

Reactions of Platinum(II) Acetylides with Organolithium Compounds: Formation of Lithium-bridged Dinuclear Platinum(II) Complexes and of Triorganoplatinatate(II) Complexes: Crystal Structure of the Complex $[\text{Pt}_2(\text{C}\equiv\text{CPh})_4(\text{PEt}_3)_2(\text{Bu}^n)_2(\mu\text{-Li})_2]^\dagger$

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Platinum(II) acetylides of the type *trans*- $[\text{Pt}(\text{C}\equiv\text{CR}^1)_2(\text{PEt}_3)_2]$ (1) ($\text{R}^1 = \text{Me}, \text{Bu}^n, \text{ or Ph}$) lose one equivalent of PEt_3 on treatment with organolithium reagents LiR^2 (2) ($\text{R}^2 = \text{Bu}^n, \text{Bu}^t, \text{ or Ph}$) in hydrocarbon solvents to give the dinuclear complexes $[\text{Pt}_2(\text{C}\equiv\text{CR}^1)_4(\text{PEt}_3)_2(\text{R}^2)_2(\mu\text{-Li})_2]$ (3), containing a PtLi_2Pt unit. In the presence of better donors (e.g. Et_2O , tetrahydrofuran, or *NNN'*-tetramethylethylenediamine) solvation of lithium breaks this dimeric structure leading to the anions (4) of the type *trans*- $[\text{Pt}(\text{C}\equiv\text{CR}^1)_2(\text{PEt}_3)\text{R}^2]^-$. Reaction of the anion (4d) ($\text{R}^1 = \text{Ph}, \text{R}^2 = \text{Bu}^n$) with a further equivalent of LiR^2 ($\text{R}^2 = \text{Bu}^n$) gave $\text{Li}(\text{C}\equiv\text{CPh})$ and another anion, *cis*- $[\text{Pt}(\text{C}\equiv\text{CPh})_2(\text{PEt}_3)(\text{Bu}^n)_2]^-$. Multinuclear n.m.r. (^1H , ^7Li , ^{13}C , ^{31}P , and ^{195}Pt) has been used to characterize the highly reactive compounds in solution. The crystal structure of complex (3d) ($\text{R}^1 = \text{Ph}, \text{R}^2 = \text{Bu}^n$) has been determined, which crystallises in space group $P2_1/n$, with $a = 14.061(4)$, $b = 18.408(4)$, $c = 19.737(7)$ Å, and $Z = 4$.

The reactivity of the metal-carbon bond $\text{M}-\text{C}\equiv$ in metal acetylides¹ stimulates numerous investigations. Our current interest in the reactions of metal acetylides with electron-deficient compounds²⁻⁵ led us to study their behaviour with organolithium reagents. The platinum(II) acetylides $[\text{Pt}(\text{C}\equiv\text{CR}^1)_2(\text{PEt}_3)_2]$ [$\text{R}^1 = \text{Me}$ (1a), Bu^n (1b), or Ph (1c)] appeared particularly suitable candidates for the following reasons: (i) several alternative reaction pathways have to be considered (Scheme 1), each leading to interesting new compounds; (ii) since the compounds (1) are slightly soluble in hydrocarbons even below 0 °C the reaction can be carried out under homogeneous conditions; (iii) reaction control and the study of the reaction products is greatly accelerated and often facilitated by obtaining readily accessible ^{31}P n.m.r. parameters [$\delta(^{31}\text{P})$ and $^1J(^{195}\text{Pt}^{31}\text{P})$]; and (iv) for this study it is expected that the n.m.r. data of all relevant nuclei present other than protons (^7Li , ^{13}C , ^{31}P , and ^{195}Pt) contribute significantly to the elucidation of the structure of the reaction products in solution.

The organolithium reagents LiR^2 [$\text{R}^2 = \text{Bu}^n$ (2a), Bu^t (2b), or Ph (2c)] were selected in order to demonstrate that the reaction proceeds in the same direction in spite of steric hindrance [(2b), $\text{R}^2 = \text{Bu}^t$] or of a differing nature of the reagent [(2c), $\text{R}^2 = \text{Ph}$], thus indicating a more general applicability of the reaction principle.

Scheme 1 shows the likely products from the reaction between compounds (1) and (2), all of which have been observed either in the case of other metals [for example, alkynylstannanes⁶ or $\text{Hg}(\text{C}\equiv\text{CR}^1)_2$]⁷ (i), other alkynes⁸ (ii), or other platinum(II) and palladium(II) compounds⁹ (iii). We show that the reaction follows exclusively pathway (iii) and that the initial product dimerizes in hydrocarbon solution (iv). This is also evidenced by the X-ray crystal structure of $[\text{Pt}_2(\text{C}\equiv\text{CR}^1)_4(\text{PEt}_3)_2(\text{R}^2)_2(\mu\text{-Li})_2]$ (3d; $\text{R}^1 = \text{Ph}, \text{R}^2 = \text{Bu}^n$). In the presence

of suitable donors ionic compounds $[\text{Pt}(\text{C}\equiv\text{CR}^1)_2(\text{PEt}_3)\text{R}^2]^-$ (4) are obtained (v).

Experimental

All compounds were prepared and handled in an atmosphere of pure dry nitrogen. The solvents were freshly distilled from sodium or potassium. Deuteriated solvents were distilled and stored over appropriate molecular sieves. The compounds (3), (4), and (5) are all extremely sensitive, both in solution and in the solid state, towards traces of moisture and oxygen.

The platinum(II) acetylides (1) have been prepared according to a modified¹⁰ literature procedure¹¹ by Cu^1 -catalysed coupling of the terminal alkynes with *trans*- $[\text{PtCl}_2(\text{PEt}_3)_2]$ in diethylamine. The organolithium compounds (2) were commercial products and have been used after determining the active lithium concentration.

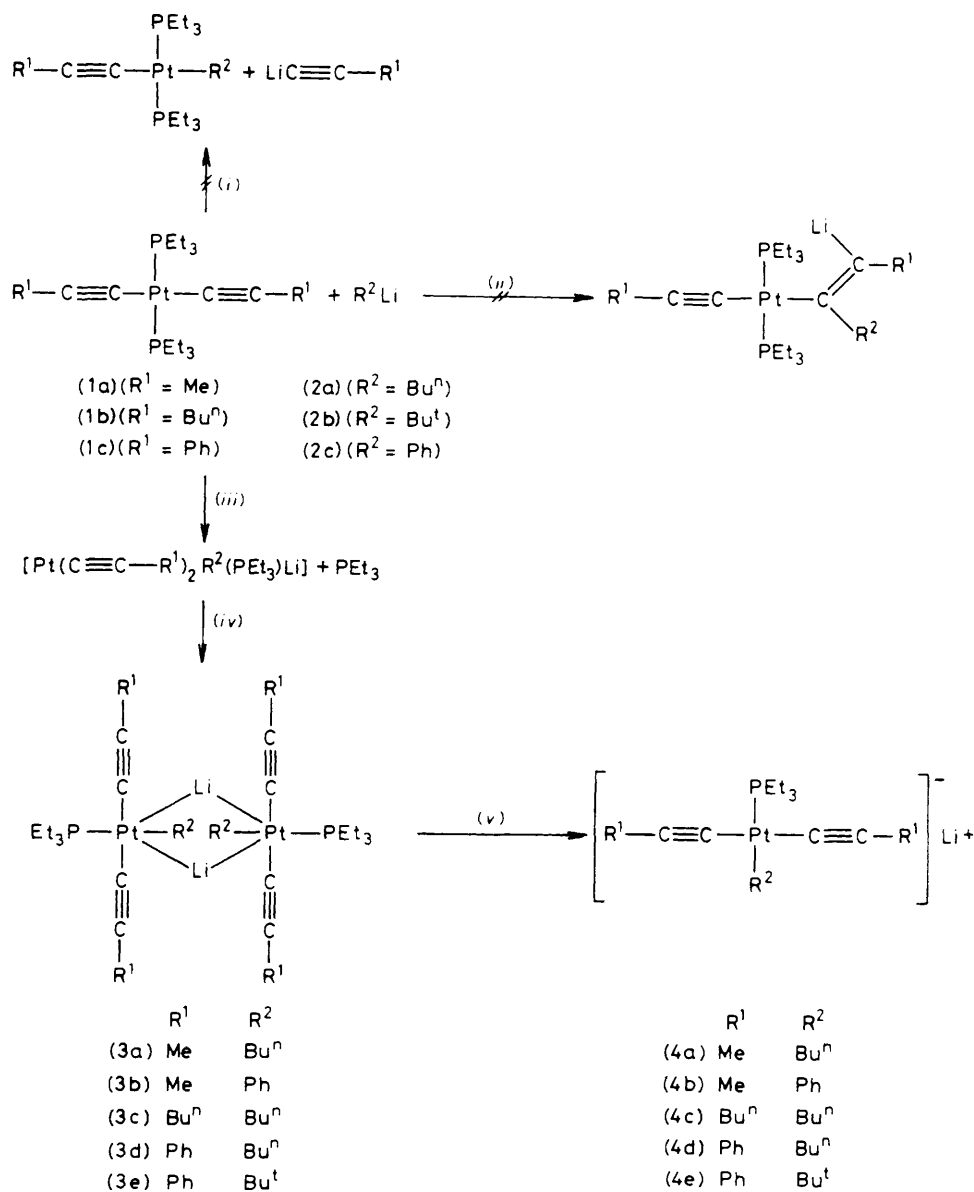
N.m.r. spectra [^1H (200), ^7Li (77.7), ^{13}C (50.3), ^{31}P (81.0), and ^{195}Pt (42.8 MHz)] were recorded using a Bruker WP 200 PFT n.m.r. spectrometer equipped with a multinuclear unit and a modified ^1H probehead (doubly tunable to receive frequencies between 35 and 82 MHz).

