Investigations of the Factors Affecting the Stability of Dihydrogen Adducts of Platinum(II)

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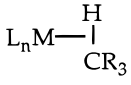
Received July 31, 1997

The preparation and study of Pt(II) H_2 adducts and Pt(IV) dihydride complexes are described. The species of interest are generated by protonation of hydridoplatinum(II) complexes of the type *trans*-$(PCy_3)_2Pt(H)X$ [X = SiH_3, H, CH_3, Ph, Cl, Br, I, CN, CF_3SO_3] and [*trans*-$(PCy_3)_2Pt(H)L][BAr^f_4]$ [L = CO, 4-picoline; BAr^f_4 = B(3,5-$C_6H_3(CF_3)_2)_4$]. The proton attacks one of three different sites on these complexes (hydride, platinum, or the trans ligand), depending on which ligand is trans to hydride. These studies reveal several factors affecting the stability and reactivity of Pt(II) σ adducts, which thus have implications for C−H activation by Pt(II).

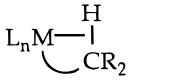
Introduction

Over the past 15 years, several successful approaches have been identified for alkane activation by transition metal complexes.[1−3] Considerable evidence from numerous laboratories supports the intermediacy of alkane σ adducts (**A**) in the C−H activation step.[4] However, because such complexes have

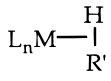


A

eluded isolation and structural characterization and typically are not directly observable,[5] several approaches have been used to examine their reactivity, including the study of *agostic* complexes (**B**) (i.e., intramolecular alkane adducts)[6−8] and of analogous, more stable σ adducts such as silanes (**C**) or dihydrogen (**D**).[7−13]



B



C (R' = SiR"$_3$)

D (R' = H)

We have been interested in studying the mechanism of C−H activation by Pt(II) complexes in aqueous solution, the first step in the homogeneous alkane oxidation system discovered by Shilov and co-workers.[14] A recent mechanistic study of the microscopic reverse of this reaction, the protonolysis of alkylplatinum(II) species, implicates the intermediacy of both alkylhydridoplatinum(IV) and alkane σ adducts (Scheme 1; the reactions are shown in the direction of C−H activation).[15,16] Unlike the ligand-trapped alkylhydridoplatinum(IV) intermediate (**I**), the σ adduct (**F**) was not detected directly at low temperatures. Consequently, our ability to explore the mechanism of its formation and its stability and reactivity was limited. For example, is the σ adduct generated through an associative or dissociative mechanism? Also, what factors affect the equilibrium between the alkane adduct (**F**) and the alkylhydridoplatinum(IV) intermediate (**G**)? We chose to investigate these issues by examining related, more stable σ adducts of Pt(II), namely, dihydrogen complexes prepared by the protonation of platinum(II) hydrides. While there are numerous examples of transition metal−H_2 complexes,[7−11,13] the vast majority are d^6 octahedral complexes. Examples of square planar d^8 complexes analogous to **F** are quite rare and have been identified only recently.[17−20]

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S0020-1669(97)00944-0 CCC: $15.00
Published on Web 04/21/1998

Scheme 1

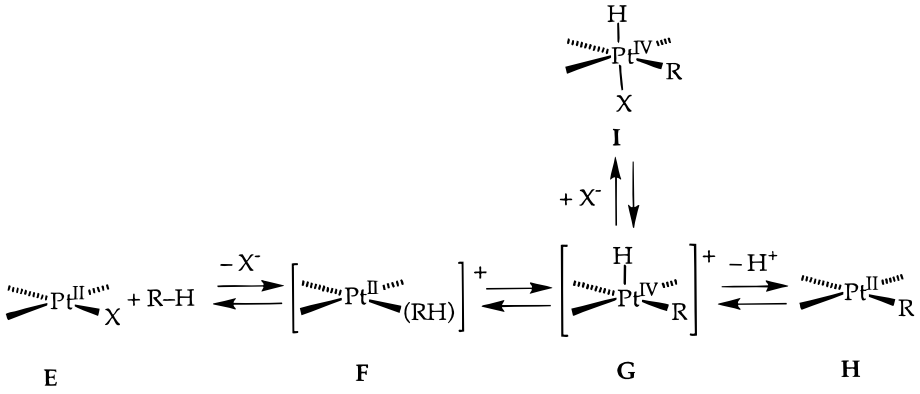

Table 1. Selected NMR Spectroscopic Data (in CD_2Cl_2 Solution)

compound	temp (°C)	peak assignment	chemical shift/ppm (multiplicity); coupling/Hz	T_1 (ms) (500 MHz)
trans-$(PCy_3)_2Pt(SiH_3)(H)$ (**1**)	22	Pt−*H*	−0.97 (t), $^1J_{Pt-H} = 760$, $^2J_{P-H} = 11$	
		Pt−Si*H*$_3$	3.13 (s)	
trans-$(PCy_3)_2Pt(H)_2$ (**2**)	22	Pt−*H*	−3.97 (t), $^1J_{Pt-H} = 796$, $^2J_{P-H} = 17$	
trans-$(PCy_3)_2Pt(CH_3)(H)$ (**3**)	−85	Pt−*H*	−6.47 (t), $^1J_{Pt-H} = 660$, $^2J_{P-H} = 17$	
		Pt−C*H*$_3$	−0.31 (s), $^2J_{Pt-H} = 44$	
trans-$(PCy_3)_2Pt(Ph)(H)$ (**4**)	22	Pt−*H*	−8.01 (t), $^1J_{Pt-H} = 595$, $^2J_{P-H} = 17$	
		Pt−C$_6$*H*$_5$	7.44 (2H, d), $^3J_{Pt-H} = 42$	
			6.84 (2H, t)	
			6.62 (1H, t)	
	25	Pt−*P*Cy$_3$	35.3, $^1J_{Pt-P} = 2850$	
trans-$(PCy_3)_2Pt(H)Cl$ (**5**)	−85	Pt−*H*	−18.86 (t), $^1J_{Pt-H} = 1300$, $^2J_{P-H} = 12$	$T_{1(min)} = \sim 480$ (−55 °C)
	−95	Pt−*P*Cy$_3$	38.6, $^1J_{Pt-P} = 2755$	
trans-$(PCy_3)_2Pt(H)Br$ (**6**)	−85	Pt−*H*	−17.58, $^1J_{Pt-H} = 1365$, $^2J_{P-H} = 12$	
		Pt−*P*Cy$_3$	37.75, $^1J_{Pt-P} = 2735$	
trans-$(PCy_3)_2Pt(H)I$ (**7**)	−85	Pt−*H*	−14.65, $^1J_{Pt-H} = 1390$, $^2J_{P-H} = 11$	
	−65	Pt−*P*Cy$_3$	36.5, $^1J_{Pt-P} = 2714$	
trans-$(PCy_3)_2Pt(H)CN$ (**8**)	22	Pt−*H*	−8.82, $^1J_{Pt-H} = 775$	
	25	Pt−*P*Cy$_3$	39.8, $^1J_{Pt-P} = 2650$	
trans-$(PCy_3)_2Pt(H)(OTf)$ (**9**)	22	Pt−*H*	−27.6 (t), $^1J_{Pt-H} = 1585$, $^2J_{P-H} = 14$	
[*trans*-$(PCy_3)_2Pt(H)(CO)]BAr^f_4$ (**10**)	22	Pt−*H*	−4.63 (t), $^1J_{Pt-H} = 920$, $^2J_{P-H} = 12$	
[*trans*-$(PCy_3)_2Pt(H)(4\text{-picoline})]BAr^f_4$ (**11**)	22	Pt−*H*	−19.60 (t), $^1J_{Pt-H} = 1070$, $^2J_{P-H} = 13.5$	
[*trans*-$(PCy_3)_2Pt(H)(H_2)]BAr^f_4$ (**12**)	−65	Pt−*H*	−10.43 (m) $^1J_{Pt-H} = 1445$	606 (−85 °C)
		Pt−(*H*$_2$)	−0.28, $^1J_{Pt-H} = 295$	36 (−85 °C)
[*trans*-$(PCy_3)_2Pt(H)(CD_2Cl_2)]BAr^f_4$ (**13**)	−80	Pt−*H*	−26.3, $^1J_{Pt-H} = 1480$	
[*trans*-$(PCy_3)_2Pt(CH_3)(H_2)]BAr^f_4$ (**14**)	−85	Pt−(*H*$_2$)	−2.35, $^1J_{Pt-H} = \sim 300$	26 (−95 °C)
		Pt−C*H*$_3$	0.87(s), $^2J_{Pt-H} = 83$	
[*trans*-$(PCy_3)_2Pt(Ph)(H_2)]BAr^f_4$ (**15**)	−80	Pt−(*H*$_2$)	−1.9, $^1J_{Pt-H} = 255$	20 (−65 °C)
$(PCy_3)_2Pt(H)_2Cl_2$ (**17**)	−85	Pt−*H*	−18.76 (s), $^1J_{Pt-H} = 1125$, $^2J_{P-H} = 6$	
	−55	Pt−*P*Cy$_3$	31.0, $^1J_{Pt-P} = 1788$	
$(PCy_3)_2Pt(H)_2I_2$ (**18**)	−45	Pt−*H*	−15.79, $^1J_{Pt-H} = 1115$	
	−55	Pt−*P*Cy$_3$	22.7, $^1J_{Pt-P} = 1715$	
$(PCy_3)_2Pt(H)_2(Cl)I$ (**19**)	−45	Pt−*H*	−15.60, $^1J_{Pt-H} = 1165$	
			−18.88, $^1J_{Pt-H} = 1075$	
	−55	Pt−*P*Cy$_3$	27.0, $^1J_{Pt-P} = 1750$	
$(PCy_3)_2Pt(H)_2Br_2$ (**20**)	−55	Pt−*H*	−17.58, $^1J_{Pt-H} = 1145$	
	−80	Pt−*P*Cy$_3$	28.2, $^1J_{Pt-P} = 1750$	
{[$(PCy_3)_2Pt(H)]_2Cl$}BAr^f_4 (**21**)	−60	Pt−*H*	−23.11, $^1J_{Pt-H} = 1559$	
	−55	Pt−*P*Cy$_3$	42.9, $^1J_{Pt-P} = 2716$	
{[$(PCy_3)_2Pt(H)]_2Br$}BAr^f_4 (**22**)	−55	Pt−*H*	−17.76, $^1J_{Pt-H} = 1655$, $^2J_{P-H} = 11$	
	−85	Pt−*P*Cy$_3$	43.08, $^1J_{Pt-P} = 2715$	
{[$(PCy_3)_2Pt(H)]_2I$}BAr^f_4 (**23**)	−75	Pt−*H*	−18.07, $^1J_{Pt-H} = 1640$	
	−60	Pt−*P*Cy$_3$	40.7, $^1J_{Pt-P} = 2670$	
trans-$(PBut_3)_2Pt(H)Cl$ (**24**)	22	C(C*H*$_3$)$_3$	1.55, $^3J_{P-H} = 6$	
		Pt−*H*	−19.9, $^1J_{Pt-H} = 1110$, $^2J_{P-H} = 12$	
[*trans*-$(PBut_3)_2Pt(H)(CD_2Cl_2)]BAr^f_4$ (**25**)	−30	C(C*H*$_3$)$_3$	1.48, $^3J_{P-H} = 5$	
		Pt−*H*	−36.3, $^1J_{Pt-H} = 2600$	

