γ-LiV$_2$O$_5$, the magnetic moments of the V^{4+} ions could not be accurately calculated from eq 4.

Conclusion

The use of LiI in acetonitrile at room temperature as a mild reducing reagent has allowed the preparation and characterization of pure Li$_x$V$_2$O$_5$ bronzes distinct from those prepared at high temperatures. These low-temperature phases appear to be structurally more similar to V$_2$O$_5$ than are the high-temperature phases. However, the electronic nature of the low-temperature phases appears to be quite similar to that of the high-temperature phases. These studies indicate that V$_2$O$_5$ should be regarded as a three-dimensional framework host for lithium rather than a two-dimensional vdW host. This view leads to the conclusion that strengthening the V–O framework should prevent extensive bond breaking under more reducing conditions while still allowing facile lithium incorporation.[25] An example is afforded by Li$_x$V$_6$O$_{13}$ bronzes.[3]

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Registry No. LiV$_2$O$_5$, 12162-92-4; V$_2$O$_5$, 1314-62-1; LiI, 10377-51-2.

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Contribution from the Guelph-Waterloo Centre for Graduate Work in Chemistry,
Guelph Campus, University of Guelph, Guelph, Ontario, Canada

Facile Intramolecular Metalation of Tri-*tert*-butylphosphine in Palladium(II) Hydride Complexes

H. C. CLARK,* A. B. GOEL, and S. GOEL

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Palladium(II) hydrides (*trans*-PdH(X)(P-t-Bu$_3$)$_2$ (I) when X = Cl or CF$_3$COO), prepared by the oxidative addition of HX to bis(tri-*tert*-butylphosphine)palladium(0), have been shown to undergo facile intramolecular metalation in solution producing complexes of the type PdX(P-t-Bu$_2$CMe$_2$CH$_2$)(P-t-Bu$_3$) (II). These complexes (II) when kept in dichloromethane or benzene solution lose 1 molar equiv of phosphine to give the bridged dimeric complexes [PdX(P-t-Bu$_2$CMe$_2$CH$_2$)]$_2$ (III). Complex III (where X = Cl) is also obtained from the reaction of tri-*tert*-butylphosphine with PdCl$_2$(NCPh)$_2$ in CH$_2$Cl$_2$. Sodium borohydride reduction of complexes I, II, or III in ethanol invariably produces bis(tri-*tert*-butylphosphine)palladium(0). Reaction of n-butyllithium with PdH(X)(P-t-Bu$_3$)$_2$ in n-hexane also gives the palladium(0) complex. The chloride bridge of complex III can be split by a variety of ligands (e.g., pyridine, Ph$_3$As, Ph$_3$P, Et$_3$P, Ph$_2$MeP, i-Pr$_3$P, t-Bu$_2$MeP, Cy$_3$P, and (C$_7$H$_7$)$_3$P) to give mononuclear species of the type *trans*-PdCl(P-t-Bu$_2$CMe$_2$CH$_2$)(L).

Introduction

The metalation of bulky phosphines in platinum(II) and palladium(II) dichlorides has been widely studied by Shaw and co-workers.[1,2] It has been suggested that the process is promoted by the facile formation of five-membered rings.[3] Compared with the intramolecular metalation of aromatic carbon atoms in coordinated phosphines, there are only a few examples known for purely aliphatic carbons.[2,4–6] Furthermore, it has been reported[4] that the n-propyl groups in the complexes PtCl$_2$(P-t-Bu-n-Pr$_2$)$_2$ and PtCl$_2$(P-t-Bu$_2$-n-Pr)$_2$ are metalated only when the complexes are heated for several hours, whereas similar palladium complexes cannot be metalated under similar conditions. Although, recently, the intramolecular metalation of *tert*-butylphosphine in the complex PdCl$_2$(P-t-Bu$_3$)$_2$ has been reported,[6] no metalation process has been reported for the corresponding palladium(II) hydrides. Palladium(II) hydride complexes *trans*-PdH(X)(P-t-Bu$_3$)$_2$ (where X = Cl or CF$_3$COO) of sufficient stability to examine metalation processes have recently been prepared by Otsuka et al.[7] We now wish to report that these palladium(II) hydrides undergo rapid intramolecular metalation with the elimination of hydrogen.

Results and Discussion

The preparation of bis(tri-*tert*-butylphosphine)palladium(0) by the reaction of *tert*-Bu$_3$P with (η^3-C$_3$H$_5$)Pd(η^5-C$_5$H$_5$) has been reported previously.[8] The latter reactant must be obtained from the reaction of thallium cyclopentadienide with allylpalladium chloride, which makes that method time consuming. We have now prepared (t-Bu$_3$P)$_2$Pd^0 in about 70% yield by the reaction of sodium naphthalenide with a mixture of PdCl$_2$(NCPh)$_2$ or (COD)PdCl$_2$ and P-t-Bu$_3$ in THF. The

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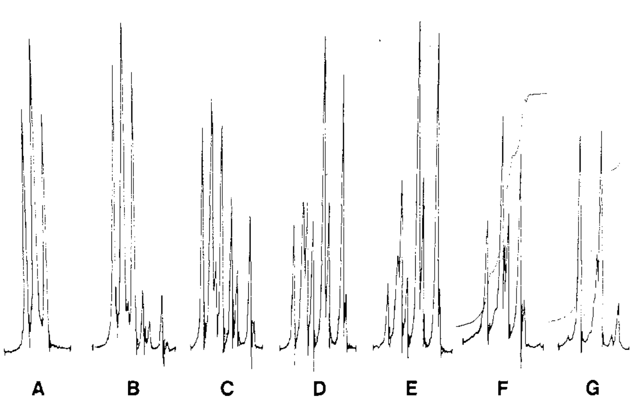


