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Registry No. 1a, 77818-75-8; **1b**, 81434-76-6; **1c**, 81434-77-7; **1d**, 81434-78-8; **1e**, 81434-79-9; **1f**, 81434-80-2; **1g**, 81434-81-3; **1h**, 81434-82-4; **1i**, 81434-83-5; **1j**, 81434-84-6; **1k**, 81446-87-9; **1l**, 81434-85-7; **1m**, 81434-86-8; **1n**, 81434-87-9; **1o**, 81434-88-0; **2a**, 81434-90-4; **2b**, 81434-92-6; **2c**, 81434-94-8; **2d**, 81434-96-0; **2e**, 81434-98-2; **2f**, 81435-00-9; **2g**, 81446-89-1; **2h**, 81435-02-1; **2i**, 81435-04-3; **2j**, 81435-06-5; **2k**, 81435-08-7; **2l**, 81435-10-1; **2m**, 81435-12-3; **2n**, 81435-14-5; **2o**, 81435-16-7; **3**, 81435-18-9; **4a**, 81435-19-0; **4b**, 81435-20-3; **4c**, 81435-21-4; **4d**, 81446-90-4; **4e**, 81456-85-2; **4f**, 81435-22-5; **4g**, 81435-23-6; **6**, 81435-25-8; **7**, 81456-88-4; **8**, 70236-70-3; **9**, 81435-26-9; $Me_3O^+PF_6^-$, 12116-05-1; $BF_3{\cdot}OEt_2$, 109-63-7; $PhCO^+SbF_6^-$, 5609-80-3; trifluoromethanesulfonic anhydride, 358-23-6.

Supplementary Material Available: Tabulations of observed and calculated structure amplitudes (Supplementary Table 1), anisotropic thermal parameters (Supplementary Table 2), and hydrogen positional and isotropic thermal parameters (Supplementary Table 3) (17 pages). Ordering information is given on any current masthead page.

Preparation, Characterization, and Some Reactions of Bis(tri-*tert*-butylphosphine)hydridoplatinum(II) Complexes

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Treatment of Pt[P(t-Bu)$_3$]$_2$ with protic acids, HX, affords the monohydrides *trans*-PtHX[P(t-Bu)$_3$]$_2$, **1a** (X = Cl), **1b** (X = Br), **1c** (X = I), and **1d** (X = O_2CCF_3). The chlorohydride **1a** is easily converted into the bromo, nitrato **1e** (X = ONO_2), and the cyano **1f** (X = CN) analogues by metathesis. The dihydride *trans*-PtH$_2$[P(t-Bu)$_3$]$_2$, **2**, is obtained from the treatment of **1a** with $NaBH_4$ in THF. The monohydrides **1a–e** undergo intramolecular metalation, at room temperature, to give the metalated complexes *trans*-PtX[P(t-Bu)$_2$CMe$_2$CH$_2$]P(t-Bu)$_3$, **3a** (X = Cl), **3b** (X = Br), **3c** (X = I), **3d** (X = O_2CCF_3), and **3e** (X = ONO_2). The complexes **3a–c** readily lose P(t-Bu)$_3$ to afford the dinuclear complexes [Pt(μ-X)-{P(t-Bu)$_2$CMe$_2$CH$_2$}]$_2$, **4a** (X = Cl), **4b** (X = Br), and **4c** (X = I). The cyanohydride **1f** and the dihydride **2** do not undergo intramolecular metalation. The hydrides **1a–e** undergo reductive elimination, in the presence of a base, to give Pt[P(t-Bu)$_3$]$_2$; **1f** and **2** are unaffected under similar conditions. The dihydride **2** is converted into **1a** upon treatment with HCl or CCl_4; **1c** is obtained upon treatment with I_2. Alcohol or phenols react with **2** to give dihydrogen and Pt[P(t-Bu)$_3$]$_2$; no reaction occurs with **1a** under similar conditions. The monohydrides **1a–e** react reversibly with CO to give *trans*-[PtH(CO){P(t-Bu)$_3$}$_2$]X, **5**, which can be isolated as salts with BF_4^- and PF_6^- as counteranions. The dihydride **2** reacts with CO and t-BuNC to afford Pt$_3$(CO)$_3$[P(t-Bu)$_3$]$_3$, **6**, and Pt$_3$[μ-CN(t-Bu)]$_3$[CN(t-Bu)]$_3$, **7**, respectively.

Introduction

In the course of our investigations[1-3] on reactions of tri-*tert*-butylphosphine with platinum(II) it was discovered that treatment of the phosphine with potassium tetrachloroplatinate(II) in alkaline ethanol affords the two-coordinate complex *trans*-Pt[P(t-Bu)$_3$]$_2$ in a very high yield. Although *trans*-Pt[P(t-Bu)$_3$]$_2$ had been prepared earlier[4] from the treatment of the phosphine with Pt(COD)$_2$[5] (COD = 1,5-cyclooctadiene), its chemical reactivity had remained unexplored. The discovery of the very facile synthesis of *trans*-Pt[P(t-Bu)$_3$]$_2$ enabled us to investigate its chemical reactivity toward a variety of substrates,[2,3] including protic acids. These investigations have shown that, contrary to the views of previous investigators,[4,6] *trans*-Pt[P(t-Bu)$_3$]$_2$ readily undergoes oxidative addition as well as ligand substitution reactions. Oxidative addition reactions of *trans*-Pt[P(t-Bu)$_3$]$_2$ with haloalkanes and iodine and its ligand substitution reaction with isocyanides and carbon monoxide have been reported recently.[3] Reactions of strong protic acids (HCl, HBr, HI, and CF_3CO_2H) with *trans*-Pt[P(t-Bu)$_3$]$_2$ and the characterization and some chemical reactions of the resulting hydridoplatinum(II) complexes are reported herein. A preliminary communication[7] on this work has appeared.

