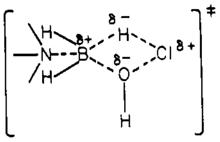
$k \approx 7 \times 10^4$ M^{-1} s^{-1} for DOCl.

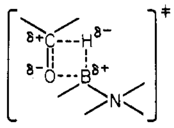
An intimate mechanism based upon these effects with HOCl substituted for OCl^- in Scheme I involves bimolecular attack of hypochlorous acid at the boron–hydrogen bond of the amine–borane. A four-center activated complex is suggested in I, wherein dashed lines depict energetically, and therefore kinetically, significant processes of bond formation and cleavage and where original and incipient bond dipoles are denoted. Collapse of I in aqueous media would lead to the formation of morpholine, BH_2OH (solvated), and chloride ion and the regeneration of H_3O^+ with rapid establishment of appropriate acid–base equilibria.



I

The normal substrate isotope effect is interpreted then as a primary effect associated with stretching of the B–H bond in the activated complex. It is in line with the relatively small boron–hydrogen isotope effects reported for other borane reactions thought to proceed via rate-limiting B–H cleavage processes, e.g., the solvolysis of substituted aryl pyridine–boranes.[17-19] As noted above, the inverse solvent isotope effect is considered to be a result simply of a lower concentration of HOCl, relative to DOCl, at comparable concentrations of lyonium ion. For reaction with molecular hypochlorous acid, therefore, the effect is normal and considered to be a secondary effect arising through perturbation of the bonding to oxygen, i.e., cleavage of the O–Cl linkage and formation of an O–B bond. Thus, in amine–borane oxidation, as in the chlorination of morpholine and other amines by hypochlorite,[20] chlorine serves as an electrophilic center reacting formally as Cl^+ (as suggested by a consideration of assigned oxidation states in HOCl).

It may be worth noting that, with respect to the distribution of bond dipoles, I is formally similar to certain four-center activated complexes that have been proposed for other boron hydride reactions, one of which involves addition of the elements of B and H across the carbonyl group in the amine–borane reduction of selected aldehydes and ketones (II).[5]



II

Although the rate of the hypochlorite chlorination of morpholine is enhanced with increasing hydrogen ion concentration, mechanistic details of this reaction have not been explored here. It is anticipated that further insight into hypochlorite and other oxyhalide oxidations of amine–boranes may be obtained through studies on borane adducts of tertiary amines wherein complications of amine chlorination are minimized or avoided. An extension to various substituted amine–borane adducts in an effort to elucidate specific substituent effects should also prove worthwhile.

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Registry No. $O(CH_2)_4NH{\cdot}BH_3$, 4856-95-5; $O(CH_2)_4NH{\cdot}BD_3$, 80584-36-7; $O(CH_2)_4ND{\cdot}BD_3$, 80584-37-8; $O(CH_2)_4NH$, 110-91-8; NaOCl, 7681-52-9.

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Contribution from the Guelph-Waterloo Centre for Graduate Work in Chemistry,
University of Guelph, Guelph, Ontario N1G 2W1, Canada

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

RAM G. GOEL,* WILLIAM O. OGINI, and RAMESH C. SRIVASTAVA[1]

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The complex *trans*-$PtH_2(As(t\text{-}Bu)_3)_2$ (**1**), which is the first dihydridoplatinum(II) complex not containing any phosphorus donor ligands, has been prepared from a facile reaction of $As(t\text{-}Bu)_3$ with K_2PtCl_4. Treatment of **1** with protic acids HX (X = Cl, Br, or CF_3CO_2) affords the monohydrido complexes $PtHX(As(t\text{-}Bu)_3)_2$ (**2**, X = Cl; **3**, X = Br; **5**, X = CF_3CO_2). A similar reaction with HI gives the dinuclear complex *trans*-$Pt_2I_2(\mu\text{-}I)_2(As(t\text{-}Bu)_3)_2$ (**6**) instead of the expected $PtHI(As(t\text{-}Bu)_3)_2$ (**4**). Complex **4** is prepared from the reaction of **1** with I_2. Complex **1** also reacts readily with CO to give a tetranuclear cluster, $Pt_4(CO)_5(As(t\text{-}Bu)_3)_4$ (**7**). Carbon monoxide reacts with **2** and displaces the chloride, but the reaction is reversible; isolable cationic complexes *trans*-$[PtH(CO)(As(t\text{-}Bu)_3)_2]X$ (**8**) (X = BF_4 or PF_6) are formed when the reaction is carried out in the presence of $LiBF_4$ or $LiPF_6$. Treatment of **2** with 1 molar equiv of $AgPF_6$ in methanol affords the cationic complex *trans*-$[PtH(MeOH)(As(t\text{-}Bu)_3)_2]PF_6$ (**9**); presence of moisture in the reaction mixture results in the formation of the aqua complex *trans*-$[PtH(H_2O)(As(t\text{-}Bu)_3)_2]PF_6$ (**10**). Complexes **9** and **10** react readily with CO to give **8** and with CH_3CN to give *trans*-$[PtH(CH_3CN)(As(t\text{-}Bu)_3)_2]X$ (**11**). Addition of 1 molar equiv of $P(t\text{-}Bu)_3$ to **2** gives a mixture of *trans*-$PtHCl(As(t\text{-}Bu)_3)(P(t\text{-}Bu)_3)$ (**12**), *trans*-$PtHCl(P(t\text{-}Bu)_3)_2$, and unreacted **2**. The infrared and ^1H NMR spectral parameters for the dihydride as well as the monohydrides are discussed.