Figure 1. Proton NMR spectra of the complex $PdH(Cl)(t\text{-}Bu_3)_2$ in benzene, at various time intervals, showing metalation to $PdCl(CH_2C_3H_6P\text{-}t\text{-}Bu_2)(P\text{-}t\text{-}Bu_3)$ (II): (A) fresh solution of $PdH(Cl)(P\text{-}t\text{-}Bu_3)_2$, (B) solution after 2 h, (C) solution after 12 h, (D) solution after 40 h, (E) solution after 4 days, (F) solution after 5 days giving pure complex II. G is the spectrum of pure $Pd_2Cl_2(CH_2C_3H_6P\text{-}t\text{-}Bu_2)_2$.

reaction proceeds smoothly to completion within about 1 h. A one-step preparation can be achieved by mixing $(COD)PdCl_2$ (COD = 1,5-cyclooctadiene) or $PdCl_2(NCPh)_2$, $P\text{-}t\text{-}Bu_3$, naphthalene, and sodium metal in dry THF under nitrogen.

$$(COD)PdCl_2 \text{ or } PdCl_2(NCPh)_2 + 2P\text{-}t\text{-}Bu_3 \xrightarrow[THF]{NaC_{10}H_8} (t\text{-}Bu_3P)_2Pd + 2NaCl + [COD \text{ or } 2PhCN] \quad (1)$$

Palladium(II) hydride complexes of the type *trans*-$PdH(X)(P\text{-}t\text{-}Bu_3)_2$ (I) (where X = Cl or CF_3COO) have been prepared by the oxidative addition of protic acids, HX, to bis(tri-*tert*-butylphosphine)palladium(0); such addition occurs readily at room temperature in benzene or hexane solutions (eq 2).

$$Pd(P\text{-}t\text{-}Bu_3)_2 + HX \rightarrow PdH(X)(P\text{-}t\text{-}Bu_3)_2 \quad (2)$$

These complexes are characterized by infrared (ν(Pd–H) = 2190–2215 cm^{-1}), proton NMR [Pd–H: δ –(16.2–18.3) (t); J(P–H) = 4.3–6.9 Hz], and ^{31}P NMR (δ –(67–79)) spectra (Table I). Although these complexes (I) are quite stable in the solid state, they undergo intramolecular metalation within a few hours when kept in benzene or methylene chloride solutions to give II (eq 3).

$$\underset{I}{trans\text{-}PdH(X)(P\text{-}t\text{-}Bu_3)_2} \rightarrow \underset{II}{PdX(P\text{-}t\text{-}Bu_2CMe_2CH_2)(P\text{-}t\text{-}Bu_3)} + H_2 \quad (3)$$

This metalation process has been followed by observing the proton NMR spectrum where the conversion of the original triplet due to *tert*-butyl groups into three sets of doublets due to metalated complexes is clearly observed (Figure 1).

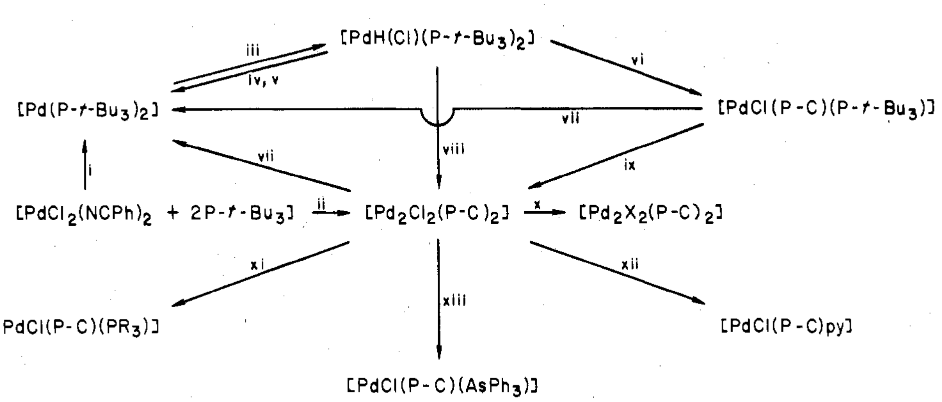
Completion of the metalation reaction is indicated by the loss of the ^1H NMR resonance due to the hydride proton as well as by the disappearance of ν(Pd–H) at (2190–2210 cm^{-1}) in the infrared spectrum. The rate of metalation is markedly enhanced by the addition of a small amount of alcohol and we find that the rate of metalation of the chloro complex is faster than that of the trifluoroacetate analogue. For example, complex I with X = Cl in benzene solution containing a small amount of alcohol was converted into the corresponding complex II within 0.5 h, while the similar metalation process in the complex I with X = CF_3COO was completed in 2–3 h. The complexes II are characterized by their proton NMR spectra which show the expected three sets of doublets due to protons of Pd–P-*t*-Bu_3, Pd–P-*t*-Bu_2, and P–CMe_2 groups. In particular, the spectrum of [$Pd(CF_3COO)(P\text{-}t\text{-}Bu_2CMe_2CH_2)(P\text{-}t\text{-}Bu_3)$] shows signals at δ 1.28 (P-*t*-Bu_3),