Preparation of $[\text{Pt}_2(\text{C}\equiv\text{CR}^1)_4(\text{PEt}_3)_2(\text{R}^2)_2(\mu\text{-Li})_2]$ [$\text{R}^1 = \text{Me}, \text{R}^2 = \text{Bu}^n$ (3a) or Ph (3b); $\text{R}^1 = \text{R}^2 = \text{Bu}^n$ (3c); $\text{R}^1 = \text{Ph}, \text{R}^2 = \text{Bu}^n$ (3d) or Bu^t (3e)].—*trans*- $[\text{Pt}(\text{C}\equiv\text{CR}^1)_2(\text{PEt}_3)_2]$ [$\text{R}^1 = \text{Me}$ (1a), Bu^n (1b), or Ph (1c)] (1.5 mmol) in hexane (60 cm³) was cooled to -78 °C. Under stirring the equivalent amount of the appropriate complex LiR^2 (2) [(2a) in hexane, (2b) in pentane, or (2c) in diethyl ether-benzene] was added and the mixture allowed to reach room temperature. After 0.5 h all the volatile compounds (solvent, PEt_3) were removed *in vacuo* leaving the compounds (3) as pale yellow-orange solids [$\nu(\text{C}\equiv\text{C})$ for (3d) at 2 085 cm⁻¹]. Single crystals of (3d) ($\text{R}^1 = \text{Ph}, \text{R}^2 = \text{Bu}^n$) were grown from a hexane solution at -20 °C. The extreme sensitivity of this compound required a comparison of the crystals with the species in solution. This was carried out as outlined in Scheme 2.

Dissolving of the solid compounds (3) in benzene gave n.m.r.

[†] *trans,trans*-Di- μ -lithio-bis[*n*-butylbis(phenylethynyl)(triethylphosphine)platinum].

Supplementary data available (No. SUP 23862, 20 pp.): structure factors, thermal parameters, full bond lengths and angles. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii-xix.

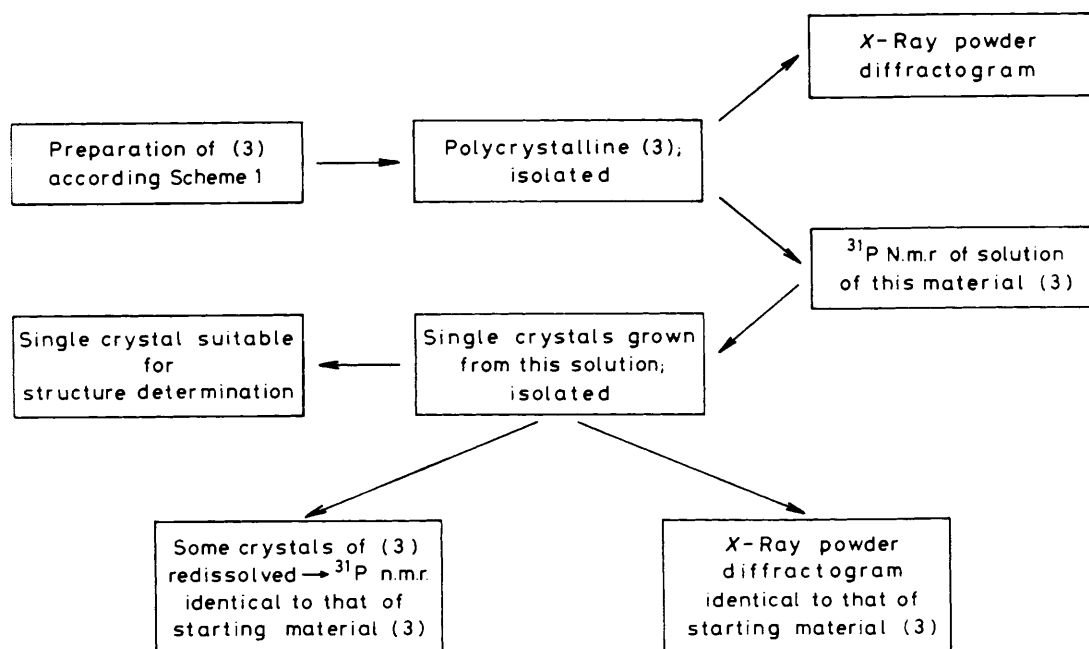


Scheme 1. Possible products of the reaction between organolithium compounds (2) and the platinum(II) acetylides (1). Elimination of phosphine [reaction (iii)] takes place

spectra identical to those of the reaction solution. In the presence of *NNN'N'*-tetramethylethylenediamine (tmen) the ionic compounds (4) were identified by n.m.r. Each lithium atom requires roughly one equivalent of tmen as shown by ^1H n.m.r. [obtained after removal of all volatile compounds *in vacuo* (5 h) and dissolving the yellow solids (4) in benzene]. In tetrahydrofuran (thf) formation of the anions (4) (^7Li n.m.r.) is accompanied by rapid decomposition at room temperature. Dissolving (3d) in diethyl ether gave a fairly stable solution of (4d) ($\text{R}^1 = \text{Ph}$, $\text{R}^2 = \text{Bu}^n$) [$\delta(^{31}\text{P})$ 8.4 p.p.m., $^1J(^{195}\text{Pt}^{31}\text{P}) = 1\ 606$ Hz]. Dissolving (3d) in dimethyl sulphide also gave a fairly stable solution, an equilibrium between (3d) and (4d) being indicated by the ^7Li resonance (broad, no ^{195}Pt satellites) and by the ^{31}P n.m.r. data [$\delta(^{31}\text{P})$ 9.3 p.p.m., $^1J(^{195}\text{Pt}^{31}\text{P}) = 1\ 580$ Hz]. A methylene chloride solution of (3d) was stable for ca. 2–4 h at room temperature as shown by ^7Li [$^1J(^{195}\text{Pt}-^7\text{Li}) = 78$ Hz] and ^{31}P n.m.r. [$\delta(^{31}\text{P})$ 9.6 p.p.m., $^1J(^{195}\text{Pt}^{31}\text{P}) = 1\ 576$ Hz].

cis-Bis(n-butyl)(phenylethynyl)(triethylphosphine)platinate(II), (5).—Compound (4d) (1 mmol), isolated from the reaction of (3d) with tmen in hexane after removal of the solvent, was redissolved in hexane (30 cm³) and cooled to -78°C . After addition of one equivalent of LiBu^n (2a) and warming the solution to room temperature the solvent was removed *in vacuo*. The solid thus obtained is only partly soluble in cyclohexane or benzene. Decanting gave a clear solution which left a dark yellow solid [compound (5)] after the solvent was removed *in vacuo*. Compound (5) was not very stable both in solution and in the solid state. Its characterization so far is based on ^1H , ^7Li , ^{13}C , ^{31}P , and ^{195}Pt n.m.r. data.

