typical for second-order quadrupolar effects,[40] indicating a large quadrupolar coupling constant. Signs and magnitudes of χ change with the σ-donor/π-acceptor strength of the ligands,[27,39] in agreement with the order Br < SO_2R < CH_2R in compounds **1**, **7**, and **4**.

Conclusions

The use of phosphorus-31 chemical shift tensors as accessible NMR parameters and their correlation to structure is only beginning.[41-43] In the present paper we have been able to demonstrate the amplified sensitivity of the different shielding components affected by the local environment of the nuclei. Examples are the different trans influences of the chlorine and the methyl group, which cause a change of 70 ppm in δ_{11} only. Also, the known dependence of the phosphorus chemical shift on the ring size in chelate systems was found to be due to a single tensor component.

We have also shown that it is possible to observe ^{55}Mn– and $^{95/97}$Mo–^{31}P coupling constants in the ^{31}P CP/MAS spectra, which are not accessible in solution because of fast relaxation processes. In the case of the manganese complex **1d**, the solid-state ^{31}P NMR spectrum has provided the opportunity to obtain the sign and magnitude of the manganese quadrupolar coupling constant and the asymmetry parameter, parameters not easily obtainable with other methods.[36] The knowledge of such quadrupolar interactions helps achieve a deeper insight into the nature of bonding in such complexes. Further investigations are in progress.

Acknowledgment. Support of this work by the Deutsche Forschungsgemeinschaft, Bonn/Bad Godesberg, by the Fonds der Chemischen Industrie, Frankfurt/Main, by BASF Aktiengesellschaft, and by Schering AG is gratefully acknowledged. Thanks are also due to C. Kingston for reading the manuscript.

---

(40) Ganapathy, S.; Schramm, S.; Oldfield, E. *J. Chem. Phys.* **1982**, *77*, 4360.
(41) Carty, A. J.; Fyfe, C. A.; Lettinga, M.; Johnson, S.; Randall, L. H. *Inorg. Chem.* **1989**, *28*, 4120.
(42) Penner, G. H.; Wasylishen, R. E. *Can. J. Chem.* **1989**, *67*, 1909.
(43) Tullius, M.; Lathrop, D.; Eckert, H. *J. Phys. Chem.* **1990**, *94*, 2145.

Contribution from the Departments of Chemistry, Indiana University,
Bloomington, Indiana 47405, and University of Vermont, Burlington, Vermont 05405

The Transient Radical $H_3Ir(PMe_2Ph)_3^+$: A Bronsted Acid

D. Eric Westerberg, Larry F. Rhodes, Joseph Edwin, William E. Geiger, and Kenneth G. Caulton*

Received September 18, 1990

Electrochemical oxidation (E_p = +0.55V vs SCE) or one-electron outer-sphere oxidation of *fac*-H_3IrP_3 (P = PMe_2Ph) by either $Fe(bpy)_3^{3+}$ or Cp_2Fe^+ yields $H_2Ir(S)P_3^+$, S = MeCN or acetone. In CH_2Cl_2, $H_4IrP_3^+$ is a detectable product. It is concluded that these are the stoichiometric (equimolar) primary products of reaction of the transient radical [$H_3IrP_3^{\bullet+}$] with *fac*-H_3IrP_3. Scavenging with NEt_3 or pyridine reveals that this reaction proceeds by proton transfer from $H_3IrP_3^+$ and that this radical is not effectively quenched by the hydrogen atom donors ^{i}PrOH or cumene nor by the H atom acceptor [$CPh_3^\bullet$]. It is proposed that the transient radical has the composition $Ir(H_2)HP_3^+$.