Table I. Crystallization, Elemental Analyses, and Proton and ^{31}P NMR Data of $PdH(X)(P\text{-}t\text{-}Bu_3)_2$, $PdX(P\text{-}C)(P\text{-}t\text{-}Bu_3)$, and $Pd_2X_2(P\text{-}C)_2$ (Where X = Cl or CF_3COO and (P-C) = $t\text{-}Bu_2PCMe_2CH_2$))

			anal. found (calcd)			^1H NMR data[c,d]			
complex[a]	solvent of crystn	dec mp,[b] °C	C	H	Cl	δ	J(P–H), Hz	^{31}P NMR data[e] δ	IR data, cm^{-1}
$PdH(Cl)(P\text{-}t\text{-}Bu_3)_2$	benzene/*n*-hexane	144–147	52.67	9.98	6.62	Pd–H –16.5 (5)	6.9	–79.7	ν(Pd–H) 2210
			(52.70)	(10.06)	(6.50)	*t*-Bu 1.51 t	12.3		ν(Pd–Cl) 247
$PdH(CF_3COO)(P\text{-}t\text{-}Bu_3)_2$	benzene/*n*-hexane	97–99	46.10	8.78		Pd–H –18.3 t	4.3	–67.8	ν(Pd–H) 2190
			(46.15)	(8.81)		*t*-Bu 1.38 t	12.5		ν(CO) 1690
$PdCl(CH_2C_3H_6P\text{-}t\text{-}Bu_2)(P\text{-}t\text{-}Bu_3)$	cold *n*-hexane	142	43.95	9.75	6.68	*t*-Bu_3 1.35 d	12.2	+11.8	ν(Pd–Cl) 250
						CMe_2 1.46 d	13.8	–61.8	
			(44.08)	(9.73)	(6.52)	*t*-Bu_2 1.56 d	14.0		
						CH_2 "F"[f]			
$Pd(CF_3COO)(CH_2C_3H_6P\text{-}t\text{-}Bu_2)(P\text{-}t\text{-}Bu_3)$	cold *n*-hexane	115	46.38	8.30		*t*-Bu_3 1.28 d	12.2	+13.8	ν(CO) 1695
						CMe_2 1.38 d	15.0	–63.9	
			(46.30)	(8.36)		*t*-Bu_2 1.45 d	14.6		
						CH_2 "F"[f]			
$Pd_2Cl_2(CH_2C_3H_6P\text{-}t\text{-}Bu_2)(P\text{-}t\text{-}Bu_3)$	benzene/*n*-hexane	172–173	41.96	7.67	10.41	CMe_2 1.25 d	13.8	+12.8	
			(42.04)	7.59	(10.36)	*t*-Bu 1.42 d	14.0		
						CH_2 "F"[f]			
$Pd_2(CF_3COO)_2(CH_2C_3H_6P\text{-}t\text{-}Bu_2)_2$	benzene/*n*-hexane	161	34.35	6.21		CMe_2 1.24 d	15.0	+13.0	ν(CO) 1696
			(34.29)	(6.19)		*t*-Bu 1.40 d	14.6		
						CH_2 "F"[f]			

[a] All complexes are light pale yellow colored crystalline solids except $PdH(Cl)(P\text{-}t\text{-}Bu_3)_2$ which is white solid. Yields of the complexes are over 80%. [b] dec = decomposition temperature. [c] Values reported are relative to Me_4Si. All spectra were obtained in benzene-d_6 except the complex $Pd_2(CF_3COO)_2(CH_2C_3H_6P\text{-}t\text{-}Bu_2)_2$ which was obtained in $CDCl_3$. [d] Key: d = doublet; t = triplet. [e] Relative to 85% H_3PO_4. [f] "F" = methylene signals could not be detected due to other strong signals in the same region.

Scheme I[a]



[a] Key to reaction conditions: (i) sodium naphthalenide, $NaC_{10}H_8$, reaction in THF at 20 °C; (ii) reaction in CH_2Cl_2 for ~2 h; (iii) HCl reaction in benzene or n-hexane; (iv) $NaBH_4$ reduction in C_2H_5OH; (v) BuLi reaction in n-hexane; (vi) metalation in benzene solution; (vii) $NaBH_4$ reduction in C_2H_6OH; (viii and ix) in CH_2Cl_2 or benzene in the presence of alcohol; (x) AgX; (xi) tertiary phosphines, PR_3, = PEt_3, PPh_3, PPh_2Me, P-i-Pr_3, PCy_3, P-t-Bu_2Me, P(o-tolyl)$_3$; (xii) pyridine; (xiii) triphenylarsine.

δ 1.45 (P-t-Bu_2), and δ 1.38 (P–CMe_2), in the ratio 9:6:2, with J(P–C–C–H) = 12.2, 14.6, and 15.0 Hz, respectively (Table I). The proton signals of the C–CH_2–Pd group could not be observed and are probably masked by other strong signals. The ^{31}P NMR spectrum in benzene shows two singlets at δ +13.8 (due to metalated phosphine) and δ −63.9 (due to unmetalated phosphine) (Table I). These complexes (II) do not show coupling between the two phosphorus nuclei, which may suggest that the coordinated phosphine in the complexes is labile.[6]

These complexes (II) are soluble in hexane and could be crystallized from cold hexane. Interestingly, when these complexes were allowed to stand in a mixture of benzene/hexane for 1 day, loss of 1 equiv of P-t-Bu_3 occurred (followed by NMR), followed by rearrangement to give halogeno- or acetato-bridged dimeric complexes Pd_2X_2(P-t-$Bu_2CMe_2CH_2$)$_2$ (III) (eq 4).

$$\underset{\text{II}}{2\text{PdX(P-}t\text{-Bu}_2\text{CMe}_2\text{CH}_2\text{)(P-}t\text{-Bu}_3\text{)}} \rightleftharpoons \underset{\text{III}}{\text{Pd}_2\text{X}_2\text{(P-}t\text{-Bu}_2\text{CMe}_2\text{CH}_2\text{)}_2} + 2\text{P-}t\text{-Bu}_3 \quad (4)$$

$$X = Cl, CF_3COO$$

This reaction is the reverse of the bridge splitting reactions reported earlier by Shaw and co-workers[3,9] for several other bridged complexes of platinum and palladium. The proton NMR spectra of complexes III invariably show three sets of doublets due to protons of Pd–P-t-Bu_2, P–CMe_2, and C–CH_2–Pd groups in a 9:3:1 ratio. The ^{31}P NMR spectra contain only one singlet at about δ +13 indicative of metalated phosphine (Table I).

