new white solid. Recrystallization of this solid from hot acetone yields the crystalline tetralithium diplatinum diphenylphosphinite complex **2** in *ca.* 45% yield. During our efforts to optimise the synthesis of complex **1** we observed that the relative yields of **1** and **2** vary with the presence of air in the reaction system (25–52% **1** to 45–11% **2**, on the Pt starting material). This fact clearly indicates that the presence of $PPh_2O^-$ ligands in complex **2** stems from the partial oxidation of the $PPh_2H$ ligand to $PPh_2OH$ under the reaction conditions employed.[9] Complex **1** was characterised analytically and spectroscopically.

The identity of complex **2** has been established by X-ray structure analysis† which revealed the unexpected tetralithiumdiplatinum species $[Pt(C{\equiv}CBu^t)_2(PPh_2O)_2Li_2(\mu\text{-}H_2O)(Me_2CO)_2]_2$.‡ Molecule A (Fig. 1) is formed by two identical dianionic fragments '*trans*-$^-OPPh_2\{Pt(C{\equiv}CBu^t)_2\}PPh_2O^-$' which act as didentate ligands, bridging the four Li centers pairwise through the oxygen atoms. Each $PPh_2O^-$ ligand is Pt–P bonded [Pt(1)–P(1,2) 2.301(2), 2.306(2) Å] and as mentioned bridges two Li centres [Li–O range 1.907(10)–1.969(10) Å], giving two planar $Li_2O_2$ rings, Li(1,2)O(1,2′) and Li(1′,2′)O(1′,2), which are rigorously coplanar. The central atoms are connected by two $H_2O$ molecules [O(5), O(5′)]. All this results in a final linear disposition of four non-bonded Li atoms [Li(2)···Li(1,2′) 2.610(13), 2.848(19) Å], Li(1)–Li(2)–Li(2′) 176.7(6)°], which is very similar to the Li disposition in the compound recently described by Roesky and coworkers,[7] $Li_4[(MeGa)_6(\mu_3\text{-}O)_2(Bu^tPO_3)_6]\cdot 4thf$. This structural feature contrasts with the most prevalent structural motif, cubane-like, found in other tetralithium derivatives[10] which has been rationalised using ring-stacking ideas.[11] The Li atoms in

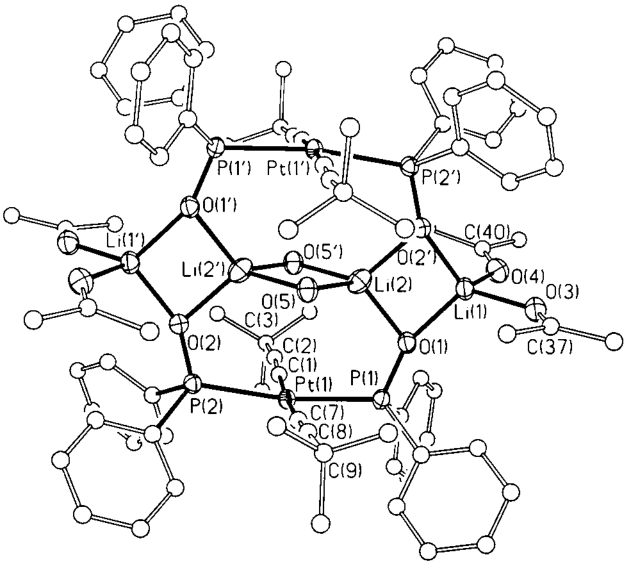

**Fig. 1** Molecular structure of **2**. Ellipsoids depicted at their 50% probability level. Important molecular geometry parameters include: interatomic distances (Å): Li(1)–O(1) 1.907(10), Li(1)–O(2′) 1.927(10), Li(2)–O(2′) 1.957(11), Li(2)–O(1) 1.969(10), Li(2)–O(5) 2.0481(10), Li(2)–O(5′) 2.048(10), Pt(1)–C(1) 2.001(6), Pt(1)–C(7) 2.006(6), C(1)–C(2) 1.207(8), C(7)–C(8) 1.203(8). Bond angles (°): O(3)–Li(1)–O(4) 99.0(4), O(1)–Li(1)–O(2′) 96.9(4), Li(1)–O(1)–Li(2) 84.6(4), Li(1)–O(2′)–Li(2) 84.4(4), O(1)–Li(2)–O(2′) 93.9(4), O(5)–Li(2)–O(5′) 91.9(4), Li(2)–O(1)–P(1) 119.1(4), O(1)–P(1)–Pt(1) 111.65(15), O(2)–P(2)–Pt(1) 112.62(15), Pt(1)–C(1)–C(2) 175.8(5), C(1)–C(2)–C(3) 173.4(7), Pt(1)–C(7)–C(8) 177.0(5), C(7)–C(8)–C(9) 175.0(7). Primed atoms are related by inversion centre to unprimed ones.