Results

Preparation of Hydridoplatinum(II) Complexes. The complexes examined in this study include those of the type *trans*-$(PCy_3)_2Pt(H)X$ [Cy = cyclohexyl; X = SiH_3 (**1**), H (**2**), CH_3 (**3**), Ph (**4**), Cl (**5**), Br (**6**), I (**7**), CN (**8**), CF_3SO_3 (**9**)] and [*trans*-$(PCy_3)_2Pt(H)L][BAr^f_4]$ [L = CO (**10**), 4-picoline (**11**); $BAr^f_4 = B\{3,5\text{-}C_6H_3(CF_3)_2\}_4$]. Only **4** and **6**−**8** have not been reported previously; they were readily prepared according to literature methods or analogous procedures.[21−28] Relevant

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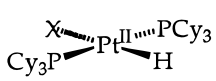
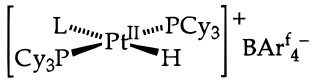
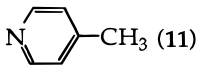


X = SiH_3 (**1**)
H (**2**)
CH_3 (**3**)
Ph (**4**)
Cl (**5**)
Br (**6**)
I (**7**)
CN (**8**)
O_3SCF_3 (**9**)



L = CO (**10**)



NMR spectral data are provided in Table 1 for these and other compounds discussed below.

Protonation of 1−4 at Low Temperature: Complexes Containing *σ* Donor Ligands Trans to Hydride. Addition of $[H(Et_2O)_2]^+BAr^f_4^-$ (abbreviated $HBAr^f_4$) to a CD_2Cl_2 solution of *trans*-$(PCy_3)_2Pt(H)_2$ (**2**) at −95 °C leads to formation of the dihydrogen adduct [*trans*-$(PCy_3)_2Pt(H_2)H]BAr^f_4$ (**12**) (Scheme 2), analogous to adducts recently reported with $P(CMe_3)_3$ and $P(CHMe_2)_3$ ligands.[17−19] The dihydrogen resonance in the ^1H NMR spectrum (Table 1) is characteristically broadened and exhibits a short T_1 (36 ms, 500 MHz) at −85 °C. In contrast, the hydride trans to the H_2 ligand has a long T_1 (606 ms, −85 °C, 500 MHz). A short H−H bond in this H_2 adduct is inferred from the large H−D coupling constant observed upon protonation of *trans*-$(PCy_3)_2Pt(D)_2$ with $HBAr^f_4$ ($^1J_{H-D}$ = 31 Hz). The solvent-coordinated complex [*trans*-$(PCy_3)_2PtH(CD_2Cl_2)]BAr^f_4$ (**13**, Table 1) and free H_2 (δ 4.55 ppm) arise subsequently and exist in equilibrium with **12** (Scheme 2). (Complex **13** was identified based on comparison with related $P(CHMe_2)_3$ and $P(CMe_3)_3$ complexes.[18,19]) This equilibrium was verified by addition of D_2 to the NMR tube containing **12** and **13**; the D_2 adduct (**12**-d_2) is observed by ^2H NMR spectroscopy.

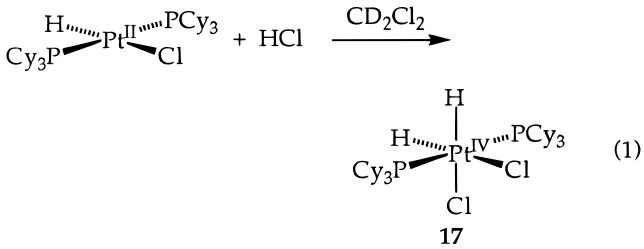
In contrast to the reactions with $HBAr^f_4$, the dihydrogen complex formed upon protonation of $(PCy_3)_2Pt(H)_2$ (**2**) with HOTf (OTf = O_3SCF_3) irreversibly loses H_2 after a few minutes at −95 °C, with formation of *trans*-$(PCy_3)_2Pt(H)(OTf)$ (**9**) (see Table 1). Protonation of **2** with HCl leads directly to *trans*-$(PCy_3)_2Pt(H)Cl$ (**5**) and H_2 at −95 °C; no intermediate H_2 adduct is observed.

Treatment of *trans*-$(PCy_3)_2Pt(SiH_3)H$ (**1**) with $HBAr^f_4$ at −95 °C in CD_2Cl_2 leads to immediate liberation of H_2. However, dihydrogen adducts *are* observed upon carrying out the same reaction with *trans*-$(PCy_3)_2Pt(CH_3)H$ (**3**) and *trans*-$(PCy_3)_2Pt(Ph)H$ (**4**) (Scheme 3 and Figure 1). The dihydrogen resonances for these complexes are shifted upfield relative to that for $[(PCy_3)_2Pt(H_2)H]BAr^f_4$ (**12**) (Table 1). While at −95 °C, methyl complex **14** slowly and irreversibly eliminates CH_4 (Scheme 3); small amounts of free H_2 are also observed in this reaction. The phenyl complex **15** is considerably more stable, however, liberating benzene only upon warming to −50 °C. Free H_2 is never observed in this case (Scheme 3).