Crystal Structure Determination of trans,trans-[Pt₂(C≡CPh)₄(PEt₃)₂(Buⁿ)₂(μ-Li)₂] (3d).—*Data collection.* A single crystal of compound (3d) (see Scheme 2) suitable for X-ray work (brick red needle, 1.00 × 0.23 × 0.28 mm) was mounted under dry argon and sealed in a Lindemann capillary. The space group



Scheme 2. Procedure to prove identity between single crystals for *X*-ray work and the material obtained by removal of all volatile compounds from the reaction solution

and approximate cell parameters were determined from oscillation and Weissenberg photographs. Accurate cell parameters and intensity data for the structure determination were measured on a Stöe four-circle diffractometer using graphite-monochromatised Mo- K_{α} radiation ($\lambda = 0.71069 \text{ \AA}$) with a 140-step ω - θ scan technique. 6660 Unique reflections [2398 observed reflections, significance test $F_o > 5\sigma(F_o)$] were collected in the region $5 < 2\theta < 45^\circ$ which were semi-empirically corrected for absorption. No crystal decay was observed during data collection. The number of parameters refined was 325. All calculations were performed using SHELX 76, PLUTO 78 (W. D. S. Motherwell), GEOM 78 (B. A. Cartwright), and private programs, on an IBM-3081 computer (University of Cambridge). Scattering factors were obtained from ref. 12.

Crystal data. $C_{52}H_{68}Li_2P_2Pt_2$, $M = 1158.94$, space group $P2_1/n$, monoclinic, $a = 14.061(4)$, $b = 18.408(4)$, $c = 19.737(7) \text{ \AA}$; $\beta = 92.18(5)^\circ$, $U = 5104.9 \text{ \AA}^3$, $D_c = 1.508 \text{ Mg m}^{-3}$, $F(000) = 2288$, $Z = 4$, $\mu = 55.97 \text{ cm}^{-1}$, $\lambda = 0.71069 \text{ \AA}$, m.p. 60° C (decomp.).

The positions of the two platinum atoms were obtained from the best E -map computed with the automatic direct methods routine in SHELX 76 (G. M. Sheldrick), and those of the lighter atoms from successive difference-Fourier maps. No hydrogen atoms were located. The structure was refined using full-matrix least-squares techniques. The platinum and phosphorus atoms were assigned anisotropic thermal parameters, as were the acetylenic and ethyl carbons. The phenyl rings were treated as rigid groups with each carbon assigned an individual thermal parameter. The carbon atom of each butyl group directly attached to platinum was refined anisotropically. Attempts at refining anisotropically the remaining atoms of the butyl groups resulted in high thermal parameters, presumably due to disorder. The R factor as well as estimated standard deviations (e.s.d.s) associated with the rest of the molecule were not altered by converting the isotropic refinement of the butyl carbons to anisotropic. Hence, these carbon atoms were left isotropic. The two lithium atoms were located, after all the other atoms had been refined, from

difference-Fourier maps, and were refined anisotropically. In the later stages of refinement, a weighting scheme was introduced. The function minimised during refinement was $\Sigma w(|F_o| - |F_c|)^2$, such that $w = [\sigma^2(F) + 0.0028F^2]^{-1}$. Convergence was achieved at $R = 0.069 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$ and $R' = 0.070 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2]^{1/2}$.

Results and Discussion

Lithium-bridged Dinuclear Pt^{II} Complexes.—As shown by Scheme 1 a quantitative reaction takes place between compounds (1) and (2) to give compounds (3) [(iii) and (iv)]. The compounds (3) are only slightly soluble in hexane, but more soluble in benzene or dichloromethane. In a pure state they form pale to dark yellow crystals which decompose above 50 – 60° C .

The structure of compounds (3) in solution follows from the n.m.r. data (see Table 1), and in particular from ^7Li and ^{195}Pt n.m.r. spectra. In the ^7Li n.m.r. spectrum of complex (3d) (Figure 1) the presence of two equivalent platinum atoms is proved by the relative intensities of the ^{195}Pt satellites due to spin-spin coupling between ^{195}Pt and ^7Li . The natural abundance ^6Li n.m.r. spectrum of compound (3d) has also been recorded in order to search for possible interactions from $J(^7\text{Li}^6\text{Li})$. However, the ^6Li n.m.r. spectrum shows the same pattern as that of the ^7Li although the linewidth is considerably reduced.¹³ In the ^{195}Pt n.m.r. spectrum of complex (3d) (Figure 2) the large doublet splitting arises from $^1J(^{195}\text{Pt}^{31}\text{P})$ while the smaller splitting is evident for spin-spin coupling between ^{195}Pt and two equivalent lithium atoms. Finally, in the ^{13}C n.m.r. spectrum of complex (3a) (Figure 3) the fairly large value¹⁴ for $^2J(^{31}\text{P}^{13}\text{C}(\text{R}^2))$ strongly indicates a *trans* position for the PEt_3 and R^2 groups, and the presence of a second set of ^{195}Pt satellites for the $^{13}\text{C}(\text{C}^1)$ and $^{13}\text{C}(\text{C}^2)$ resonances of the *n*-butyl groups also shows that there are two platinum atoms in the molecule. The $^{13}\text{C}_\alpha$ resonances are broad at ambient temperature presumably as a result of partially relaxed scalar coupling $J(^{13}\text{C}^7\text{Li})$. At -10° C in $[\text{H}_8]\text{toluene}$ a fairly sharp doublet is observed instead, indi-

Table 1. N.m.r. parameters (^{13}C , ^{31}P , and ^{195}Pt) ^{a,b,c} of the platinum(II) complexes (1), (3), (4), and (5)

Complex	R ¹	R ²	$\delta(^{13}\text{C}_\alpha)$	$\delta(^{13}\text{C}_\beta)$	$\delta[^{13}\text{C}(\text{R}^1)]$		$\delta[^{13}\text{C}(\text{R}^2)]$		$\delta(^{31}\text{P})$	$\delta(^{195}\text{Pt})$
(1a)	Me		91.5 (942.0) [15.0]	100.4 (268.0) [1.5]	6.7 (21.4) [—]				12.2 (2 460.0)	-274.9
(3a)	Me	Bu ^a	96.8 (987.0) [10.0]	103.1 (311.0) [—]	6.2 (24.3) [—]		19.1(C ¹) (490.0; 32.0) [97.3]	35.1(C ²) (25.8; —) [5.2]	9.3 (1 632.0)	-11.3
(4a)	Me	Bu ^a	100.0 (1 009.0) [13.3]	97.4 (304.0) [—]	7.0 (20.6) [—]		15.3(C ¹) (555.0) [105.0]	35.9(C ²) (21.0) [4.4]	8.1 (1 687.0)	-10.9
(4b)	Me	Ph	101.6 (1 009.0) [13.9]	97.3 (293.0) [—]	7.0 (24.4) [—]		155.5(C _i) (758.0) [110.0]	143.2(C _o) (52.0) [—]	6.6 (1 779.0)	108.2
(1b)	Bu ^a		92.3 (939.0) [15.2]	106.3 (263.0) [—]	22.0(C ¹) (21.0) [—]	33.4(C ²) (10.0) [—]			9.0 (2 456.0)	-269.7
(3c)	Bu ^a	Bu ^a	98.1 (1 000.0) [10.0]	109.1 (306.0) [—]	21.8(C ¹) (24.0) [—]	33.2(C ²) (10.0) [—]	19.4(C ¹) (488.0; 33.0) [97.0]	35.3(C ²) (26.7; —) [4.8]	9.0 (1 622.0)	-11.6
(1c)	Ph		108.3 (961.0) [15.2]	110.0 (269.0) [—]	130.1(C _i) (25.0) [—]	131.2(C _o) (—) [—]			12.1 (2 392.0)	-245.0
(3d) ^d	Ph	Bu ^a	109.8 (1 012.0) [10.0]	112.4 (310.0) [—]	127.2(C _i) (27.6) [1.5]	131.7(C _o) (8.8) [1.5]	18.5(C ¹) (483.4; 29.0) [94.0]	35.1(C ²) (27.0; 6.0) [4.9]	9.7 (1 576.0)	40.7
(3e)	Ph	Bu ^t			128.3(C _m) (—) [—]	126.4(C _p) (—) [—]	28.3(C ³) (62.0) [6.9]	14.6(C ⁴) (—) [—]	6.2 (1 006.0)	
(4d) ^d	Ph	Bu ^a	117.3 (1 026.0) [13.3]	108.1 (306.0) [0.5]	130.5(C _i) (27.6) [1.0]	131.4(C _o) (5.8) [—]	14.9(C ¹) (545.0) [101.0]	35.9(C ²) (20.0) [4.3]	8.4 (1 644.0)	29.3
(4e)	Ph	Bu ^t	121.9 (1 080.0) [11.3]	107.2 (307.0) [—]	131.1(C _i) (28.6) [—]	131.4(C _o) (10.8) [—]	23.1(C ¹) (625.0) [105.0]	38.4(C ²) (20.0) [1.5]	6.4 (1 215.0)	159.3