Shaw has suggested that the intramolecular metalation process in complexes $MX_2(PR_3)_2$ (M = Pd, Pt) involves oxidative addition of 2C–H or 3C–H to the metal, followed by elimination of hydrogen halide. The acidic nature of 2C–H in the phosphine has been demonstrated by Kiffen et al.,[10] who have reported that complexes of the type $Pt_2Cl_4L_2$ (L = n-Bu_3P, n-Pr_3P, and t-Bu_2-n-PrP) undergo hydrogen–deuterium exchange at the C-3 position of n-butyl or n-propyl groups and also at the C-2 position of the *tert*-butyl groups. Otsuka et al.,[8] in their structure determination of Pd(P-t-Bu_2Ph)$_2$, have observed a short distance (2.70 Å) between Pd and the hydrogen of the *tert*-butyl group. They infer an interaction between Pd and the hydrogen of the *tert*-butylphosphine. Such an interaction is probably also present in $PdHCl$(P-t-Bu_3)$_2$ which contains the more bulky P-t-Bu_3 ligand. Moreover, the occurrence of such an interaction combined with the presence of the hydridic ligand[11] and with the steric crowding about Pd suggests that intramolecular metalation may well occur as a consequence of the direct facile elimination of molecular hydrogen rather than by oxidative addition of C–H to Pd–H followed by H_2 elimination.

The conversion of complexes II into the dimeric bridged complexes III is presumably a consequence of the steric crowding at Pd in II, resulting from the presence of both the bidentate, metalated phosphine ligand and the monodentate tertiary phosphine or arsine ligand. Dissociation of the monodentate ligand relieves the steric crowding and gives the more stable III.

Bridge-Splitting Reactions of the Complex $[Pd_2Cl_2(P\text{-}C)_2]$ (III), Where (P-C) = $CH_2C_3H_6P$-t-Bu_2

The chlorine bridges of the binuclear compound III are readily cleaved by various ligands to give the mononuclear complexes [Pd(Cl)(P-C)L] (IV). Similar bridge-splitting reactions of other halogen-bridged binuclear platinum(II) and palladium(II) complexes have previously been reported.[3,12-14] The present reactions are summarized in Scheme I, and analytical, ^1H NMR, and ^{31}P NMR data are given in Table II.

Complex IV with L = pyridine shows, in its infrared spectrum, a band due to ν(Pd–Cl) at ~280 cm^{-1} indicative of *trans*-[PdCl(P-C)py].[3] Its proton NMR spectrum shows three sets of sharp doublets at δ 1.52, 1.44, and 0.95 ppm in ratios 9:3:1 due to t-Bu_2–P, C–Me_2, and C–CH_2–Pd (J(P–H) = 14.0, 13.8, and 4.0 Hz, respectively). The ^{31}P NMR spectrum also shows only one singlet at δ +13.1 ppm which supports the presence of only one isomer.

The addition of a tertiary phosphine, R_3P (where R_3P = Et_3P, Ph_3P, Ph_2MeP, i-Pr_3P, Cy_3P, t-Bu_2MeP, or $(C_7H_7)_3P$), to a solution of $[Pd_2Cl_2(P\text{-}C)_2]$ in benzene also gave complex IV with a trans configuration. This geometry is indicated by the ^{31}P NMR spectra (Table II) which show two doublets due to each nonequivalent phosphorus nucleus, with a large coupling constant ^2J(P–P′) (402–440 Hz) characteristic of mutually trans phosphorus atoms.[3] For example, the ^{31}P NMR spectrum of the complex [PdCl(P-C)(Ph_3P)] shows two sets of doublets at δ +19.6 ppm (due to metalated phosphorus) and δ −19.2 ppm (due to unmetalated P of Ph_3P) with ^2J(P–P′) = 422 Hz. The ^1H NMR spectral parameters for these complexes [PdCl(P-C)(R_3P)] (IV) are given in Table II. The signals due to di-*tert*-butyl protons are observed as a double doublet due to splitting by both phosphorus nuclei. For example, the spectrum of complex IV (R_3P = Ph_3P) shows a double doublet due to the *tert*-butyl group at δ 1.64 ppm with ^3J(P–H) = 12.8 Hz and ^5J(P–H) = 1.1 Hz. However, the methyl protons (P–CMe_2) show only one doublet at δ 1.34 ("J" = ^3J(P–H) + ^5J(P–H) = 12.5). The methylene protons

Table II. Crystallization, Elemental Analysis, and Proton and ^{31}P NMR Data of Complexes PdCl(P-C)L (Where (P-C) = *t*-Bu$_2$PCMe$_2$CH$_2$)

