3912 Inorg. Chem. 1981, 20, 3912-3918

Contribution from the Department of Chemistry,
University of Victoria, Victoria, British Columbia, Canada V8W 2Y2

Synthesis and ^{31}P NMR Studies of Platinum Complexes of $[R_2P(O)CHP(O)R_2]^-$ Ligands, R = Ph or OEt. Crystal and Molecular Structure of Lithium *trans*-Dichloro(triethylphosphine)(bis(diphenylphosphinyl)methyl)platinate(II), an Unusual Case of Chloro Bridging between Platinum and Lithium

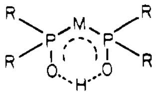
JANE BROWNING, GORDON WILLIAM BUSHNELL, and KEITH ROGER DIXON*

Received February 17, 1981

The anions $[CH(PR_2O)_2]^-$ are formally phosphorus analogues of acetylacetonate. The lithium salts, $Li[CH(PR_2O)_2]$, react under mild conditions with the chloro-bridged dimers $[M_2Cl_4(PR'_3)_2]$ to form *trans*-$[MCl_2(PR'_3)(CH(PR_2O)_2Li)]$ (**5**; M = Pd, R = Ph, R' = Et; M = Pt, R = Ph, R' = Et or *n*-Bu; M = Pt, R = OEt, R' = Et, *n*-Bu, or Ph). Crystals of **5** (M = Pt, R = Ph, R' = Et) are orthorhombic, of space group *Pbca*, with $a = 19.247$ (8) Å, $b = 21.918$ (8) Å, $c = 15.942$ (4) Å, and $Z = 8$. The structure shows square-planar platinum coordination (Pt–Cl(1) 2.282 (9), Pt–Cl(2) 2.32 (1), Pt–P(3) 2.25 (1), Pt–C(1) 2.14 (3) Å) with the lithiated bis(diphenylphosphinyl)methyl ligand bonded to Pt via the methine carbon. The remarkable feature of the structure is that this six-membered ring ligand adopts a boat conformation with C(1) and Li in the prows so that Li is also coordinated by Cl(2) which is itself bound to Pt. The complex is thus tridentate toward Li within the mononuclear unit, but Li and O(1) lie close to a crystallographic center of symmetry which generates a dimer containing two Pt and two Li atoms. The Li coordination is approximately tetrahedral with Li–O(1) = 2.09 (6), Li–O(2) = 1.84 (6), Li–O(1)' = 1.98 (7), and Li–Cl(2) = 2.19 (6) Å. The accuracy of the structure refinement was limited by a disorder or thermal motion problem within the PEt_3 group, and $R = 0.100$ and $R_w = 0.109$ with use of 2123 observations and 331 variables. ^{31}P and ^{1}H NMR data for the complexes **5** are reported and discussed, an important feature being ^1J(Pt–PR'$_3$) in the range 2750–2827 Hz trans to the methine carbon. This indicates a comparatively small trans influence for the $[CH(PR_2O)_2Li]$ ligand relative to normal C-bonded ligands. Other important coupling constants are ^3J(P–P) = 11.8–15.4, ^2J(Pt–P) = 83.8–99.8, ^3J(P–H) = 8.6–14.3, ^3J(P–H) = 6.7–22.8, ^2J(Pt–H) = 72.5–125 Hz, where H is the methine proton. Comparison of NMR parameters for Na^+ and Li^+ salts suggests that the Li^+ ion in **5** remains intimately associated with the complex in solution. The lithium cations are displaced by reactions of **5** with $[M_2Cl_2(PEt_3)_4][BF_4]_2$ to form the unstable cations $[(R'_3P)Cl_2Pt(\mu\text{-}CH(PR_2O)_2)M(PEt_3)_2]^+$ (R' = Et, R = Ph, M = Pd; R' = *n*-Bu, R = OEt, M = Pt).

Introduction

Recent studies in this laboratory and by several other research groups have shown that, whenever PR_2OH and PR_2O^- ligands occupy cis positions in the coordination sphere of a complex, a hydrogen bonded system, **1**, is formed.[1,2] Removal of the hydrogen-bonded proton results in an anionic coordination compound which may itself act as a ligand, formally analogous to acetylacetonate and capable of forming similar complexes, e.g., $[VO(PtCl(PEt_3)(PPh_2O)_2)_2]$.[1] Other workers have carried out extensive investigations on system **2** derived from carbonyl complexes of manganese and rhenium.[3]



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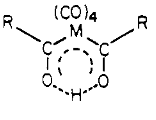

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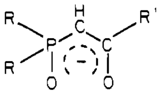

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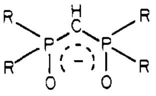

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Metal acetylacetonates have, of course, been the subject of extensive investigation, but in contrast the analogues **3** and **4**, containing one and two phosphorus atoms, respectively, have been accorded comparatively little attention. **3** and **4** are derived by deprotonation of $R_2P(O)CH_2C(O)R'$ and $R_2P(O)CH_2P(O)R_2$, respectively, and alkali-metal and alkaline-earth salts of **3**[4-6] and alkali-metal salts of **4**[5-8] are well established. Spectroscopic evidence for the delocalized nature of anions of both types has been presented.[6] Transition-metal derivatives are less well studied. Chromium,[6] cobalt,[6] and nickel[9] complexes of **3** (R = OEt, R' = CH_3) are known, the last two having been characterized by X-ray diffraction as trinuclear complexes, $[M_3L_6]$,[9,10] and this type of anion (R = OBu, R' = Ph) has also been used as an extraction agent for uranium.[11] However, for type **4** anions, there appear to be no reports of transition-metal complexes.

Anion **4** is similar to acetylacetonate in that both can potentially coordinate to a metal through either the methine carbon or through oxygen chelation. As the first step in a continuing study of this potential we chose to work with platinum derivatives since both modes of coordination are well established for acetylacetonates of this metal. This paper reports synthesis and ^{31}P NMR studies of a series of complexes $MCl_2(PR'_3)[CH(PR_2O)_2Li]$ (M = Pd, R = Ph, R' = Et; M = Pt, R = Ph, R' = Et or *n*-Bu; M = Pt, R = OEt, R' = Et, *n*-Bu, or Ph) and an X-ray diffraction study of the platinum complex with R = Ph and R' = Et. The structural work shows coordination of the new ligand to platinum via the methine carbon and to lithium via oxygen chelation. The lithium is additionally coordinated by a remarkable chlorobridge from platinum to lithium and by dimerization so that approximately tetrahedral geometry about lithium is attained.