Introduction

Following the discovery of the first stable hydridoplatinum(II) complex,[2] *trans*-$PtHCl(PEt_3)_2$, there has been rapid development in the chemistry of transition-metal hydrides.[3-10] Undoubtedly, much of the interest in these com-

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Table I. Analytical Molecular Weight and Conductance Data

		% C		% H		% X[b]		mol wt[c]		
compound	mp[a]	calcd	found	calcd	found	calcd	found	calcd	found	Λ[d]
$PtH_2(As(t\text{-}Bu)_3)_2$	173	41.80	41.66	8.12	7.86			689	670	0.7
$PtHCl(As(t\text{-}Bu)_3)_2$	270	39.91	39.42	7.60	7.90	4.91	4.73	724	712	0.2
$PtHBr(As(t\text{-}Bu)_3)_2$	208	37.40	37.22	7.15	7.28	10.42	10.29	768	760	2.1
$PtHI(As(t\text{-}Bu)_3)_2$	205	35.34	35.24	6.47	6.42	15.58	15.24	815	800	3.0
$PtH(O_2CCF_3)(As(t\text{-}Bu)_3)_2$	160	38.95	38.90	6.87	6.77			802	798	1.3
$Pt_2I_4(As(t\text{-}Bu)_3)_2$	190	20.72	20.70	3.88	4.20	36.55	36.11	1390	1360	7.5
$Pt_4(CO)_5(As(t\text{-}Bu)_3)_4$	128	33.40	33.17	5.67	6.00			1904	1895	0
$[PtH(MeOH)(As(t\text{-}Bu)_3)_2]PF_6$	>200	34.70	33.66	6.82	6.74					
$[PtH(H_2O)(As(t\text{-}Bu)_3)_2]PF_6$	>200	33.87	34.20	6.60	6.50					
$[PtH(CO)(As(t\text{-}Bu)_3)_2]PF_6$	180–185	34.84	34.70	6.45	6.34					41.8
$[PtH(CO)(As(t\text{-}Bu)_3)_2]BF_4$	220–225	37.37	37.10	6.91	6.83					42.2
$[PtH(CO)(As(t\text{-}Bu)_3)_2]ClO_4$	>190	36.79	36.84	6.81	6.70					40.8
$[PtH(MeCN)(As(t\text{-}Bu)_3)_2]PF_6$[e]	176–180	35.70	35.58	6.70	6.54					39.9
$[PtH(MeCN)(As(t\text{-}Bu)_3)_2]ClO_4$[f]	>190	37.65	37.80	7.06	7.15					41.8
$[PtH(MeCN)(As(t\text{-}Bu)_3)_2]BF_4$[g]	170	38.24	38.12	7.17	7.20					42.8

[a] Compound decomposed. [b] X = Cl, Br, or I. [c] In benzene except for $Pt_2I_4(As(t\text{-}Bu)_3)_2$, which is in 1,2-dichloroethane. [d] In Ω^{-1} cm^2 mol^{-1} for 10^{-3} solutions in dichloromethane. [e] % N calcd, 1.60; found, 1.55. [f] % N: calcd, 1.69; found, 1.65. [g] % N: calcd, 1.72; found, 1.69.

pounds has been due to the recognition[11-19] that transition-metal hydrides are intimately involved in many reactions catalyzed by these metals. Until recently our knowledge of stable platinum(II) hydrides[20,21] had been limited to the monohydridoplatinum(II) complexes, which have been now well investigated. Recently it was discovered[22] that thermally stable dihydridoplatinum(II) complexes of the type *trans*-PtH_2L_2 can be prepared if the ligands L are sterically demanding tertiary phosphines. Synthetic routes for such complexes have now been explored by several workers.[22-28] Stabilization of *cis*-dihydridoplatinum(II) complexes by bulky chelating phosphines has also been reported,[29,30] but no dihydridoplatinum(II) complex without auxiliary phosphorus donor ligands has hitherto been known.

Due to our interest in the insertion of CO into the metal–hydrogen bond, synthesis and reactions of the dihydride *trans*-$PtH_2(P(t\text{-}Bu)_3)_2$, as well as the monohydrides *trans*-$PtHX(P(t\text{-}Bu)_3)_2$, have been investigated[28] recently in this laboratory. To extend the range of the known platinum(II) dihydrides and to modify the reactivity of the Pt–H bond, we have been interested in the synthesis and chemical reactivity of dihydridoplatinum(II) complexes not containing any phosphorus donor ligands. In our continuing investigations on platinum metal complexes of tri-*tert*-butylarsine[31] we discovered that a remarkably stable dihydridoplatinum(II) complex, *trans*-$PtH_2(As(t\text{-}Bu)_3)_2$ (**1**), can be prepared in very high yield from the reaction of the arsine with K_2PtCl_4. This preparation, to our knowledge, represents the most facile synthesis of a dihydridoplatinum(II) complex. A preliminary communication on this work has appeared.[32]

Results and Discussion

Treatment of $As(t\text{-}Bu)_3$ with an alcoholic solution of K_2PtCl_4 and KOH at ~40 °C afforded **1** in 80% yield. Acetaldehyde was produced in the reaction, which was isolated as its 2,4-dinitrophenylhydrazine derivative. Thus, the overall reaction can be represented by eq 1. Although formation of

$$K_2PtCl_4 + 2As(t\text{-}Bu)_3 + 2C_2H_5OH + 2KOH \rightarrow PtH_2(As(t\text{-}Bu)_3)_2 + 2CH_3CHO + 4KCl + 2H_2O \quad (1)$$

the monohydridoplatinum(II) complex *trans*-$PtHCl(PEt_3)_2$ from the treatment of *cis*-$PtCl_2(PEt_3)_2$ with KOH in ethanol has been known,[33] there is no precedent for the formation of a dihydridoplatinum(II) complex from such a reaction.