Complex PdCl(P-C)L where L =	Solvent of Crystallization	Melting Point °C	Analysis(%) found (calc)			^{31}P N.M.R. Data^k			^{1}H N.M.R. Data^N							
									Signals due to [CH$_2$C(Me)$_2$PBu$^t_2$]							Signals due to Ligand (L)
			C	H	Cl	Metalated Phosphine, P, (δppm)	Ligated unmetalated Phosphine P' (δppm)	J(P-P') (Hz)	t-butyl (P-Bu$^t_2$)			dimethyl[P-C(Me)$_2$		Methylene(P-C-CH$_2$Pd)		
--	--	--	--	--	--	--	--	--	Bu^t(δ) (ppm)	^{3}J(P-H) or 'J'(P-H) (Hz)	^{5}J(P-H) (Hz)	Me (δppm)	^{3}J(P-H) or 'J'(P-H) (Hz)	CH$_2$ (δppm)	J(P-H) (Hz)	(δ) and J(P-H) (Hz)
Et$_3$P	benzene/hexane	90	46.92 (46.90)	8.85 (8.90)	7.80 (7.71)	+14.1	-14.1	441	1.68(dd)	11.5	1.7	1.50(d)	12.0	'F'	--	Et$_3$P: Et = 0.87-1.57(m) J(P-H) = 6Hz
Ph$_3$P	benzene/hexane	165^c	59.43 (59.55)	6.92 (6.80)	6.03 (5.88)	+19.6	-19.2	422	1.64(dd)	12.8	1.1	1.34(d)	12.5	0.71(t)	11.8	Ph$_3$P: Ph=8.3-7.8(m); 7.5-7.1(m)
Ph$_2$MeP	benzene/pentane	160^e	55.19 (55.30)	7.24 (7.19)	6.62 (6.54)	+18.0	- 7.2	440	1.62(dd)	11.3	2.1	1.30(dd)	^{3}J(P-H) 11.9 ^{5}J(P-H) 2.1	0.60(t)	13.6	Ph$_2$MeP: Ph=7.62-7.42(m) Me=1.98(t); ^{2}J(P-H)=7; ^{4}J(P-H)=6.5
Bu$^t_2$MeP	benzene/hexane	168-170^c	50.23 (50.15)	9.46 (9.35)	7.09 (7.06)	+17.1	-27.3	413	1.51(dd)	12.7	1.0	1.36(d)	12.2	0.83(dd)	J(P-H) 5.5 J(P'-H) 5.0	Bu$^t_2$MeP: Bu^t=1.31(dd) ^{3}J(P-H)=12.2; ^{5}J(P-H)=1.0 Me =0.78(t) 'J'(P-H)=13.1
Pr$^i_3$P*	benzene/hexane	148-150^c	50.20 (50.15)	9.42 (9.35)	7.04 (7.06)	+13.8	-35.3	403	1.52(dd)	12.5	0.7	1.40(d)	12.4	0.92(d) 0.80(d)	J(P-H) 5.4 J(P-H) 5.0	Pr$^i_3$: (CH$_3$)$_2$C = 1.18(d)J(P-H)=14.3; 1.23(d)J(P'-H)=13.2 CH = 2.2(m&b)
Cy$_3$P	cold hexane	170-73^c	57.90 (57.83)	9.46 (9.48)	5.82 (5.70)	+14.5	-25.3	409	1.59(d)	'J' 12.2	--	1.50	12.5	1.04(d) 0.95	^{3}J(P-H) 5.6 ^{3}J(P'-H) 5.0	Cy$_3$P: Cy=1.0-2.5(b)
C$_7$H$_7$P	cold hexane	144	64.85 (64.81)	7.71 (7.69)	5.86 (5.81)	+16.4	-20.3	413	1.57(d)	'J' 12.8	--	1.42(d)	12.9	0.60(t)	'J'=12.5	(C$_7$H$_7$)P: Ph=7.1(m); 8.0(m) CH$_3$=2.48(s)
Ph$_3$As$^{(\dagger)}$	benzene/hexane	150-153^c	55.26 (55.51)	6.37 (6.32)	5.52 (5.47)	+16.2	--	--	1.40(d)	'J' 14.0	--	1.24(d)	14.2	'F'	--	Ph$_3$As: Ph=7.7-7.2(m)
Py(C$_5$H$_5$N)$^{*(\dagger)}$	benzene/pentane	162-64^e	39.20 (39.11)	6.02 (5.94)	Cl= 6.91 (6.80) N = 2.71 (2.68)	+13.1	--	--	1.52(d)	'J' 14.0	--	1.44(d)	13.8	0.95(d)	J(P-H) 4.0	Py(C$_5$H$_5$N): N-(CH$_2$=8.75(b) 3&5CH=7.17(b) 4CH=7.5(b)

a - All complexes are white crystalline solids; b = broad; c = melts with decomposition; d = doublet; dd = doublet of doublets; e = decomposed.

F = Signals could not be detected due to strong signals of the other groups; t = triplet; s = singlet; m = multiplet.

Me = Methyl; Et = ethyl; Ph = Phenyl; Pr^i = isopropyl; Bu^t = t-butyl; Py = pyridine; Cy = Cyclohexyl; 'J' = 3J(P-H) + ^{5}J(P-H).

K = Relative to 85% H$_3$PO$_4$; spectra were recorded in benzene except the complexes * which were recorded in CDCl$_3$.

N = Spectra recorded at ca 35°C and 60 MHz; Spectra were recorded in C$_6$D$_6$ except the complexes (†) which were recorded in CDCl$_3$.

(C–CH$_2$–Pd) are observed as a triplet due to the splitting by both phosphorus nuclei at δ 0.71 with J(P–H) = 11.8 Hz.

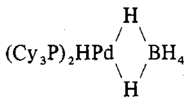
For complex IV with L = AsPh$_3$ the ^{31}P NMR spectrum shows a strong singlet at δ +16.2 ppm and a weaker singlet at δ +12.7 ppm. The former is due to the metalated phosphorus of the pure complex and the weak singlet at δ –12.7 ppm is due to dimeric [Pd$_2$Cl$_2$(P-C)$_2$] suggesting that the complex dissociates in solution (eq 5). This dissociation is

$$2[\mathrm{PdCl(P\text{-}C)(Ph_3As)}] \rightleftharpoons [\mathrm{Pd_2Cl_2(P\text{-}C)_2}] + 2\mathrm{Ph_3As} \qquad (5)$$

not observed in the tertiary phosphine complexes. This may be due to the weaker coordination tendency of the arsine compared with that of a phosphine. No complex formation was observed when a mixture of Ph$_3$Sb was added to a benzene or CH$_2$Cl$_2$ solution of [Pd$_2$Cl$_2$(P-C)$_2$]. The ^{31}P NMR spectrum of the resulting solution at various temperatures from –60 to +60 °C showed the presence of only unreacted [Pd$_2$Cl$_2$(P-C)$_2$]. Similarly, no complex of the type [PdCl(P-C)(CO)] could be obtained by bubbling carbon monoxide into a solution of complex IV in benzene.