Platinum(II) hydrides have played an important role in the development of the chemistry of transition metal hydrides. Soon after the discovery[8] of the first stable platinum hydride *trans*-PtHCl(PEt$_3$)$_2$, there has been rapid development in the chemistry of transition metal hydrides.[9-17] Many monohydridoplatinum(II) complexes[18,19]

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Table I. Analytical and Molecular Weight Data for the Hydrido Complexes

compd	Mp,[a] °C	% C calcd	% C found	% H calcd	% H found	% X calcd	% X found	mol wt[b] calcd	mol wt[b] found
trans-$PtHCl[P(t\text{-}Bu)_3]_2$	215	45.32	45.40	8.65	8.61	5.59	5.60	636	630
trans-$PtHBr[P(t\text{-}Bu)_3]_2$	210	42.35	42.12	8.09	8.05	11.76	11.78	680	670
trans-$PtHI[P(t\text{-}Bu)_3]_2$	195	39.61	39.58	7.58	7.48	17.48	18.00	727	730
trans-$PtH(CF_3CO_2)[P(t\text{-}Bu)_3]_2$	167	43.76	43.56	7.71	7.70			713	702
trans-$PtHNO_3[P(t\text{-}Bu)_3]_2$[c]	190	43.49	43.25	8.38	8.20			663	656
trans-$PtHCN[P(t\text{-}Bu)_3]_2$[d]	230	47.90	47.84	8.86	8.80			627	615
trans-$PtH_2[P(t\text{-}Bu)_3]_2$	283	47.92	47.90	9.32	9.36			601	595

[a] Decomposition temperature. [b] In benzene; concentration range 10^{-2}–10^{-3} M. [c] % N: calcd, 2.11; found, 2.10. [d] % N: calcd, 2.24; found, 2.18

of the type *trans*-$PtHXL_2$, where X = an anionic ligand and L = tertiary phosphine or tertiary arsine, are now known. A few dihydridoplatinum(II) complexes, *trans*-PtH_2L_2 (L = bulky tertiary phosphine) have also been prepared[6,20–22] recently, but little has been known about their chemistry. Reactions of several platinum(II) monohydrides, *trans*-$PtHX[P(t\text{-}Bu)_3]_2$, **1**, as well as the dihydride *trans*-$PtH_2[P(t\text{-}Bu)_3]_2$, **2**, have been examined in the present work. Unlike the other platinum(II) monohydrides, the monohydrides **1a–e** undergo facile intramolecular metalation. After the completion of this work, platinum(II) hydride stabilized by tri-*tert*-butylarsine have also been prepared[23] in this laboratory.

Results and Discussion

Protic acids, HX (X = Cl, Br, I, O_2CCF_3), react readily with $Pt[P(t\text{-}Bu)_3]_2$ to give the monohydrides *trans*-$PtHX[P(t\text{-}Bu)_3]_2$, **1a** (X = Cl), **1b** (X = Br), **1c** (X = I), and **1d** (X = O_2CCF_3). Metathesis of **1a** with $AgNO_3$ and AgCN affords the nitrato **1e** (X = NO_3) and the cyano **1f** (X = CN) analogues, respectively. Complex **1a** also reacts with LiBr to give **1b**. The monohydrides **1** are readily converted to the dihydride *trans*-$PtH_2[P(t\text{-}Bu)_3]_2$, **2** by treatment with $NaBH_4$ in THF. A similar reaction in ethanol gives a mixture of **2** (90%) and $Pt[P(t\text{-}Bu)_3]_2$ (10%).

The monohydrides **1a–f** as well as the dihydride **2** are air-stable white crystalline solids which are very soluble in solvents such as hexane, benzene, and dichloromethane but only sparingly soluble in solvents such as ethanol. Analytical and molecular weight data for these compounds are given in Table I, and the characteristic infrared and ^1H and $^{31}P\{H\}$ NMR spectral data in Table II.

The trans configuration for all the hydrides is deduced from their ^1H NMR spectra which exhibited a 1:2:1 triplet[24] at ca. δ 1.50 attributable to the *tert*-butyl hydrogens and another 1:2:1 triplet upfield from Me_4Si attributable to the hydride hydrogens which are coupled to the two equivalent ^{31}P nuclei. In each case, the hydride triplet was accompanied by a pair of satellite triplets due to ^{195}Pt–^1H spin–spin coupling. The $^{31}P\{^1H\}$ NMR spectrum of each compound showed a main resonance (δ 73–101) and a pair of satellite resonances due to ^{195}Pt–^{31}P spin–spin coupling. A band of medium intensity at ca. 2250–2400 cm^{-1}, attributable to the Pt–H stretching frequency,[13,19,20] was observed in the infrared spectra of the compounds **1a–f**. The infrared spectra of **1d**, **1e**, and **1f** also showed characteristic bands due to the coordinated O_2CCF_3,[25] ONO_2,[26] and CN[27] ligands, respectively. The infrared spectrum of the dihydride **2** showed a strong band at 1820 cm^{-1} due to the antisymmetric Pt–H stretching frequency; the observation of only one Pt–H stretching frequency in the infrared is consistent with the proposed trans structure.

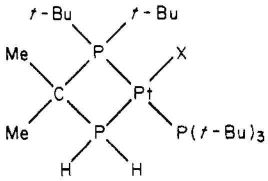

Figure 1.