The dihydride **1** is an air-stable white solid soluble in hexane, benzene, and dichloromethane. It behaves as a monomeric molecular species in benzene, and its solution in dichloromethane is nonconducting (data in Table I). Its infrared

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Table II. ^{1}H NMR and IR Spectral Data

	IR,[a] cm^{-1}		^{1}H NMR[b]		
compound	ν(Pt–H)	ν(Pt–X) or ν(CO)	δ(*t*-Bu)	δ(Pt–H)	^1J(Pt–H), Hz
$PtH_2(As(t\text{-}Bu)_3)_2$	1775 s		1.54	−3.78	725
$PtHCl(As(t\text{-}Bu)_3)_2$	2348 m	261 ms	1.51	−21.10	970
$PtHBr(As(t\text{-}Bu)_3)$	2338 m	174 m	1.55	−20.00	1000
$PtHI(As(t\text{-}Bu)_3)$	2330 m	131 m	1.52	−17.50	996
$PtH(O_2CCF_3)(As(t\text{-}Bu)_3)_2$[c]	2341 m		1.33	−27.20	1026
$Pt_2I_4(As(t\text{-}Bu_3)_3)_2$		192 m, 153 w, 130 w	1.40[d]		
$Pt_4(CO)_5(As(t\text{-}Bu)_3)_4$[f]		2018 s, 1797 s, 1750 s, 1740 vs	1.46[e]		
$[PtH(CO)(As(t\text{-}Bu)_3)_2]PF_6$[g]	2210 m	2045 vs	1.60[h]	−5.39[h]	641
$[PtH(CO)(As(t\text{-}Bu)_3)_2]BF_4$[i]	2220 m	2040 vs	1.57[j]	−5.40[j]	645
$[PtH(CO)(As(t\text{-}Bu)_3)_2]ClO_4$[k]	2215 m	2050 vs	1.58[h]	−5.38[h]	643
$[PtH(MeCN)(As(t\text{-}Bu)_3)_2]PF_6$[l]	*m*		1.52[j]	−20.68[j]	930
$[PtH(MeCN)(As(t\text{-}Bu)_3)_2]BF_4$[n]	*m*		1.51[j]	−20.64[j]	928
$[PtH(MeOH)(As(t\text{-}Bu)_3)_2]PF_6$[o]	2410 w		1.44[p]	−31.74[p]	1361
$[PtH(H_2O)(As(t\text{-}Bu)_3)_2]PF_6$[q]	2410 w		1.46[p]	−30.36[p]	1263

[a] Measured in Nujol mulls. [b] In benzene-d_6 at ambient temperatures unless stated otherwise. [c] Antisymmetric ν(CO_2) = 1706 cm^{-1}. [d] In dichloromethane at ambient temperature. [e] At −30 °C the spectrum in dichloromethane shows three resonances, at δ 1.08, 1.28 and 1.44, with integrated intensities in the ratio 1:1:2, respectively. [f] ν(CO) for $Pt_4(^{13}CO)_5(As(t\text{-}Bu)_3)_4$: 1980 m, 1752 vs, 1720 s, 1695 vs cm^{-1}. [g] ν(PF) = 840 vs cm^{-1}, δ(PF) = 555 s cm^{-1}. [h] In $(CD_3)_2CO$. [i] ν(BF) = 1060 vs cm^{-1}, δ(BF) = 520 s cm^{-1}. [j] In $CDCl_3$. [k] ν(ClO) = 1100 vs cm^{-1}, δ(ClO) = 620 s cm^{-1}. [l] ν(PF) = 835 vs cm^{-1}, δ(PF) = 555 s cm^{-1}. [m] Too weak to see. [n] ν(BF) = 1060 vs cm^{-1}, δ(BF) = 515 s cm^{-1}. [o] ν(PF) = 840 vs cm^{-1}, δ(PF) = 555 s cm^{-1}; ν(OH) = 3510 s cm^{-1}, δ(OH) = 1610 w cm^{-1}. [p] In CD_2Cl_2. [q] ν(OH) = 3580 s, 3500 s cm^{-1}, δ(OH) = 1590 m cm^{-1}; ν(PF) = 855 vs cm^{-1}, δ(PF) = 555 s cm^{-1}.

Table III. Pt-H Stretching Frequencies, Hydride Chemical Shifts, and $^1J(^{195}Pt\text{-}^1H)$ Values for the Known *trans*-PtH_2L_2 Complexes

L	ν(Pt-H), cm^{-1}	δ(Pt-H)	$^1J(^{195}Pt\text{-}^1H)$, Hz
$As(t\text{-}Bu)_3$[a]	1775	−3.78	725
$P(t\text{-}Bu)_3$[b]	1820	−2.95	775
$P(t\text{-}Bu)_2Ph$[c]	1780	−3.05	790
$P(cy)_3$[c]	1710	−3.05	798
$P(cy)_2Ph$[d]	1765	−3.18	787
$P(i\text{-}Pr)_3$[c]	1735	−3.22	790
$P(Et)_3$[c]	1725	−2.22	792

[a] This work. [b] Data from ref 28 and 37. [c] Data from ref 26. [d] Data from ref 25.

spectrum, in the solid state, showed only one band attributable to the Pt–H stretching frequency, indicating a trans structure. Its ^{1}H NMR spectrum (in benzene-d_6) showed a singlet in the *tert*-butyl region and another singlet with accompanying satellites (due to the ^{195}Pt–^{1}H spin–spin coupling) in the upfield region. Thus, only one isomeric form is indicated to be present in solution. The pertinent spectral data are given in Table II. The known Pt–H stretching frequencies, hydride chemical shifts, and ^1J(Pt–H) values for the dihydridoplatinum(II) complexes are compiled in Table III. As can be seen from the data in Table III, the upfield chemical shift for **1** is slightly higher than that for *trans*-$PtH_2(P(t\text{-}Bu)_3)_2$, but its Pt–H stretching frequency is 45 cm^{-1} lower than that for the phosphine complex; the magnitude of ^1J(Pt–H) for **1** is also lower than that for the phosphine analogue. The chemical shifts and the ^1J(Pt–H) values for the complexes *trans*-PtH_2L_2, where L = $P(t\text{-}Bu)_2Ph$, $P(cy)_3$, $P(cy)_2Ph$, and $P(i\text{-}Pr)_3$, fall in a very narrow range, but their Pt–H stretching frequencies vary from 1710 to 1780 cm^{-1}. Thus, neither the hydride chemical shift nor the magnitude of ^1J(Pt–H) for the dihydridoplatinum(II) complexes shown in Table III seems to correlate well with the Pt–H stretching frequency. Since the Pt–H stretching frequencies for these complexes are not likely to be coupled to other vibrations, they provide a more reliable measure of the strength of the Pt–H bonds than the ^{1}H NMR parameters. On this basis the strength of the Pt–H bonds in **1** seems to be comparable to that of those in *trans*-$PtH_2(P(t\text{-}Bu)_2Ph)_2$.