Introduction

Recently, we suggested[1] the use of a strong outer-sphere oxidant, $Fe(bpy)_3(PF_6)_3$, as a method for quantitating the number of metal-bound ligands M–H (as H_2) or M–CO (as CO) by Toepler pumping of the noncondensable gases evolved following oxidation. For the polyhydride *fac*-$H_3Ir(PMe_2Ph)_3$, oxidation by 2 or more equiv of $Fe(bpy)_3(PF_6)_3$ resulted in the liberation of 1 mol of H_2/Ir (eq 1, P = PMe_2Ph, S = MeCN). This stoichiometry raises the possibility of an intramolecular mechanism for elimination of H_2 from some cationic iridium trihydride radical. Such a mechanism has been shown[2] to fold for H_2 elimination from *diamagnetic* $H_5OsP_3^+$. However, further study of eq 1 revealed that 1 equiv of oxidant results in complete consumption of H_3IrP_3 but the loss of only $^1/_2$ mol of H_2/Ir (eq 2, S = MeCN). This result is totally unexpected on the basis of an intramolecular H_2 elimination mechanism and suggests instead that an intermolecular mechanism may be operative. Also relevant is the fact that paramagnetic polyhydrides devoid of π-donor ligands are unknown. The implied high reactivity of such species has been verified for the transient radical $ReH_6(PMe_2Ph)_2$.[3] Even dimetal paramagnetic polyhydrides are highly reactive.[4] To gain a better understanding of the results and mechanistic implications of eq 2, we have explored in more detail this oxidation and report our findings here.

$$fac\text{-}H_3IrP_3 + 2Fe(bpy)_3^{3+} \xrightarrow[S]{} \underset{\mathbf{2}}{cis,mer\text{-}H(S)_2IrP_3^{2+}} + H_2 + 2Fe(bpy)_3^{2+} \quad (1)$$

$$H_3IrP_3 + Fe(bpy)_3^{3+} \xrightarrow[S]{} \underset{\mathbf{3}}{cis,mer\text{-}H_2(S)IrP_3^{+}} + \tfrac{1}{2}H_2 + Fe(bpy)_3^{2+} \quad (2)$$

Results

Oxidation in Coordinating Solvents. In order to avoid the possibility of "overoxidation" of *fac*-H_3IrP_3[5] by $Fe(bpy)_3^{3+}$ (eq 1), the stoichiometry of eq 2 was studied by using the milder oxidant, Cp_2FeBF_4 ($E°$ = +0.55 V vs $E°$ = +1.21 V for $Fe(bpy)_3^{3+}$ (vs SCE)). The potential of oxidation of H_3IrP_3 (+0.55 V) is coincidentally the same as that of ferrocene in these media. In spite of this, ferrocenium is able to exhaustively oxidize the Ir complex because the irreversibility of the H_3IrP_3 oxidation allows the reaction to proceed to completion. We have also employed two different solvents, acetonitrile and acetone. At low temperature, the reactions were complete in minutes with quantitative consumption of ferrocenium ion (as judged by the absence of its blue color) to yield the corresponding solvento cations (eq 3). In both cases, vigorous gas evolution was noted when the reaction was carried out at room temperature. Thus, the ferro-

$$\underset{\mathbf{1}}{fac\text{-}H_3IrP_3} + Cp_2Fe^+ \xrightarrow[S]{} cis,mer\text{-}H_2(S)IrP_3^+ + Cp_2Fe + \tfrac{1}{2}H_2 \quad (3)$$

4a; S = MeCN
4b; S = Me_2CO

---

*To whom correspondence should be addressed at Indiana University.

(1) Lemmen, T. H.; Lundquist, E. G.; Rhodes, L. F.; Sutherland, B. R.; Westerberg, D. E.; Caulton, K. G. *Inorg. Chem.* **1986**, *25*, 3915.
(2) Bruno, J. W.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1984**, *106*, 1663.
(3) Bruno, J. W.; Caulton, K. G. *J. Organomet. Chem.* **1986**, *315*, C13.
(4) Allison, J. D.; Walton, R. A. *J. Am. Chem. Soc.* **1984**, *106*, 163.
(5) We have chosen to study the oxidation reactions of the facial isomer (vis-à-vis the meridional isomer) only because of its ease of isolation and purification. The cyclic voltammogram of a mixture of *fac* and *mer* isomers is identical with that of pure *fac*, suggesting no dramatic difference in behavior for the *mer* isomer.