The influence of the anionic ligand X on the Pt–H stretching frequency,[28] the hydride chemical shift,[29] and the magnitude of $^1J(^{195}Pt\text{–}^1H)$[29] and $^1J(^{195}Pt\text{–}^{31}P)$[30] has been investigated for the *trans*-$PtHX(PEt_3)_2$ complexes.[13,18] The results seem to indicate that the Pt–H stretching frequencies as well as the upfield hydride shifts for these complexes decrease with increasing trans influence of the ligand X. However, neither of these trends is evident for the tri-*tert*-butyl complexes for which the Pt–H stretching frequency decreases in the order Cl ≈ NO_3 > I > CF_3CO_2 > Br > CN, and the hydride chemical shift (upfield) in the order NO_3 > CF_3CO_2 > Cl > Br > I > CN. Furthermore, whereas the Pt–H stretching frequency for the tri-*tert*-butylphosphine complexes is ca. 150–200 cm^{-1} higher than that for the analogous triethylphosphine complexes, the hydride chemical shifts for the analogous compounds in the two series are not markedly different. The magnitude of ^1J(Pt–H) for the triethylphosphine complexes decrease in the order I > Br > NO_3 > Cl ≫ CN showing no simple dependence of ^1J(Pt–H) upon the trans influence of X. A similar situation is seen for the tri-*tert*-butylphosphine complexes. For complexes in both series, the magnitude of ^1J(Pt–P) appears to decrease with

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Table II. Infrared and ^{1}H and ^{31}P{^{1}H}NMR Data for the Hydrido Complexes

compd	$\nu_{\text{Pt-H}}$,[a] cm^{-1}	^{1}H NMR data[b] δ(Pt-H)	^2J(P-H), Hz	^1J(Pt-H), Hz	δ(*t*-Bu)	[^3J(P-H) + ^5J(P-H)], Hz	^{31}P{^{1}H}NMR data[c] δ	^1J(Pt-P), Hz
trans-PtHCl[P(*t*-Bu)$_3$]$_2$	2402 mw	−19.23 (t)	12.7	1070	1.52 (t)	12.7	75.0 76.5[d]	2952 2946
trans-PtHBr[P(*t*-Bu)$_3$]$_2$	2382 mw	−18.35 (t)	12.2	1100	1.55 (t)	12.2	75.4 76.9[d]	2932 2925
trans-PtHI[P(*t*-Bu)$_3$]$_2$	2396 mw	−16.36 (t)	11.6	1096	1.56 (t)	12.2	76.6	2903
trans-PtH(CF$_3$CO$_2$)[P(*t*-Bu)$_3$]$_2$[e]	2390 mw	−24.77 (t)	14.0	1105	1.38 (t)	12.4	79.0	3010
trans-PtHCN[P(*t*-Bu)$_3$]$_2$[f]	2250 m	−10.22 (t)	13.9	609	1.49 (t)	11.6	81.2	2808
trans-PtHNO$_3$[P(*t*-Bu)$_3$]$_2$[g]	2400 mw	−25.50 (t)	12.5	1155	1.39 (t)	12.5	79.3[d]	3001
trans-PtH$_2$[P(*t*-Bu)$_3$]$_2$	1820 s	−2.95 (t)	15.5	774	1.52 (t)	12.5	100.9	3003
trans-[PtH(CO){P(*t*-Bu)$_3$}$_2$]Cl		−5.30 (t)[h]	9.8	746	1.58 (t)	13.7	89.9[d]	2405
trans-[PtH(CO){P(*t*-Bu)$_3$}$_2$]Br		−5.27 (t)[h]	9.8	747	1.55 (t)	13.4	89.9[d]	2407
trans-[PtH(CO){P(*t*-Bu)$_3$}$_2$]CF$_3$CO$_2$		−5.70 (t)[h]	10.0	744	1.18 (t)	13.0	89.3[d]	2406
trans-[PtH(CO){P(*t*-Bu)$_3$}$_2$]NO$_3$		−5.30 (t)[h]	9.9	746	1.58 (t)	13.9	89.9[d]	2410

[a] For the solid state (Nujol mulls). [b] In C_6D_6. [c] In C_6H_6 containing 20% C_6D_6. [d] In CH_2Cl_2 containing 20% C_6D_6. [e] $\nu_{as}(CO_2)$ = 1680 s cm^{-1}. [f] ν(CN) = 2085 s cm^{-1}. [g] $\nu(NO_2)$ = 1450 s and 1275 s; ν(NO) = 1015ms. [h] In CD_2Cl_2.

Table III. Analytical and ^{1}H and ^{31}P{^{1}H} NMR Data[a] for the Internally Metalated Complexes[b]