Samples of the dihydride **1** were unchanged when stored at room temperature for several months; benzene solutions of **1** also remained unchanged when kept at room temperature for 1 week. Reactions of the dihydride **1** with HCl, HBr, and CF_3CO_2H (eq 2) afforded the monohydrides $PtHX(As(t\text{-}Bu)_3)_2$ (**2**, X = Cl; **3**, X = Br; **5**, X = O_2CCF_3) in almost quantitative yields. The resulting monohydrides did not react with excess acid.

$$PtH_2(As(t\text{-}Bu)_3)_2 + HX \rightarrow PtHX(As(t\text{-}Bu)_3)_2 + H_2 \quad (2)$$

Addition of HI to an acetone solution of **1**, however, resulted in the precipitation of a dark red solid which was characterized to be *trans*-$Pt_2I_2(\mu\text{-}I)_2(As(t\text{-}Bu)_3)_2$ (**6**). The metathetical reaction of **2** with sodium iodide gave the expected hydridoplatinum(II) complex $PtHI(As(t\text{-}Bu)_3)_2$ (**4**), but the reaction did not go to completion. Reaction of **1** with iodine (eq 3), however, gave **4** in quantitative yield.

$$2PtH_2(As(t\text{-}Bu)_3)_2 + I_2 \rightarrow 2PtHI(As(t\text{-}Bu)_3)_2 + H_2 \quad (3)$$

The monohydrides **2**–**5**, like the dihydride, are also air-stable white solids soluble in hexane, benzene, and dichloromethane. As shown by the data in Table I, they also behave as monomeric molecular species in benzene and their solutions in dichloromethane are also nonconducting. The Pt–H and Pt–X stretching frequencies and the ^{1}H NMR parameters for these complexes are listed in Table II, which also shows the antisymmetric CO_2 stretching frequency for **5**.

Although it is difficult to distinguish between the cis and trans isomers of complexes **2**–**5** on the basis of their spectral data, all four complexes are expected to adopt a trans structure due to the bulky nature of the $As(t\text{-}Bu)_3$ ligands. The spectral data for all four compounds are certainly consistent with the trans structure. The Pt–X stretching frequency for complexes **2**–**4** is markedly lower than that for similar complexes of platinum(II) dihalides,[34] and this is in accord with the high trans influence[35] of the hydride ligand. The Pt–Cl stretching frequency[36] for **2** is comparable to that reported[26] for *trans*-$PtHCl(P(t\text{-}Bu)_2Ph)_2$ and *trans*-$PtHCl(P(i\text{-}Pr)_3)_2$. The anti-

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symmetric CO_2 stretching frequency for **5** is comparable to that for *trans*-$PtH(O_2CCF_3)(P(t\text{-}Bu)_3)_2$ and is indicative of the presence of the monodentate CF_3CO_2 group.

The effects of the trans ligand X on the Pt–H stretching frequency, the Pt–H chemical shift, and the magnitude of ^1J(Pt–H) for monohydrides **2–5** appear to be similar to those observed for the well-studied[7,38–40] series of the complexes *trans*-$PtHX(PEt_3)_2$. The hydride chemical shifts for complexes **2–5** are more upfield than those for other analogues.[7,26,28,38,39] The Pt–H stretching frequencies for **2–5** are also higher than those for other analogues except the tri-*tert*-butylphosphine complexes, for which the Pt–H stretching frequencies are about 50 cm^{-1} higher.

Formulation of **6** as a dinuclear molecular species is supported by the molecular weight data; its conductance data in dichloromethane are also indicative of a nonionic species (Table II). Its trans structure is deduced from the infrared data (Table II), which show the presence of only one frequency (192 cm^{-1}) assignable to the stretching vibrations involving terminal Pt–I bonds. The weak bands at ca. 150 and 130 cm^{-1} can be assigned to the stretching frequencies involving the bridging Pt–I bonds. The proposed assignments are consistent with those reported for other dinuclear *trans*-$Pt_2I_2(\mu\text{-}I)_2L_2$ complexes.[34]

When CO was bubbled through a solution of **1** in hexane or pentane at room temperature, a dark red solid corresponding to the formula $Pt_4(CO)_5(As(t\text{-}Bu)_3)_4$ (**7**) precipitated rapidly. Exposure of **1**, in the solid state, to an atmosphere of CO at room temperature also resulted in the formation of **7**. Proton NMR spectral measurements showed that **7** is also formed upon passing CO through a toluene-d_8 or CD_2Cl_2 solution of **1** at 203 K; there was no spectral evidence for the insertion of CO into a Pt–H bond to form a formyl complex. Thus **1**, like the other dihydridoplatinum(II) complexes *trans*-PtH_2L_2[28b,41–43] (L = a bulky phosphine), undergoes a facile reductive elimination in the presence of CO. However, unlike the phosphine complexes, which give the trinuclear carbonyl clusters of the types $Pt_3(CO)_3L_3$ (L = $P(t\text{-}Bu)_3$,[28b,44] $P(cy)_3$[42,43]) or $Pt_3(CO)_3(P(cy)_3)_4$,[41] **1** appears to form the tetranuclear cluster.

Complex **7** is air stable and is only sparingly soluble in solvents such as pentane or hexane but dissolves readily in benzene or dichloromethane. The proposed tetranuclear formulation is supported by molecular weight measurements in benzene (Table I). Like other compounds in Table I, its solution in dichloromethane is also nonconducting. Its ^1H NMR spectrum (Table II) at ambient temperature (in benzene-d_6) consists of a single resonance at δ 1.46. The spectrum at −30 °C (in CD_2Cl_2), however, shows three resonances, at δ 1.08, 1.28 and 1.44, with relative intensities of 1:1:2, respectively. The ^{13}C NMR spectrum of $Pt_4(^{13}CO)_5(As(t\text{-}Bu)_3)_4$ (prepared by using ^{13}CO) at −80 °C consists of a central peak at 231.2 ppm, which is flanked on each side by two satellites due to the ^{195}Pt–^{13}C spin–spin coupling [^1J(Pt–C) = 758 and 801 Hz]. The spectrum also shows a peak at 177.5 ppm, but due to its low intensity the satellites due to ^{195}Pt–^{13}C spin–spin coupling are not observed. The peak at 231.2 ppm is assigned to a bridging carbonyl group, and the peak at 177.5 ppm may be attributed to a terminal carbonyl group.[45a] The infrared spectrum of **7** (Table II), in the solid state, in the carbonyl stretching region shows bands due to bridging as well as terminal CO groups.[45b] Although a complete structural characterization of **7** must await a structure determination by X-ray diffraction, it appears to be similar to the previously reported[46] clusters $Pt_4(CO)_5L_4$ (L = $AsPh_3$, PPh_2PhCH_2, Et_3). However, its facile formation as well as its stability is surprising in view of the observation of earlier workers[46] that the lability of the $Pt_4(CO)_5L_4$ clusters increases markedly upon substitution of arsenic for phosphorus.