© 1991 American Chemical Society

cenium ion effected the oxidation in the same manner as $Fe(bpy)_3(PF_6)_3$[1] and we conclude that the subsequent reaction steps are those of free $[IrH_3P_3^{\bullet+}]$ independent of its method of generation.

Further support for this contention comes from electrochemical (CV) experiments which show that (one-electron) oxidation of *fac*-H_3IrP_3 in Me_2CO proceeds irreversibly. The peak observed on a second cycle has a peak potential identical with that exhibited by an authentic sample of *cis,mer*-$H_2Ir(Me_2CO)P_3^+$ (vide infra).

We have attempted to increase the stability of the radical $[H_3IrL_3^{\bullet+}]$ by going to the analogue where L = PPh_3. This approach permits isolation of the radical $Fe(CO)_3(PPh_3)_2^{\bullet+}$, for example.[6] However, oxidation of $H_3Ir(PPh_3)_3$ with Cp_2Fe^+ in acetonitrile gives only rapid conversion to *cis,mer*-$H_2Ir(S)(PPh_3)_3^+$, with no spectroscopic or visual evidence for a persistent radical.

Oxidation in Dichloromethane. To evaluate the role of the coordinating solvents MeCN and Me_2CO on the course of the reaction, the oxidation was also performed in the "noncoordinating" solvent CH_2Cl_2. This permits detection of an intermediate, $H_4IrP_3^+$, in eq 3. The reaction again proceeds rapidly to completion even at −70 °C, but to products which are more diverse than in eq 3. These products (eq 4) are produced in relative yields

$$fac\text{-}H_3IrP_3 + Cp_2Fe^+ \xrightarrow{CH_2Cl_2} \underset{\mathbf{5}}{H_4IrP_3^+} + \underset{\mathbf{4c}}{cis,mer\text{-}H_2Ir(CH_2Cl_2)P_3^+} + \mathbf{6} \tag{4}$$

which depend upon experimental conditions (reaction time, reactor geometry, and efficiency of agitation).

The key product in eq 4 is $H_4IrP_3^+$. We believe that this is not only the simplest product but also one of two primary products formed from the radical cation $[H_3IrP_3^{\bullet+}]$. A previous report[7] on the formation of $H_4IrP_3^+$ (by protonation of H_3IrP_3) in CH_2Cl_2 established that this undergoes immediate displacement of 1 mol of H_2 by S = MeCN or THF, yielding *cis,mer*-$H_2Ir(S)P_3^+$. This reaction explains why $H_4IrP_3^+$ is not detected in eq 3. The production of $H_4IrP_3^+$ in eq 4 gives the appearance of the action of a Bronsted acid on (unreacted) H_3IrP_3, the acid apparently being $[H_3IrP_3^{\bullet+}]$ (eq 5). The source of the proton in **5** must be

$$[H_3IrP_3^{\bullet+}] + H_3IrP_3 \rightarrow [H_2IrP_3^{\bullet}] + \underset{\mathbf{5}}{H_4IrP_3^+} \tag{5}$$

an iridium hydride, since the ^2H NMR spectrum shows no deuteron on iridium when eq 4 is carried out in CD_2Cl_2; thus neither CD_2Cl_2 nor any (necessarily deuterated) impurities in the solvent can be the source of the additional hydride ligand in **5**.