Results

(A) Synthesis and NMR Results. As noted in the Introduction, alkali-metal salts of type **4** anions have been reported

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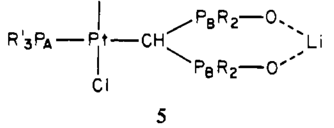
Table I. Nuclear Magnetic Resonance Data

		^{31}P spectra[b]					^1H spectra[c]			
compd	solvent[a]	$\delta(P_A)$	$\delta(P_B)$	$^3J(P-P)$	$^1J(Pt-P_A)$	$^2J(Pt-P_B)$	δ	$^3J(P_A-H)$	$^2J(P_B-H)$	$^2J(Pt-H)$
$Ph_2P(O)CH_2P(O)Ph_2$	A		−116.4				3.46		14.9	
$(EtO)_2P(O)CH_2P(O)(OEt)_2$	A		−120.8				2.51		22.8	
$[PtCl_2(PEt_3)(CH(PPh_2O)_2Li)]$	A	−136.1	−100.0	13.4	2756	86.1	3.92	8.6[d]		72.5
	B	−136.6	−103.6	14.0	2772	88.1				
$[PtCl_2(PEt_3)(CH(PPh_2O)_2Na)]$	B	−136.7	−105.7	13.4	2749	84.0				
$[PtCl_2(P\text{-}n\text{-}Bu_3)(CH(PPh_2O)_2Li)]$	B	−145.0	−102.3	13.9	2769	87.8	4.41	8.6[d]		73.0
	A	−143.6	−98.8	13.6	2750	86.9				
$[PtCl_2(P\text{-}n\text{-}Bu_3)(CH(PPh_2O)_2Na)]$	A	−145.4	−105.2	13.6	2721	83.8				
$[PtCl_2(PEt_3)(CH(P(OEt)_2O)_2Li)]$	A	−136.0	−103.0	12.0	2769	93.4	2.69	9.1	21.5	118
	B	−137.4	−104.3	12.8	2781	94.9				
$[PtCl_2(PEt_3)(CH(P(OEt)_2O)_2Na)]$	B	−137.9	−105.3	11.8	2751	91.4				
$[PtCl_2(P\text{-}n\text{-}Bu_3)(CH(P(OEt)_2O)_2Li)]$	A	−143.6	−102.9	12.6	2761	92.8	2.63	9.1	21.5	117
	B	−145.0	−104.1	12.2	2769	94.8				
$[PtCl_2(PPh_3)(CH(P(OEt)_2O)_2Li)]$	A	−126.5	−104.9	13.1	2827	99.8	3.06	9.7	21.6	125
$[PdCl_2(PEt_3)(CH(PPh_2O)_2Li)]$	B	−121.4	−103.9	15.4			3.54	14.3	6.7	
$[Pt(PEt_3)_2(acac)][BF_4]$	A	−135.6			3583					

[a] Solvents given in this column are for ^{31}P spectra: A = dichloromethane; B = tetrahydrofuran. All ^1H spectra were recorded in deuteriochloroform. [b] Data from proton decoupled ^{31}P spectra. Chemical shifts in ppm with negative values upfield of the external $P(OMe)_3$ reference. Coupling constants in hertz. P_A is phosphorus in the PR_3 ligands, and P_B is phosphorus in the PR_2O groups. [c] Only data for the methine proton in the $[CH(PR_2O)_2M]$ ligand is shown. Chemical shifts in ppm with positive values downfield of the internal $SiMe_4$ reference. Coupling constants in hertz. Spectra were recorded in deuteriochloroform. [d] These resonances appeared as quartets showing only a single $J(P,H)$ coupling due to accidental near equality of the two couplings.

by several authors.[5-8] We have worked mainly with lithium, and occasionally sodium, salts prepared in situ by reaction of butyllithium or sodium hydride with $R_2P(O)CH_2P(O)R_2$, R = Ph or OEt, in tetrahydrofuran solution. The choice of the transition-metal complex to react with the ligand proved much more difficult. For example, in attempted metathetical syntheses using *cis*-$[PtCl_2(PEt_3)_2]$ some reaction clearly occurred, but no tractable or readily identifiable products were obtained except for a single reaction with $Na[CH(PPh_2O)_2]$ which yielded ^{31}P spectra consistent with formation of *cis*-$[PtCl(PEt_3)_2(CH(PPh_2O)_2Na)]^+$ or *cis*-$[PtCl(PEt_3)_2(CH(PPh_2O)_2)]$. The spectrum was assigned as follows but the product was unstable and could not be fully characterized: δ (PO) −111.5 (broad), δ(P trans to Cl) −138.0 ($^1J(Pt-P) = 3880$ Hz, $^2J(P-P) = 19.3$ Hz), δ(P trans to C) −131.7 ($^1J(Pt-P) = 2350$ Hz). Reactions of $M[CH(PR_2O)_2]$ salts with cationic chloro-bridged complexes, $[M_2Cl_2(PEt_3)_4][BF_4]_2$, were similarly unsuccessful even though we were able to show that sodium acetylacetonate reacts rapidly with $[Pt_2Cl_2(PEt_3)_4][BF_4]_2$ to give an oxygen-bonded chelate complex, $[Pt(PEt_3)_2(acac)][BF_4]$, in high yield. An attempted ligand exchange reaction of $LiCH(PPh_2O)_2$ with $[Pt(PEt_3)_2(acac)][BF_4]$ also failed to yield stable identifiable products.

In contrast to the results with chloro-bridged cations, the neutral chloro-bridged dimers, $M_2Cl_4(PR_3)_2$, reacted cleanly and rapidly with $LiCH(PR_2O)_2$ salts according to the equation $2LiCH(PR_2O)_2 + M_2Cl_4(PR'_3)_2 \rightarrow$ *trans*-$PtCl_2(PR'_3)[CH(PR_2O)_2Li]$ (M = Pd, R = Ph, R′ = Et; M = Pt, R = Ph, R′ = Et or *n*-Bu; M = Pt, R = OEt, R′ = Et, *n*-Bu, or Ph). These products were characterized by microanalysis, by infrared, ^{31}P, and ^1H NMR spectroscopy, and by an X-ray diffraction study of **5** (R = Ph, R′ = Et). As described in detail below, the solid-state structure of **5** is more complex than the simple formula suggests with additional lithium coordination arising from both chloro bridging and by dimerization.



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Proton-decoupled ^{31}P NMR spectra of complexes **5** showed two basic resonances: a triplet assignable to P_A (the R'_3P ligand) and a doublet due to P_B (the PR_2O groups), with the multiplet structure caused by mutual coupling, $^3J(P-P)$. Each multiplet has side bands, intensity one-fourth of the main peaks, due to coupling to ^{195}Pt ($I = {}^1/_2$, 33.8% abundant), and as expected the one-bond coupling to P_A (ca. 2700–2800 Hz) is much larger than the two-bond coupling to P_B (ca. 90 Hz). Data characterizing these spectra are collected in Table I. We are not aware of any data on two-bond Pt–P couplings which can be directly compared[12] with $^2J(Pt-P)$. However, the values (ca. 90 Hz) seem entirely consistent with the well-known range for $^1J(Pt-P)$ (1500–4000 Hz encompasses the majority of values)[15] and the limited data on $^3J(Pt-P)$ which indicates a range from −27 to +63 Hz with the majority of values <+30 Hz.[14,16,17]

Proton NMR spectra of $[PtCl_2(PEt_3)(CH(PPh_2O)_2Li)]$ show three regions of absorption in the correct relative intensities for the phenyl, ethyl, and methine protons. The methine proton appears as a 1:3:3:1 quartet with ^{195}Pt side bands. The quartet is relatively broad and may be assigned as due to overlap of a doublet of triplets caused by accidental near equality of the couplings to phosphorus in the PEt_3 ligand and in the PPh_2O groups. This interpretation is confirmed by spectra of the $CH(P(OEt)_2O)_2Li$ derivatives where the coupling to phosphorus in the $P(OEt)_2O$ group is larger and the methine proton appears as a resolved doublet of triplets. Data for the methine proton spectra of the various complexes studied are collected in Table I. The coupling constants to phosphorus, $^3J(P_A-H)$ and $^2J(P_B-H)$, and to platinum, $^2J(Pt-H)$, are entirely consistent with previous results. They may be compared, for example, with 6.4 Hz for ^3J(P–H

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(12) Some data are available on $^2J(Pt-P)$ in complexes containing Pt–Pt bonds (e.g., $[Pt_2Cl_2(\mu\text{-dppm})_2]$ −136 Hz;[13] $[Pt_3(\mu\text{-CO})_3(P\text{-}t\text{-}Bu_2Me)_3]$ 413 Hz[14]), but the metal-metal bonds make these complexes very different to the present examples.