A pentane solution of **2** became yellowish when CO was passed through. Removal of the solvent in vacuo, however, afforded the starting material. When carbon monoxide was bubbled into a solution of **2** in CD_2Cl_2 for 1 h, the ^1H NMR spectrum of the solution showed a hydride resonance at −5.3 ppm and the accompanying satellite doublet due to ^{195}Pt–^1H spin–spin coupling [^1J(Pt–H) = 640 Hz]. The markedly low values of δ(Pt–H) and ^1J(Pt–H) are very similar to those found for the cationic hydridocarbonyl complexes *trans*-$[PtH(CO)(As(t\text{-}Bu)_3)_2]X$ (vide infra) and indicate the presence of the *trans*-$[PtH(CO)(As(t\text{-}Bu)_3)_2]^+$ species. However, **2** was recovered quantitatively upon removal of the solvent in vacuo. These observations suggest that the reaction of **2** with CO is reversible (eq 4).

$$trans\text{-}PtHCl(As(t\text{-}Bu)_3)_2 + CO \rightleftarrows trans\text{-}[PtH(CO)(As(t\text{-}Bu)_3)_2]Cl \quad (4)$$

Displacement of the chloride ligand from **2** by a noncoordinating anion is expected to shift the equilibrium (4) toward the right completely. The cationic complexes *trans*-$[PtH(CO)(As(t\text{-}Bu)_3)_2]X$ (**8**) (X = BF_4, PF_6) were indeed obtained in quantitative yields when CO was bubbled through a solution of **2** containing 1 molar equiv of $LiBF_4$ or $LiPF_6$.

We have recently reported[47] the preparation of a three-coordinate Pt(II) hydride, $[PtH(P(t\text{-}Bu)_3)_2]PF_6$, from the reaction of *trans*-$PtHCl(P(t\text{-}Bu)_3)_2$ with $AgPF_6$ in acetone or methanol. In an attempt to prepare the corresponding arsine analogue, *trans*-$PtHCl(As(t\text{-}Bu)_3)_2$ was treated with $AgPF_6$ in methanol. The resulting product, however, is best formulated as *trans*-$[PtH(MeOH)(As(t\text{-}Bu)_3)_2]PF_6$ (**9**). Its infrared spectrum (Nujol mull) shows characteristic bands at 3510, 2410, and 1610 cm^{-1} due to ν(OH), ν(Pt–H), and δ(OH), respectively. The band at 2410 cm^{-1} is comparable to the Pt–H stretching frequency observed at 2400 cm^{-1} for the four-coordinate complex *trans*-$[PtH(Me_2CO)(P(t\text{-}Bu)_2Ph)_2]PF_6$.[48] In the ^1H NMR spectrum (in CD_2Cl_2) of **8**, the Pt–H proton gives rise to a singlet at δ −31.7, which is accompanied by a satellite doublet due to ^{195}Pt [^1J(Pt–H) = 1361 Hz]. The high values of ν(Pt–H), δ(Pt–H), and ^1J(Pt–H) for **8** are consistent with a very weak trans influence[49,50] of MeOH. However, good analytical data for **9** could not be obtained, presumably due to the difficulty of obtaining the exact stoichiometric content of methanol. If the silver salt or the solvent in the above reaction is not very dry, then the corresponding aqua complex *trans*-$[PtH(H_2O)(As(t\text{-}Bu)_3)_2]PF_6$ (**10**) is formed. The values of ν(Pt–H), δ(Pt–H), and ^1J(Pt–H) (Table II) for **10** are similar to those for **9**.

The dichloromethane solutions of **9** (and its BF_4 and ClO_4 analogues) react readily with MeCN and CO to afford *trans*-$[PtH(L)(As(t\text{-}Bu)_3)_2]X$ (**11** L = MeCN; **8**, CO; X = PF_6, BF_4, or ClO_4). The infrared and ^1H NMR data for these complexes are listed in Table II. The ν(Pt–H), δ(Pt–H), and

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^1J(Pt–H) values are expected to decrease with increasing trans influence of the ligand L.[49,50] From the data in Table II it can be seen that the CO group, as expected, exhibits the strongest trans influence in the series MeOH < H_2O < Cl < MeCN ≪ CO.

The arsine ligand(s) in the complexes $MCl_2(As(t\text{-}Bu)_3)_2$ and $M_2Cl_4(As(t\text{-}Bu)_3)_2$ (M = Pt, Pd) can be easily displaced by tertiary phosphines.[31] For preparation of the mixed phosphine–arsine hydride *trans*-$PtHCl(As(t\text{-}Bu)_3)(P(t\text{-}Bu)_3)$ (**12**), **2** was treated with an equimolar amount of $P(t\text{-}Bu)_3$ in pentane. The resulting solid, after removal of the solvent, showed three Pt–H stretching frequencies, at 2348 m, 2400 m, and 2360 m cm^{-1}. The first two frequencies can be attributed to unreacted **2** and *trans*-$PtHCl(P(t\text{-}Bu)_3)_2$,[28] respectively, and the third frequency may be assigned to **12**. The ^{1}H NMR spectrum of the product in C_6D_6 showed a singlet at δ 21.7 [^1J(Pt–H) = 970 Hz], a doublet at δ 19.99 [^1J(P–H) = 1047 Hz; ^2J(P–H) = 11.7 Hz], and a triplet at δ 19.23 [^1J(Pt–H) = 1068 Hz; ^2J(P–H) = 12.2 Hz] due to the Pt–H protons. While the singlet and the triplet are due to the Pt–H proton of the complexes **2** and *trans*-$PtHCl(P(t\text{-}Bu)_3)_2$, the doublet can be attributed to the Pt–H proton of **12**. It is interesting to note that the values of ν(Pt–H), δ(Pt–H), and ^1J(Pt–H) for **12** fall between the values for **2** and its phosphine analogue. Unfortunately, attempts to separate the individual components by repeated crystallization failed. The amount of **12** in the product seemed to decrease with increasing rate of addition of the phosphine.