	% C		% H		% X		^{1}H NMR data		^{31}P{^{1}H} NMR data		
	calcd	found	calcd	found	calcd	found	δ	^3J(P-H$_2$), Hz	δ	^2J(P-P′), Hz	^1J(Pt-P), Hz
PtCl(P-C)P(*t*-Bu)$_3$	45.44	45.50	8.43	8.51	5.88	6.01	1.48 (d) [P(*t*-Bu)$_3$] 1.56 (d) [P(*t*-Bu)$_2$] 1.62 (d) [Me$_2$]	12.7 11.5 12.4	66.8 −12.8	382	2680 2360
PtBr(P-C)P(*t*-Bu)$_3$	42.48	42.68	7.81	7.62	11.80	11.70	1.75 (d) [P(*t*-Bu)$_3$] 1.82 (d) [P(*t*-Bu)$_2$] 1.55 (d) [CMe$_2$]	12.0 12.5 13.5	69.4 −15.7	376	2717 2329
PtI(P-C)P(*t*-Bu)$_3$	39.72	39.58	7.31	7.29	17.51	17.85	1.45 (d) [P(*t*-Bu)$_3$] 1.53 (d) [P(*t*-Bu)$_2$] 1.64 (d) [CMe$_2$]	13.5 14.0 14.6	69.7 −16.3	372	2729 2314
Pt(CF$_3$CO$_2$)(P-C)P(*t*-Bu)$_3$	43.88	43.75	7.45	7.57			1.68 (d) [P(*t*-Bu)$_3$] 1.86 (d) [P(*t*-Bu)$_2$] 1.75 (d) [CMe$_2$]	10.5 12.5 12.0			
[PtNO$_3$(P-C)]P(*t*-Bu)$_3$							1.53 (d) [P(*t*-Bu)$_3$] 1.67 (d) [P(*t*-Bu)$_2$] 1.20 (d) [CMe$_2$]		68.4 0.6	364	2783 2441
[PtCl(P-C)]$_2$	33.40	33.36	6.03	6.03	8.23	8.22	1.50 (d) (*t*-Bu) 1.46 (d) [CMe$_2$] 1.40 (d) (CH$_2$)	13.8 14.4 13.0	−15.8 −16.2		3740 3760
[PtBr(P-C)]$_2$	30.25	30.15	5.46	5.40	17.01	17.59	1.53 (d) [*t*-Bu] 1.48 (d) [CMe$_2$] 1.45 (d) [CH$_2$]	13.9 14.5 13.0	−13.7		3920
[PtI(P-C)]$_2$	27.53	27.16	4.97	4.82	24.28	24.13	1.31 (d) [*t*-Bu] 1.26 (d) [CMe$_2$] 1.20 (d) [CH$_2$]	13.7 11.0 11.7	−10.7 −11.7		3558 3536

[a] Spectra were recorded in C_6H_6 containing 20% C_6D_6 at ambient temperature. [b] (P-C) = [P(*t*-Bu)$_2$CMe$_2$CH$_2$].

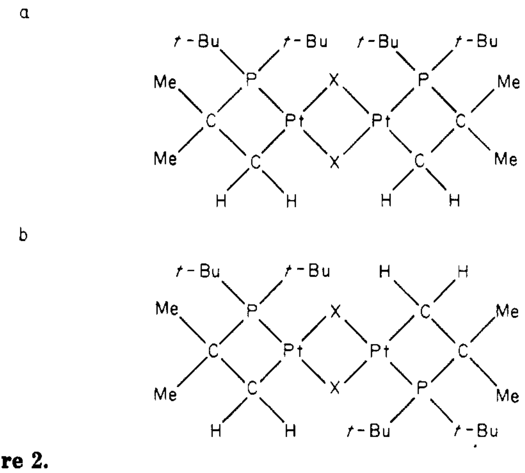

Figure 2.

increasing trans influence of X; the tri-*tert*-butylphosphine analogues have, however, significantly higher ^1J(Pt–P) values.

As expected, the Pt-H stretching frequency, upfield hydride chemical shift, and the magnitude of ^1J(Pt–H) for the dihydride **2** are appreciably lower than those for the monohydrides **1**. Trends in the antisymmetric Pt–H stretching frequency and the ^{1}H NMR parameters for **2** and other trans platinum(II) dihydrides[6,21,23] have been examined in a recent publication from this laboratory;[23] the study shows little correlation between the Pt–H stretching frequencies and the ^{1}H NMR parameters.

In marked contrast to the other platinum(II) hydrides, the monohydrides **1a–e** undergo intramolecular metalation in solution, at room temperature. Although recent work[1,2,31] in this laboratory has shown that tri-*tert*-butylphosphine is readily metalated upon treatment with platinum(II) chloride, intramolecular metalation of a phosphine ligand in a platinum(II) hydride has hitherto not been observed.

The complexes **1a–e** were quantitatively converted into the internally metalated complexes *trans*-PtX[P(*t*-Bu)$_2$CMe$_2$CH$_2$]P(*t*-Bu)$_3$, **3a** (X = Cl), **3b** (X = Br), **3c** (X = I), **3d** (X = O$_2$CCF$_3$), and **3e** (X = NO$_3$) (Figure 1), when their solutions in benzene or dichloromethane were kept at room temperature. The ease of metalation decreased in the order I > Br > Cl > O$_2$CCF$_3$ ≈ NO$_3$. For example, conversion of **1c** into **3c** was complete within 24 h whereas 2 weeks were required for complete conversion of **1d** to **3d**. Benzene solutions of the cyanohydride **1f** were unchanged when kept at room temperature for about a month or refluxed for 1 h. The loss of the hydride hydrogen from the monohydride upon intramolecular metalation was evident from the absence of the high-field resonance signal in the ^{1}H NMR spectra of the solutions and the Pt–H stretching frequency in the infrared spectra of the resulting solids. Thus, the intramolecular metalation involves the reaction represented by eq 1.

$$\textit{trans}\text{-PtHX[P(}t\text{-Bu)}_3]_2 \rightarrow \textit{trans}\text{-}\overline{\text{PtX[P(}t\text{-Bu)}_2\text{CMe}_2\text{C}}\text{H}_2]\text{P(}t\text{-Bu)}_3 + \text{H}_2 \quad (1)$$

Analytical and the ^{1}H and ^{31}P NMR spectral data for the metalated complexes **3a–e** are listed in Table III. Complex **3a** has been characterized unequivocally in a previous study.[1] The ^{1}H and ^{31}P NMR spectral data for **3a** listed in Table III are identical with those reported previously;[1] the ^{1}H and/or ^{31}P NMR spectral data for **3b–e** are similar to those for **3a**. Thus, all the five metalated complexes are indicated to be structurally similar.