The second product in eq 4, **4c**, has been identified on the basis of the following data: (a) **4c** has a rigid *cis,mer*-$H_2IrLP_3^+$ framework, as judged from ^1H and ^{31}P NMR spectroscopy; (b) purging a CH_2Cl_2 solution of the pure compound of **5**, $[H_4IrP_3]BF_4$, with argon to remove H_2, yields **4c**; (c) L (see point a, above) cannot be coordinated BF_4^-, since the PF_6^- analogue (from $Fe(bpy)_3(PF_6)_3$) is identical by ^1H NMR and since low-temperature $^{31}P\{^1H\}$, ^{19}F, and ^{11}B NMR spectra all show only free, not coordinated, BF_4^- or PF_6^-; (d) H_2O (D_2O) impurity in the solvent cannot be L, since addition of D_2O to **4c** yields new compounds, one of which is the D_2O complex $H_2Ir(D_2O)P_3^+$, whose spectral data are distinct from **4c**.

Attempts to synthesize and isolate **4c** by an independent route have been unsuccessful, and detection of coordinated CH_2Cl_2 by ^1H NMR has been hampered because CD_2Cl_2 is the only nondestructive solvent for the complex.[8a] Coordinated halocarbons have been proposed in other (very similar) systems and have been structurally characterized.[9]

The third product of the reaction in eq 4, **6**, has been formulated as a dimer. The detection ($^{31}P\{^1H\}$ NMR) of *two* sets of meridional phosphines at −80 °C is consistent with a dimer with inequivalent iridium centers. These begin to coalesce to a single AM_2 pattern at 25 °C. At −80 °C, two hydride chemical shifts are evident, and integration of the PMe_2 and hydride hydrogens permits deduction of an $H_4Ir_2P_6^{2+}$ stoichiometry.[8b] We feel that **6** is a secondary product when oxidation is conducted in CH_2Cl_2 (eq 4), since dissolution of **4c** in benzene yields some **6**. Loss of a weak ligand such as CH_2Cl_2 from **4c** would be expected to lead to dimerization (e.g., formation of **6**). Alternatively, H_2IrP_3 may undergo aggregation to $Ir_2H_nP_6$ (*n* = 4 or 5) in a weakly coordinating solvent and then experience oxidation.

We conclude that the primary products of the one-electron oxidation of *fac*-H_3IrP_3 in CH_2Cl_2 are equimolar $H_4IrP_3^+$ and $H_2Ir(CH_2Cl_2)P_3^+$. In effect, the $[H_3IrP_3^{\bullet+}]$ radical has undergone a solvent-assisted disproportionation, yielding an oxidation product,[10] $IrH_4P_3^+$, and Ir(III).

Reactivity of the Transient $[H_3IrP_3^{\bullet+}]$. At this point, the working hypothesis is that, regardless of solvent, the mechanism of oxidation involves eqs 5–7 (bracketed species were not directly observed).

$$fac\text{-}H_3IrP_3 \xrightarrow{-e^-} \underset{\mathbf{7}}{[H_3IrP_3^{\bullet+}]} \tag{6}$$

$$\underset{\mathbf{7}}{[H_3IrP_3^{\bullet+}]} + fac\text{-}H_3IrP_3 \rightarrow [H_2IrP_3^{\bullet}] + \underset{\mathbf{5}}{H_4IrP_3^+} \tag{5}$$

$$[H_2IrP_3^{\bullet}] \xrightarrow[+S]{-e^-} \underset{\mathbf{4}}{cis,mer\text{-}H_2Ir(S)P_3^+} \tag{7}$$