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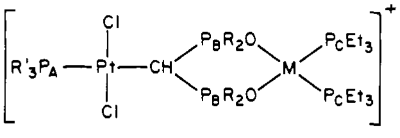
(trans)) in $[PtCH_3(PMe_2Ph)_3]^+$,[18] 7-9 Hz for ^3J(P-H) in a range of PMe_2Ph complexes,[19] 49.5-88 Hz (depending on the trans ligand) for ^2J(Pt-H) in *trans*-$PtMeXL_2$ and *trans*-$[PtMeL_2L']^+$ complexes,[20] and with ca. 120 Hz for ^2J(Pt-H) in carbon-bonded acetylacetonate complexes of platinum.[21]

Examination of the structure of **5** shows that the two R groups attached to a single phosphorus in the ring ligand are chemically nonequivalent since they are respectively syn and anti relative to the platinum. This difference is clearly observed both in proton and ^{13}C NMR spectra. For example, ^1H spectra of $[PtCl_2(PEt_3)(CH(PPh_2O)_2Li)]$ show four broad but distinct phenyl absorptions at δ 8.24, 7.66, 7.40, and 7.07; the two low-field resonances being due to the protons ortho to phosphorus in the two nonequivalent phenyl groups and the high-field resonances to the remaining phenyl protons. Similarly, the methylene resonances of the ethoxy groups in $[PtCl_2(PEt_3)(CH(P(OEt)_2O)_2Li)]$ appear as two distinct ^1H multiplets at δ 4.49 and 4.04 and as ^{13}C absorptions at 61.7 and 62.9 ppm downfield from $Si(CH_3)_4$. Unfortunately, these observations do not show whether the ring ligand structure is maintained in solution because the groups in question remain nonequivalent even if there is free rotation about the C-P bonds of the ring.

The evidence for the presence of the lithium atom in the structure requires some comment. This was first suggested by preliminary X-ray diffraction results and confirmed by subsequent flame tests and finally by an atomic absorption analysis of $[PtCl_2(PEt_3)(CH(PPh_2O)_2Li)]$. The oxygen chelation to lithium is evidenced by a lowering of the ν(P=O) stretching frequencies in the infrared; from 1190 and 1204 cm^{-1} in $Ph_2P(O)CH_2P(O)Ph_2$ to ca. 1152 and 1168 cm^{-1} in the complexes $[PtCl_2(PR'_3)(CH(PPh_2O)_2Li)]$ and from 1265 (broad) cm^{-1} in $(EtO)_2P(O)CH_2P(O)(OEt)_2$ to ca. 1170 and 1200 cm^{-1} in the complexes, $[PtCl_2(PR'_3)(CH(P(OEt)_2O)_2Li)]$. Moreover, reactions using $[Pt_2Cl_4(PR_3)_2]$ substrates with $[CH(PR_2O)_2Na]$ salts resulted in markedly less-stable products with ^{31}P NMR spectra showing identifiable differences from the corresponding lithium products. These data are shown in Table I. In each case comparison of data in the same solvent shows that replacement of Li by Na causes a small upfield shift of $\delta(P_A)$ accompanied by decreases in $^1J(Pt-P_A)$ and $^2J(Pt-P_B)$. The sodium salts tended to decompose in solution and during attempted crystallization and in consequence were not isolated. The cation dependence of the NMR parameters suggests that the specific coordination of the lithium atom found in the solid-state structure is maintained in solution. Measurements of molar conductance for the lithium salts in nitromethane solution confirmed this view, giving values <15 Ω^{-1} cm^2.

The unusual ring ligand structure **5** revealed by the X-ray diffraction study also suggested that removal of the lithium ion should yield an anionic complex capable of chelation to another metal via the oxygens of the PR_2O groups. This possibility was tested by reactions of $[M_2Cl_2(PEt_3)_4][BF_4]_2$ (M = Pd or Pt) with the $[PtCl_2(PR'_3)(CH(PR_2O)_2Li)]$ complexes. By analogy with the preparation of $[Pt(PEt_3)_2(acac)]^+$ described above, we expected formation of the cations **6**.



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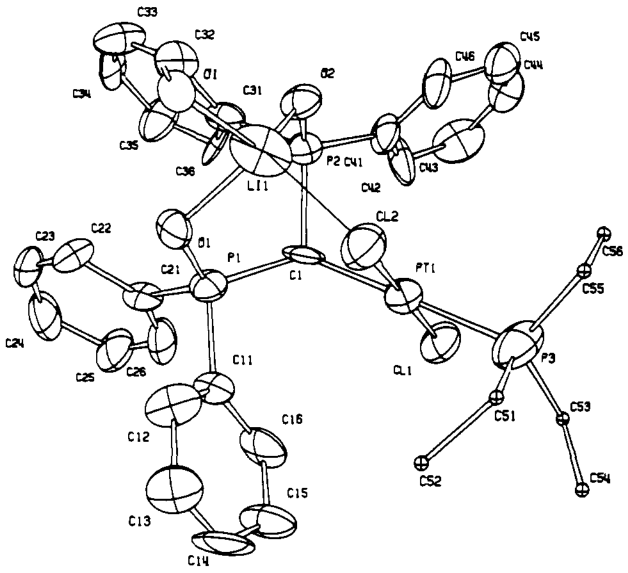

Figure 1. ORTEP plot of the molecular structure of *trans*-$[PtCl_2(PEt_3)(CH(PPh_2O)_2Li)]$. One extra atom, O(1)', belonging to the adjacent molecule, is included to show the complete lithium coordination.

Reaction of $[Pd_2Cl_2(PEt_3)_4][BF_4]_2$ with $[PtCl_2(PEt_3)(CH(PPh_2O)Li)]$ gave an impure product showing three ^{31}P principal NMR absorptions in tetrahydrofuran solution. These may be assigned respectively to phosphorus nuclei A, B, and C in structure **6** (R' = Et, R = Ph, M = Pd). The A resonance is a triplet (δ_A 136.3, $^3J(P_A-P_B)$ = 13.2 Hz) with ^{195}Pt side bands ($^1J(Pt-P_A)$ = 2883 Hz), B is a doublet (δ_B -93.3, $^3J(P_A-P_B)$ = 13.2 Hz) with ^{195}Pt side bands ($^2J(Pt-P_B)$ = 81.1 Hz), and C is a singlet at δ_c -97.8. A similar reaction using $[Pt_2Cl_2(PEt_3)_4][BF_4]_2$ with $[PtCl_2(P\text{-}n\text{-}Bu_3)(CH(P(OEt)_2O)_2Li)]$ also gave products with ^{31}P NMR spectra assignable to structure **6** (R' = *n*-Bu, R = OEt, M = Pt). In this case the A resonance was a triplet (δ_A -144.0, $^3J(P_A-P_B)$ = 12.5 Hz), B was a poorly resolved doublet ($J \approx 12$ Hz) of triplets ($J \approx 7$ Hz) at δ_B -97.5, and C was a triplet (δ_C -133.9, $^3J(P_B-P_C)$ = 7.2 Hz). All three resonances showed ^{195}Pt side bands: $^1J(Pt-P_A)$ = 2948 Hz, $^2J(Pt-P_B)$ = 92.8 Hz, and $^1J(Pt-P_C)$ = 3992 Hz. In line with the data described above for **6** (R' = Et, R = Ph, M = Pd), we assume that the $^2J(Pt-P_B)$ coupling involves the platinum atom which is bound to the bridging ligand via carbon. The absence of any apparent coupling of P_B to the platinum atom bound to the bridging ligand via oxygen is consistent with our results on the related complex $[(Et_3P)ClPt(\mu\text{-}PPh_2O)_2Pt(PEt_3)_2]^+$ where no coupling is observed (i.e., presumably the coupling constant is very small) between phosphorus in the bridging ligands and the platinum bound to the bridging ligands via oxygen.