It has been shown[31,32] that the complex **3a** can lose the coordinated P(*t*-Bu)$_3$ to give the chloro-bridged dinuclear metalated complex, **4a** (Figure 2), according to eq 2 (where X = Cl). The bromo and the iodo analogues **3b** and **3c** were also found to behave in a similar manner to give **4b** and **4c**.

$$2\,\textit{trans}\text{-}\overline{\text{PtX[P(}t\text{-Bu)}_2\text{CMe}_2\text{C}}\text{H}_2]\text{P(}t\text{-Bu)}_3 \rightarrow [\overline{\text{Pt(}\mu\text{-X)\{P(}t\text{-Bu)}_2\text{CMe}_2\text{C}}\text{H}_2\}]_2 + 2\text{P(}t\text{-Bu)}_3 \quad (2)$$

Crystals of the dinuclear complexes **4a–c** were obtained when benzene solutions of the complexes **3a–c** containing some hexane were allowed to stand at room temperature. Crystals of the iodo complex **4c** appeared when the solution was allowed to stand overnight whereas several days were required to get crystals of **4b** or **4a**. Under similar conditions, **3d** and **3e** were recovered unchanged. Thus, the ease of formation of the dinuclear metalated complexes appears to decrease in the order I > Br > Cl > O$_2$CCF$_3$ ≈ NO$_3$, indicating that the formation of the dinuclear metalated complexes **4** is also promoted by the steric bulk of the phosphine.

Analytical and the ^{1}H and ^{31}P NMR spectral data for **4a–4c** are included in Table III. The ^{1}H and ^{31}P NMR spectral data for **4a** have been reported[31,32] elsewhere. As shown by the data in Table III, the spectral features for **4b** and **4c** are similar to those for **4a**. The ^{31}P NMR data for **4a** and **4c** indicate the presence of both the cis and trans isomers.

Like the cyano hydride **1f**, the dihydride **2** does not undergo intramolecular metalation either at room temperature or in refluxing benzene. The preliminary report[7] on its conversion to $\{\overline{\text{Pt(}\mu\text{-H)[P(}t\text{-Bu)}_2\text{CMe}_2\text{C}}\text{H}_2]\}_2$ has been found to be erroneous; benzene solutions of the dihydride did not show any change when either kept at room temperature for up to 1 month or refluxed for 2 h.

The monohydrides **1a–e** undergo a facile reductive elimination in the presence of a base such as OH$^-$ or OMe$^-$. Addition of alcoholic KOH or NaOMe to the benzene solutions of **1a–e** resulted in the quantitative formation of the platinum(0) complex Pt[P(*t*-Bu)$_3$]$_2$. The facile synthesis[3] of Pt[P(*t*-Bu)$_3$]$_2$ from the reaction of tri-*tert*-butylphosphine with K$_2$PtCl$_4$ in the presence of alcoholic KOH, thus, seems to involve initial formation of **1a** and its subsequent conversion to the platinum(0) complex. The observed reductive elimination of **1a** also accounts for the formation of Pt[P(*t*-Bu)$_3$]$_2$ in the preparation of **2** from **1a** and alcoholic NaBH$_4$. The cyano hydride **1f** as well as the dihydride **2** were unaffected when treated, in a similar manner, with either KOH or NaOMe. Little is known about the reactivity of the dihydridoplatinum(II) complexes with bases. The observed stability of **1f** in the presence of OH$^-$ is, however, in marked contrast to the reported[33] conversion of *trans*-PtH(CN)(PPh$_3$)$_2$ to Pt(PPh$_3$)$_2$ upon treatment with KOH.

The dihydride **2** was converted readily into **1a** upon treatment with HCl in benzene, but the resulting **1a** did not react with excess acid. A solution of **2** in CCl$_4$ was also converted completely into **1a** within 15 h as shown by the ^{1}H NMR measurements which also showed the formation of CHCl$_3$. There was no subsequent reaction of **1a** with either CCl$_4$ or CHCl$_3$ for at least 3 days. The lack of reactivity of **1a** toward HCl or CCl$_4$ is in marked contrast

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to the reactivity of *trans*-$PtHCl(PEt_3)_2$[34] toward these substrates and is explicable in terms of the steric bulk of the $P(t\text{-}Bu)_3$ ligands. The iodohydride **1c** was formed upon addition of I_2 to a benzene solution of **2**.

With the objective of isolating the unknown hydridoalkoxyplatinum(II) complexes, reactions of **2** with C_6Cl_5OH, C_6H_5OH, and C_2H_5OH were examined. Immediate evolution of dihydrogen occurred upon adding C_6Cl_5OH to a benzene solution of **2**, and the $^{31}P\{^1H\}$ NMR spectrum of the solution showed the presence of only $Pt[P(t\text{-}Bu)_3]_2$ as the phosphorus-containing species. The dihydride **2** was also found to react with C_6H_5OH and C_2H_5OH, at room temperature, to give $Pt[P(t\text{-}Bu)_3]_2$. The reaction with C_6H_5OH was complete within 3 h, but the reaction with ethanol was much slower; only 70% of **2** was converted into $Pt[P(t\text{-}Bu)_3]_2$ when its solution in ethanol was kept at room temperature for 3 weeks. The rate of the reaction of the dihydride **2** with alcohols, thus, seems to depend upon their acidity. The overall reaction probably involves reactions 3 and 4. The failure to isolate the hydridoalkoxyplatinum(II) complexes is explicable in terms of very high lability of such species which have as yet not been isolated.