^a In C₆D₆ [(5) in C₆D₁₂], 27 °C. $\delta(^{13}\text{C})$: external SiMe₄ (C₆D₆ = 128.0 p.p.m., C₆D₁₂ = 27.8 p.p.m.). $\delta(^{31}\text{P})$: external H₃PO₄. $\delta(^{195}\text{Pt})$ Ξ ^{195}Pt = 21.4 MHz (R. K. Harris and B. E. Mann, 'NMR and the Periodic Table,' Academic Press, London, 1978). Coupling constants, $J(^{195}\text{Pt}^{13}\text{C})$, are given in parentheses, and $J(^{31}\text{P}^{13}\text{C})$ in square brackets. ^b $\delta(^7\text{Li})$ of (3), (4), and (5) within 1 = 1 p.p.m. relative to LiCl-H₂O. ^c $\delta(^{13}\text{C})$ of P(CH₂CH₃)₃ of (1)–(5): $\delta[^{13}\text{C}(\text{CH}_2)] = 17.0 \pm 0.7$ p.p.m., $\delta[^{13}\text{C}(\text{CH}_3)] = 8.6 \pm 0.2$ p.p.m. ^d Relevant ¹H n.m.r. data for (3d) (internal SiMe₄): C¹H₂ 2.02 (37.2) [4.0]; C²H₂ 2.44 (38.0) [6.5]; C³H₂ 1.85; CH₃ 1.16; C₆H₅ 6.85–6.97 and 7.28–7.38; P(CH₂CH₃)₃ 1.08 and 1.87 p.p.m. ¹H n.m.r. data for (4d) (internal SiMe₄): C¹H₂ 1.40 (52.7) [5.7]; C²H₂ 2.55 (44.4) [8.8]; C³H₂ 1.95; CH₃ 1.22; C₆H₅ 6.89–7.13 and 7.46; P(CH₂CH₃)₃ 1.15 and 1.94 p.p.m. (tmen: 1.83 and 1.99 p.p.m.).

Table 1 (continued)

Complex	R ¹	R ²	$\delta(^{13}\text{C}_\alpha)$	$\delta(^{13}\text{C}_\beta)$	$\delta(^{13}\text{C}(\text{R}^1))$		$\delta(^{13}\text{C}(\text{R}^2))$		$\delta(^{31}\text{P})$	$\delta(^{195}\text{Pt})$
(5)	Ph	Bu ⁿ	114.0 (—) [<5]	108.5 (217.0) [1.0]	130.6(C _t) (21.0) [1.4] 128.3(C _m) (—) [—]	131.4(C _o) (—) [—] 124.7(C _p) (—) [—]	20.8(C ¹ , <i>trans</i>) (644.0) [106.6] 28.8(C ³ , <i>trans</i>) (75.2) [6.8] 14.0(C ¹ , <i>cis</i>) (604.0) [6.8] 30.3(C ³ , <i>cis</i>) (92.0) [—]	35.4(C ² , <i>trans</i>) (24.1) [4.6] 14.8(C ⁴ , <i>trans</i>) (—) [—] 36.4(C ² , <i>cis</i>) (17.8) [—] 15.1(C ⁴ , <i>cis</i>) (—) [—]	8.4 (1 931.0)	84.5

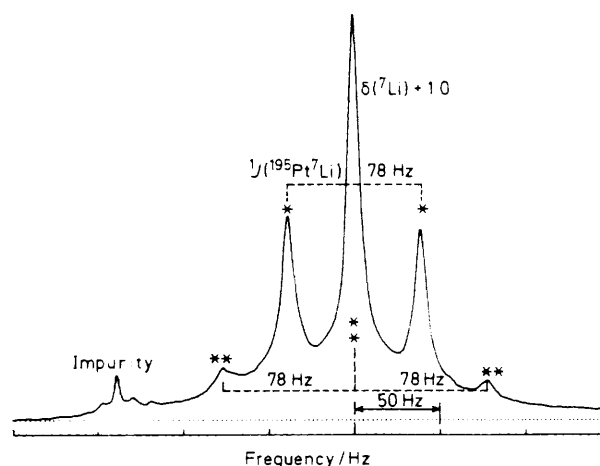


Figure 1. 77.7-MHz ⁷Li n.m.r. spectrum of compound (3d) (in C₆D₆, 27 °C). Asterisks indicate the ⁷Li resonances due to the presence of one (*) and two (**) ¹⁹⁵Pt nuclei in the molecule

cating the expected increase in the ⁷Li quadrupolar relaxation rate. The signal-to-noise ratio of the ³¹P n.m.r. spectrum would have been sufficient to observe lines of an AA'XX' spin system (in the presence of two ¹⁹⁵Pt isotopes). The simplicity of the ³¹P n.m.r. data shows that both coupling constants $J(^{31}\text{P}^{31}\text{P})$ and $J(^{195}\text{Pt}^{195}\text{Pt})$ must be close to zero.

The ¹H n.m.r. spectra of compound (3d) have been studied by ¹H-³¹P and ¹H-¹H,³¹P heteronuclear double and triple resonance experiments in order to assign the ¹H resonances and the coupling constants $J(^{31}\text{P}^1\text{H})$ and $J(^{195}\text{Pt}^1\text{H})$ of the butyl group. In the ¹H-¹H,³¹P experiment two sets of ¹⁹⁵Pt satellites due to $J(^{195}\text{Pt}^1\text{H})$ can be assigned to the ¹H resonance of the Pt-CH₂ group. Selective ¹H-¹H,³¹P experiments with the correct ³¹P irradiation frequencies for the ¹⁹⁵Pt satellites in the ³¹P n.m.r. spectrum showed that the sign of $^2J(^{195}\text{Pt}^1\text{H})$ is negative, while the sign of $^3J(^{195}\text{Pt}^1\text{H})$ is positive with respect to the positive sign of $^1J(^{195}\text{Pt}^{31}\text{P})$.¹⁴

The n.m.r. evidence is fully corroborated by the crystal structure of compound (3d). Figure 4 indicates the atomic numbering scheme, and Figures 5 and 6 show the molecule and the co-ordination around one platinum. Table 2 contains the final positional parameters for all atoms and Tables 3 and 4 selected bond lengths and angles.

The four platinum-lithium distances are, within standard deviations the same. The rather large value of this distance [*e.g.* Li(1)-Pt(2) 2.807(64) Å] suggests that this is a rather weak interaction. Close contact exists between the lithium atoms and the acetylenic carbons directly bonded to the platinum atoms [C(210)-Li(2) 2.074(51), C(110)-Li(2) 2.147(64), C(130)-

Li(1) 2.161(73), and C(230)-Li(1) 2.238(69) Å]. The distance between the acetylenic carbons not bonded to platinum and the lithium atoms is in excess of 2.5 Å. The Pt...Pt distance of 4.350 Å indicates that no direct bonding exists between the two platinum atoms. The Li...Li distance is 3.610 Å.

The angle Pt(2)-Li(1)-Pt(1) [101.3(17)°] is not significantly different to Pt(2)-Li(2)-Pt(1), nor is Li(2)-Pt(1)-Li(1) [79.5(19)°] to Li(2)-Pt(2)-Li(1). Furthermore, Pt(1), Li(1), Pt(2), Li(2), and the four acetylenic groups form a planar moiety, with maximum deviation from the mean plane of 0.27 Å. The triethylphosphine groups are *trans* to one another with respect to the platinum-lithium plane. The n-butyl group on each platinum atom is on the opposite side of the Pt-Li ring to the triethylphosphine bonded to the same platinum. Since the angle Li(1)-Pt(1)-P(1) [117.5(14)°] is not significantly different to Li(2)-Pt(1)-P(1) and also to the equivalent angles round Pt(2), the two triethylphosphines are at equivalent positions on either side of the platinum-lithium ring. The same is true for the n-butyl groups. It would therefore appear at first that this compound may be described as possessing two octahedrally co-ordinated platinum atoms. The equality of the corresponding bond lengths and angles from each platinum to its ligands means that the Pt-Li ring possesses a pseudo-centre of symmetry (Figure 5). However, Pt(1), C(110), C(120), C(130), and P(1) are coplanar (Figure 6) as are Pt(2), C(210), C(220), C(230), and P(2), with a maximum deviation from planarity in each case of less than 0.1 Å. These two squares, each with a ligand at each corner and a platinum atom at the middle, are almost parallel, subtending a dihedral angle of only 10°. Furthermore, n.m.r. data presented elsewhere in this paper are compatible with platinum(II) being in a square-planar environment. Clearly, given the rather long Pt-Li contact the molecule can be considered as comprising two platinum atoms each in a square-planar environment, the two halves being held together by the two lithium atoms. Given that (a) the short acetylene-Li contacts found here are of the same order as C-Li bond lengths observed in other structures (2.28 Å in Li₄Me₄,^{15a} 2.19-2.47 Å in Li₄Et₄,^{15b} and 2.20 Å in [(Li(C≡CPh))₄(Me₂N(CH₂)₆NMe₂)₂]^{15c}), (b) the associated bond angles [*e.g.* C(112)-C(111)-C(110) 170.7(43) and C(132)-C(131)-C(130) 165.4(45)°] indicate that the acetylenic carbons are not in the ideal *sp* geometry, and (c) the presence of ¹³C⁷Li spin-spin coupling, it may be that C-Li interactions take part in the bonding between the two halves of the molecule. This interaction between lithium and carbon may be more important than that of Pt-Li.