Equation 7 is a one-electron oxidation of a neutral radical, certainly easier than oxidation of cationic $[H_3IrP_3^{\bullet+}]$ but necessarily also easier than of H_3IrP_3 itself. Given the demonstrated tendency[12] of 17-electron radicals to add a donor ligand and thereby become more easily oxidized (i.e., 19 valence electrons), eq 7 may actually be oxidation of $H_2Ir(S)P_3^{\bullet}$. Thus, the overall reaction is net removal of H^- from *half* of the H_3IrP_3 by a three-step ECE process ($-e^-$, $-H^+$, $-e^-$). The other half of the H_3IrP_3 reagent is consumed in the (non-electron-transfer) step, eq 5. Note, however, that this mechanism incorporates a step (eq 5) which is deceptive in that it could proceed by H^+ transfer from the radical to H_3IrP_3 *or* by hydrogen atom transfer from H_3IrP_3 to the radical cation. Is $[H_3IrP_3^{\bullet+}]$ a Bronsted acid or a hydrogen atom abstractor? Discrimination between these two mechanisms for eq 5 is possible by generation of the reactants in the presence of scavengers of known reactivity. For example, if proton transfer is the actual mechanism, then any base can substitute for H_3IrP_3 in eq 5, with the result that the Cp_2Fe^+:H_3IrP_3 stoichiometry will change from the 1:1 of eq 4 to 2:1 (all H_3IrP_3 must now be consumed by the electron transfer of eq 6). Indeed, oxidation in acetone in the presence of 7–8 equiv of added pyridine or 25 equiv of NEt_3 consumes 2 equiv of ferrocenium ion (eq 8). The reaction is now a net two-electron oxidation of one H^- to H^+.

$$fac\text{-}H_3IrP_3 + 2Cp_2Fe^+ + :B \rightarrow \underset{\mathbf{4}}{cis,mer\text{-}H_2Ir(L)P_3^+} + BH^+ + 2Cp_2Fe \tag{8}$$

if B = NEt_3, L = Me_2CO in **4b**

if B = py, L = py in **4d**

While the acidity of transient $[H_3IrP_3^{\bullet+}]$ has been demonstrated, we also explored the possibility that $[H_3IrP_3^{\bullet+}]$ could act

---

[6] Baker, P. K.; Connelly, N. G.; Jones, B. M. R.; Maher, J. P.; Somers, K. R. *J. Chem. Soc., Dalton Trans.* **1980**, 579.

[7] Rhodes, L. F.; Caulton, K. G. *J. Am. Chem. Soc.* **1985**, *107*, 259.

[8] (a) It is noteworthy that both $[H_4Ir(PMe_2Ph)_3]BF_4$ and [*cis,mer*-$H_2Ir(CH_2Cl_2)(PMe_2Ph)_3]BF_4$ are benzene soluble. (b) Attempted determination of the number of hydride ligands in this dimer by integration of the ^1H NMR spectrum has given results with enough scatter (x = 5–7) that we are reluctant to choose any one. Attempts at answering the question by observing the number of lines in a selectively hydride-*coupled* ^{31}P NMR spectrum resulted only in a broad resonance, presumably due to the small (14 Hz) average J_{PH}. The fluxionality of this species would suggest that it is *not* of the form $P_3Ir(\mu\text{-}H)_3IrP_3^+$.

[9] Burk, M. J.; Segemuller, B.; Crabtree, R. *Organometallics* **1987**, *6*, 2241. Winter, C. H.; Veal, W. R.; Garner, C. M.; Arif, A. M.; Gladysz, J. A. *J. Am. Chem. Soc.* **1989**, *111*, 4766. Cutler, A. R.; Todaro, A. B. *Organometallics* **1988**, *1*, 1782.

[10] We have shown[11] that $IrH_4P_3^+$ is in actuality $Ir(H)_2(H_2)P_3^+$ and thus formally Ir(III). However, since this involves H_2 as a ligand, it is properly called an oxidation product.

[11] Lundquist, E. G.; Folting, K.; Streib, W. E.; Huffman, J. C.; Eisenstein, O.; Caulton, K. G. *J. Am. Chem. Soc.* **1990**, *112*, 855.

[12] Donovan, B. T.; Geiger, W. E. *J. Am. Chem. Soc.* **1988**, *111*, 2335.

as a radical toward hydrogen atom donors and acceptors.