Both $[(PCy_3)_2Pt(H_2)CH_3]BAr^f_4$ (**14**) and $[(PCy_3)_2Pt(H_2)Ph]BAr^f_4$ (**15**) exhibit characteristically short T_1 values for the H_2 signals (**14**, 26 ms, −95 °C; **15**, 20 ms, −65 °C). (Elimination of methane and benzene from **14** and **15**, respectively, prevented determination of the minimum T_1 values.) Protonation of $(PCy_3)_2Pt(CH_3)H$ (**3**) and $(PCy_3)_2Pt(Ph)H$ (**4**) with $DBAr^f_4$ generates the HD adducts, **14**-d_1 and **15**-d_1, which exhibit large H−D coupling constants of 30.5 and 33.6 Hz, respectively. Addition of HCl to **4** at −80 °C immediately liberates H_2 along with formation of *trans*-$(PCy_3)_2Pt(Ph)Cl$ (**16**) (no benzene is observed). Correspondingly, addition of chloride to the H_2 adduct, **15**, at −80 °C results in rapid substitution of H_2 by chloride (Scheme 4).

No multiple deuterium incorporation is observed in the methane liberated from the reaction between *trans*-$(PCy_3)_2Pt(CH_3)D$ and 10 equivalents of $DBAr^f_4$ at −80 °C. In the presence of a large excess of $HBAr^f_4$ and $DBAr^f_4$, a deuterium kinetic isotope effect of 2.5 (±0.4) was determined for protonolysis of the Pt−CH_3 bond based on the ratio of CH_4/CH_3D generated.

Protonation of 5−7 at Low Temperature: Complexes Containing *σ* and *π* Donor Ligands Trans to Hydride. Protonation of *trans*-$(PCy_3)_2Pt(H)Cl$[28] (**5**) with HCl at −80 °C slowly forms the oxidative addition product $(PCy_3)_2Pt(H)_2Cl_2$ (**17**) (eq 1 and Table 1). The stereochemistry of the Pt(IV)



(1)

17

product is presumably that shown in eq 1, however, other less likely structures are also consistent with NMR data. Adding HCl to a CD_2Cl_2 solution of *trans*-$(PCy_3)_2Pt(H)I$ (**7**) leads to three Pt(IV) products, reflecting facile halide exchange between the complexes: $(PCy_3)_2Pt(H)_2Cl_2$ (**17**), $(PCy_3)_2Pt(H)_2I_2$ (**18**), and $(PCy_3)_2Pt(H)_2(Cl)I$ (**19**) (Table 1). While **17** and **18** were prepared independently to verify this assignment, formation of **19** is inferred from mass balance and chemical shifts of the hydride resonances, which are consistent with such an assignment.

Protonation of *trans*-$(PCy_3)_2Pt(H)X$ [X = Cl (**5**), Br (**6**), I (**7**)] with $HBAr^f_4$ rather than HCl leads to different products. In each case, three separate platinum-hydride resonances are observed in the ^1H NMR spectrum of the reaction mixture. These peaks correspond to the three platinum complexes shown in eq 2. For example, upon addition of $HBAr^f_4$ to **7** at −80 °C, resonances appear at δ −14.65 ppm ($^1J_{Pt-H}$ = 1390) (**7**), −15.79 ppm ($^1J_{Pt-H}$ = 1115 Hz) (**18**), and −18.07 ppm ($^1J_{Pt-H}$ = 1640 Hz) (**23**). The peaks associated with **18** and **23** are of equal intensity (Figure 2). The ^1H NMR resonance for "H^+" in this reaction appears at 16.7 ppm. The chloride-bridged dimer **21** was prepared independently by mixing one equivalent of $(PCy_3)_2Pt(H)Cl$ (**5**) and $[(PCy_3)_2PtH(solvent)]BAr^f_4$ in CH_2Cl_2. The reversibility of the equilibrium in eq 2 was qualitatively verified by warming and recooling the reaction mixture between −95 and −45 °C, and observing that the relative concentrations of [**18**] + [**23**] vs [**7**] change depending on the temperature,

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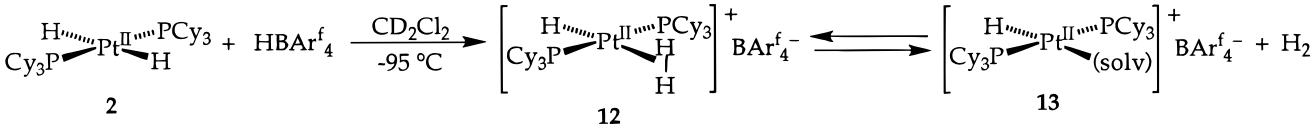
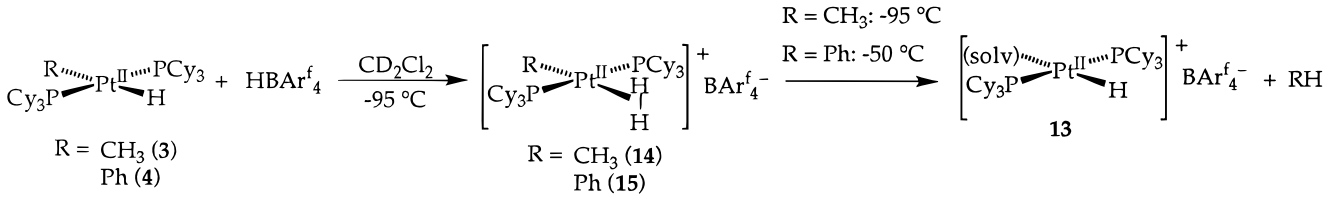
Scheme 2



Scheme 3



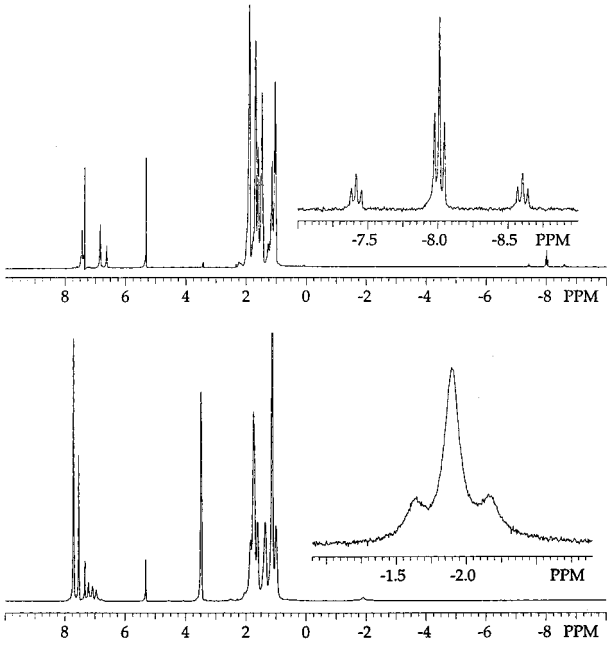
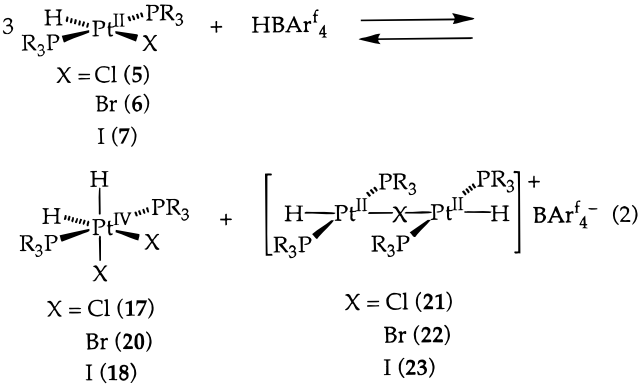


Figure 1. ^{1}H NMR spectra of *trans*-$(PCy_3)_2Pt(Ph)H$ (**4**) (top spectrum) and the H_2 adduct $[(PCy_3)_2Pt(H_2)Ph]BAr^f_4$ (**15**) generated upon protonation of **4** with $HBAr^f_4$.



with the left side of the equilibrium being favored at lower temperatures. Upon warming the reaction mixture above ~−40 °C, irreversible protonation of the phosphine ligands causes decomposition of the products. (^{1}H NMR $[Cy_3PH]^+$: 5.1 ppm (d), $^1J_{P-H}$ = 440 Hz) Addition of NBu_4Cl to the reaction mixture containing **5**, **17**, and **21**, or addition of NBu_4I to the mixture of **7**, **18**, and **23** results in complete formation of the Pt(IV) dihydride products **17** and **18**, respectively. Monitoring the reactions in eq 2 using ^{31}P NMR verified the identity of the products and confirmed the absence of nonhydride containing products (see data in Table 1).