In each of the four phenylacetylides, the two carbon atoms making up the acetylenic group are coplanar with the phenyl ring, indicating that delocalisation operates throughout, a fact also indicated by the relatively short single bond linking the acetylene with the phenyl ring.

In the butyl groups, disorder, which can be correlated to

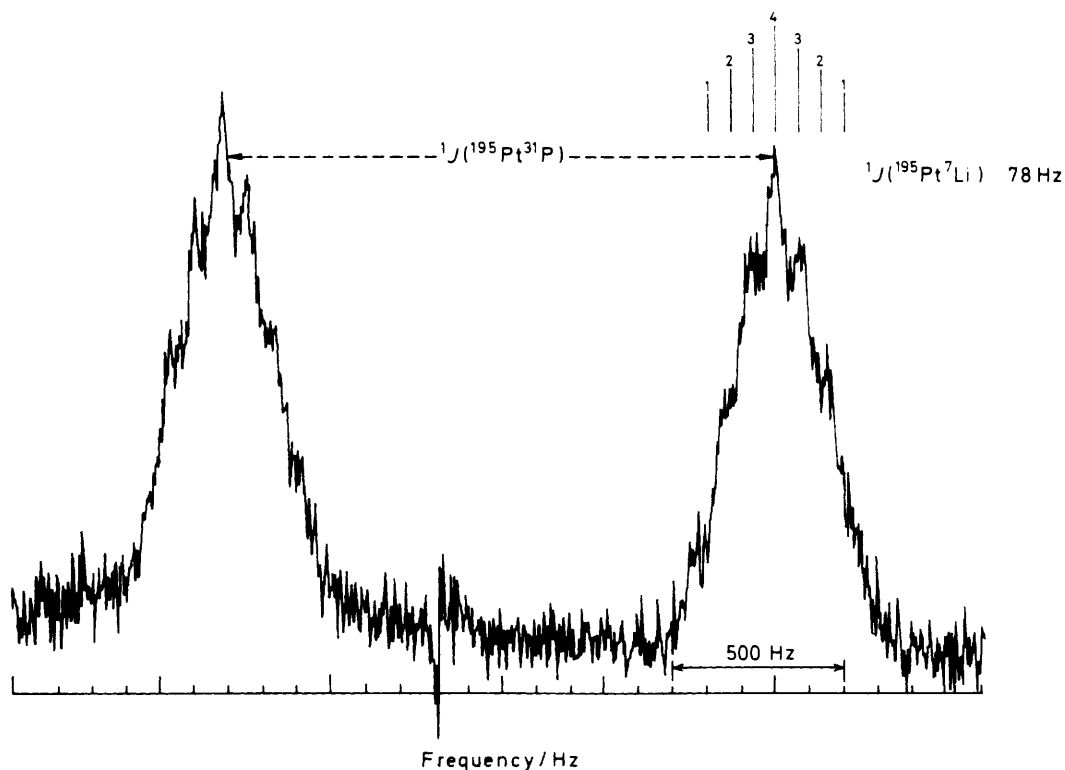


Figure 2. 42.8-MHz ^{195}Pt n.m.r. spectrum of compound (3d) (in C_6D_6 , 27 $^\circ\text{C}$, ^1H broad band decoupled). The splitting pattern due to spin-spin coupling between ^{195}Pt and two equivalent ^7Li nuclei ($I = \frac{3}{2}$) is shown. The presence of ^6Li (natural abundance 7.42%, $I = 1$) will contribute to the intensities, in particular to those of the inner lines since $J(^{195}\text{Pt}^6\text{Li}) = 0.38 J(^{195}\text{Pt}^7\text{Li})$

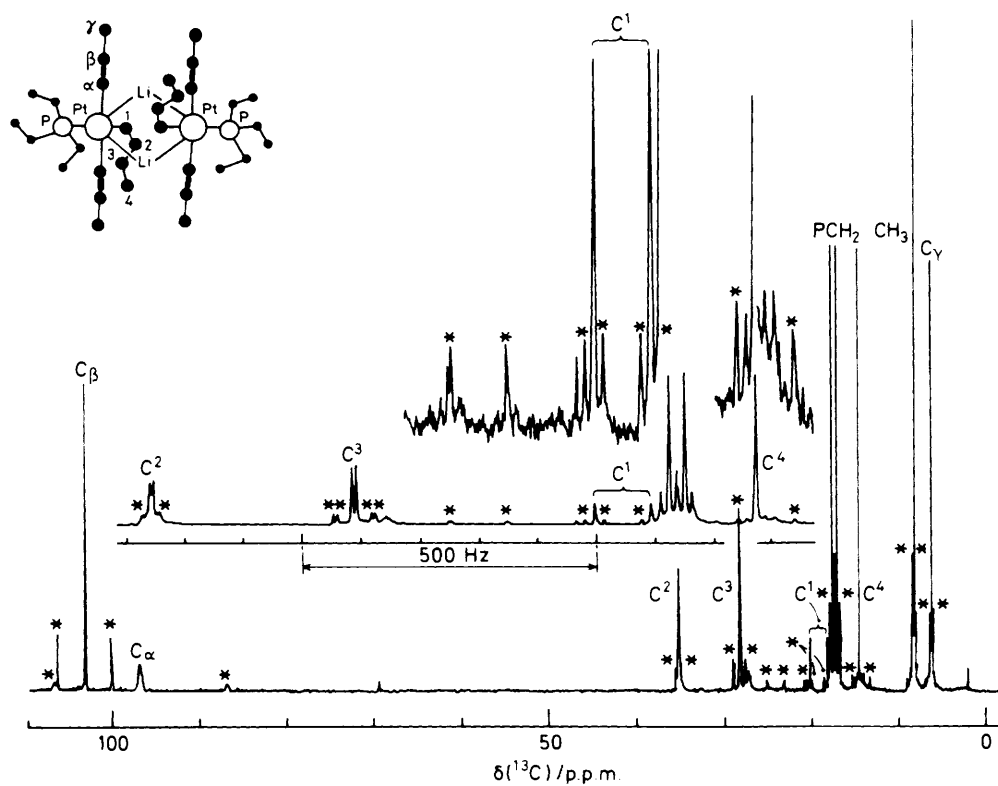


Figure 3. 50.3-MHz ^{13}C n.m.r. spectrum of compound (3a) (in C_6D_6 , 27 $^\circ\text{C}$, ^1H broad band decoupled.) Asterisks indicate the ^{195}Pt satellites due to $J(^{195}\text{Pt}^{13}\text{C})$. Note the second set of ^{195}Pt satellites which is clearly visible for the $^{13}\text{C}(\text{C}^1)$ resonance of the n-butyl group

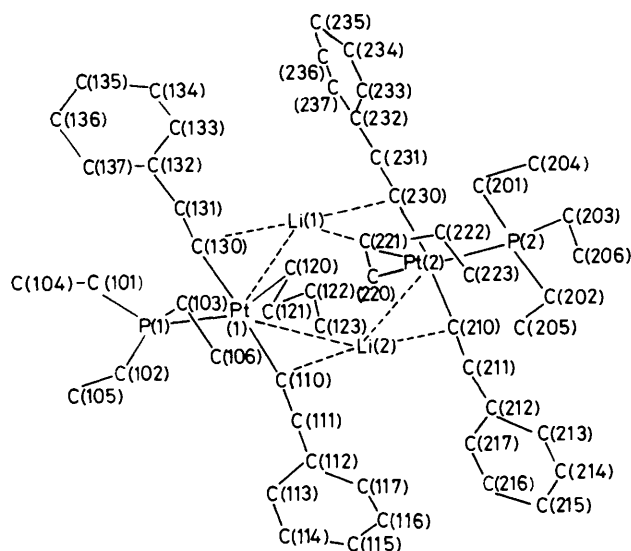


Figure 4. Numbering scheme for the molecular structure of compound (3d)