Oxidation of *fac*-H_3IrP_3 by 1 equiv of trityl cation in dichloromethane (eq 9) creates a geminate pair, and the trityl radical will serve as a probe of the willingness of $[H_3IrP_3^{\bullet+}]$ to donate a hydrogen atom.

$$H_3IrP_3 + CPh_3^+ \rightarrow [H_3IrP_3^{\bullet+}, CPh_3^{\bullet}] \qquad (9)$$

The observed products of this reaction include $H_4IrP_3^+$ and *cis,mer*-$H_2Ir(CH_2Cl_2)P_3^+$ (**4c**), while hydrogen atom abstraction by the trityl radical would require no $H_4IrP_3^+$ product, but only **4c**.[13]

The transient radical **7** is similarly unreactive toward hydrogen atom donors. When 2-propanol was used as the solvent for the ferrocenium oxidation, it acted only as a coordinating solvent (eq 10, S = ^iPrOH). This claim rests on quantification of the evolved hydrogen by Toepler pumping.

$$fac\text{-}H_3IrP_3 + Cp_2Fe^+ \xrightarrow[S]{} \underset{\mathbf{4e}}{cis,mer\text{-}H_2(^iPrOH)IrP_3^+} + Cp_2Fe + \tfrac{1}{2} H_2 \qquad (10)$$

If 2-propanol had trapped $[H_3IrP_3^{\bullet+}]$ as $H_4IrP_3^+$, 1 mol of H_2/mol of *fac*-H_3IrP_3 should have been liberated. Only $^1/_2$ mol was observed. Similarly, the reaction was unaffected by being executed in the presence of a large excess of the hydrogen atom donor cumene.

The above experiments demonstrate that the transient $[H_3IrP_3^{\bullet+}]$ shows no hydrogen atom donor or acceptor behavior. We suggest that these results also allow us to discount a mechanism (eq 11) based on disproportionation of $[H_3IrP_3^{\bullet+}]$ directly

$$2[H_3IrP_3^{\bullet+}] \rightarrow H_4IrP_3^+ + H_2IrP_3^+ \xrightarrow[S]{} H_2Ir(S)P_3^+ \qquad (11)$$

to the two observed products via hydrogen atom transfer. Although this mechanism appears to be unattractive because it relies on a reaction of two like-charged species, such reactions have precedent.[14-16]

The transient $[H_2IrP_3^{\bullet}]$ produced in eq 5 should be diverted to different products if Cp_2Fe^+ is less abundantly available, since its consumption by eq 7 is then diminished. $[H_2IrP_3^{\bullet}]$, if present, should then react with itself of with other available scavengers; in particular, reaction with a C–Cl bond might give H_2ClIrP_3. When Cp_2Fe^+ was reacted with H_3IrP_3 in CH_2Cl_2 at a 1:2 mol ratio (eq 12), this was indeed observed,[17] along with dimer **11**,

$$2H_3IrP_3 + Cp_2Fe^+ \rightarrow \underset{17\%}{\mathbf{5}} + \underset{56\%}{\mathbf{4c}} + \underset{\mathbf{10},\ 17\%}{cis,mer\text{-}H_2ClIrP_3} + \underset{\mathbf{11},\ 3\%}{Ir_2H_5P_6^+} + \underset{7\%}{fac\text{-}H_3IrP_3} + Cp_2Fe \qquad (12)$$

a known product of condensation of $H_4IrP_3^+$, and H_3IrP_3.[18] That a small amount of *fac*-H_3IrP_3 detected is truly unreacted reagent (and not a product of hydrogen atom donation by solvent) is proven by the absence of deuterium in this product when eq 12 is executed in CD_2Cl_2.

Electrooxidation. The oxidation of H_3IrP_3 is a diffusion-controlled but irreversible one-electron process in both acetone and CH_2Cl_2 (E_p = +0.55 V with scan rate v = 0.20 V/s). The number of electrons transferred was established by bulk coulometry at ambient temperatures. The anodic peak potential shift with v (+50–60 mV/10-fold increase) and the breadth of the wave ($E_p - E_{p/2}$ = 100 mV, consistent with αn = 0.5)[19] are indicative of a slow heterogeneous charge-transfer reaction for H_3IrP_3 at the Pt electrode. No chemical reversibility was seen for this process, even at temperatures as low as 220 K in CH_2Cl_2.