Attempts to prepare **12** from a redistribution reaction as shown in eq 5 also failed; the ^{1}H NMR spectrum of the reaction mixture in benzene showed the presence of only the starting materials even after 72 h.

$$trans\text{-}PtHCl(As(t\text{-}Bu)_3)_2 + trans\text{-}PtHCl(P(t\text{-}Bu)_3)_2 \nrightarrow 2trans\text{-}PtHCl(As(t\text{-}Bu)_3)(P(t\text{-}Bu)_3) \quad (5)$$

Experimental Section

General Data. Tri-*tert*-butylarsine was prepared as reported previously.[31] It was handled in an atmosphere of oxygen-free dry nitrogen. Potassium tetrachloroplatinate was prepared by the procedure of Livingstone.[51] The solvents were dried prior to use with standard methods. Carbon monoxide from Matheson was purified by passing through a column of KOH pellets. Other chemicals were reagent grade and were used as received.

Physical Measurements. Elemental analyses were performed by Guelph Chemical Laboratory, Guelph. Molecular weights were determined with a Hitachi Perkin-Elmer 115 osmometer. Infrared spectra were recorded with a Perkin-Elmer 180 spectrometer. ^{1}H NMR spectra were recorded on a Varian A-60 spectrometer or a Bruker WP-60 Fourier-transform spectrometer, with either Me_4Si or the solvent as internal reference. All the chemical shifts are reported relative to Me_4Si. Conductances were measured with a Yellow Springs Instrument Model 31 conductivity bridge using a glass conductivity cell with platinized platinum electrodes.

Preparation of *trans*-$PtH_2(As(t\text{-}Bu)_3)_2$. Tri-*tert*-butylarsine (2.5 mmol) was added to a solution of KOH (3.5 mmol) in ethanol (25 mL). Crystals of K_2PtCl_4 (1 mmol) were added to the solution, and the mixture was stirred for 24 h at 40 °C. Hexane (60 mL) was added to the reaction mixture, which was then filtered, and the residue was washed twice with 10-mL portions of hexane. The colorless filtrate and the washings were mixed and concentrated in vacuo to give pale white *trans*-$PtH_2(As(t\text{-}Bu)_3)_2$, which was recrystallized from hexane; yield 80%.

Reactions of *trans*-$PtH_2(As(t\text{-}Bu)_3)_2$. 1. With CF_3COOH. A solution of CF_3COOH (0.2 mmol) in 10 mL of hexane was added dropwise, with stirring, to a solution of $PtH_2(As(t\text{-}Bu)_3)_2$ (0.2 mmol) in 20 mL of hexane. After the reaction mixture was stirred for about 40 min at room temperature, the solvent was removed and the resulting white solid residue was recrystallized from hexane to give $PtH(CF_3COO)(As(t\text{-}Bu)_3)_2$, yield 96%.

2. With HCl. A solution of HCl in benzene was prepared by adding dropwise 5 mL of CH_3OH (0.11 mol) to a solution of CH_3COCl (0.10 mol) in 20 mL of cold benzene with stirring. The resulting solution was diluted to 1000 mL with benzene, and 2 mL of the diluted solution was added dropwise, with stirring, to a solution of $PtH_2(As(t\text{-}Bu)_3)_2$ (0.2 mmol) in 15 mL of benzene. The reaction mixture was stirred at room temperature for 30 min. Removal of the solvent gave a white solid, which was recrystallized from hexane to give $PtHCl(As(t\text{-}Bu)_3)_2$, yield 90%.

3. With HBr. A solution of HBr (0.2 mmol) in 10 mL of acetone was added dropwise with stirring to an ice-cold solution of $PtH_2(As(t\text{-}Bu)_3)_2$ (0.2 mmol) in 15 mL of acetone. After being stirred for about 10 min, the solution was concentrated to half the original volume and filtered. The solid product was washed with cold benzene to give $PtHBr(As(t\text{-}Bu)_3)_2$, yield 88%.

4. With HI. A solution of HI (0.2 mmol) in 10 mL of cold acetone was added dropwise, with stirring, to a solution of $PtH_2(As(t\text{-}Bu)_3)_2$ (0.2 mmol) in 20 mL of cold acetone, and the resulting mixture was stirred for about 30 min. The solution turned dark and turbid. The dark, greenish solid was filtered, washed three times with 10 mL of cold acetone, dried, and characterized to be $[PtI_2(As(t\text{-}Bu)_3)]_2$, yield 50%. The filtrate and the washings were combined, and upon removal of the solvent an oily residue of free arsine with some uncharacterized material was obtained.

5. With I_2. A solution of I_2 (0.1 mmol) in 30 mL benzene was added dropwise with stirring to a cold solution of $PtH_2(As(t\text{-}Bu)_3)_2$ (0.2 mmol) in 15 mL of benzene, and the reaction mixture was stirred for ~1 h to give a dark, brownish solution, which was filtered. No solid residue was obtained. Removal of the solvent from the filtrate gave $PtHI(As(t\text{-}Bu)_3)_2$ as a gray solid, which was recrystallized from hexane; yield 80%.