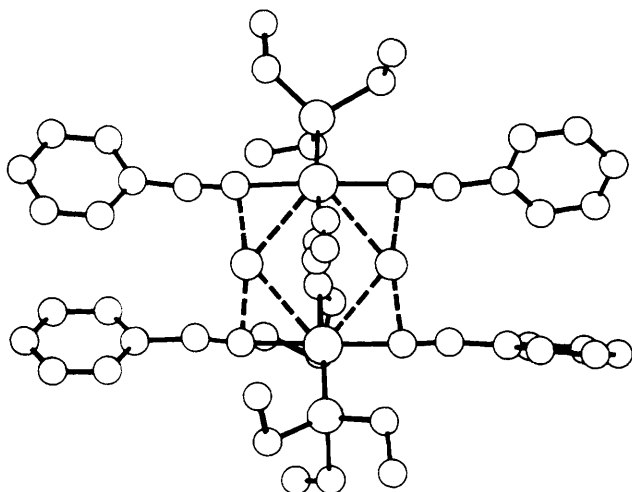


Figure 5. The molecule of (3d), viewed perpendicular to the mean plane

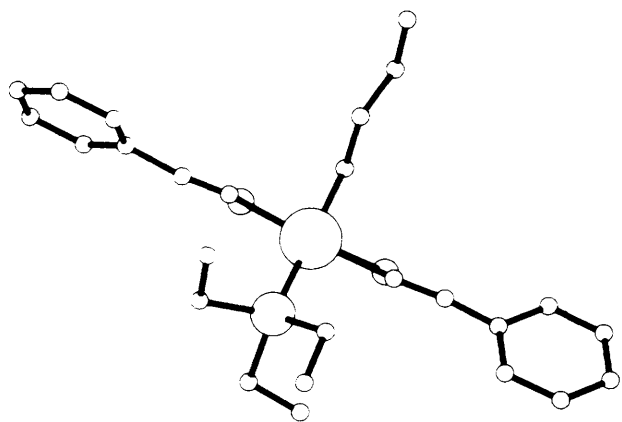


Figure 6. Co-ordination around one platinum in (3d), viewed along the Pt...Pt axis

Table 2. Atom co-ordinates ($\times 10^4$)

Atom	X/a	Y/b	Z/c
Pt(1)	5 489(1)	-429(1)	1 995(1)
P(1)	5 446(8)	823(5)	2 122(6)
C(101)	4 691(31)	1 344(21)	1 492(31)
C(102)	6 655(31)	1 203(17)	2 070(26)
C(103)	4 754(40)	1 099(29)	2 953(19)
C(104)	5 103(46)	1 278(32)	836(30)
C(105)	6 687(37)	2 040(27)	2 168(32)
C(106)	5 411(47)	1 027(41)	3 474(36)
C(110)	6 665(29)	-486(20)	2 653(26)
C(111)	7 385(28)	-555(19)	3 011(23)
C(112)	8 205(17)	-513(19)	3 401(13)
C(113)	3 620(17)	155(19)	3 568(13)
C(114)	9 470(17)	179(19)	3 956(13)
C(115)	9 903(17)	-465(19)	4 178(13)
C(116)	9 488(17)	-1 132(19)	4 010(13)
C(117)	3 639(17)	-1 157(19)	3 622(13)
C(120)	5 542(27)	-1 569(15)	1 856(19)
C(121)	6 017(39)	-1 755(28)	1 211(31)
C(122)	6 214(46)	-2 569(29)	1 157(36)
C(123)	6 567(62)	-2 826(45)	610(48)
C(130)	4 309(27)	-441(20)	1 319(23)
C(131)	3 607(25)	-405(17)	1 017(24)
C(132)	2 864(16)	-337(11)	485(11)
C(133)	1 923(16)	-512(11)	616(11)
C(134)	1 210(16)	-418(11)	112(11)
C(135)	1 438(16)	-149(11)	-522(11)
C(136)	2 379(16)	26(11)	-653(11)
C(137)	3 092(16)	-68(11)	-150(11)
Pt(2)	4 016(1)	-1 954(1)	3 272(1)
P(2)	3 911(8)	-3 200(5)	3 218(6)
C(201)	3 354(39)	-3 551(22)	2 430(27)
C(202)	4 898(36)	-3 810(25)	3 489(35)
C(203)	2 976(39)	-3 481(34)	3 954(33)
C(204)	3 168(38)	-4 423(21)	2 369(32)
C(205)	5 667(39)	-3 624(24)	2 967(29)
C(206)	3 369(52)	-3 376(39)	4 460(40)
C(210)	5 250(23)	-2 012(17)	3 835(15)
C(211)	5 945(27)	-1 979(17)	4 186(16)
C(212)	6 771(14)	-2 038(14)	4 650(12)
C(213)	7 277(14)	-2 685(14)	4 738(12)
C(214)	8 074(14)	-2 710(14)	5 180(12)
C(215)	8 365(14)	-2 088(14)	5 535(12)
C(216)	7 859(14)	-1 441(14)	5 447(12)
C(217)	7 062(14)	-1 416(14)	5 004(12)
C(220)	4 027(23)	-840(18)	3 404(17)
C(221)	3 289(49)	-581(45)	3 879(37)
C(222)	2 927(61)	-994(46)	4 475(44)
C(223)	3 716(62)	-687(46)	4 927(44)
C(230)	2 804(23)	-1 833(17)	2 709(14)
C(231)	2 154(24)	-1 815(17)	2 317(16)
C(232)	1 203(14)	-1 739(12)	1 977(12)
C(233)	479(14)	-1 312(12)	2 231(12)
C(234)	-403(14)	-1 274(12)	1 884(12)
C(235)	-560(14)	-1 663(12)	1 283(12)
C(236)	165(14)	-2 090(12)	1 030(12)
C(237)	1 047(14)	-2 128(12)	1 377(12)
Li(1)	3 762(37)	-1 187(33)	2 051(34)
Li(2)	5 822(50)	-1 254(26)	3 188(18)

the low melting point, is reflected in large thermal parameters, as well as large e.s.d. values for the bond lengths and angles. Thus, although the bond angles are not equal to the expected value of 109° , they do not deviate significantly from that value, except for C(223)-C(222)-C(221). The butyl group C(220)-C(223) appears to be more disordered than C(120)-C(123) as can be seen from Figure 5. This is reflected in the bond angle C(223)-C(222)-C(221) [$90.6(64)^\circ$] and the increased deviation of the atoms from the mean plane of the group

(maximum 0.43 Å) when compared with the Buⁿ group C(120)–C(123) (maximum 0.1 Å). It is noteworthy that Pt(2)···C(121) is only 3.00 Å and Pt(1)···C(221) 2.99 Å.

A literature survey was carried out using the Cambridge crystallographic Data Base.¹⁶ Some 579 structures were found of molecules possessing both platinum and phosphorus atoms, whilst 70 structures contained a phenylacetylide moiety. The average of the Pt–P bond lengths found in this

survey (calculated using GEOM 78) was found to be 2.290(42) Å, individual values varying from 2.151 to 2.399 Å. The average Pt–C bond in the structures containing phenylacetylide was found to be 2.047(88) Å, with minimum and maximum values of 1.801 and 2.198 Å. Similarly, the average C≡C bond in published structures bearing a phenylacetylide was found to be 1.227(43) Å, the values varying from 1.120 to 1.290 Å. Comparison of these values with those found for compound (3d) indicates that in spite of the bonding present in the latter, these particular bonds (Pt–P, Pt–C, C≡C) are 'normal'. A further 150 structures were found which contained C≡C bonds linked *via* a π bond to a metal atom. The mean C≡C bond length in these structures was found to be 1.257(35) Å, only slightly longer than the average value for phenylacetylides. In compound (3d), however, the average C≡C value is 1.177(40) Å, *i.e.* lower (but only just significantly) than the average value found for phenyl acetylides. It is therefore likely that Li···C interaction present in this compound is not purely a π bond, a conclusion further supported by the fact that the contacts between Li and the carbons in each acetylenic group are unequal.

All the n.m.r. evidence for compounds (3) in solution points to a square-planar environment for each platinum atom which is only slightly distorted by the lithium atoms. This is clearly seen by comparison with the data for compounds (1)¹⁰ and (4) as shown in Table 1.

In addition the crystal structure serves to explain several interesting features in the n.m.r. spectra: (i) the fairly large coupling constant $|J(^{195}\text{Pt}^1\text{Li})|$, and (ii) the 'long range' coupling between ¹⁹⁵Pt and ¹³CH₂, and between ¹⁹⁵Pt and ¹H(CH₂) of the butyl group linked to the other platinum atom, respectively.