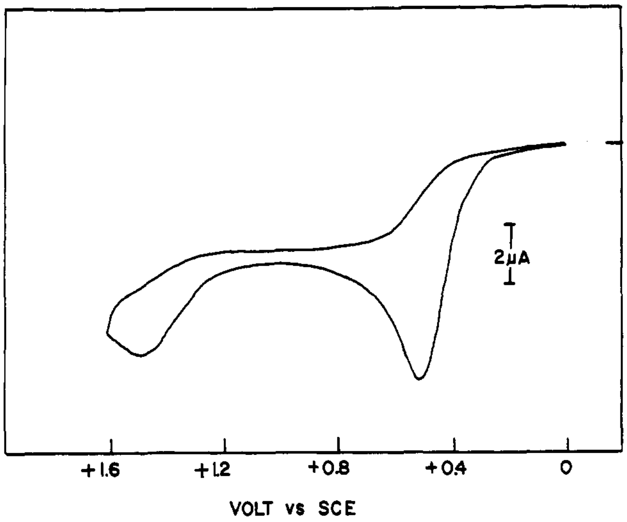


Figure 1. Cyclic voltammogram of 1.15 mM $H_3Ir(PMe_2Ph)_3$ in acetone/0.1 M Bu_4NPF_6 at Pt electrode, v = 0.16 V/s, T = 273 K.

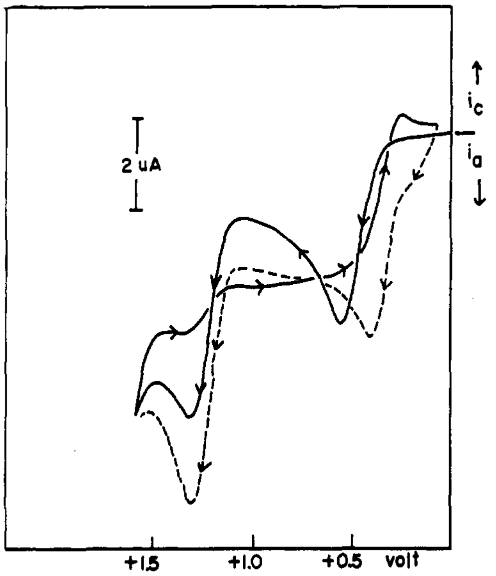


Figure 2. Two successive cyclic scans of 0.35 mM $H_3Ir(PMe_2Ph)_3$ in CH_2Cl_2/0.1 M Bu_4NPF_6 at Pt electrode, v = 0.10 V/s, T = ambient. Dashed line is second scan.

Continuing the voltammetry sweep to more positive potentials reveals a second anodic wave at +1.50 V (acetone) or +1.32 V (CH_2Cl_2) (Figures 1 and 2). At ambient temperatures and slow scan rates (<0.2 V/s) the height of the second wave is roughly equal to that of H_3IrP_3. The identity of the complex responsible for the second wave in acetone is $H_2Ir(Me_2CO)P_3^+$, deduced by this matching peak potential of the acetone complex in this solvent. Bulk oxidation of H_3IrP_3 also gives $H_2Ir(Me_2CO)P_3^+$ in high yield as the only identifiable product. This result confirms the overall stoichiometry of eq 3 and demonstrates (eq 13) that electrochemical and ferrocenium-initiated oxidations of H_3IrP_3 give identical results.

$$fac\text{-}H_3IrP_3 \rightarrow cis,mer\text{-}H_2Ir(Me_2CO)P_3^+ + \tfrac{1}{2} H_2 + e^- \qquad (13)$$

Electrolysis in CH_2Cl_2 at 298 K gives only the peak at +1.32 V, which we assign to **4c**, isolated from the chemical oxidation of H_3IrP_3 (eq 4).