$$PtH_2[P(t\text{-}Bu)_3]_2 + ROH \rightarrow PtH(OR)[P(t\text{-}Bu)_3]_2 + H_2 \quad (3)$$

$$PtH(OR)[P(t\text{-}Bu)_3]_2 \rightarrow Pt[P(t\text{-}Bu)_3]_2 + ROH \quad (4)$$

$$R = C_6Cl_5,\ C_6H_5,\ C_2H_5$$

To explore the possibility of insertion of CO into the Pt–H bonds, we examined reactions of CO with the monohydrides **1a–f** as well as the dihydride **2**. When CO was passed through solutions of **1a** in chloroform or dichloromethane, the hydrido chloride was partially converted into the cationic complex *trans*-$[PtH(CO)\{P(t\text{-}Bu)_3\}_2]Cl$,[35] **5a**, as shown by the ^1H and ^{31}P NMR spectral data. Removal of the volatiles, however, gave back **1a** quantitatively, indicating that the reaction of **1a** with CO is reversible (eq 5). Under similar conditions, the complexes **1b–e** were completely converted to the corresponding carbonyl complexes *trans*-$[PtH(CO)\{P(t\text{-}Bu)_3\}_2]X$, **5b–e**, which were characterized by their ^1H and ^{31}P NMR data; attempts to isolate these complexes gave mixtures of the monohydride and the corresponding carbonyl complex **5**. Substitution of Cl^- by a weakly coordinating anion such as BF_4^- or PF_6^- is expected to displace the equilibrium 5 completely toward right. Reaction of **1a** with CO in the presence of equimolar amounts of LiX (X = BF_4, PF_6) indeed afforded the cationic complexes *trans*-$\{PtH(CO)[P(t\text{-}Bu)_3]_2\}X$, both of which have also been isolated independently from the treatment of the three-coordinate cationic hydrides[35] $[PtH\{P(t\text{-}Bu)_3\}_2]X$ (X = BF_4 or PF_6) with CO.

$$trans\text{-}PtHCl[P(t\text{-}Bu)_3]_2 + CO \rightleftharpoons trans\text{-}[PtH(CO)\{P(t\text{-}Bu)_3\}_2]Cl \quad (5)$$

Unlike the monohydrides **1a–e**, the cyano hydride **1f** does not react with CO. This is not surprising in view of strong affinity of cyanide for platinum(II).

On passing CO through a pentane solution of **2**, the trinuclear complex $Pt_3(CO)_3[P(t\text{-}Bu)_3]_3$, **6**, was obtained as the sole platinum-containing species. Its infrared and ^1H and $^{31}P\{^1H\}$ NMR spectra were identical with those for an authentic sample prepared from the reaction[3] of $Pt[P(t\text{-}Bu)_3]_2$ with CO. There was no spectral evidence for the insertion of CO into the Pt–H bond(s) even at −80 °C; the NMR spectra showed the presence of only the cluster **6** and free $P(t\text{-}Bu)_3$. The dihydride **2** also undergoes facile reductive elimination upon treatment with *t*-BuNC which not only causes reductive elimination of H_2 from **2** but also displaces both the $P(t\text{-}Bu)_3$ ligands from the resulting $Pt[P(t\text{-}Bu)_3]_2$ to give the trinuclear complex $Pt_3(\mu\text{-}CN\text{-}t\text{-}Bu)_3(CN\text{-}t\text{-}Bu)_3$, **7**. The infrared and ^1H NMR spectra for **7** were identical with those for an authentic sample[3,36] prepared from the reaction of *t*-BuNC with $Pt[P(t\text{-}Bu)_3]_2$.

Experimental Section

Materials. Tri-*tert*-butylphosphine[37] and bis(tri-*tert*-butylphosphine)platinum(0)[3] were prepared as reported previously. Reagent grade carbon monoxide from Matheson was purified by passing through a column of potassium hydroxide pellets. Other chemicals were used as received. All solvents were reagent grade and were dried prior to use following standard procedures.

Physical Measurements. Elemental analyses were performed by M.H.W. Laboratories, Phoenix, AZ, and by Guelph Chemical Laboratories, Guelph, Ontario. Infrared spectra were recorded on a Beckman IR-12 or a Perkin-Elmer IR-180 spectrophotometer using samples prepared as mulls in Nujol or halocarbon oil. ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded in the fourier transform mode with a Brucker WP-60 spectrometer. Me_4Si was used as internal reference for ^1H NMR spectral measurements and 85% H_3PO_4 as external reference for ^{31}P NMR measurements. The positive chemical shifts are downfield from the reference.