Table 3. Bond lengths (Å)

P(1)–Pt(1)	2.319(12)	C(110)–Pt(1)	2.067(53)
C(120)–Pt(1)	2.118(30)	C(130)–Pt(1)	2.089(47)
Li(1)–Pt(1)	2.818(54)	Li(2)–Pt(1)	2.826(13)
C(101)–P(1)	1.870(46)	C(102)–P(1)	1.845(43)
C(103)–P(1)	2.003(12)	C(104)–C(101)	1.443(62)
C(105)–C(102)	1.554(54)	C(106)–C(103)	1.361(71)
C(111)–C(110)	1.219(53)	Li(2)–C(110)	2.147(64)
C(112)–C(111)	1.363(46)	C(121)–C(120)	1.501(60)
C(122)–C(121)	1.527(21)	C(123)–C(122)	1.296(92)
C(131)–C(130)	1.136(50)	Li(1)–C(130)	2.161(73)
C(132)–C(131)	1.458(47)	P(2)–Pt(1)	2.300(11)
C(210)–Pt(2)	2.026(34)	C(220)–Pt(2)	2.068(36)
C(230)–Pt(2)	2.011(32)	Li(1)–Pt(2)	2.807(64)
Li(2)–Pt(2)	2.858(69)	C(201)–P(2)	1.833(48)
C(202)–P(2)	1.849(45)	C(203)–P(2)	2.062(62)
C(204)–C(201)	1.630(52)	C(205)–C(202)	1.561(64)
C(206)–C(203)	1.132(67)	C(211)–C(210)	1.178(36)
Li(2)–C(210)	2.074(51)	C(212)–C(211)	1.455(37)
C(221)–C(220)	1.502(21)	C(222)–C(221)	1.505(22)
C(223)–C(222)	1.506(22)	C(231)–C(230)	1.176(34)
Li(1)–C(230)	2.238(69)	C(232)–C(231)	1.479(37)

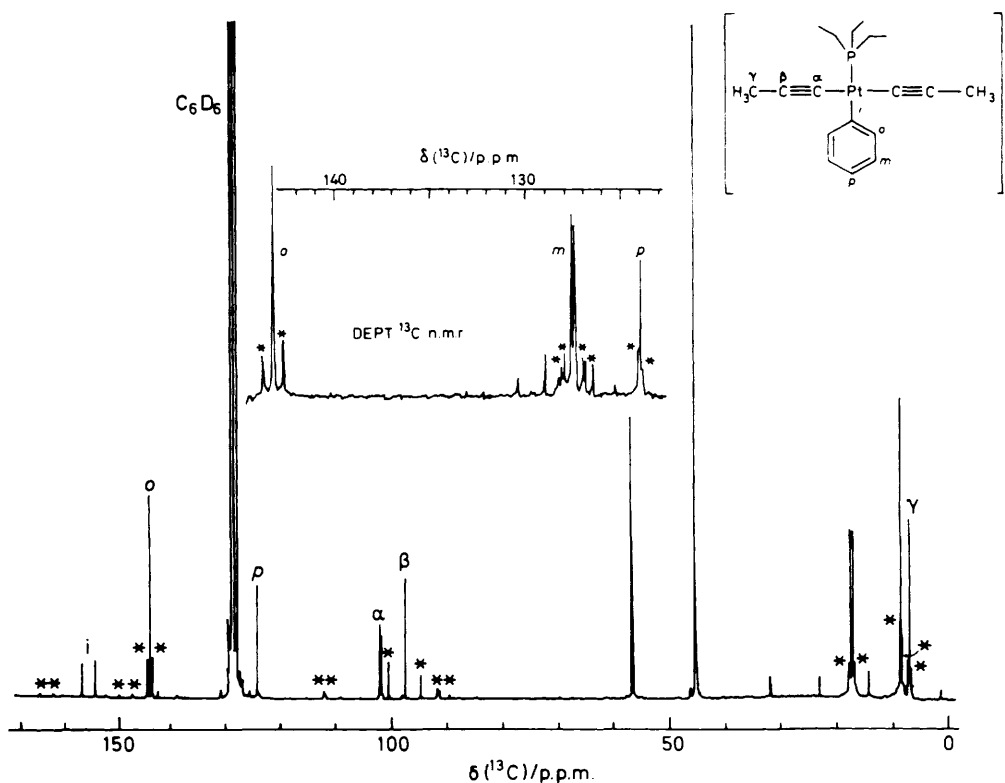
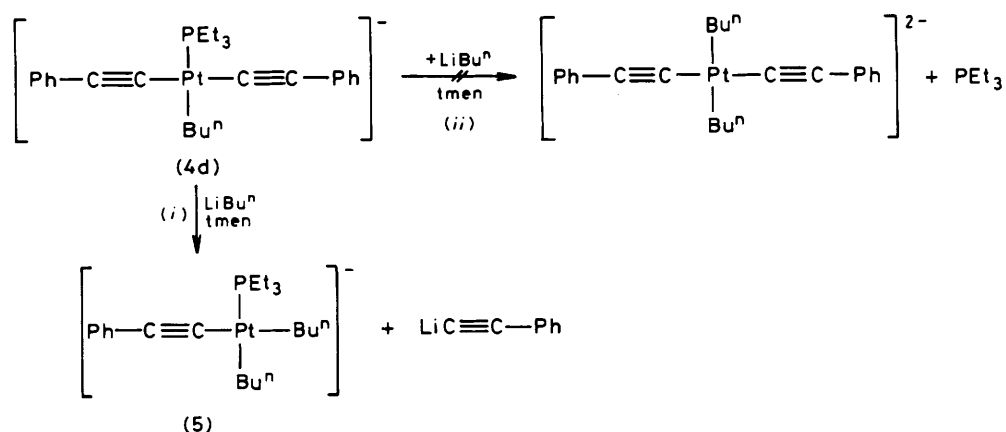


Figure 7. 50.3-MHz ¹³C n.m.r. spectrum of compound (4b) (in C₆D₆, 27 °C, ¹H broad band decoupled). Asterisks indicate the ¹⁹⁵Pt satellites due to $J(^{195}\text{Pt}^{13}\text{C})$. The ¹³C_m resonance as shown in the insert has been obtained by using the DEPT pulse sequence for the spectral editing of CH resonances (D. M. Doddrell, D. T. Pegg, and M. R. Bendall, *J. Magn. Reson.*, 1982, **48**, 323) in order to suppress the solvent signal



Scheme 3. Possible products of the reaction between the anion (4d) and the organolithium compound (2a). Elimination of lithium acetylide [reaction (i)] takes place

Table 4. Bond angles (°)