Unfortunately, the complex cations of structure **6** were not stable to normal workup and purification procedures, and their characterization therefore rests on the solution ^{31}P NMR evidence.

(B) Crystal and Molecular Structure of *trans*-$[PtCl_2(PEt_3)(CH(PPh_2O)_2Li)]$. The atomic labeling scheme and the structure of a single molecule are depicted in Figure 1, and the interatomic distances, bond angles, and mean plane calculations are collected in Tables II-IV, respectively.

Figure 1 shows the basic structure, **5**, in agreement with the chemical and NMR results. The platinum coordination is closely planar (Table IV) with the $CH(PPh_2O)_2$ group bound to platinum via carbon and with the lithium coordinated by the two oxygens so that the group forms a bridge between the two dissimilar metals. The remarkable feature of the structure is that the lithium is further coordinated in a highly unusual

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Table II. Interatomic Distances (Å × 10^2)[a]

atoms	length	atoms	length
Pt–Cl(1)	228.2 (9)	Pt–Cl(2)	232 (1)
Pt–P(3)	225 (1)	Pt–C(1)	214 (3)
C(1)–P(1)	177 (3)	C(1)–P(2)	182 (2)
P(1)–O(1)	146 (2)	P(2)–O(2)	148 (2)
O(1)–Li	209 (6)	O(2)–Li	184 (6)
O(1)′–Li	198 (7)	Cl(2)–Li	219 (6)
Cl(2)–O(1)	337 (2)	O(1)–O(2)	301 (3)
Cl(2)–O(2)	326 (2)	O(2)–O(1)′	331 (3)
Cl(2)–O(1)′	372 (2)	O(1)′–O(1)	293 (4)
P(1)–C(11)	182 (3)	P(1)–C(21)	179 (3)
C(11)–C(12)	131 (4)	C(21)–C(22)	139 (4)
C(12)–C(13)	141 (5)	C(22)–C(23)	127 (4)
C(13)–C(14)	134 (5)	C(23)–C(24)	142 (6)
C(14)–C(15)	127 (5)	C(24)–C(25)	139 (5)
C(15)–C(16)	136 (5)	C(25)–C(26)	131 (5)
C(16)–C(11)	137 (4)	C(26)–C(21)	143 (4)
P(2)–C(31)	183 (3)	P(2)–C(41)	172 (3)
C(31)–C(32)	135 (4)	C(41)–C(42)	136 (5)
C(32)–C(33)	131 (4)	C(42)–C(43)	142 (5)
C(33)–C(34)	127 (5)	C(43)–C(44)	141 (6)
C(34)–C(35)	135 (5)	C(44)–C(45)	129 (4)
C(35)–C(36)	143 (5)	C(45)–C(46)	138 (5)
C(36)–C(31)	130 (4)	C(46)–C(41)	137 (4)
P(3)–C(51)	199	C(51)–C(52)	163
P(3)–C(53)	169	C(53)–C(54)	129
P(3)–C(55)	167	C(55)–C(56)	167

[a] Atom O(1)′ is the inverse of O(1). Estimated standard deviations are given in parentheses.

Table III. Bond Angles (Deg)

atoms	angle	atoms	angle
Cl(1)–Pt–C(1)	86.8 (9)	Cl(2)–Pt–C(1)	94.4 (9)
Cl(1)–Pt–P(3)	89.6 (4)	Cl(2)–Pt–P(3)	89.1 (4)
Cl(1)–Pt–Cl(2)	178.4 (4)	C(1)–Pt–P(3)	176.5 (9)
Pt–C(1)–P(1)	114 (2)	Pt–C(1)–P(2)	110 (1)
P(1)–C(1)–P(2)	112 (1)	O(1)–Li–O(2)	100 (2)
P(1)–O(1)–Li	115 (2)	P(2)–O(2)–Li	118 (2)
C(1)–P(1)–O(1)	111 (1)	C(1)–P(2)–O(2)	112 (1)
C(1)–P(1)–C(11)	111 (1)	C(1)–P(2)–C(31)	112 (1)
C(1)–P(1)–C(21)	112 (1)	C(1)–P(2)–C(41)	108 (2)
O(1)–P(1)–C(11)	110 (1)	O(2)–P(2)–C(31)	107 (1)
C(11)–P(1)–C(21)	103 (1)	C(31)–P(2)–C(41)	107 (2)
C(21)–P(1)–O(1)	110 (1)	C(41)–P(2)–O(2)	111 (2)
P(1)–C(11)–C(12)	119 (2)	P(2)–C(31)–C(32)	120 (2)
P(1)–C(11)–C(16)	126 (2)	P(2)–C(31)–C(36)	121 (2)
P(1)–C(21)–C(22)	123 (2)	P(2)–C(41)–C(42)	126 (3)
P(1)–C(21)–C(26)	122 (2)	P(2)–C(41)–C(46)	118 (3)
C(11)–C(12)–C(13)	121 (3)	C(31)–C(32)–C(33)	119 (3)
C(12)–C(13)–C(14)	118 (3)	C(32)–C(33)–C(34)	125 (4)
C(13)–C(14)–C(15)	124 (4)	C(33)–C(34)–C(35)	120 (3)
C(14)–C(15)–C(16)	116 (4)	C(34)–C(35)–C(36)	117 (4)
C(15)–C(16)–C(11)	126 (3)	C(35)–C(36)–C(31)	121 (3)
C(16)–C(11)–C(12)	115 (3)	C(36)–C(31)–C(32)	119 (3)
C(21)–C(22)–C(23)	123 (3)	C(41)–C(42)–C(43)	125 (4)
C(22)–C(23)–C(24)	123 (3)	C(42)–C(43)–C(44)	114 (3)
C(23)–C(24)–C(25)	115 (4)	C(43)–C(44)–C(45)	123 (4)
C(24)–C(25)–C(26)	122 (4)	C(44)–C(45)–C(46)	121 (3)
C(25)–C(26)–C(21)	122 (3)	C(45)–C(46)–C(41)	122 (3)
C(26)–C(21)–C(22)	115 (3)	C(46)–C(41)–C(42)	115 (3)
Cl(2)–Li–O(1)	104 (3)	O(1)–Li–O(2)	100 (2)
Cl(2)–Li–O(1)′	126 (2)	O(2)–Li–O(1)′	120 (3)
Cl(2)–Li–O(2)	108 (3)	O(1)′–Li–O(1)	92 (3)
Pt–P(3)–C(51)	113	C(51)–P(3)–C(53)	102
Pt–P(3)–C(53)	119	C(53)–P(3)–C(55)	117
Pt–P(3)–C(55)	115	C(55)–P(3)–C(51)	82
P(3)–C(51)–C(52)	106	P(3)–C(53)–C(54)	120
P(3)–C(55)–C(56)	89		