The stability of complexes IV, obtained by the bridge-splitting reactions of III with tertiary phosphines, depends on the size of the tertiary phosphine and follows the trend Et$_3$P $\sim$ Ph$_2$MeP $\sim$ Ph$_3$P > i-Pr$_3$P > Cy$_3$P $\sim$ t-Bu$_2$Me > t-Bu$_3$P. Thus, compared to complexes PdCl(P-C)(L) (where L = Et$_3$P, Ph$_2$MeP, Ph$_3$P), which are quite stable in the solid state as well as in solution, the complexes of IV (L = Cy$_3$P, t-Bu$_2$Me, or t-Bu$_3$P) are less stable and tend to dissociate in solution, giving the starting dimeric complex III over 1–5 days. These observations support our earlier statement that the conversion of the complex PdCl(P-C)(P-t-Bu$_3$) (II) to Pd$_2$Cl$_2$(P-C)$_2$ is driven by the steric crowding at Pd in II, which is relieved by dissociation of the bulky P-t-Bu$_3$ ligand.

In the reaction of sodium borohydride with PtH(Cl)(P-t-Bu$_3$)$_2$, we have observed the formation of the stable dihydridoplatinum complex PtH$_2$(P-t-Bu$_3$)$_2$[15] (V). However, in the reaction of PdH(Cl)(PCy$_3$)$_2$ with NaBH$_4$, Green et al.[16] obtained the borohydride complex



VI

In an effort to prepare an analogous complex of type V or VI, we attempted the reduction of PdH(Cl)(P-t-Bu$_3$)$_2$ with NaBH$_4$ in ethanol but found, surprisingly, that the palladium(0) complex Pd(P-t-Bu$_3$)$_2$ is obtained.

$$\mathrm{PdH(Cl)(P\text{-}}t\mathrm{\text{-}Bu_3)_2} + \mathrm{NaBH_4} \xrightarrow{\text{ethanol}} \mathrm{Pd(P\text{-}}t\mathrm{\text{-}Bu_3)_2} + \mathrm{NaCl}$$

Similarly, in the reaction of PdCl(P-t-Bu$_2$CMe$_2$CH$_2$)(P-t-Bu$_3$) (II) with NaBH$_4$, Pd(P-t-Bu$_3$)$_2$ is also obtained, although the similar reaction of the platinum analogue produced PtH$_2$(P-t-Bu$_3$)$_2$ and PtH(P-t-Bu$_2$CMe$_2$CH$_2$)(P-t-Bu$_3$).[17] Palladium analogues of V and VI may be transient products of the above reactions but then undergo reductive elimination to give the stable zerovalent palladium product. In support of this, we have observed that when n-butyllithium is allowed to react with a solution of PdH(Cl)(t-Bu$_3$)$_2$ in n-hexane, the only stable product was bis(tri-*tert*-butylphosphine)palladium(0), Pd(P-t-Bu$_3$)$_2$, and not the expected PdH(n-Bu)(P-t-Bu$_3$)$_2$. The same zerovalent palladium complex was also obtained in low yield in the reaction of the dimeric complex III with NaBH$_4$.

Experimental Section

Reactions involving tri-*tert*-butylphosphine and the oxidative reactions of (t-Bu$_3$P)$_2$Pd^0 with acids were carried out under nitrogen at room temperature. However, other manipulations such as purifications were carried out under open conditions. Tetrahydrofuran (THF) was dried and distilled over NaAlH$_4$; other solvents used were of spectroanalytical grade and used without further purification. (Benzonitrile)palladium(II) dichloride, PdCl$_2$(NCPh)$_2$,[18] and allylpalladium(II) cyclopentadiene, (η^3-C$_3$H$_5$)Pd(η^5-C$_5$H$_5$),[19] were prepared as reported earlier. Bis(tri-*tert*-butylphosphine)palladium, (t-Bu$_3$P)$_2$Pd, was prepared by the reaction of t-Bu$_3$P with allylpalladium(II) cyclopentadiene in hexane at room temperature.[8]

Elemental analyses were performed by M.H.W. Laboratories, Phoenix, Ariz. Proton NMR spectra were recorded on a Varian A-60 or a Bruker HFX-90 Fourier transform spectrometer. ^{31}P NMR spectra were recorded on a Bruker PW-60 Fourier transform spectrometer. Phosphoric acid (85%) was used as external standard; those ^{31}P chemical shifts to high field (low frequency) are reported as positive. Infrared spectra were obtained on a Beckman IR-12 spectrophotometer. Melting points were determined with a Gallenkamp melting point apparatus in glass capillary tubes.

Physical, analytical, and spectroscopic data are given in Table I.

Preparation of (t-Bu$_3$P)Pd^0 from the Reaction of PdCl$_2$(NCPh)$_2$ with Sodium Naphthalenide in THF. To a well-stirred slurry of PdCl$_2$(NCPh)$_2$ (6.0 mmol) and t-Bu$_3$P (12 mmol) in THF (20 mL) was added dropwise a solution of sodium naphthalenide (12.0 mmol) in THF (10 mL) under nitrogen. The reaction mixture was stirred at room temperature for $\sim$30 min and the solvent was removed in vacuo. The residue was extracted with 50 mL of n-hexane and filtered under nitrogen. The complex (t-Bu$_3$P)$_2$Pd^0 was crystallized in $\sim$70% yield upon cooling the concentrated solution. Anal. Calcd for (t-Bu$_3$P)$_2$Pd: C, 56.4; H, 10.67. Found: C, 56.5; H, 10.71. The proton NMR spectrum shows a triplet at δ 1.51 ppm due to *tert*-butyl protons with J(P–H) = 12.0 Hz.

