

Formation of an unusual tetralithium diplatinum complex [Pt(C≡C^tBu)₂(PPh₂O)₂Li₂(μ-H₂O)(Me₂CO)₂]₂ containing μ₃-PPh₂O⁻ Ligands

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The very unusual complex [Pt(C≡C^tBu)₂(PPh₂O)₂Li₂(μ-H₂O)(Me₂CO)₂]₂ **2** is obtained by the reaction of 'Li₂[Pt(C≡C^tBu)₄]' with an excess of PPh₂H in acetone-ethanol and possesses an unusual linear chain of four Li atoms sandwiched between two square planar dianionic units *trans*-O⁻PPh₂{Pt(C≡C^tBu)₂}PPh₂O⁻, to which it is bound through μ₃-PPh₂O⁻ bridging ligands.

Platinum-alkynyl chemistry has long been the subject of intensive study¹ and recently there has been a growing interest in the synthesis of polymetallic species derived from dianionic (C₂²⁻, C₂RC₂²⁻, 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.^{1,2d,e,3} The chemistry of monomeric derivatives containing other types of ligands is comparatively less developed^{1,3a,4} and analogous complexes containing secondary phosphines as additional ligands have not been explored. The presence of acidic protons in this type of ligand (PR₂H) probably prevents the use of the most general synthetic routes such as the reaction of halides with alk-1-yne (base, Cu-catalysed)^{1,2d,e,3b,4d} or with metal acetylide reagents.^{1,4} Recently, we have reported the preparation of *trans*-[Pt(C≡C^tBu)₂(PPh₃)₂]₂⁵ in high yield by partial displacement of the alkynyl groups with PPh₃ from the reactive species Li₂[Pt(C≡C^tBu)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≡C^tBu)₂(PPh₂H)₂]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 μ₃-PPh₂O⁻ and μ-OH₂ 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 tetraalkynylplatinate lithium species 'Li₂[Pt(C≡C^tBu)₄]' was initially formed by addition of LiC≡C^tBu to [PtCl₂(tht)₂] (molar ratio 5.5 : 1) as previously reported.^{5,8} Treatment of the colourless solution obtained by dissolving Li₂[Pt(C≡C^tBu)₄] in acetone-ethanol with an excess of PPh₂H (1 : 3, N₂ atmosphere) causes the slow precipitation (7 h of stirring) of *trans*-[Pt(C≡C^tBu)₂(PPh₂H)₂]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 PPh₂O⁻ ligands in complex **2** stems from the partial oxidation of the PPh₂H ligand to PPh₂OH 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 tetralithium diplatinum species [Pt(C≡C^tBu)₂(PPh₂O)₂Li₂(μ-H₂O)(Me₂CO)₂]₂.[‡] Molecule A (Fig. 1) is formed by two identical dianionic fragments '*trans*-O⁻PPh₂{Pt(C≡C^tBu)₂}PPh₂O⁻' which act as didentate ligands, bridging the four Li centers pairwise through the oxygen atoms. Each PPh₂O⁻ 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 Li₂O₂ 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 H₂O 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 Li₄[(MeGa)₆(μ₃-O)₂(Bu^tPO₃)₆]-4thf. This structural feature contrasts with the most prevalent structural motif, cubane-like, found in other tetralithium derivatives¹⁰ which has been rationalised using ring-stacking ideas.¹¹ The Li atoms in

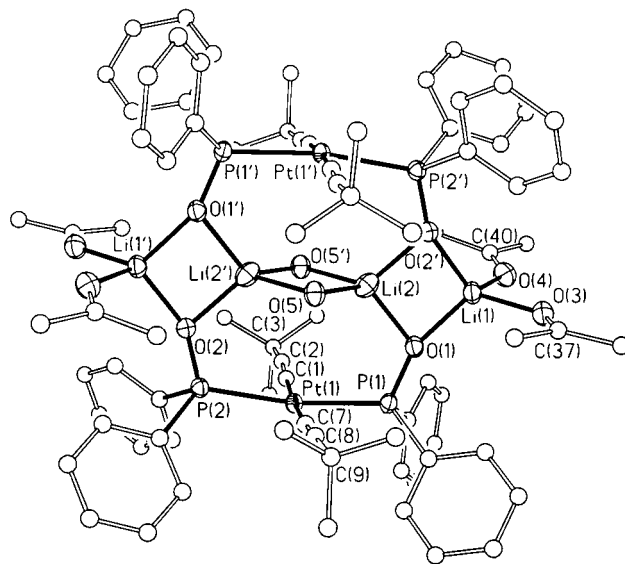


Fig. 1 Molecular structure of **2**. Ellipsoids depicted at their 50% probability level. Important molecular geometry parameters include: interatomic distances (Å): Li(1)–O(1) 1.907(10), Li(1)–O(2') 1.927(10), Li(2)–O(2') 1.957(11), Li(2)–O(1) 1.969(10), Li(2)–O(5) 2.0481(10), Li(2)–O(5') 2.048(10), 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)–Pt(1) 119.1(4), O(1)–Pt(1)–Pt(1) 111.65(15), O(2)–Pt(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)O₂] 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 LiO₄ 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 diorgano-phosphinite ligands,^{9a,12b,13} to our knowledge, complex **2** is the first example in which this ligand acts with a $\mu_3\text{-}\kappa^3\text{:P,O,O'}$ bonding mode, bridging two hard Li atoms ($\mu\text{-O}$) 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 [PPh₂O][–] complexes displaying a $\mu\text{-O},\mu\text{-P}$ 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 $\nu(\text{C}\equiv\text{C})$ band at 2092 cm^{–1}, the presence of water (3646, 3402, 1611 cm^{–1}) and typical absorptions for $\nu(\text{P}=\text{O})$ (996, 1006, 1030 cm^{–1}), characteristic of phosphinito-bridged complexes.¹³ In the ³¹P NMR spectrum a singlet shifted far downfield (δ 67.37, ¹J_{PTP} 2510 Hz) is observed, indicative of P oxidation to P^V.¹³ The ¹H NMR spectrum of **2** in CD₃COCD₃ exhibits a singlet at δ 0.46 due to equivalent alkynyl groups (C₂Bu^t); however, the difficulty in assigning OH bands, even after addition of D₂O, does not allow us to determine with certainty whether the H₂O 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 LiO₄ derivatives.¹⁵

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Footnotes and References

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† Crystal data for 2·0.5Me₂CO: C_{43.50}H₅₃Li₂O_{5.50}Pt, *M* = 934.77, triclinic, space group *P*1 (no. 2), *a* = 13.858(3), *b* = 13.858(3), *c* = 24.693(7) Å, α = 83.79(3), β = 87.53(2), γ = 65.02(2)°, *U* = 4590(2) Å³, *Z* = 2, *T* = 173 K, μ = 3.166 mm^{–1}, graphite monochromated Mo-K α radiation, λ = 0.71073 Å, colourless prism with dimensions 0.56 × 0.46 × 0.30 mm, Siemens AED2/STOE diffractometer with Oxford Cryogenics low-temperature attachment, ω - θ scans, data collection range 4 < 2 θ < 48°, semiempirical absorption correction based on ψ 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 93¹⁶) 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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