Table IV

The Mean Planes[a]

plane	description	definition
1	benzene ring 1	C(11)–C(16)
2	benzene ring 2	C(21)–C(26)
3	benzene ring 3	C(31)–C(36)
4	benzene ring 4	C(41)–C(46)
5	Pt coordination plane	Pt, Cl(1), Cl(2), P(3), C(1)

Equations of the Planes $Ax + By + Cz = D$ (Å)

plane	A	B	C	D	χ^2 [b]
1	−0.4116	0.8217	−0.3943	−1.3767	1.67
2	0.7036	0.3669	−0.6085	−0.1065	7.88
3	0.5482	0.5380	−0.6403	2.5150	0.32
4	0.4773	−0.5325	−0.6990	0.3089	2.82
5	0.3921	0.4506	−0.8020	0.2187	6.69

[a] Angles between planes (deg): 1,5 = 58.3; 2,5 = 21.7; 3,5 = 13.9; 4,5 = 59.5; 1,2 = 75.4; 3,4 = 65.0. Perpendicular distances of the adjacent P atoms to phenyl planes 1–4 are −0.032 (8), −0.046 (8), 0.000 (8), and 0.083 (8) Å, respectively. [b] $\chi^2 = \Sigma_i P_i^2/\sigma^2(P_i)$, the summation being over all atoms in the plane.

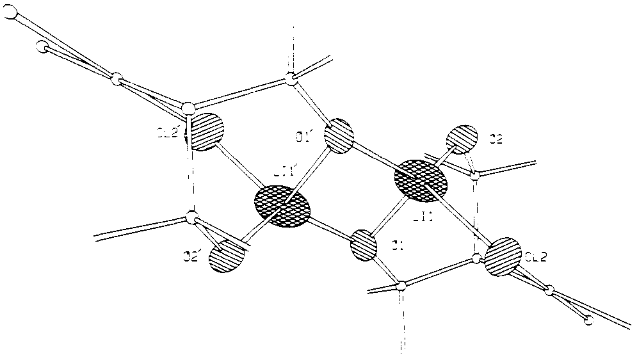

Figure 2. The lithium coordination, showing how the tetrahedra share an edge to link two molecules into a dimeric unit. The phenyl rings have been omitted for clarity.

manner involving one of the chlorines on platinum forming a bridge to the lithium. The arrangement is shown in Figure 2. Thus, the six-membered $\overline{\mathrm{C(H)P(Ph_2)OLiOP(Ph_2)}}$ ring lies approximately perpendicular to the coordination plane and adopts a boat conformation so that the lithium atom is brought close (2.19 Å) to Cl(2). An approximately tetrahedral coordination (three oxygens and a chlorine) about lithium is completed by an oxygen atom (O(1)′ at 1.98 Å) from a second molecule of the complex. The tetrahedron is repeated in the second molecule by inversion in the crystallographic center of symmetry between O(1) and O(1)′. The two tetrahedra share a common edge O(1)---O(1)′, and the overall effect is for the lithium coordination to link two molecules into a compact dimeric unit.

The distances (Table II) between the lithium and the surrounding atoms (O–Li 1.97 Å (average), C(2)–Li 2.19 Å) appear reasonable, although the unusual bonding in this complex means that comparisons neither with Pauling ionic radii (O^{2-}, 1.40 Å; Cl^-, 1.81 Å; Li^+, 0.60 Å)[22] nor with covalent radii (Cl, 0.99 Å; O, 0.74 Å; Li, 1.34 Å (in Li_2))[23] are entirely appropriate. The coordination about lithium shows significant distortions from tetrahedral angles (Table III), and it is interesting that the smallest angle at Li is subtended by the shared edge O(1)---O(1)′, a feature commonly found in oxide chemistry.[24] The Pt–Cl lengths are typical for a *trans*-dichloroplatinum(II) fragment, and the Pt–Cl(2) length (2.32 (1) Å) is slightly greater than Pt–Cl(1) (2.282 (1) Å) as might be expected in the presence of an Li---Cl(2) interaction. It

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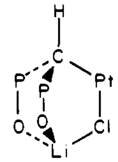
is also noteworthy that, although the Cl–Pt–Cl group is close to linearity and the Pt–P(3) bond is at right angles to this line, the Cl–Pt–C(1) angles are significantly distorted (86.8 (9) and 94.4 (9)°) as might be expected from the geometry of the ring systems. Within the $CH(PPh_2O)Li$ ligand, the P═O (average 1.47 Å) and P–C (average 1.795 Å) bond lengths are typical[25] for respectively double and single bonds involving these elements and indicate localized bonding. This ligand is comparatively weakly bound to platinum (2.14 (1) Å) and exhibits only a modest trans influence (Pt–P(3) 2.25 (1) Å), two points which are developed in detail in the Discussion section.

The remaining interatomic distances and angles are all normal and require no further comment except to note that, as described in the Experimental Section, the carbon atoms of the triethylphosphine ligand are only roughly determined, and for this reason no standard deviations are given for parameters associated with these atoms. The apparently large thermal ellipsoid for P(3) in Figure 1 is probably associated with this problem.

Discussion

As we noted in the Introduction, the $[R_2P(O)CHP(O)R_2]^-$ ligands studied in the present work are formally analogous to the acetylacetonate anion and are thus potentially capable of coordination to a metal via either oxygen or carbon. In platinum acetylacetonates, the two modes of coordination occur with about equal frequency and stability, and there are several examples where both types occur in a single complex.[26] Our reactions indicate that, relative to acetylacetonate, the $[R_2P(O)CHP(O)R_2]^-$ anions may have a greater preference for bonding to platinum via carbon. Thus, reaction of acetylacetonate with $[Pt_2Cl_2(PEt_3)_4][BF_4]_2$ produced a stable, oxygen-bonded chelate, $[Pt(PEt_3)_2(acac)_2][BF_4]$, in high yield whereas similar reactions of $[R_2P(O)CHP(O)R_2]^-$ anions gave no identifiable products. Moreover, none of our other reactions of $[R_2P(O)CHP(O)R_2]^-$ with platinum substrates yielded any evidence of Pt–O-bonded species. The reactions of $[R_2P(O)CHP(O)R_2]Li$ salts with $[Pt_2Cl_4L_2]$ substrates did lead to the stable carbon-bonded species **5**, which are the main subject of this paper. However, the novel structure of these complexes, in which the entire lithium salt functions as an essentially neutral ligand, makes it clear that the nature of the alkali-metal cation plays a crucial role in these reactions. Consequently, any conclusions about the inherent coordination preferences of the $[R_2P(O)CHP(O)R_2]^-$ ligands should be approached with caution. Certainly the ligand is unusual in bridging two such dissimilar metals, and the lithium cation appears to be essential to the stability of the system since our attempts to make analogous sodium salts all led to unstable complexes. It is, however, also interesting that when bonded to platinum via carbon the $[R_2P(O)CHP(O)R_2]^-$ ligands do exhibit some slight "soft" donor character in forming the unstable complexes, **6**, in which the oxygens bind to a second platinum center.