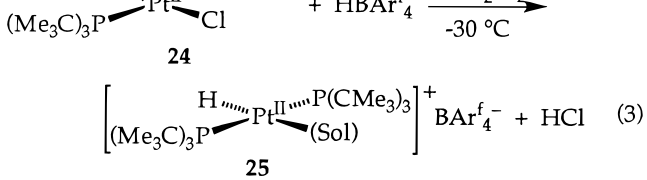
The reaction between $HBAr^f_4$ and $(PCy_3)_2Pt(H)Cl$ (**5**) is, in fact, more complex than indicated by eq 2. At −95 °C, the Pt−*H* ^{1}H NMR resonance corresponding to **5** broadens significantly and shifts upfield slightly upon addition of $HBAr^f_4$. This peak is assigned to a new species (or mixture of species), **5**·$HBAr^f_4$. Upon slight warming of the reaction mixture (e.g., at −80 °C), the products **17** and **21** arise in an equilibrium with **5**·$HBAr^f_4$, in accord with eq 2 (Figure 3).

The upfield shift of **5**·$HBAr^f_4$ (peak A′ in Figure 3) relative to **5** is dependent on the H^+ concentration, with higher $[H^+]$ leading to a greater upfield shift. The origin of this behavior is not entirely clear but possibly originates from equilibrium protonation of either the chloride or hydride in **5** (see discussion below). The ^{1}H NMR resonance associated with **5**·$HBAr^f_4$ exhibits a significantly reduced $T_{1(min)}$ relative to **5** (**5**, $T_{1(min)}$ = 480 ms at −55 °C; **5**·$HBAr^f_4$, $T_{1(min)}$ = 80 ms at −32 °C). Furthermore, addition of $DBAr^f_4$ to **5** results in rapid H/D exchange between D^+ and the platinum hydride.

The same behavior does not appear for the bromide and iodide complexes, **6** and **7**. Addition of $HBAr^f_4$ to **6** or **7** has very little effect on their respective ^{1}H NMR signals (cf. Figure 2). Verification of this observation is the relatively long T_1 observed for **6** in the presence of $HBAr^f_4$: $T_{1(min)}$ = ~350 ms at −40 °C.

Unfortunately, these results (i.e., the equilibria in eq 2) are complicated by the presence of adventitious H_2O in the $HBAr^f_4$ (see Experimental Section). Water acts as a base in the reaction and shifts the equilibrium in eq 2 toward the starting materials.

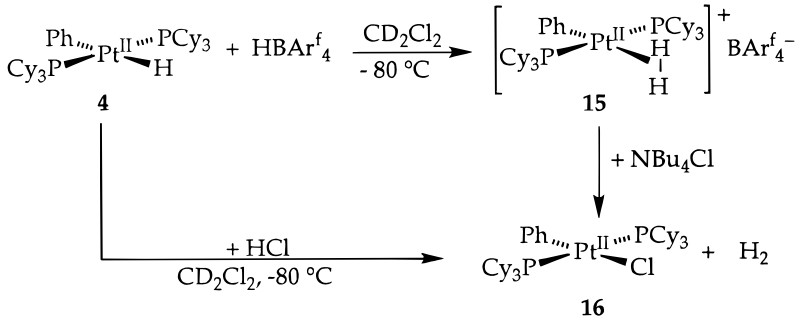
Treating the related $P(CMe_3)_3$-ligated complex, *trans*-$\{P(CMe_3)_3\}_2Pt(H)Cl$ (**24**),[24,26] with $HBAr^f_4$ generates the solvated hydridoplatinum(II) complex (**25**) at −30 °C reflecting electrophilic attack at the chloride (eq 3). Gusev et al. have recently



examined this reaction in much more detail and suggest the presence of an intermediate η^1-HCl adduct prior to loss of HCl.[18]

Protonation of 8, 10, and 11: Complexes Containing a Cationic Charge and/or a π Acid Ligand Trans to Hydride. No reaction is observed between $HBAr^f_4$ and the cationic complexes [*trans*-$(PCy_3)_2Pt(H)L][BAr^f_4]$ [L = CO (**10**), 4-picoline (**11**)] in CD_2Cl_2, even after 2 days at room temperature.

Scheme 4



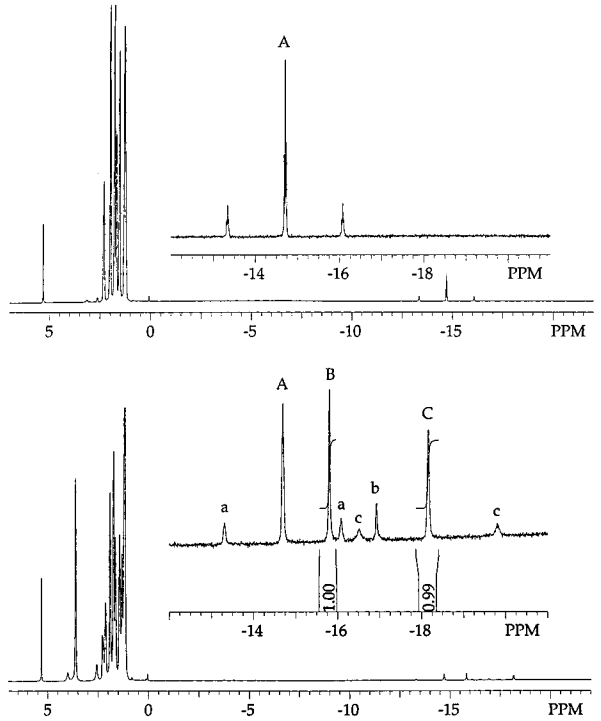


Figure 2. ^{1}H NMR spectra of *trans*-$(PCy_3)_2Pt(H)I$ (**7**) (top spectrum) and of the products generated upon addition of $HBAr^f_4$ to **7** in CD_2Cl_2. The labeled peaks correspond to the following compounds: **A**, *trans*-$(PCy_3)_2Pt(H)I$ (**7**); **B**, $(PCy_3)_2Pt(H)_2I_2$ (**18**); and **C**, $\{[(PCy_3)_2Pt(H)]_2I\}BAr^f_4$ (**23**). The lowercase letters correspond to platinum satellites of the peaks labeled with uppercase letters.

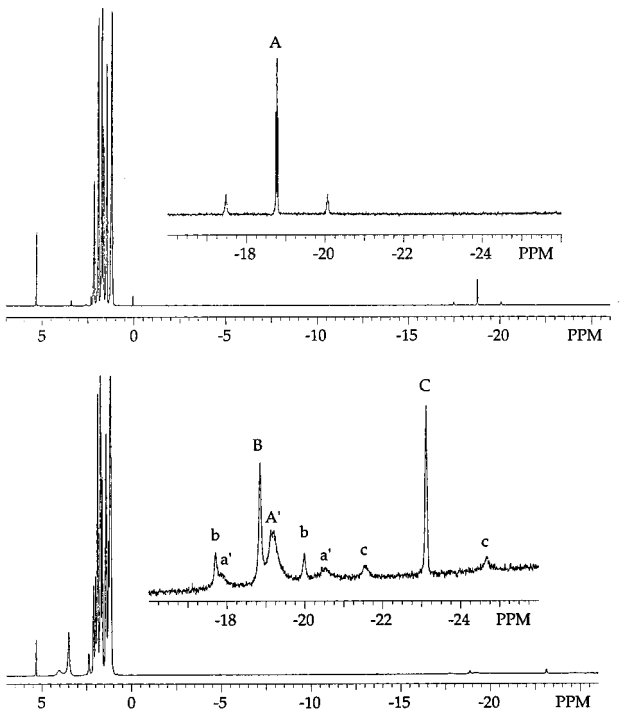


Figure 3. ^{1}H NMR spectra of *trans*-$(PCy_3)_2Pt(H)Cl$ (**5**) (top spectrum) and of the products generated upon addition of $HBAr^f_4$ to **5** in CD_2Cl_2. The labeled peaks correspond to the following compounds: **A**, *trans*-$(PCy_3)_2Pt(H)Cl$ (**5**); **A′**, "$(PCy_3)_2Pt(H)Cl{\cdot}HBAr^f_4$"; **B**, $(PCy_3)_2Pt(H)_2Cl_2$ (**17**); and **C**, $\{[(PCy_3)_2Pt(H)]_2Cl\}BAr^f_4$ (**21**). The lowercase letters correspond to platinum satellites of the peaks labeled with uppercase letters.

Moreover, no reaction is observed between **10** and hydrogen chloride, even in the presence of 15 equiv of HCl. In contrast, formation of a dihydrido Pt(IV) product is observed upon addition of HCl to **11**.