C(110)-Pt(1)-P(1)	90.3(12)	C(120)-Pt(1)-P(1)	178.6(11)
C(120)-Pt(1)-C(110)	90.0(15)	C(130)-Pt(1)-P(1)	93.2(11)
C(130)-Pt(1)-C(110)	176.4(14)	C(130)-Pt(1)-C(120)	86.4(15)
Li(1)-Pt(1)-P(1)	117.5(14)	Li(1)-Pt(1)-C(110)	128.6(17)
Li(1)-Pt(1)-C(120)	63.2(17)	Li(1)-Pt(1)-C(130)	49.6(16)
Li(2)-Pt(1)-P(1)	116.6(13)	Li(2)-Pt(1)-C(110)	49.1(17)
Li(2)-Pt(1)-C(120)	64.5(16)	Li(2)-Pt(1)-C(130)	129.0(18)
Li(2)-Pt(1)-Li(1)	79.5(19)	C(101)-P(1)-Pt(1)	117.0(17)
C(102)-P(1)-C(101)	105.7(21)	C(102)-P(1)-Pt(1)	110.1(13)
C(103)-P(1)-Pt(1)	110.9(18)	C(103)-P(1)-C(101)	97.7(25)
C(103)-P(1)-C(102)	115.3(26)	C(104)-C(101)-P(1)	108.4(36)
C(105)-C(102)-P(1)	113.0(34)	C(106)-C(103)-P(1)	104.9(38)
C(111)-C(110)-Pt(1)	175.4(39)	Li(2)-C(110)-Pt(1)	84.2(21)
Li(2)-C(110)-C(111)	96.3(36)	C(112)-C(111)-C(110)	170.7(43)
C(113)-C(112)-C(111)	121.4(22)	C(117)-C(112)-C(111)	118.6(22)
C(121)-C(120)-Pt(1)	110.8(30)	C(122)-C(121)-C(120)	111.8(49)
C(123)-C(122)-C(121)	119.5(71)	C(131)-C(130)-Pt(1)	171.1(42)
Li(1)-C(130)-Pt(1)	83.1(21)	Li(1)-C(130)-C(131)	93.3(36)
C(132)-C(131)-C(130)	165.4(45)	C(133)-C(132)-C(131)	120.3(18)
C(137)-C(132)-C(131)	119.6(18)	C(210)-Pt(2)-P(2)	91.5(10)
C(220)-Pt(2)-P(2)	174.3(10)	C(220)-Pt(2)-C(210)	88.9(14)
C(230)-Pt(2)-P(2)	91.9(10)	C(230)-Pt(2)-C(220)	87.8(14)
Li(1)-Pt(2)-P(2)	117.1(14)	Li(1)-Pt(2)-C(210)	125.4(14)
Li(1)-Pt(2)-C(220)	67.0(17)	Li(1)-Pt(2)-C(230)	52.2(14)
Li(2)-Pt(2)-P(2)	120.2(13)	Li(2)-Pt(2)-C(210)	46.5(9)
Li(2)-Pt(2)-C(220)	63.8(16)	Li(2)-Pt(2)-C(230)	130.8(9)
Li(2)-Pt(2)-Li(1)	79.2(12)	C(201)-P(2)-Pt(2)	114.6(16)
C(202)-P(2)-Pt(2)	123.1(18)	C(202)-P(2)-C(201)	108.8(27)
C(203)-P(2)-Pt(2)	105.0(20)	C(203)-P(2)-C(201)	104.2(26)
C(203)-P(2)-C(202)	97.8(27)	C(204)-C(201)-P(2)	118.2(38)
C(205)-C(202)-P(2)	101.9(34)	C(206)-C(203)-P(2)	106.4(62)
C(211)-C(210)-Pt(2)	173.5(32)	Li(2)-C(210)-Pt(2)	88.4(21)
Li(2)-C(210)-C(211)	89.7(30)	C(212)-C(211)-C(210)	172.2(35)
C(213)-C(212)-C(211)	122.2(18)	C(217)-C(212)-C(211)	117.8(18)
C(221)-C(220)-Pt(2)	113.1(40)	C(222)-C(221)-C(220)	126.1(74)
C(223)-C(222)-C(221)	90.6(64)	C(230)-Pt(2)-C(210)	176.6(12)
C(231)-C(230)-Pt(2)	171.2(33)	Li(1)-C(230)-Pt(2)	82.5(18)
Li(1)-C(230)-C(231)	93.9(28)	C(232)-C(231)-C(230)	165.5(36)
C(233)-C(232)-C(231)	123.4(18)	C(237)-C(232)-C(231)	116.6(18)
C(130)-Li(1)-Pt(1)	47.4(16)	Pt(2)-Li(1)-Pt(1)	101.3(17)
Pt(2)-Li(1)-C(130)	148.6(25)	C(230)-Li(1)-Pt(1)	145.2(27)
C(230)-Li(4)-C(130)	164.7(30)	C(230)-Li(1)-Pt(2)	45.3(14)
C(110)-Li(2)-Pt(1)	46.7(14)	Pt(2)-Li(2)-Pt(1)	99.9(17)
Pt(2)-Li(2)-C(110)	146.5(20)	C(210)-Li(2)-Pt(1)	144.9(30)
C(210)-Li(2)-C(110)	168.4(32)	C(210)-Li(2)-Pt(2)	45.1(16)

In these cases we assume that a 'through space' coupling mechanism¹⁷ has to be considered. This accounts for the value of $|J(^{195}\text{Pt}^7\text{Li})|$ (78 Hz) which appears to be too large for a solely geminal 'through bond' interaction. Similarly, we find a second set of ^{195}Pt satellites only for those nuclei which are in the close neighbourhood of the platinum.

Triorganoplatinatate(II) Complexes.—Solvation of the lithium atoms in the lithium-bridged compounds (3) by Et_2O , thf, or tmen breaks the dimeric structure to give the anions (4) [Scheme 1, reaction (v)]. This becomes immediately apparent from the change in the ^7Li n.m.r.: there is only a single sharp signal without any ^{195}Pt satellites. Similarly, the ^{195}Pt n.m.r. spectrum shows only a doublet [$J(^{195}\text{Pt}^{31}\text{P})$] without further fine structure. Since the ^{31}P n.m.r. spectra do not change significantly ^7Li n.m.r. in this case is an extremely sensitive tool (even in very diluted solutions) to distinguish quickly between compounds (3) and (4).

Figure 7 shows the ^{13}C n.m.r. spectrum of the anion (4b). The *trans* position of the PEt_3 and the phenyl group is proved by the large splitting of the $^{13}\text{C}_i$ resonance due to $^2J(^{31}\text{P}^{13}\text{C})$. Interestingly, the coupling constant $^3J(^{31}\text{P}^{13}\text{C}_o)$ is close to zero while $^4J(^{31}\text{P}^{13}\text{C}_m)$ is of considerable magnitude. Similar behaviour is observed for $^nJ(^{31}\text{P}^{13}\text{C})$ ($n = 2, 3, \text{ or } 4$) in (4a) and (4d) with the butyl group and R^1 in a *trans* position.

The ^1H n.m.r. spectrum of the anion (4d) has been recorded using essentially the same techniques as for (3d). The coupling constants $J(^{31}\text{P}^1\text{H})$ and $J(^{195}\text{Pt}^1\text{H})$ are of comparable magnitude to those in (3d) and also the signs of $^2J(^{195}\text{Pt}^1\text{H})$ (–) and $^3J(^{195}\text{Pt}^1\text{H})$ (+) are opposite.

While treatment of compounds (3) with a second equivalent of (2) leads mainly to decomposition it was hoped that the anions (4) behave differently. Indeed, reaction of compound (4d) with (2a) in the presence of tmen leads to the anion (5) (Scheme 3). Previous studies of the system $[\text{PtMe}_2(\text{PPh}_3)_2]\text{-LiMe}$ have shown the formation of the anion $[\text{PtMe}_3(\text{PPh}_3)]^-$ and of the dianion $[\text{PtMe}_4]^{2-}$.^{9a} However, in our case there is no elimination of the second phosphine [(ii)] but elimination of one alkynyl group [(i)] leading to the new anion (5). The configuration of (5) is proved by the ^{13}C n.m.r. spectrum which shows two sets of ^{13}C resonances for butyl groups with a large coupling constant $|^2J(^{31}\text{P}^{13}\text{C})|_{\text{trans}}$ and a small value of $|^2J(^{31}\text{P}^{13}\text{C})|_{\text{cis}}$. The comparison of the ^{13}C n.m.r. parameters for the alkynyl carbon atoms in (4d) and in (5) is also instructive: (i) the shielding of the $^{13}\text{C}_\alpha$ atom in (5) is much reduced which is typical for the replacement of an alkynyl group by an alkyl group in a *trans* position; (ii) the decrease in the magnitude of $|^1,^2J(^{195}\text{Pt}(^{13}\text{C}\equiv))|$ in (5) is also a typical *trans*-effect of the alkyl groups as compared to the alkynyl group (e.g. in the case of $\text{Hg}(\text{C}\equiv\text{CBu}^n)_2$ $\{^1J[^{199}\text{Hg}(^{13}\text{C}\equiv)] = 2\,391, ^2J[^{199}\text{Hg}(^{13}\text{C}\equiv)] = 628\text{ Hz}\}$ and $\text{HgMe}(\text{C}\equiv\text{CBu}^n)$ $\{^1J[^{199}\text{Hg}(^{13}\text{C}\equiv)] = 1\,400, ^2J[^{199}\text{Hg}(^{13}\text{C}\equiv)] = 404\text{ Hz}\}$).¹⁸ The similar *trans*-effects of an alkynyl group and a trialkylphosphine have been noted.¹⁰ This is also evident from the comparable magnitudes of the coupling constants $^1J(^{195}\text{Pt}^{13}\text{CH}_2)$ in (5). There is too much overlap of various ^1H resonances in the ^1H n.m.r. spectrum of the anion (5) at 200 MHz, precluding the assignment of the ^1H resonances of the two different butyl groups.

Conclusions

The formation of compounds (3) and (4) shows that PEt_3 competes successfully with the alkynyl group as a leaving

group as shown in Scheme 1. This may have some bearing on the reaction between organolithium compounds and Pt^{II} compounds similar to (1) in general. In Scheme 3 it is shown that under these conditions the alkynyl ligand is the preferred leaving group. This indicates a delicate balance of the reaction pathway depending on the reagents and reaction conditions. The utility of multinuclear n.m.r. has been demonstrated in this study and it is hoped to be of great value in the investigation of similar systems currently under investigation.

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