The novel coordination to lithium (Figures 1 and 2) merits further comment. Chloride is, of course, well-known to form stable bridges with many metals, and examples in which it bridges two different metals are well established (e.g., $[PdPt(\mu\text{-}Cl)_2Cl_2(PBu_3)_2]$).[27] Compounds containing weak intermolecular bridging by halide ligands have also been reported (e.g., *trans*-$[PdI_2(PMe_2Ph)_2]$).[28] However, the role of chloride in the present complexes in bridging two such dissimilar metals is certainly highly unusual and to our knowledge unprecedented. Interestingly, the Pt–Cl(1) (2.282 (9) Å) and Pt–Cl(2) (2.32 (1) Å) lengths are very similar to those found in more conventional chloride-bridged compounds. For example, in $[Pt_2(\mu\text{-}Cl)_2Cl_2(PPr_3)_2]$, the terminal Pt–Cl bond is 2.279 (9) Å and the platinum to bridge chloride length (trans to terminal Cl) is 2.315 (8) Å.[29] In complex **5**, the chloride and lithium are brought into proximity by a boat conformation of the six-membered $\overline{\text{CPOLiOP}}$ ring. Formation of the Cl(2)---Li linkage completes two further six-membered rings, and the whole molecule may thus be regarded as a very unusual "tripod" ligand coordinated to lithium.



The presence of the lithium atom as an essentially integral part of the ligand in these complexes raises questions as to the nature of the platinum–carbon bond. The observed Pt–C(1) length is 2.14 (3) Å, and the coordination around C(1) is tetrahedral. A survey of literature examples of Pt–C(sp^3) bonds trans to phosphorus ligands shows a fairly wide variation from 2.01 Å in *cis*-$[Pt(PPh_3)_2(EtOC_6H_7)]$[30] to 2.175 Å for the bond to the CH_2COPh ligand in $[Pt(CH_2COPh)(C_6H_9)(diphos)]$,[31] with the majority of values in the lower part of this range (<2.10 Å). Although the relatively low precision of our measurement makes it difficult to be definitive, it appears that the Pt–Cl(1) bond in our complex is long but by no means exceptionally so. In the case of the $PtCH_2COPh$ complex, it was suggested that the long bond was due to significant contribution from a dipolar structure, $Pt^+\text{---}CH_2{=}CPh{=}O^-$, a view which was supported by shortening of the C–C bond, lengthening of the C–O bond, and a lowering of ν(C═O) in the infrared spectrum.[31] In view of the bonding to the lithium ion in our structure, this type of contribution would be an attractive hypothesis, but there seems no real evidence for it. There is a lowering of ν(P═O) in the infrared spectra, as would be expected from the interaction of oxygen with lithium, but the C—P and P═O lengths are entirely consistent[25] with localized single and double bonds, respectively.

Finally, the trans influence of the $CH(PPh_2O)_2Li$ ligand is of interest since both the NMR studies and the structural work suggest that it is considerably smaller than normally found for C-bonded ligands. Thus, the Pt–P(3) bond length of 2.25 Å occupies an intermediate position in the values tabulated by Mather, Pidcock, and Rapsey[32] and is, for example, more closely comparable with the 2.247 Å (trans to Cl) found in *cis*-$[PtCl_2(PMe_3)_2]$ than with the 2.298 Å (trans to P) in *trans*-$[PtCl_2(PEt_3)_2]$.[32] More extensive and precise data is available for NMR trans influences, and the ^1J(Pt–P) value of 2756 Hz in $[PtCl_2(PEt_3)(CH(PPh_2O)_2Li)]$ may be compared with 3520 Hz (trans to Cl in *cis*-$[PtCl_2(PEt_3)_2]$),[33] 2409 Hz (trans to PEt_3 in *trans*-$[PtCl_2(PBu_3)(PEt_3)]$,[34] and 1856 Hz (trans to CH_3 in *cis*-$[Pt(CH_3)_2(PEt_3)_2]$.[35] On the ^1J-

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(Pt–P)-based scale of trans influence[36] listed by Allen and Sze,[34] the $CH(PPh_2O)Li$ ligand would lie somewhere between the tertiary phosphines and nitrogen donors such as *p*-toluidine, in contrast to the more usual carbon-bonded ligands which are found at the extreme high end of the scale.[36]

Experimental Section

(A) Synthesis and Characterization. Data relating to the characterization of the complexes are given in the tables and in the Results section. Phosphorus-31 NMR spectra were recorded at 24.29 MHz on a Nicolet TT14 Fourier-transform spectrometer using a Varian HA60 magnet. Protons were decoupled by broad band ("noise") irradiation at appropriate frequencies. $P(OCH_3)_3$ was used as external reference and C_6D_6 as external lock. Negative chemical shifts are upfield from the reference. Usually 4096 real-time data points were used in a 6 kHz sweep, giving resolution of 1.46 Hz, and data are thus subject to errors of this magnitude. ^1H NMR spectra were recorded on the Nicolet TT14 at 60.0 MHz.

Microanalyses were by D. L. McGillivray of this department or by Canadian Microanalytical Service Ltd., Vancouver, B.C. Infrared spectra were recorded from 4000 to 200 cm^{-1} with accuracy of ±3 cm^{-1} on a Perkin-Elmer 283 spectrophotometer calibrated against polystyrene film. Solid samples were examined as Nujol mulls between cesium iodide plates.

$(EtO)_2P(O)CH_2P(O)(OEt)_2$ (Alfa-Ventron Corp.) and $Ph_2PCH_2PPh_2$ (PCR Research Chemicals Inc.) were commercially available. $Ph_2P(O)CH_2P(O)Ph_2$ was prepared by stirring a benzene solution of $Ph_2PCH_2PPh_2$ with aqueous sodium hypochlorite solution, and it was recrystallized from benzene. *cis*-$[PtCl_2(PEt_3)_2]$,[37] $[M_2Cl_2(PEt_3)_4][BF_4]_2$[38] (M = Pt or Pd), and $[M_2Cl_4(PR_3)_2]$[39] (M = Pt, R = Et or *n*-Bu; M = Pd, R = Et) were all prepared as previously described.

$MCl_2(PR'_3)(CH(PR_2O)_2Li)$ Complexes. Preparations of these complexes were all conducted in an atmosphere of dry nitrogen using tetrahydrofuran solvent which had been freshly distilled from a potassium/benzophenone mixture. All were similar to the following representative example.

A solution (1.4 M in hexane) of *n*-butyllithium (0.46 mL, 0.64 mmol) was added dropwise to a stirred suspension of $Ph_2P(O)CH_2P(O)Ph_2$ (0.27 g, 0.64 mmol) in tetrahydrofuran (2 mL). The resulting orange solution was added to a solution of $[Pt_2Cl_4(P\text{-}n\text{-}Bu_3)_2]$ (0.30 g, 0.32 mmol) in tetrahydrofuran (10 mL). After 30 min of stirring, the solvent was removed in vacuo and the residue washed with hexane before recrystallization by dropwise addition of hexane to a tetrahydrofuran solution of the product. Et_3P and Ph_3P analogues were recrystallized by dropwise addition of diethyl ether to tetrahydrofuran solutions of the products, and yields for all preparations were in the range 75–90% based on conversion of the $[M_2Cl_4(PR_3)_2]$ substrates.