Protonation of the neutral cyanide complex (**8**) with 1 equiv of $HBAr^f_4$ at room temperature results in a downfield shift of the Pt−*H* ^{1}H NMR resonance (**8** [CD_2Cl_2], δ −8.82 ppm, $^1J_{Pt-H}$ = 775 Hz; **8** + $HBAr^f_4$, −7.24 ppm, $^1J_{Pt-H}$ = 835 Hz). The data were not consistent with formation of a dihydrogen adduct or a Pt(IV) dihydride species (e.g., no reduction in the T_1 of the platinum hydride). However, upon cooling the reaction mixture to ∼−120 °C a new "H^+" peak is observed at 13.3 ppm. (Probe temperatures were calibrated using the $\Delta\nu$ for CH_3OH ^{1}H NMR resonances. Reaction temperatures below the nominal freezing point of CD_2Cl_2 are presumably attainable by freezing point depression and/or supercooling of the solution.) If 3 equiv of HCl is added to **8**, two "H^+" peaks are observed at −115 °C in a 2:1 ratio at 12.9 and 14.4 ppm, respectively. Since 12.9 ppm corresponds to the chemical shift of HCl in CD_2Cl_2 not containing **8** at −115 °C, the peak at 14.4 is assigned to a hydrogen isocyanide (HNC) ligand (eq 4). This assignment is supported by IR spectroscopy. Upon protonation of **8**, the C−N stretch shifts to higher energy, from ν = 2128 to 2156 cm^{-1}. This shift is consistent with other examples of Lewis acid complexation of coordinated cyanides.[29−33]

Reactions between CH_3OTf and Hydridoplatinum(II) Complexes. Electrophilic attack by CH_3OTf on hydridoplatinum(II) complexes was also briefly examined. Whereas methane is liberated at −45 °C in the reaction between CH_3OTf and *trans*-$(PCy_3)_2Pt(H)Ph$ (**4**), electrophilic attack at chloride is observed in the CH_3OTf reaction with *trans*-$(PCy_3)_2Pt(H)Cl$ (**5**) and *trans*-$(PBu^t_3)_2Pt(H)Cl$ (**24**) at +15 °C, leading

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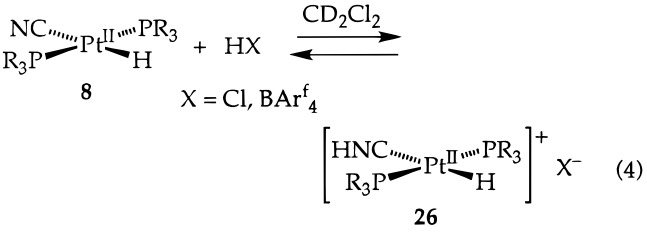
(30) Evans, D. F.; Jones, D.; Wilkinson, G. *J. Chem. Soc.* **1964**, 3164−3167.
(31) Siebert, H. *Z. Anorg. Allg. Chem.* **1964**, *327*, 63−70.
(32) Eaton, D. R.; Sandercock, A. C. *J. Phys. Chem.* **1982**, *86*, 1371−1375.
(33) Markwell, A. J.; Pratt, J. M.; Shaikjee, M. S.; Toerien, J. G. *J. Chem. Soc., Dalton Trans.* **1987**, 1349−1357.



(4)

to formation of CH_3Cl and the corresponding solvated cationic hydridoplatinum(II) complexes (**9** and **25**).

Discussion

Sites of Electrophilic Attack: Evidence for Protonation at all Three Possible Sites. In 1994, Gusev et al. reported the first example of a platinum(II) dihydrogen complex, [*trans*-{P(CMe$_3$)$_3$}$_2$Pt(H$_2$)H]OTf.[17] Because platinum(IV) dihydrides are also known,[34−36] we undertook a systematic investigation of related hydridoplatinum(II) complexes to examine the factors which dictate the site of electrophilic attack in protonation reactions. Despite the steric stabilization provided by the P(CMe$_3$)$_3$ ligand, its extreme bulk (cone angle > 180° [37]) limits the range of complexes that can be readily prepared. Consequently, we chose to investigate complexes containing the PCy$_3$ ligand. Tricyclohexylphosphine also exhibits a very large cone angle (170°), and its electronic effects are very similar to P(CMe$_3$)$_3$.[37]

Protonation of the hydridoplatinum(II) complexes discussed above reveals electrophilic attack at all three possible sites (Scheme 5): hydride (**K**, **1**−**4**), platinum (**J**, **5**−**7**), and the trans ligand (e.g., cyanide) (**I**, **8** and **24**). We know of no other class of complexes where protonation at *all three* sites has been observed.[38] In addition, irreversible protonation at a fourth site, the phosphine ligands, is also observed for the halide complexes **5**−**7** at higher temperatures. It should be noted that protonation at platinum to give Pt(IV) (**J**) is only observed in the presence of a good sixth ligand (halide) to stabilize the d^6 octahedral metal center. We do not observe interconversion between any of our products with the other possible "tautomers," except possibly in the protonation of (PCy$_3$)$_2$Pt(H)Cl as discussed below. (The products shown in Scheme 5 are not rigorously tautomers, that is, complexes differing only in the position of the proton, because the Pt(IV) dihydride product contains an extra ligand.) Also, we can generally identify only the *thermodynamic* sites of protonation; in some cases, unobserved kinetic products may precede those we have characterized (see further discussion below).

Pt(II) Dihydrogen Complexes: Effect of Trans Ligands and the Reversibility of Protonation. All of the complexes which lead to formation of an H_2 adduct (**2**−**4**) bear a strong σ donor ligand trans to the hydride. Presumably the strong donating ability of these ligands enhances the basicity of the trans hydride, making it more susceptible to protonation (relative to the platinum center). For complexes (PCy$_3$)$_2$Pt(CH$_3$)H (**3**) and (PCy$_3$)$_2$Pt(Ph)H (**4**), we find that the products of protonation at hydride (i.e., H_2 adducts **14** and **15**) eventually decompose by irreversible protonolysis of the Pt−C bond.

As expected, the lability of the Pt−(H$_2$) bond tracks with the trans effect of this ligand: −SiH$_3$ > −H ∼ −CH$_3$ > −Ph. Competitive formation of methane from [*trans*-(PCy$_3$)$_2$Pt(H$_2$)CH$_3$]BAr$^f_4$ (**14**) even at −95 °C limits our ability to compare this complex with [*trans*-(PCy$_3$)$_2$Pt(H$_2$)H]BAr$^f_4$ (**12**) more precisely. The large $^1J_{H-D}$ values observed for the deuterated analogues of **12**, **14** and **15** indicate they have a rather short, "unactivated" H−H bond (∼0.8−0.9 Å) based on the correlation between $^1J_{H-D}$ and the H−H bond distances noted in other H_2 complexes.[13,39]

In principle, rather than protonation at hydride (Path A, Scheme 6), protonation at platinum could lead to formation of the thermodynamically favored H_2 adduct (Path B, Scheme 6); however we have no evidence for such a route. Similarly, loss of methane on protonation of *trans*-(PCy$_3$)$_2$Pt(H)CH$_3$ may occur either by a sequence involving preequilibrium deprotonation of [*trans*-(PCy$_3$)$_2$Pt(H$_2$)CH$_3$]$^+$ (**14**) followed by direct attack at the Pt−C bond to give **L** (Path C, Scheme 6), or via preequilibrium formation of a five-coordinate methyldihydridoplatinum(IV) complex (**M**) which reductively eliminates methane (Path D, Scheme 6). The deuterium kinetic isotope effect (k_H/k_D = 2.5) does not permit a distinction. A recent theoretical study indicates that the (five-coordinate) Pt(IV) tautomer (**M**) is much higher in energy than either σ adduct (**14** or **L**).[17,18]

Lack of deuterium incorporation into the methyl group in the presence of excess DBAr$^f_4$ indicates that if the methane σ adduct (**L**) is on the reaction pathway, it must lose methane faster than it reverts via either path C or D. In contrast, protonation of **3** at hydride to give **14** is reversible. Two factors likely contribute to this result: (1) a larger barrier for displacement of H_2 versus methane (probably due to a stronger Pt−H$_2$ bond) and (2) a higher *kinetic* acidity of coordinated H_2 versus coordinated methane. Recent theoretical results suggest bound H_2 would also be *thermodynamically* more acidic than coordinated methane.[18]

The reaction between "CH_3^+" (as CH_3OTf) and three different platinum(II) hydrides also failed to provide evidence for a methane σ adduct. In fact, for the complexes *trans*-(PCy$_3$)$_2$Pt(H)Cl (**5**) and *trans*-{P(CMe$_3$)$_3$}$_2$Pt(H)Cl (**24**), CH_3^+ attacks chloride rather than hydride, generating CH_3Cl. The chloride in **24** is also attacked when H^+ is the electrophile.[18] These results likely arise from steric effects in the transition state for electrophilic attack. For example, the extreme steric bulk of P(CMe$_3$)$_3$ effectively prevents formation of a six-coordinate Pt(IV) product. The transition state for attack at the Pt−H bond in **24** would also be extremely sterically congested, thus leaving the chloride lone pairs as the only accessible site for electrophilic attack. Steric effects may also play a role in the electrophilic attack on **5**, with H^+ preferring attack at platinum and CH_3^+ at chloride.