Reaction of *trans*-$PtHCl(As(t\text{-}Bu)_3)_2$ with NaI. A solution of NaI (0.25 mmol) in 20 mL of ethanol was added to a solution of *trans*-$PtHCl(As(t\text{-}Bu)_3)_2$ (0.2 mmol) in 15 mL of ethanol, and the reaction mixture was stirred for 24 h to give a dark brown solution. Precipitated NaCl was filtered off and washed twice with 10 mL of benzene. The filtrate and washings were mixed and evaporated in vacuo to give a brown solid, which upon extraction with hexane yielded a mixture of *trans*-$PtHI(As(t\text{-}Bu)_3)_2$ and *trans*-$PtHCl(As(t\text{-}Bu)_3)_2$.

Reaction of CO with *trans*-$PtH_2(As(t\text{-}Bu)_3)_2$. Carbon monoxide was passed slowly through a flask containing *trans*-$PtH_2(As(t\text{-}Bu)_3)_2$ (0.2 mmol). The white dihydride immediately turned dark red. Carbon monoxide was passed over the solid dihydride for about 24 h. The dark red solid was then washed twice with a 10-mL portion of cold pentane, in which it was found only slightly soluble. The resulting dark red solid product was characterized to be $Pt_4(CO)_5(As(t\text{-}Bu)_3)_4$, yield 95%. The same tetranuclear complex was obtained when carbon monoxide was passed into a benzene or pentane solution of *trans*-$PtH_2(As(t\text{-}Bu)_3)_2$.

Reaction of CO with *trans*-$PtHCl(As(t\text{-}Bu)_3)_2$. Carbon monoxide was passed for about 2 h into a pentane solution of *trans*-$PtHCl(As(t\text{-}Bu)_3)_2$ (1 mmol) in 50 mL of pentane. The solution quickly turned yellow. However, removal of pentane in vacuo gave *trans*-$PtHCl(As(t\text{-}Bu)_3)_2$.

Reaction of CO with *trans*-$PtHCl(As(t\text{-}Bu)_3)_2$ in the Presence of $LiBF_4$ or $LiPF_6$. Carbon monoxide was bubbled into a suspension of *trans*-$PtHCl(As(t\text{-}Bu)_3)_2$ (0.5 mmol) in acetone (10 mL) containing LiX (X = BF_4, PF_6) (1 mmol) for ~2 h. The volatiles were removed under reduced pressure. Dichloromethane (5 mL) was added, and the reaction mixture was filtered to remove the lithium salts. Addition of pentane to the filtrate and cooling gave colorless crystals of *trans*-$[PtH(CO)(As(t\text{-}Bu)_3)_2]BF_4$, yield 90%.

Reactions of *trans*-$PtHCl(As(t\text{-}Bu)_3)_2$ with AgX (X = PF_6, BF_4, ClO_4). To a suspension of the platinum complex (0.5 mmol) in methanol (10 mL) was added a solution of $AgPF_6$ (0.5 mmol) at room temperature. After the reaction mixture was stirred for ~1 h, the AgCl was filtered off. The filtrate was freed from the solvent in vacuo and the residue dissolved in dichloromethane (5 mL). The solution was passed through a small column of Florisil. Addition of pentane gave a pale yellow solid of *trans*-$[PtH(MeOH)(As(t\text{-}Bu)_3)_2]PF_6$, yield 75%.

Reactions of *trans*-$[PtH(solvent)(As(t\text{-}Bu)_3)_2]X$ (X = PF_6 or BF_4) with MeCN and CO. A solution containing equimolar amounts of *trans*-$PtHCl(As(t\text{-}Bu)_3)_2$ and AgX (X = PF_6, BF_4, ClO_4) in methanol or acetone was stirred for ~1 h. The AgCl was filtered off, and the

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filtrate was treated with an excess of MeCN or CO. Removal of the volatiles and crystallization of the residual solid from dichloromethane/pentane afforded *trans*-$[PtH(MeCN)(As(t\text{-}Bu)_3)_2]X$ or *trans*-$[PtH(CO)(As(t\text{-}Bu)_3)_2]X$, respectively, in 90% yield.

Reaction of *trans*-$PtHCl(As(t\text{-}Bu)_3)_2$ with $P(t\text{-}Bu)_3$. A solution of the phosphine (0.5 mmol) in pentane (5 mL) was added dropwise to the platinum complex (0.5 mmol) in pentane (15 mL). The reaction mixture was stirred for 2 h and then freed from the solvent. Infrared and ^1H NMR spectra of the residual colorless solid showed it to be a mixture of *trans*-$PtHCl(As(t\text{-}Bu)_3)(P(t\text{-}Bu)_3)$, *trans*-$PtHCl(P(t\text{-}Bu)_3)_2$, and *trans*-$PtHCl(As(t\text{-}Bu)_3)_2$.

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Registry No. **1**, 80630-41-7; **2**, 80630-42-8; **3**, 80630-43-9; **4**, 80630-44-0; **5**, 80630-45-1; **6**, 80630-46-2; **7**, 80630-47-3; **8**, X = BF_4, 80630-49-5; **8**, X = PF_6, 80630-50-8; **8**, X = ClO_4, 80630-51-9; **9**, 80630-53-1; **10**, 80630-55-3; **11**, X = PF_6, 80630-57-5; **11**, X = ClO_4, 80630-58-6; **11**, X = BF_4, 80630-59-7; **12**, 80630-60-0; *trans*-$PtHCl(P(t\text{-}Bu)_3)_2$, 67901-08-0; K_2PtCl_4, 10025-99-7.