Microanalytical results were as follows. Anal. Calcd for $[PtCl_2(PEt_3)(CH(PPh_2O)_2Li)]$: C, 46.2; H, 4.50; P, 11.5; Cl, 8.8; Li, 0.86. Found: C, 46.4; H, 4.41; P, 11.4; Cl, 9.1; Li, 0.74. (Mp > 230 °C dec.) Anal. Calcd for $[PtCl_2(P\text{-}n\text{-}Bu_3)(CH(PPh_2O)_2Li)]$: C, 49.9; H, 5.43. Found: C, 50.2; H, 5.47. (Mp = 207–208 °C dec.) Anal. Calcd for $[PtCl_2(PEt_3)(CH(P(OEt)_2O)_2Li)]$: C, 26.6; H, 5.35. Found: C, 26.35; H, 5.26. (Mp = 157–158 °C.) Anal. Calcd for $[PtCl_2(P\text{-}n\text{-}Bu_3)(CH(P(OEt)_2O)_2Li)]$: C, 33.1; H, 6.35. Found: C, 33.1; H, 6.45. (Mp = 98–100 °C.) Anal. Calcd for $[PtCl_2(PPh_3)(CH(P(OEt)_2O)_2Li)]$: C, 39.4; H, 4.41. Found: C, 39.7; H, 4.43. (Mp > 179 °C dec.) Anal. Calcd for $[PdCl_2(PEt_3)(CH(PPh_2O)_2Li)]$: C, 51.9; H, 5.06. Found: C, 51.4; H, 5.19. (Mp = 252–253 °C dec.)

$[Pt(PEt_3)_2(acac)][BF_4]$. Sodium acetylacetonate (0.036 g, 0.29 mmol) in acetone solution and $[Pt_2Cl_2(PEt_3)_4][BF_4]_2$ (0.16 g, 0.144 mmol) in dichloromethane solution were mixed and stirred together for 15 min. A very fine white precipitate was removed by filtration. Evaporation of the filtrate under reduced pressure gave a colorless oil which was dissolved in dichloromethane and shaken with aqueous $NaBF_4$ solution to remove chloride. The dichloromethane extract was recrystallized by the dropwise addition of diethyl ether to a chilled tetrahydrofuran solution to give *the complex* as colorless crystals (0.165 g, 0.27 mmol). Anal. Calcd for $C_{17}H_{37}BF_4O_2PtP_2$: C, 33.1; H, 6.04. Found: C, 33.1; H, 5.99.

Table V. Fractional Atomic Coordinates ($\times 10^3$)

atom	x	y	z
Pt	78.6 (1)	160.8 (1)	153.5 (1)
Cl(1)	173.4 (6)	187.3 (4)	231.3 (6)
Cl(2)	−19.5 (6)	135.2 (5)	77.2 (6)
P(1)	86.7 (4)	10.8 (4)	145.7 (5)
P(2)	161.8 (5)	80.5 (4)	13.9 (5)
P(3)	26.7 (7)	248.6 (6)	190.8 (8)
O(1)	43.5 (11)	−8.0 (9)	74.7 (11)
O(2)	102.9 (10)	84.1 (9)	−45.1 (12)
C(1)	133 (2)	79 (1)	123 (1)
C(11)	33 (1)	20 (1)	238 (2)
C(12)	−29 (2)	−5 (2)	241 (2)
C(13)	−72 (2)	2 (2)	311 (3)
C(14)	−48 (2)	33 (3)	377 (2)
C(15)	11 (2)	60 (2)	378 (2)
C(16)	50 (2)	55 (2)	308 (2)
C(21)	144 (1)	−50 (1)	175 (2)
C(22)	149 (2)	−104 (1)	129 (2)
C(23)	189 (3)	−148 (1)	151 (2)
C(24)	232 (3)	−145 (2)	223 (3)
C(25)	235 (3)	−89 (2)	263 (2)
C(26)	194 (2)	−44 (2)	240 (3)
C(31)	212 (2)	12 (2)	−14 (2)
C(32)	190 (2)	−24 (2)	−78 (2)
C(33)	226 (2)	−73 (2)	−96 (2)
C(34)	281 (2)	−89 (1)	−60 (3)
C(35)	306 (2)	−56 (2)	5 (3)
C(36)	267 (2)	−3 (1)	27 (2)
C(41)	217 (2)	142 (1)	3 (2)
C(42)	278 (2)	151 (1)	43 (3)
C(43)	323 (2)	201 (2)	30 (3)
C(44)	301 (2)	240 (2)	−34 (3)
C(45)	242 (2)	235 (2)	−71 (2)
C(46)	201 (2)	185 (1)	−58 (2)
C(51)	−74	238	214
C(52)	−80	180	277
C(53)	54	286	277
C(54)	12	296	337
C(55)	−4	291	111
C(56)	77	314	90
Li	16 (2)	63 (3)	−7 (4)

Other Reactions. The other attempted syntheses mentioned in the Results section all used procedures similar to those described above. Reactions were conducted at ambient temperature in tetrahydrofuran or dichloromethane solution, and the products were examined by ^{31}P NMR.

(B) Crystal Measurements. Crystals of $[PtCl_2(PEt_3)(CH(PPh_2O)_2Li)]$ suitable for study by X-ray diffraction were grown by vapor diffusion of diethyl ether into a solution of the complex in dichloromethane. Preliminary X-ray photographs were taken with use of Weissenberg and precision cameras and Cu Kα radiation. Systematic absences established the space group as *Pbca* (No. 61). The crystal was mounted approximately along the *a* axis. The goniometer head was transferred to a Picker four-circle diffractometer automated with a PDP-11 computer. Twenty pairs of centering measurements were done at $\pm 2\theta$, with $|2\theta|$ in the range 22–40° with use of Mo K$\bar{\alpha}$ radiation ($\lambda = 0.71069$ Å). The matrix and the unit cell dimensions were refined by least-squares methods. The crystal data at approximately 25 °C were $a = 19.247$ (8) Å, $b = 21.918$ (8) Å, $c = 15.942$ (4) Å, $V = 6725$ (4) Å^3, $D_m = 1.608$ g cm^{-3} (flotation in CCl_4 and $CHBr_3$), $D_c = 1.593$ g cm^{-3}, formula = $C_{31}H_{36}Cl_2LiO_2P_3Pt$, $M_r = 806.48$, and $Z = 8$.

Intensities were measured with the use of a $\theta/2\theta$ step scan of 70 steps of 0.03° in 2θ, counting for 1 s at each step. Background measurements were for 35 s at each end of the scan. Measurements were completed in one octant out to 40° in 2θ with use of Zr-filtered Mo K$\bar{\alpha}$ radiation. Three standards were measured preceding each batch of 50 reflections, and the sum of these standards decreased

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(35) Allen, F. H.; Pidcock, A. *J. Chem. Soc. A* **1968**, 2700.

(36) $MePh_2Si > Ph > Me \gg Et_3P, Bu_3P > Me_2PhP > Ph_3P > (PhO)_3P, CN > Et_3As > NO_2 > p\text{-tol} > EtNH_2 > Et_2NH > py, N_3, NCO, NCS > Cl, Br, I > NO_3$.

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linearly with time and X-ray exposure to about 64% of the original intensity. Each of the standards behaved in a similar manner, and the stability constant estimates were 0.013, 0.011, and 0.011, indicating that the decline was at least a steady effect. The intensities were corrected with the Lorentz and polarization factors.

Absorption corrections were applied with the use of numerical integration over an (8 × 8 × 8) Gaussian grid. The crystal had 12 well-formed faces, and the shape is given by the following indices and perpendicular distances (in parentheses) in millimeters from an internal origin: 1,1,1 (0.244); –1,–1,–1 (0.152); –1,1,1 (0.195); 1,–1,–1 (0.141); 1,–1,1 (0.211); –1,1,–1 (0.170); 1,1,–1 (0.098); –1,–1,1 (0.177); 0,1,0 (0.175); 0,–1,0 (0.118); 1,0,0 (0.203); –1,0,0 (0.216). The indexing and measurements were done on the diffractometer, and the crystal orientation was given to the program in the form of the diffractometer matrix. The absorption coefficient was 47.5 cm^{-1}, and the corrections were in the range 0.296–0.348.