Preparation of *trans*-$PtHX[P(t\text{-}Bu)_3]_2$. (a) To a well-stirred solution of $Pt[P(t\text{-}Bu)_3]_2$ (2.0 mmol) in benzene (30 mL) was added, dropwise, a benzene solution of equimolar amount of the acid HX. The reaction mixture was stirred at room temperature for 15 min, and the solvent was removed in vacuo to give a white solid which was crystallized from hexane to give colorless needles. (b) A mixture containing 0.5 mmol of $Pt[P(t\text{-}Bu)_3]_2$ and 0.25 mmol of $N_2H_4{\cdot}2HCl$ in 10 mL of acetone was stirred for 24 h. The solvent was removed in vacuo and the residue extracted with benzene (15 mL). Removal of the benzene under reduced pressure gave *trans*-$PtHCl[P(t\text{-}Bu)_3]_2$ in 90% yield. (c) A suspension of *trans*-$PtHCl[P(t\text{-}Bu)_3]_2$ (0.5 mmol) and LiBr (1 mmol) in acetone (15 mL) was stirred at room temperature for 4 days. The solvent was removed under reduced pressure. The residue was extracted with benzene (20 mL). Removal of the benzene afforded *trans*-$PtHBr[P(t\text{-}Bu)_3]_2$; yield 90%. (d) Equimolar amounts of *trans*-$PtHCl[P(t\text{-}Bu)_3]_2$ and AgX (X = CN, NO_3) were stirred together for 24 h in a mixture of acetone and dichloromethane (2:1). The volatiles were removed under reduced pressure, and the residual solid was extracted with benzene. Removal of the benzene in vacuo afforded the colorless hydrides *trans*-$PtHX[P(t\text{-}Bu)_3]_2$ in 90% yield.

Preparation of *trans*-$PtH_2[P(t\text{-}Bu)_3]_2$. To a well-stirred solution of *trans*-$PtHCl[P(t\text{-}Bu)_3]_2$ (1 mmol) in dry THF (10 mL) was added $NaBH_4$ (5 mmol). The mixture was stirred for 30 min; then the solvent was removed in vacuo. The residue was extracted with pentane (30 mL), and the resulting solution was evaporated under reduced pressure to give the colorless dihydride **2**, which was recrystallized from hexane; yield 90%. Use of ethanol instead of THF in the above reaction afforded a mixture containing 90% **2** and 10% $Pt[P(t\text{-}Bu)_3]_2$.

Intramolecular Metalation of *trans*-$PtHX[P(t\text{-}Bu)_3]_2$ (1a–f). Benzene solutions of complexes **1** were kept at room temperature, and their ^1H NMR spectra were recorded each day until their conversion into the internally metalated complexes **3** was complete. The solution was then evaporated under vacuum, and the resulting solid was recrystallized from hexane.

Conversion of the Complexes 3 into 4. Complexes **3** were dissolved in a 1:1 mixture of benzene and hexane, and the solutions were allowed to stand at room temperature. Solution of **3c** gave crystals of **4c** after standing overnight. Crystals of **4b** and **4a** were obtained in a similar manner after 5 and 8 days, respectively.

Reactions of *trans*-$PtHX[P(t\text{-}Bu)_3]_2$ (1a–f) with CO. (a) CO was bubbled through dichloromethane or chloroform solutions of **1a–f** (0.4 mmol in 25 mL) for 1 h. Removal of the solvent in vacuo and recrystallization of the resulting off-white solid from

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hexane afforded the unreacted starting material when X = Cl. For X = Br, CF_3CO_2, or NO_3, a mixture of the starting material and the cationic hydride complex *trans*-[PtH(CO){P(*t*-Bu)$_3$}$_2$]X was obtained upon evaporation of the solvent as shown by the infrared and ^1H and $^{31}P\{^1H\}$ NMR spectral measurements. (b) CO was passed through a stirred suspension of **1a** (0.5 mmol) and LiX (X = BF_4, PF_6) in a mixture (15 mL) of acetone/dichloromethane (2:1). After 4 h, the volatiles were removed and the residue was extracted with dichloromethane (5 mL). The resulting solution was diluted with pentane and then cooled to give colorless plates of *trans*-[PtH(CO){P(*t*-Bu)$_3$}$_2$]X; the infrared ^1H and $^{31}P\{^1H\}$ NMR spectral data were identical with those for authentic samples.[35]

Reaction of *trans*-PtH$_2$[P(*t*-Bu)$_3$]$_2$ with CO. A colorless solution of *trans*-PtH$_2$[P(*t*-Bu)$_3$]$_2$ (0.4 mmol) in pentane (40 mL) became orange upon bubbling with CO for ca. 1 h. Bubbling of CO was continued until all the solvent evaporated to give a dark orange solid which was washed twice with 10 mL of hexane and then recrystallized from a mixture of hexane and benzene: mol wt calcd 1265, found 1237; IR (Nujol mull) 2200–1700 cm^{-1} region: 1785 (vs), 1730 (vs) cm^{-1}. Anal. Calcd for $C_{39}H_{81}P_3O_3Pt_3$: C, 36.7; H, 6.41. Found: C, 37.01; H, 6.31.

Reaction of *trans*-PtH$_2$[P(*t*-Bu)$_3$]$_2$ with *t*-BuNC. A solution of the isocyanide (1.1 mmol) in pentane (5 mL) was added dropwise to that of the dihydride (0.5 mmol) in the same solvent (10 mL). An orange-red solid gradually separated which was filtered, washed with pentane, and dried. It was characterized to be Pt$_3$(μ-CN-*t*-Bu)$_3$(CN-*t*-Bu)$_3$: yield 90%; IR (Nujol mull) 2200–1700 cm^{-1} region: 2142 (vs), 2092 (sh), 1728 (s, sh), and 1704 (vs) cm^{-1}. Anal. Calcd for $C_3OH_{54}N_6Pt_3$: C, 33.25; H, 4.98. Found: C, 33.40; H, 4.85.