Mechanism of H_2 Ligand Substitution. Our earlier investigation of the protonolysis of various alkylplatinum(II) complexes[16] provided evidence for methane σ adducts as intermediates in the reaction. Methane displacement from these intermediates appears to follow both associative (for [*trans*-(PEt$_3$)$_2$Pt(CH$_4$)Cl]$^+$) and dissociative (for [(tmeda)Pt(CH$_4$)Cl]$^+$, tmeda = tetramethylethylenediamine) pathways based on kinetics of the protonolysis reaction. However, because the intermediate σ adducts are not observed, these conclusions remain somewhat tentative. In the reactions described here, H_2 displacement from [*trans*-(PCy$_3$)$_2$Pt(H$_2$)H]$^+$ (**12**) appears to

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(36) Blacklaws, I. M.; Ebsworth, E. A. V.; Rankin, D. W. H.; Robertson, H. E. *J. Chem. Soc., Dalton Trans.* **1978**, 753−758.
(37) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313−348.
(38) Kuhlman, R. *Coord. Chem. Rev.* **1997**, *167*, 205−232.
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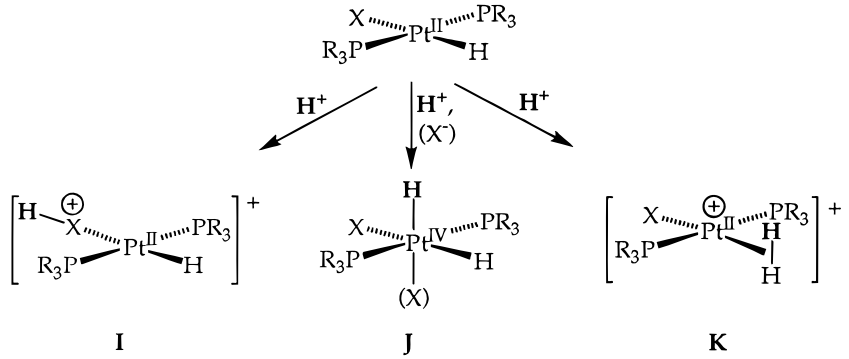
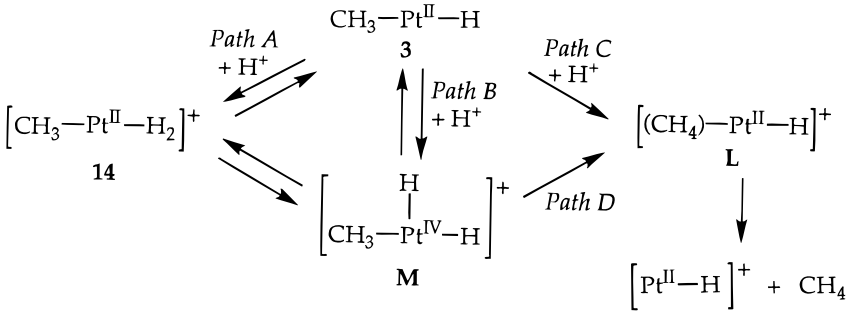
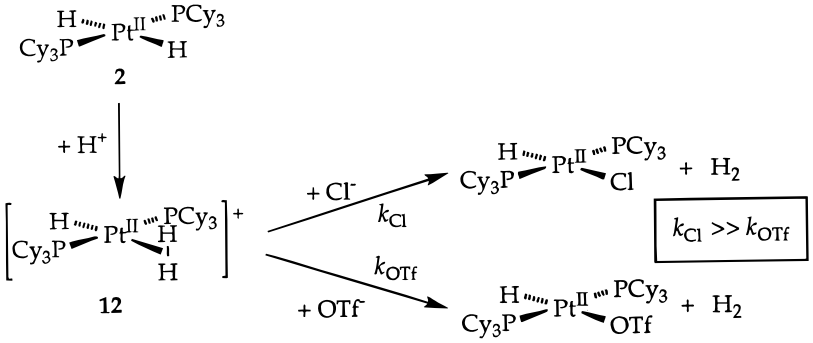
Scheme 5



Scheme 6



Scheme 7



proceed through an *associative* pathway, based on the dependence of the substitution rate on the incoming ligand. Liberation of H_2 from **12** proceeds considerably faster in the presence of chloride (k_{Cl}) than triflate (k_{OTf}) (Scheme 7), as determined by comparing the reaction of **2** with HCl versus HOTf. However, it is not possible to rule out a mechanism involving preequilibrium loss of H_2 (i.e., through a *dissociative* pathway). Different incoming ligands will then trap the cationic intermediate at different rates.

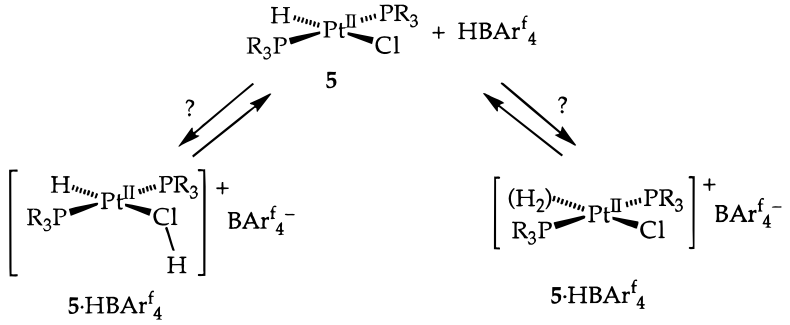
Protonation of Halide Complexes 5−7: Observation of Pt(IV) Dihydride Complexes. Substitution of the strong σ donor ligand with a halide appears to dramatically reduce the basicity of the trans hydride relative to the platinum center; a dihydrogen adduct is no longer observed as the thermodynamic product. Instead, protonation at platinum results. Importantly, the Pt(IV) dihydride product observed upon protonation of all three halide complexes (**5**−**7**) is *six*-coordinate. When $HBAr^f_4$ is the proton source, the sixth ligand is acquired by halide abstraction from the starting material. We obtain no evidence for a five-coordinate, Pt(IV) dihydride product in any of our reactions. Our observations are consistent with the proposal by Falk and Halpern[40] for the mechanism of H/D exchange between D_2O and *trans*-$(PEt_3)_2Pt(H)Cl$. On the basis of kinetic studies they suggested a Pt(IV) hydride/deuteride intermediate stabilized by chloride or solvent in the sixth coordination site.

The Pt(II) chloride complex (**5**) appears to interact with $HBAr^f_4$. At this point we cannot definitively identify the nature of this interaction; however, the ^1H NMR behavior seems consistent with rapid, reversible protonation of either the hydride or chloride ligands (Scheme 8).

The rapid H/D exchange between $DBAr^f_4$ and the platinum hydride supports protonation at the hydride (although the chloride−H^+ interaction still could be thermodynamically favored). Similar observations, namely (1) a reduced T_1 relaxation time and (2) an upfield shift in the hydride resonance, were recently reported for a series of tungsten hydride complexes in the presence of acidic alcohols.[41] These data were interpreted as *intermolecular* hydrogen bonding between the alcohols and the tungsten hydride. Several other examples of hydrogen bonding to transition metal hydrides have been reported recently,[42] although most are *intramolecular* interactions. In our case, such interaction would lead to a "stretched" H_2 adduct.

(40) Falk, C. D.; Halpern, J. *J. Am. Chem. Soc.* **1965**, *87*, 3523−3524.
(41) Shubina, E. S.; Belkova, N. V.; Krylov, A. N.; Vorontsov, E. V.; Epstein, L. M.; Gusev, D. G.; Niedermann, M.; Berke, H. *J. Am. Chem. Soc.* **1996**, *118*, 1105−1112.