(C) Crystal Structure Solution and Refinement. The structure was solved by the use of the Patterson function and heavy-atom method. The atomic scattering factors for uncharged atoms were used.[40] The programs used were supplied by Penfold[41] and are based on ORFLS, FORDAP, ORFFE, and ORTEP. The structure was refined by the method of least squares minimizing $\sum w(|F_o| - |F_c|)^2$. A weighting scheme was devised in the final stages of the refinement: $w = (A + Bx + Cx^2 + Dx^3)^{-1}$ where $x = |F_o|$ and $A = 41.388$, $B = -0.53721$, $C = 0.38642 \times 10^{-2}$, and $D = -0.40782 \times 10^{-5}$. This weighting scheme gives a reasonably constant mean value of $w\Delta^2$ when the reflections are analyzed in batches according to the amplitudes of the structure factors. Because of program size limitations, the refinement was done by alternately refining two large blocks of parameters chosen according to chemical grouping and with the six heavy atoms always included. Convergence was reached, and the estimated standard deviations of the anisotropic temperature parameters were obtained. The standard deviations of the bond lengths and angles were then obtained from the inverted matrix of a final cycle including all the fractional coordinate variables. The lithium atom was easily located in difference maps, although the evidence for its identity rests mainly upon the chemical preparation and subsequent analysis of the compound. The final discrepancy indices were $R = 0.100$ and $R_w = 0.109$. There were 2123 observations and 331 variables in the model and $(\sum w\Delta^2/(N_{obsd} - N_{var}))^{1/2} = 2.14$.

We were not able to refine the structure further owing to a difficulty in precisely locating the carbon atoms of the triethylphosphine ligand. This ligand is either in disorder or in high thermal motion, and we finally chose to contour the difference map based on structure factors calculated for all atoms except the six carbons of the triethylphosphine ligand. These were then positioned with the use reasonable torsion angles, molecular models, and our previous experience of the most likely conformation for PEt_3 in square-planar complexes.

Notwithstanding the uncertainty in the PEt_3 ligand, the final difference map has a maximum of 2.11 e $Å^{-3}$ and a minimum of –1.25 e $Å^{-3}$, and we are confident that the structure is not significantly in error. The fractional atomic coordinates are given in Table V, and tables of structure factors, anisotropic temperature parameters, and intermolecular distances have been deposited.

Acknowledgment. We thank the Natural Science and Engineering Research Council of Canada and the University of Victoria for research grants and Mrs. K. Beveridge for technical assistance in the crystal structure determination.

Registry No. **5** (R′ = Et, R = Ph, M = Pt), 78610-29-4; **5** (R′ = *n*-Bu, R = Ph, M = Pt), 78610-30-7; **5** (R′ = Et, R = OEt, M = Pt), 78610-31-8; **5** (R = *n*-Bu, R = OEt, M = Pt), 78610-32-9; **5** (R′ = Ph, R = OEt, M = Pt), 78610-33-0; **5** (R′ = Et, R = Ph, M = Pd), 78610-34-1; **6** (R′ = Et, R = Ph, M = Pd), 78610-35-2; **6** (R′ = *n*-Bu, R = OEt, M = Pt), 78610-36-3; $[Pt(PEt_3)_2(acac)][BF_4]$, 78610-38-5; $(EtO)_2P(O)CH_2P(O)(OEt)_2$, 1660-94-2; $Ph_2P(O)CH_2P(O)Ph_2$, 2071-21-8; $Pt_2Cl_4(P(n\text{-}Bu)_3)_2$, 15670-38-9; $Pt_2Cl_4(PEt_3)_2$, 15692-96-3; $Pd_2Cl_4(PEt_3)_2$, 15684-59-0; $Pt_2Cl_4(PPh_3)_2$, 15349-80-1; $[Pt_2Cl_2(PEt_3)_4][BF_4]_2$, 19394-82-2; $[Pd_2Cl_2(PEt_3)_4][BF_4]_2$, 22180-55-8; *cis*-$[PtCl_2(PEt_3)_2]$, 15692-07-6; $PtCl_2(PEt_3)(CH(PPh_2O)_2Na)$, 78610-39-6; $PtCl_2(P\text{-}n\text{-}Bu_3)(CH(PPh_2O)_2Na)$, 78610-40-9; $PtCl_2(PEt_3)(CH(P(OEt)_2O)_2Na)$, 78610-41-0.

Supplementary Material Available: Listings of observed and calculated structure factor amplitudes (Table S1), intermolecular distances (Table S2), and anisotropic temperature parameters (Table S3) (10 pages). Ordering information is given on any current masthead page.

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[40] "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2B, p 99.

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Contribution No. 2890 from the Central Research and Development Department,
E. I. du Pont de Nemours and Company, Experimental Station, Wilmington, Delaware 19898

Magnesium Butadiene as a Reagent for the Preparation of Transition-Metal Butadiene Complexes: Molecular Structure of Bis(η-butadiene)[1,2-bis(dimethylphosphino)ethane]hafnium

S. S. WREFORD* and J. F. WHITNEY

Received March 9, 1981

The conveniently prepared reagent $Mg(C_4H_6)\cdot 2THF$ reacts readily with transition-metal halides, forming butadiene complexes. Thus $Hf(\eta\text{-}C_4H_6)_2(dmpe)$, $Ti(\eta\text{-}C_4H_6)_2(depe)$, $Ti(\eta\text{-}C_4H_6)_2[(MeO)_2PC_2H_4P(OMe)_2]$, $Ti(\eta\text{-}C_4H_6)_2(diphos)$, and $Zr(\eta\text{-}C_4H_6)_2(dmpe)$ are formed when MCl_4 (M = Ti, Zr, Hf) and the appropriate bidentate phosphine (dmpe = 1,2-bis(dimethylphosphino)ethane, depe = 1,2-bis(diethylphosphino)ethane, diphos = 1,2-bis(diphenylphosphino)ethane) are treated with $Mg(C_4H_6)\cdot 2THF$. Similarly, $NbCl_4(dmpe)_2$, WCl_6, and $FeCl_2$ or $FeCl_3$ adducts of trimethylphosphine react with the reagent, affording $NbCl(C_4H_6)(dmpe)_2$, $W(\eta\text{-}C_4H_6)_3$, and $Fe(\eta\text{-}C_4H_6)(PMe_3)_3$, respectively. $Ti(C_4H_6)_2(diphos)$ polymerizes ethylene. $Hf(\eta\text{-}C_4H_6)_2(dmpe)$ is triclinic, space group $P\bar{1}$, with $a = 13.274$ (2) Å, $b = 14.952$ (2) Å, $c = 9.319$ (1) Å, $\alpha = 97.14$ (1)°, $\beta = 101.82$ (1)°, $\gamma = 109.76$ (1)°, $Z = 4$, and ρ(calcd) = 1.742 g cm^{-3}. The complex has no crystallographically imposed symmetry but has a structure based on a distorted C_2 octahedral geometry. The $Zr–C_4H_6$ arrangement is η^4 but distorted toward a $1,4\text{-}\eta^2\text{-}C_4H_6$ structure, reflecting substantial π interaction.

Transition-metal butadiene complexes are generally prepared by reducing a metal halide or halo complex in the presence of butadiene, by thermal or photolytic ligand displacements, or by metal atom evaporation techniques. All of these methods, although quite useful, have limitations; more general methods would be helpful, especially for the preparation of thermally unstable complexes on a moderate scale. Magnesium is known to react with butadiene in THF under