Oxidative Addition of Protic Acids HX (X = Cl or CF$_3$COO) to P(t-Bu$_3$P)$_2$Pd^0. To a solution of (t-Bu$_3$P)$_2$Pd^0 (2 mmol) in hexane ($\sim$50 mL) was added slowly with continuous stirring a solution of hydrogen chloride prepared by the reaction of acetyl chloride (2 mmol) with methanol. The reaction mixture was stirred for $\sim$15 min and the solvent was removed in vacuo; *trans*-PdH(Cl)(t-Bu$_3$P)$_2$ was obtained as colorless crystals in almost quantitative yield.

trans-PdH(CF$_3$COO)(t-Bu$_3$P)$_2$ was prepared similarly by the reaction of CF$_3$COOH with the palladium(0) complex. Analyses and spectroscopic data are given in Table I.

Metalation Reactions of Complexes PdH(X)(t-Bu$_3$P)$_2$ (X = Cl or CF$_3$COO) in Benzene. The internal metalation of the complexes was followed by recording the ^{1}H NMR spectra of the solutions at various time intervals, at room temperature. When the metalation was complete, the solution was transferred into a flask, benzene was removed, and the resulting pale yellow solid was extracted with hexane to give light, pale yellow crystals on cooling. The analytical data for these crystals corresponded to the formula PdX(CH$_2$C$_3$H$_6$P-t-Bu$_2$)(P-t-Bu$_3$). The complete conversion of the complexes PdH(X)(t-Bu$_3$P)$_2$ into the corresponding PdX(CH$_2$C$_3$H$_6$P-t-Bu$_2$)(t-Bu$_3$P) took place over 5 days and 1 week, respectively, for X = chloride and trifluoroacetate. Figure 1 shows the ^{1}H NMR spectra for the metalation reaction of PdH(Cl)(t-Bu$_3$P)$_2$ at different time intervals in benzene.

Preparation of PdX(CH$_2$C$_3$H$_6$P-t-Bu$_2$)(t-Bu$_3$P). In a typical reaction, to a solution of PdH(Cl)(t-Bu$_3$P)$_2$ (1 mmol) in benzene ($\sim$25 mL) was added a few drops of ethanol. The colorless solution turned yellow immediately. After 30 min the solvent was removed under reduced pressure and the residue obtained was extracted with hexane. The extract on drying gave a pale yellow crystalline solid. The ^{1}H NMR spectrum and analyses of this product showed it to be PdCl(CH$_2$C$_3$H$_6$P-t-Bu$_2$)(t-Bu$_3$P).

The complex Pd(CF$_3$COO)(CH$_2$C$_3$H$_6$P-t-Bu$_2$)(t-Bu$_3$P) was obtained similarly from its hydride in 2–3 h under similar conditions.

Preparation of [Pd$_2$X$_2$(CH$_2$C$_3$H$_6$P-t-Bu$_2$)$_2$] (X = Cl or CF$_3$COO). (A) From [PdX(CH$_2$C$_3$H$_6$P-t-Bu)$_2$(t-Bu$_3$P)]. In a typical reaction, a solution of [PdCl(CH$_2$C$_3$H$_6$P-t-Bu$_2$)(t-Bu$_3$P)] (2 mmol) in a mixture of benzene and n-hexane was left overnight for slow crystallization. The unmetalated phosphine was cleaved and the resulting pale yellow crystals were identified as Pd$_2$Cl$_2$(CH$_2$C$_3$H$_6$P-t-Bu$_2$)$_2$. Other complexes were obtained similarly.

(B) By the Reaction of t-Bu$_3$P with (PhCN)$_2$PdCl$_2$ in CH$_2$Cl$_2$. To a solution of (PhCN)$_2$PdCl$_2$ (2 mmol) in CH$_2$Cl$_2$ ($\sim$40 mL) was added slowly t-Bu$_3$P (2 mmol) with continuous stirring. The reaction mixture was further stirred for $\sim$2 h, during which the color turned dark brown-red. The solvent was removed and the blackish mass obtained was extracted with benzene. The complex was crystallized from a benzene/*n*-hexane mixture to give pale yellow crystals identified as $[Pd_2Cl_2(CH_2C_3H_6P\text{-}t\text{-}Bu_2)_2]$.

Preparation of $[PdCl(CH_2C_3H_6P\text{-}t\text{-}Bu_2)(L)]$ (L = PEt_3, PPh_3, PCy_3, PPh_2Me, *t*-PBu_2Me, $P(o\text{-}CH_3C_6H_4)_3$ *i*-PPr_3, and $AsPh_3$). In a typical reaction to a solution of $[Pd_2Cl_2(CH_2C_3H_6P\text{-}t\text{-}Bu_2)_2]$ (0.2 mmol) was added PPh_3 (0.4 mmol) and the reaction mixture was stirred overnight. Benzene was removed, and the white solid was crystallized from a benzene/*n*-hexane mixture.

All other complexes were prepared similarly. Physical, analytical and spectroscopic data are given in Table II.

Reaction of $[Pd_2Cl_2(CH_2C_3H_6P\text{-}t\text{-}Bu_2)_2]$ with Pyridine. To a solution of $[Pd_2Cl_2(CH_2C_3H_6P\text{-}t\text{-}Bu_2)_2]$ (0.15 mmol) in benzene was added pyridine (0.45 mmol) and the reaction mixture was refluxed for ~2 h. The solvent was removed in vacuo, and the white solid was crystallized from a benzene/*n*-pentane mixture.