Scheme 8



The origin of the *upfield* shift is currently unexplained; formation of dihydrogen adducts **12**, **14**, and **15** results in downfield shifts (see Table 1), approaching the value of free H_2 (δ 4.55 ppm). Direct determination of the pK_a value for an osmium adduct of H_2 trans to chloride and bromide revealed that the bromide complex is more acidic.[43] This result is consistent with our results, since no interaction is observed between H^+ and the bromide and iodide complexes **6** and **7**.

An alternative explanation for our observations is protonation at chloride. The proposal is in accord with protonation of chloride of the $P(CMe_3)_3$ complex **24**.[18] Formation of an HCl adduct would account nicely for an upfield shift in the Pt−*H* ^{1}H NMR resonance relative to **5** since HCl is a weaker ligand than Cl^-. Furthermore, the greater basicity of chloride relative to bromide and iodide consistently predicts that **6** and **7** should exhibit a weaker interaction with H^+. However, this proposal does not explain the reduced $T_{1(min)}$ value. At this point, we cannot definitively identify the nature of this interaction. Our inability to completely exclude adventitious water also limits our ability to interpret these results.

Protonation of Complexes Containing a Cationic Charge and/or a π Acid Ligand Trans to Hydride. The CO complex **10** exhibits no affinity for H^+. Presumably the cationic charge of this complex combined with the strong π acidity of the CO ligand dramatically reduces its basicity. The other cationic complex examined here (**11**) has picoline, a relatively weak σ donor, trans to the hydride. In this case, a Pt(IV) dihydride product can be observed, but again, only in the presence of a sixth ligand (chloride) to stabilize the d^6 product. No reaction is observed in the absence of chloride (i.e., upon addition of $HBAr^f_4$).

An isocyanide ligand is formed upon protonation of the cyanide complex, **8**. This is the only example where we directly observe H^+ interaction with the ligand trans to hydride. Morris and co-workers recently observed a similar reaction with *trans*-$[FeH(CN)L_2]$ (L = a diphosphine ligand). In their case, protonation at either hydride or the cyanide nitrogen can be observed depending on the phosphine ligand used.[44]

Contrast between Square-Planar d^8 and Octahedral d^6 Dihydrogen Adducts. Because of the rarity of d^8 dihydrogen complexes, it may be valuable to compare our results with those of better known octahedral d^6 complexes. Homolytic cleavage (*i.e.*, oxidative addition) of a dihydrogen ligand appears more facile in the d^6 complexes, as suggested by several examples of reversible dihydride/dihydrogen adduct equilibria that have been reported for such complexes.[11,13] In these cases, the equilibrium exists between six-coordinate d^6 (H_2 adduct) and seven-coordinate d^4 (dihydride) structures. In our case, the corresponding equilibrium between four-coordinate d^8 and five-coordinate d^6 structures appears energetically prohibitive. In fact, the dihydride "tautomer" is only observed in the presence of a sixth ligand. We never observe interconversion between an H_2 adduct and a Pt(IV) dihydride complex. Notably, addition of chloride to the dihydrogen complexes **12**, **14**, and **15** promotes ligand substitution rather than conversion to the dihydride structure. There is evidence for such interconversion between the corresponding tautomers in alkane interactions with platinum (although the alkane adduct is not observed directly).[16,45]

Other features, however, demonstrate the qualitative similarities between octahedral d^6 and square-planar d^8 dihydrogen complexes. Several studies have examined the impact of the ligand trans to H_2 in octahedral ruthenium and osmium complexes.[39,43,46−49] Longer *d*(H−H) is observed in complexes having halides (σ *and* π donors) trans to H_2 versus hydride (σ-only donor). Our studies reveal similar behavior. Dihydrogen complexes are observed with trans σ donor ligands (CH_3, Ph, H), whereas the Pt(IV) dihydride structure, the limit of homolytic activation, is stabilized by halide ligands. This trend is typically attributed to a "π effect" in which π symmetry electron density from the halide leads to more back-bonding into the σ* orbital of bound H_2.

Relative to a hydride ligand, halides enhance the acidity of coordinated dihydrogen. Use of neutral trans ligands, which increase the positive charge on the complex, lowers the pK_a even further.[39,43,46,47,50] Although the pK_a's of our complexes have not yet been determined, this qualitative trend is borne out. Protonation of the hydride ligand occurs readily when it is trans to a strong σ donor (as for **2**, **3**, and **4**). Although there may be some affinity between protons and the hydride ligand in the chloride complex (**5**), this interaction appears quite weak. Furthermore, no direct proton−hydride interaction is ever observed for the bromide and iodide complexes (**6** and **7**) or the cationic complexes (**10** and **11**). Such observations are intuitively reasonable: a strong σ donor should enhance the basicity of the trans hydride, and further, cationic hydride complexes should be less basic than related neutral species.

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Conclusion

This study has allowed us to address several questions regarding Pt(II) σ adducts. As expected the strength and lability of the interaction depends directly on the nature of the trans ligand. Also, substitution of coordinated H_2 from the complexes examined here probably proceeds through an associative mechanism. This result may not be general for other Pt(II) σ adducts, however, since the mechanism is likely influenced by the ancillary ligands and the strength of the Pt(II)$-\sigma$ adduct bond.

The variation of the site of electrophilic attack with the ligand trans to hydride seems particularly relevant to alkane activation. C−H activation by Pt(II) appears to proceed through *both* an alkane σ adduct and a Pt(IV) alkyl hydride intermediate; however, deprotonation only occurs from the Pt(IV) hydride.[16] Shilov chemistry takes place in the presence of good ligands for Pt(IV) (Cl^- and H_2O), the same types of ligands that promote electrophilic attack at platinum in the hydride complexes discussed above. Thus, the success of the Shilov system may, in part, depend on appropriate ligands to access the *kinetically* more acidic Pt(IV) alkyl hydride intermediate. Such considerations suggest that an extremely electrophilic platinum(II) complex, one which strongly destabilizes Pt(IV), may not be the best candidate for C−H activation.

For systems in which C−H oxidative addition is not a viable option (e. g., with Pd(II)[51] and Hg(II)[52]), alkane activation has only been observed in strong acid solvents which dramatically enhance the electrophilicity of the metal ions. (Attempts to reproduce the recently reported oxidative addition of C−H bonds by Pd(II)[53] were unsuccessful in our laboratory.[54]) Deprotonation of a coordinated alkane may be the most plausible mechanism in these reactions.

Experimental Section

General Considerations. All syntheses and reactions were carried out under air-free conditions using standard Schlenk, inert-atmosphere glovebox, or high-vacuum techniques. NMR spectral data was obtained using a Bruker AM500 NMR spectrometer. All solvents used were dried prior to use: CD_2Cl_2, distilled from fresh CaH_2 and stored over 4 Å molecular sieves; CH_2Cl_2, distilled from P_2O_5; toluene, predried over 4 Å molecular sieves and then distilled from sodium. Preparation of the following compounds was carried out according to literature procedures or slight modifications thereof: $[H(Et_2O)_2][BAr^f_4]$ [BAr^f_4 = B(3,5-$C_6H_3(CF_3)_2)_4$], *trans*-$(PCy_3)_2Pt(H)X$ [X = SiH_3 (**1**),[23] H (**2**),[25] CH_3 (**3**),[28] Cl (**5**),[28] CF_3SO_3 (**9**)[21]], [*trans*-$(PCy_3)_2Pt(H)L][BAr^f_4]$ [L = CO (**10**),[21] 4-picoline (**11**)[21]], and *trans*-$\{P(CMe_3)_3\}_2Pt(H)Cl$ (**24**).[26]

Warning: *SiH_4 used in the preparation of **1** is explosive on contact with air. Thus, minimal excess should be used in this reaction.*

Preparation of *trans*-$(PCy_3)_2Pt(Ph)H$ (4). $(PCy_3)_2Pt(H)Cl$ (200 mg, 0.25 mmol) was dissolved in dry toluene in a Schlenk flask. After the solution was cooled to 0 °C, PhMgBr (210 μL, 3.0 M solution, 0.63 mmol) was added via syringe. The reaction mixture was then stirred for several hours while slowly warming to room temperature. The reaction was then quenched with water. The organic layer was then separated, filtered through Celite, and dried with $MgSO_4$. Removal of the solvent afforded the product in moderate yield (60%). The solid was purified by washing with diethyl ether. See Table 1 for NMR data. Anal. Calcd for $C_{42}H_{72}P_2Pt$: C, 60.48; H, 8.70. Found: C, 60.34; H, 8.50. IR: ν(Pt−H) = 1958 cm^{-1} (s).