Contribution from the Department of Chemistry,
Tulane University, New Orleans, Louisiana 70118

Binuclear Cationic Complexes of Rhodium. 6. Carboxylate and Acetylene Derivatives[1]

JOEL T. MAGUE* and STEVEN H. DEVRIES

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The A-frame complexes $[Rh_2(CO)_2(\mu\text{-}Cl)(L_2)_2]PF_6$ ($L_2 = (C_6H_5)_2PCH_2P(C_6H_5)_2$ (DPM), $(C_6H_5)_2AsCH_2As(C_6H_5)_2$ (DAM)) react with silver carboxylates to yield the carboxylate-bridged dimers $[Rh_2(CO)_2(\mu\text{-}O_2CR)(L_2)_2]PF_6$ (L_2 = DPM, R = CH_3; L_2 = DAM, R = CH_3, C_2H_5). All three complexes rapidly exchange carbon monoxide at room temperature, but only for the phosphine complex could a μ-carbonyl adduct be detected. Reaction of the carboxylate dimers with electronegatively substituted acetylenes yields the vinylidene-bridged species $[Rh_2(CO)(\mu\text{-}CO)(\mu\text{-}RC_2R)(O_2CR')(L_2)_2]PF_6$ (L_2 = DPM, DAM, R = CO_2CH_3, CF_3, R′ = CH_3; L_2 = DAM, R = CO_2CH_3, CF_3, R′ = C_2H_5). These in turn react with other ligands L (L = $CNC(CH_3)_3$, $P(OCH_3)_3$) to yield $[Rh_2(L)(\mu\text{-}CO)(\mu\text{-}RC_2R)(O_2CCH_3)(L_2)_2]PF_6$. The complex $[Rh_2(CNC(CH_3)_3)_4(DPM)_2](B(C_6H_5)_4)_2$ also reacts with electronegatively substituted acetylenes to give $[Rh_2(CNC(CH_3)_3)_4(RC_2R)(DPM)_2](B(C_6H_5)_4)_2$. The infrared and ^1H, ^{13}C, and ^{31}P NMR spectra of these complexes are also discussed.

Introduction

In the course of our study of the face-to-face dimers $[Rh(CO)ClL_2]_2$ ($L_2 = (C_6H_5)_2PCH_2P(C_6H_5)_2$ (DPM), $(C_6H_5)_2AsCH_2As(C_6H_5)_2$ (DAM))[1] it was observed that they reacted readily with hexafluorobut-2-yne to yield an extremely insoluble olive green product.[2] More recently a very similar product was obtained in the reaction of this acetylene with the A-frame complexes $[Rh_2(CO)_2(\mu\text{-}Cl)(L_2)_2]B(C_6H_5)_4$ (L_2 = DPM, DAM).[3] Because of our interest in the mode of interaction of carbon–carbon multiple bonds with binuclear complexes, we sought related acetylene adducts that would be sufficiently soluble to permit adequate characterization. We report here on the results of this study.

Experimental Section

All solvents were appropriately dried and distilled prior to use and were stored under an atmosphere of dinitrogen. Reactions were carried out in a dinitrogen atmosphere with use of standard Schlenk techniques. Literature procedures were used to prepare $[Rh_2(CO)_2(\mu\text{-}Cl)(L_2)_2]PF_6$[1] and $[Rh_2(CNC(CH_3)_3)_4(DPM)_2](B(C_6H_5)_4)_2$[4]. Infrared spectra were obtained on Beckman IR-18A and Perkin-Elmer 298 spectrophotometers. Carbon-13 and phosphorus-31 NMR spectra were obtained on a JEOL FX-60 spectrometer operating at 15.03 MHz (30° flip angle, 5-s repetition rate) and 24.15 MHz (45° flip angle, 5-s repetition rate), respectively. Chemical shifts are referred to external tetramethylsilane (^{13}C) and external H_3PO_4 (^{31}P), respectively, and are positive downfield. Proton NMR spectra were obtained on JEOL MH-100 and Varian EM-390 spectrometers at 100 and 90 MHz, respectively, and are referenced to internal tetramethylsilane (τ 10.0). Simulation of NMR spectra was accomplished with use of a local version of the LAOCOON-3[14] program. Melting points were determined in open capillaries on a Mel-Temp apparatus and are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Conductance measurements were made on a Thomas-Serfass Model RCM 15B1 bridge with a cell containing platinized electrodes, which had been calibrated with 0.01 M aqueous potassium chloride.

Synthesis of $[Rh_2(CO)_2(\mu\text{-}O_2CR)(L_2)_2]PF_6$ (L_2 = DPM, DAM, R = CH_3; L_2 = DAM, R = C_2H_5). In a typical experiment, 0.300 mmol of the appropriate $[Rh_2(CO)_2(\mu\text{-}Cl)(L_2)_2]PF_6$ complex was dissolved in 20 mL of a 1:1 (v/v) mixture of dichloromethane and tetrahydrofuran and treated with an equimolar quantity of solid silver carboxylate. The resulting suspension was stirred vigorously for 4 h while protected from light during which time the color changed from red orange to dark red. Following filtration through a pad of diatomaceous earth the solution was concentrated under reduced pressure until solid formed. The precipitation was completed by addition of diethyl ether, and the resulting product recrystallized from dichloromethane/diethyl ether to yield red-orange to dark red crystals, which were collected and dried in vacuo. All products appear to be air-stable.

Synthesis of Acetylene Adducts, $[Rh_2(CO)(\mu\text{-}CO)(\mu\text{-}RC{=}CR)(O_2CR')(L_2)_2]PF_6$ (L_2 = DPM, DAM, R = CF_3, CO_2CH_3, R′ = CH_3; L_2 = DAM, R = CF_3, CO_2CH_3, R′ = C_2H_5). In a typical experiment, 0.200 mmol of $[Rh_2(CO)_2(\mu\text{-}O_2CR')(L_2)_2]PF_6$ was dissolved in 5 mL of dichloromethane and treated with an excess of the appropriate acetylene. After 2 h of stirring, the solution had become light orange, and addition of diethyl ether precipitated the product, which was collected and recrystallized from dichloromethane/diethyl ether to yield yellow air-stable microcrystals.

Synthesis of $[Rh_2(L)(\mu\text{-}CO)(\mu\text{-}RC{=}CR)(O_2CCH_3)(L_2)_2]PF_6$ (L = $CNC(CH_3)_3$, $P(OCH_3)_3$; R = CF_3, CO_2CH_3; L_2 = DPM, DAM). In a typical experiment, 0.200 mmol of $[Rh_2(CO)_2(RC{=}CR)(O_2CCH_3)(L_2)_2]PF_6$ was dissolved in 10 mL of dichloromethane and 1.5 equiv of the ligand (*tert*-butyl isocyanide or trimethyl phosphite) was added. For the reactions with the isocyanide the

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