Reaction of $NaBH_4$ with $PdH(Cl)(t\text{-}Bu_3P)_2$ (I), $PdCl(P\text{-}C)(P\text{-}t\text{-}Bu_3)$ (III), and $[Pd_2Cl_2(P\text{-}C)_2]$ (III) [(P-C) = *t*-$Bu_2PCMe_2CH_2$]. To a solution of $PdH(Cl)(t\text{-}Bu_3P)_2$ (I) (1.0 mmol) in dried ethanol was added excess of $NaBH_4$ (5.0 mmol) and the reaction mixture was stirred for ~2 h. The ethanol was removed under reduced pressure and the residue was extracted with *n*-hexane. On cooling of the *n*-hexane solution, white crystals were obtained in 65% yield. Physical, analytical, and spectroscopic data for this product showed it to be $(t\text{-}Bu_3P)_2Pd^0$.

Similarly, the reaction of $NaBH_4$ with $PdCl(P\text{-}C)(t\text{-}Bu_3P)$ (II) or $[Pd_2Cl_2(P\text{-}C)_2]$ (II) gave the complex $(t\text{-}Bu_3P)_2Pd^0$ in 62 and 30% yields, respectively.

Reaction of $PdH(Cl)(t\text{-}Bu_3P)_2$ with BuLi. To a suspension of $PdH(Cl)(t\text{-}Bu_3P)_2$ (1.0 mmol) in dry *n*-hexane (30 mL) was slowly added a solution of *n*-BuLi (1.1 mmol) in *n*-hexane with continuous stirring. The reaction mixture was stirred overnight and the contents were filtered. The filtrate was concentrated and cooled, and the white crystals thus obtained were identified as $(t\text{-}Bu_3P)_2Pd^0$.

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Registry No. *trans*-$PdH(Cl)(t\text{-}Bu_3P)_2$, 63166-71-2; *trans*-$PdH(CF_3COO)(t\text{-}Bu_3P)_2$, 62922-33-2; $PdCl(P\text{-}C)(t\text{-}Bu_3P)$, 63230-80-8; $Pd(CF_3COO)(P\text{-}C)(t\text{-}Bu_3P)$, 69721-10-4; $Pd_2Cl_2(P\text{-}C)_2$, 69393-58-4; $Pd_2(CF_3COO)_2(P\text{-}C)_2$, 69796-89-0; $PdCl(P\text{-}C)(Et_3P)$, 71000-98-1; $PdCl(P\text{-}C)(Ph_3P)$, 71000-99-2; $PdCl(P\text{-}C)(Ph_2MeP)$, 71001-00-8; $PdCl(P\text{-}C)(t\text{-}Bu_2MeP)$, 71031-53-3; $PdCl(P\text{-}C)(i\text{-}Pr_3P)$, 71001-01-9; $PdCl(P\text{-}C)(Cy_3P)$, 71001-02-0; $PdCl(P\text{-}C)((C_7H_7)P_3)$, 71001-03-1; $PdCl(P\text{-}C)(Ph_3As)$, 71001-04-2; $PdCl(P\text{-}C)(py)$, 71001-05-3; $PdCl_2(NCPh)_2$, 14873-63-3; $(t\text{-}Bu_3P)_2Pd$, 53199-31-8; HCl, 7647-01-0; CF_3COOH, 76-05-1.

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Contribution from The Donnan Laboratories, Liverpool University, Liverpool L69 3BX, United Kingdom,
and The Department of Inorganic Chemistry, Oxford University, Oxford OX1 3QR, United Kingdom

Synthesis and Characterization of Bis[μ-[bis(diphenylphosphino)methane]]-μ-methylene-dichlorodiplatinum and Related Complexes. Insertion of Methylene into a Pt–Pt Bond

MICHAEL P. BROWN,*[1a] JOHN R. FISHER,[1a] RICHARD J. PUDDEPHATT,[1a,c] and KENNETH R. SEDDON[1b]

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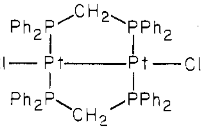
Reaction of the diplatinum(I) complex $[Pt_2Cl_2(\mu\text{-dppm})_2]$, dppm = bis(diphenylphosphino)methane, with CH_2N_2, SO_2, and S_8 gives the adducts $[Pt_2Cl_2(\mu\text{-}X)(\mu\text{-dppm})_2]$ where X = CH_2, SO_2, or S, respectively. Where X = CH_2, this represents the first example of simple addition of methylene to a metal–metal bond. Reaction of $[Pt_2H_2(\mu\text{-}H)(\mu\text{-dppm})_2][PF_6]$ with MeSH gives $[Pt_2H_2(\mu\text{-SMe})(\mu\text{-dppm})_2][PF_6]$. The structures of the complexes were deduced primarily with ^1H and ^{31}P NMR spectroscopy, and it is concluded that Pt–Pt bonding is absent or very weak in all cases.

Introduction

Recently we have shown that platinum, when complexed with bis(diphenylphosphino)methane (dppm), readily forms a number of binuclear complexes in which the ligand adopts a bridging role.[2-5] An example is $[Pt_2Cl_2(\mu\text{-dppm})_2]$ (I), an air-stable complex containing two directly bonded platinum atoms in the formal oxidation state of I.[2,3]



I

The platinum–platinum bond in this complex may, as we have previously shown, be reversibly protonated[4] or undergo reversible addition of carbon monoxide[3,5] to give complexes in which the added group, viz., H^+ or CO, bridges the two platinum atoms. The related ligand bis(diphenylarsino)methane (dpam) also gives a similar platinum–carbonyl complex, namely, $[Pt_2Cl_2(\mu\text{-CO})(\mu\text{-dpam})_2]$, although the dpam analogue of I is unknown.[5] The ability of dppm and similar ligands to promote the formation of binuclear complexes by bridging two atoms rather than chelating to one is demonstrated by the chemistries of other metals. Indeed, recent publications show that a concurrent and independent investigation of palladium gave remarkably similar results. Thus X-ray structural studies show that $[Pd_2Br_2(\mu\text{-dppm})_2]$[6,7]

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