Preparation of *trans*-$(PCy_3)_2Pt(H)X$, X = Br (6), I (7). $(PCy_3)_2$-Pt(H)Cl (60 mg, 0.076 mmol) was added to a pear-shaped flask containing a stir bar and suspended in acetone (3−5 mL) under argon. Lithium bromide (66 mg, 0.76 mmol) or LiI (100 mg, 0.75 mmol) was then added to the flask, and the reaction mixture was stirred for 2 days (this duration is likely not necessary to complete the reaction). The acetone was removed under vacuum, and the product was extracted from the resulting solid with toluene. Subsequent evaporation of the toluene afforded the analytically pure products in high (80−90%) yield. See Table 1 for NMR data. Anal. Calcd for $C_{36}H_{67}BrP_2Pt$: C, 51.67; H, 8.07. Found: C, 51.96; H, 8.04. Anal. Calcd for $C_{36}H_{67}IP_2Pt$: C, 48.62; H, 7.64. Found: C, 48.72; H, 7.34. IR: (**6**) ν(Pt−H) = 2176 cm^{-1} (m); (**7**) ν(Pt−H) = 2153 cm^{-1} (m).

Preparation of *trans*-$(PCy_3)_2Pt(H)CN$ (8). $(PCy_3)_2Pt(H)Cl$ (100 mg, 0.13 mmol) was dissolved in CH_2Cl_2 (5 mL) in a Schlenk flask under argon, and a solution of AgOTf (32.4 mg, 0.13 mmol) in methanol (3 mL) was added via syringe. The mixture was stirred for 80 min, and the solvent was then removed under vacuum. A dichloromethane extract of the resulting solid was filtered through Celite to remove suspended AgCl. The CH_2Cl_2 was removed under vacuum, and the residue was dissolved in methanol (5 mL). Sodium cyanide (6.2 mg, 0.13 mmol) was added to this solution, and the reaction mixture was stirred for 15 min. Solvent was removed and the solid was partitioned between water and CH_2Cl_2. The CH_2Cl_2 fraction was dried over $MgSO_4$. Removal of CH_2Cl_2 led to an oily product which solidified upon washing with pentane. Yield: 52%. See Table 1 for NMR data. Anal. Calcd for $C_{37}H_{67}NP_2Pt$: C, 56.76; H, 8.63; N, 1.79. Found: C, 56.90; H, 8.73; N, 1.64. IR: ν(Pt−H) = 2043 cm^{-1} (mw), ν(C−N) = 2128 cm^{-1} (mw).

Preparation of dry $[H(Et_2O)_2][BAr^f_4]$ [BAr^f_4 = B(3,5-C_6H_3-$(CF_3)_2)_4$]. This reagent was prepared according to procedures reported previously.[55] As mentioned in the text above, the product was often contaminated with varying amounts of water, primarily arising from incomplete removal of H_2O from $NaBAr^f_4 \cdot xH_2O$. Although elemental analysis of the $HBAr^f_4$ reagent is consistent with the formulation $[H(Et_2O)_2][BAr^f_4]$, inspection of the ^1H NMR spectrum at low temperature revealed the presence of two "H^+" peaks at ∼16.6 and 13.1 ppm. Addition of a few equivalents of H_2O to the solution converted all of the "H^+" to the upfield resonance. This complication can be alleviated in part by drying the $NaBAr^f_4 \cdot xH_2O$ *several times* over activated 4 Å molecular sieves (we had previously done this only once); however, adventitious water is difficult to exclude completely.

General Procedure for Low-Temperature Protonation Experiments. Except where indicated otherwise, reaction mixtures for low-temperature NMR experiments were prepared by loading the solid starting material into a 5 mm NMR tube equipped with a screw cap and silicone/PTFE septum (available from Wilmad Glass Company). The reagent was then dissolved in CD_2Cl_2 (∼450 μL) and cooled to −95 °C. The $HBAr^f_4$ was loaded into a vial in the glovebox and sealed with a rubber septum. It too was dissolved in CD_2Cl_2 (∼200 μL) and added to the precooled NMR tube via syringe. Alternatively, for reactions with HCl, a solution of HCl in diethyl ether-d_{10} (1.8 M) was added to the pre-cooled NMR tube via syringe. The combined reagents were vigorously shaken while at −95 °C prior to inserting the tube into a precooled NMR probe. An identical procedure was used for the reaction of **4**, **5**, and **23** with CH_3OTf.

Preparation and Characterization of [*trans*-$(PCy_3)_2Pt(H_2)R]$-BAr^f_4, R = H (12), CH_3 (14), Ph (15). The H_2 adducts **12**, **14**, and **15** were prepared by addition of $HBAr^f_4$ to the hydride complexes **2**−**4** according to the general procedures outlined above. T_1 measurements for these compounds were obtained at 500 MHz at various temperatures using the inversion recovery method. The $^1J_{HD}$ values for **14**-d_1 and **15**-d_1 were obtained by addition of $DBAr^f_4$ to the corresponding hydrides (**3** and **4**). The $^1J_{HD}$ value for **12**-d_2 was obtained by adding $HBAr^f_4$ to the dideuteride *trans*-$(PCy_3)_2Pt(D)_2$ (**2**-d_2). Compound **2**-d_2 was prepared in identical manner to **2**,[25] except using $NaBD_4$ instead of $NaBH_4$ in the reaction. The reversibility of H_2 coordination to the $[(PCy_3)_2Pt(H)]^+$ fragment was verified by freezing a CH_2Cl_2 solution of **12** in a J. Young NMR tube and placing a D_2 atmosphere over the frozen solution using a high-vacuum line. Upon warming the solution

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to −80 °C, a ^{2}H NMR spectrum revealed the presence of the bound D_2 (i.e., **12**-d_2). No deuterium was incorporated into the hydride position (see Results section). See Table 1 for low-temperature characterization of **12**−**15**.

Determination of Isotope Effect for Protonolysis of *trans*-$(PCy_3)_2Pt(CH_3)D$ (3-d_1). Compound **3**-d_1 was prepared from $LiCH_3$ and **5**-d_1 according to the methods used for **3**.[28] Solid $HBAr^f_4$ (216 mg, 0.21 mmol) and $DBAr^f_4$ (500 mg, 0.49 mmol) were combined in flask A, and $(PCy_3)_2Pt(CH_3)D$ (27.3 mg, 0.035 mmol) was added to flask B. After the ball joint was sealed using grease and a joint clamp, the apparatus was evacuated on a high-vacuum line connected to a Toepler pump. Dichloromethane (degassed and dried) was then vacuum transferred into both flasks (∼10 mL into flask A and 5 mL into flask B), and the apparatus was then sealed using the Kontes PTFE valve. After both solids were dissolved, the solutions were cooled to −60 °C. Rapid rotation of flask B around the ball joint allowed the contents of both flasks to be mixed at low temperature. The mixture was allowed to stir for approximately 2 h, after which the gas evolved in the reaction was collected using a Toepler pump and transferred into an NMR tube containing CD_2Cl_2. The relative quantity of CH_4 and CH_3D generated in the reaction was determined by integrating their respective ^{1}H NMR resonances. The reaction was carried out twice, and identical results were obtained. A control experiment was carried out to determine the level of H/D exchange between $DBAr^f_4$ and the glass surface. In this experiment (tmeda)$Zn(CH_3)_2$ (150 mg, 0.71 mmol) was added to the flask and $DBAr^f_4$ (500 mg, 0.49 mmol) was added to another flask. Sufficient (tmeda)$Zn(CH_3)_2$ was used to ensure consumption of all the H^+/D^+ in the reaction mixture. After dissolving the reagents in CH_2Cl_2 (added by vacuum transfer), the solutions were mixed, and the gas produced in the reaction was collected. A subsequent ^{1}H NMR spectrum of the methane generated revealed CH_4 (28.3%) and CH_3D (71.7%) (these percentages are the average of two successive experiments). This ratio was used in calculating the isotope effect for the reaction with **3**-d_1.

Acknowledgment. We thank the Army Research Office and the National Science Foundation for providing financial support for this work; S.S.S. thanks the National Science Foundation for a predoctoral fellowship. We thank Professor Ken Caulton for sharing research results prior to publication.

IC970944Y