each [Li(1,2)$O_2$] unit are chemically different. Thus the internal Li atoms [Li(2), Li(2′)] have tetrahedral coordination, being bonded to the O atoms [O(5), O(5′)] of the two bridging water ligands, while the external Li atoms [Li(1), Li(1′)] interact with two terminal acetone molecules [Li(1)–O(3),(4) 1.981(10), 1.997(10) Å]. Both the distortion from tetrahedral geometry at the Li centres and the Li–O bond lengths are in good agreement with those observed in other Li compounds containing similar $LiO_4$ tetrahedral coordination environments.[10–12] On the other hand, it is also remarkable that although a variety of metal coordination modes have been observed for diorganophosphinite ligands,[9a,12b,13] to our knowledge, complex **2** is the first example in which this ligand acts with a $\mu_3$-$\kappa^3$:P,O,O′ bonding mode, bridging two hard Li atoms (μ-O) and also being P-bonded to a soft Pt centre. The P–O bond distances in **2** [1.537(4), 1.539(4) Å] are comparable to those observed for structurally characterised $[PPh_2–O]^-$ complexes displaying a μ-O,μ-P metal bridging mode.[13] The square-planar coordination at Pt is unexceptional, exhibiting, as expected, essentially linear acetylenic fragments (see Fig. 1).

In accord with the solid structure, the IR spectrum of **2** shows, in addition to a medium $\nu$(C≡C) band at 2092 $cm^{-1}$, the presence of water (3646, 3402, 1611 $cm^{-1}$) and typical absorptions for $\nu$(P=O) (996, 1006, 1030 $cm^{-1}$), characteristic of phosphinito-bridged complexes.[13] In the $^{31}P$ NMR spectrum a singlet shifted far downfield ($\delta$ 67.37, $^1J_{PtP}$ 2510 Hz) is observed,indicative of P oxidation to $P^V$.[13] The $^1H$ NMR spectrum of **2** in $CD_3COCD_3$ exhibits a singlet at $\delta$ 0.46 due to equivalent alkynyl groups ($C_2Bu^t$); however, the difficulty in assigning OH bands, even after addition of $D_2O$, does not allow us to determine with certainty whether the $H_2O$ molecules remain coordinated in solution.

The Li-ionic conductivity of the Li derivative **2** has also been measured using the well known complex impedance method,[14] but it is near zero. This fact is in agreement with previous results obtained for other tetrahedral $LiO_4$ derivatives.[15]

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## Footnotes and References

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† *Crystal data* for **2**·0.5$Me_2CO$: $C_{43.50}H_{53}Li_2O_{5.50}Pt$, $M$ = 934.77, triclinic, space group $P1$ (no. 2), $a$ = 13.858(3), $b$ = 13.858(3), $c$ = 24.693(7) Å, $\alpha$ = 83.79(3), $\beta$ = 87.53(2), $\gamma$ = 65.02(2)°, $U$ = 4590(2) $Å^3$, $Z$ = 2, $T$ = 173 K, $\mu$ = 3.166 $mm^{-1}$, graphite monochromated Mo-K$\alpha$ radiation, $\lambda$ = 0.710 73 Å, colourless prism with dimensions 0.56 × 0.46 × 0.30 mm, Siemens AED2/STOE diffractometer with Oxford Cryogenics low-temperature attachement, $\omega$–$\theta$ scans, data collection range $4 < 2\theta < 48°$, semiempirical absorption correction based on $\psi$ scans, transmission factors 0.889–0.577, 1001 refined parameters with 13 628 unique ($R_{int}$ = 0.026) reflections (15 247 measured). Full-matrix least-squares refinement of this model against $F^2$ (program SHELXL 93[16]) converged to final residual indices $R_1$ = 0.033, $wR_2$ = 0.070. ($R$ factors defined in ref. 16), GOF 1.05. Final difference electron density maps showed four peaks $> 1$ e $Å^{-3}$ (1.98, 1.43, 1.31, 1.03; largest diff. hole −1.21) lying closer than 1.12 Å from the Pt atoms. CCDC 182/698.

‡ The crystal structure determination† reveals that there are two independent, but very similar, half-molecules per asymmetric unit. For simplicity, we will discuss here only the molecule denoted by **A**.

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