Reactions of the Hydrides with Strong Bases. (a) To a solution of *trans*-PtHX[P(*t*-Bu)$_3$]$_2$ (X = Cl, Br) (50 mg) in benzene (4 mL) was added a drop of the saturated solution of KOH in ethanol. The $^{31}P\{^1H\}$ NMR spectra of the solutions, after 1 h, showed the presence of Pt[P(*t*-Bu)$_3$]$_2$ as the only phosphorus-containing species. Removal of the volatiles in vacuo and recrystallization of the resulting solid gave Pt[P(*t*-Bu)$_3$]$_2$ in 90% yield. Neither *trans*-PtHCN[P(*t*-Bu)$_3$]$_2$ nor *trans*-PtH$_2$[P(*t*-Bu)$_3$]$_2$ reacted with KOH/EtOH under similar conditions. (b) *trans*-PtHCl[P(*t*-Bu)$_3$]$_2$ (0.5 mmol) in benzene (5 mL) was added to a solution of NaOMe (0.5 mmol) in methanol (10 mL). The reaction mixture was stirred for 5 h. The volatiles were removed in vacuo, and the residue was extracted with pentane (25 mL). Removal of the pentane gave colorless Pt[P(*t*-Bu)$_3$]$_2$ in 95% yield.

Reactions of *trans*-PtH$_2$[P(*t*-Bu)$_3$]$_2$ with ROH (R = C_6Cl_5, C_6H_5, C_2H_5). To a solution of the dihydride in benzene was added a slight excess of the phenol. Immediate evolution of dihydrogen occurred in the case of C_6Cl_5OH; the reaction with C_6H_5OH was complete in about 3 h. In both cases, the $^{31}P\{^1H\}$ NMR spectrum of the resulting solution showed the presence of Pt[P(*t*-Bu)$_3$]$_2$ as the only phosphorus-containing species. About 70% *trans*-PtH$_2$[P(*t*-Bu)$_3$]$_2$ was converted into Pt[P(*t*-Bu)$_3$]$_2$ when its solution in ethanol was kept at room temperature for about 3 weeks.

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Registry No. **1a**, 67901-03-3; **1b**, 67871-27-6; **1c**, 67950-30-5; **1d**, 67871-28-7; **1e**, 81476-54-2; **1f**, 81476-55-3; **2**, 67870-05-7; **3a**, 63230-78-4; **3b**, 67870-02-4; **3c**, 67870-03-5; **3d**, 67870-04-6; **3e**, 81476-56-4; **4a**, 69393-57-3; **4b**, 81476-57-5; **4c**, 79138-87-7; **5a**, 81476-58-6; **5b**, 81476-59-7; **5d**, 81476-60-0; **5e**, 81476-61-1; **6**, 79136-89-9; 1, 55664-26-1; Pt[P(*t*-Bu)$_3$]$_2$, 60648-70-6.

Addition of Carbon Monoxide and Methyl Isocyanide to Methylpalladium A-Frame Complexes and Some Reactions of the Product Acyl Complexes

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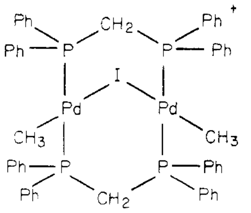
Addition of carbon monoxide to [Pd$_2$(dpm)$_2$(μ-X)(CH$_3$)$_2$]X (X = I$^-$, Br$^-$; dpm = Ph$_2$PCH$_2$PPh$_2$) produces the A-frame acyls [Pd$_2$(dpm)$_2$(μ-X)(COCH$_3$)$_2$]X which have been isolated as crystalline solids and characterized by ^1H and ^{31}P NMR spectroscopy and infrared spectroscopy. Reaction of [Pd$_2$(dpm)$_2$(μ-I)(COCH$_3$)$_2$]X with dioxygen yields acetic anhydride and Pd$_2$(dpm)$_2$I$_2$. With iodine, bromine, and diphenyl disulfide, the binuclear acyl complex yields acetyl iodide, acetyl bromine, and (*S*)-phenyl thioacetate, respectively, as the organic products. Addition of carbon monoxide to [Pd$_2$(dpm)$_2$(μ-I)(CH$_3$)I]BF$_4$ yields brown, crystalline [Pd$_2$(dpm)$_2$(μ-I)(COCH$_3$)I][BF$_4$] which appears to retain the weak metal–metal bond found in [Pd$_2$(dpm)$_2$(μ-I)(CH$_3$)I][BF$_4$]. Methyl isocyanide reacts with [Pd$_2$(dpm)$_2$(μ-I)(CH$_3$)I][BF$_4$] to form [Pd$_2$(dpm)$_2$(μ-CH$_3$C=NCH$_3$)(CNCH$_3$)$_2$]$^{3+}$, a complex with a bridging iminoacyl ligand, which has been isolated as a hexafluorophosphate salt.

Introduction

Recently the binuclear palladium methyl complexes [Pd$_2$(dpm)$_2$(μ-X)(CH$_3$)$_2$]$^+$ (X = I, Br) **1** and [Pd$_2$(dpm)$_2$(μ-I)CH$_3$I]$^+$ **2** (dpm is bis(diphenylphosphino)methane) have become available.[1] The dimethyl complex **1** is prepared from Pd$_2$(dpm)$_3$ and alkyl halides, while **2** is obtained upon protonation of Pd$_2$(dpm)$_2$(μ-CH$_2$)I$_2$. While these two cations are valence isoelectronic, **2**, which has been structurally characterized by X-ray crystallography, possesses an unusual metal–metal separation of 3.0 Å and appears to have a greater degree of metal–metal bonding than **1**.[2]



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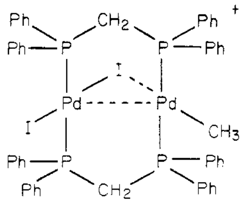

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