The voltammetry is more complicated in CH_2Cl_2 than in acetone. At 233 K the primary oxidation wave at +0.55 V is still irreversible, but the anodic peak at +1.3 V virtually disappears. This result implies that an intermediate occurs prior to formation of $H_2Ir(CH_2Cl_2)P_3^+$. Its possible identity is discussed below. A second prominent feature of slow CV scans in CH_2Cl_2 is the curve

---

(13) The absence of ^1H NMR evidence for 2-propanol in oxidation reactions carried out in acetone also demonstrates the lack of hydrogen atom donation by $[H_3IrP_3^{\bullet+}]$.

(14) Droege, M. W.; Harman, W. D.; Taube, H. *Inorg. Chem.* **1987**, *26*, 1309.

(15) Fonseca, E.; Geiger, W. E.; Bitterwolf, T. E.; Rheingold, A. L. *Organometallics* **1988**, *7*, 567.

(16) DeLaet, D. L.; Powell, D. R.; Kubiak, C. P. *Organometallics* **1985**, *4*, 954.

(17) The deficiency of **5** relative to **4c** from the expected equimolar value is due in part to the conversion of **5** to **11**.

(18) This conversion was proven by treatment of H_3IrP_3 with 0.5 equiv of $HBF_4 \cdot Et_2O$ (generating a solution initially equimolar in IrH_3P_3 and $IrH_4P_3^+$). Rhodes, L. F. Doctoral thesis, Indiana University, 1984.

(19) Bard, A. J.; Faulkner L. R. *Electrochemical Methods*; John Wiley and Sons: New York, 1980; p 222.

crossing that is observed upon scan reversal (Figure 2). A cathodic feature is evident at $E_p = +0.27$ V, apparently coupled to an anodic wave at $E_p = +0.41$ V, which appears on a second scan. Curve crossings are generally indicative of homogeneous redox reactions taking place in the reaction layer adjacent to the electrode surface.[20] Given the mechanistic complexity of the H_3IrP_3 oxidation and the transient nature of the intermediate with $E°_{app} = +0.34$ V, we did not attempt to identify the mechanism leading to the curve crossings. This phenomenon was somewhat dependent on sample history and experimental conditions (rigor or solvent dryness, purity of purge gases, etc.). It is no longer present at faster sweep rates or lower temperatures, as expected for relatively slow homogeneous redox reactions in the electrode reaction layer.

Electrochemical results are consistent with a reaction scheme in acetone consisting of the ECE mechanism of eqs 5–7 (vide ante) which yields the overall one-electron stoichiometry of eq 13. The intermediate evident but not identified in CH_2Cl_2 undoubtedly has to do with the products of eq 5, $H_4IrP_3^+$ and the H_2IrP_3 radical. Recall that the former goes spontaneously to $H_2Ir(Me_2CO)P_3^+$ in acetone but is stable in CH_2Cl_2. The fate of the 17-electron radical H_2IrP_3 is therefore the key in unraveling the nature of the homogeneous reactions leading to the curve-crossing phenomenon. Several routes are possible. One would involve formation of a neutral dimer $H_4Ir_2P_6$, which could be oxidizable to $H_2Ir(CH_2Cl_2)P_3^+$. Another involves formation of a 19-electron unstable intermediate $H_2Ir(S)P_3$, which could be oxidized to the corresponding cation by the electrode or by oxidants generated in the electrode reaction layer.

Discussion

One-electron oxidation of *fac*-H_3IrP_3, using either electrochemistry or the outer-sphere chemical oxidants Cp_2Fe^+ or $Fe(bpy)_3^{3+}$, can be interpreted as producing the transient radical $[H_3IrP_3^{\bullet +}]$, which behaves as a Bronsted acid but not effectively as a hydrogen atom donor or acceptor. Subsequent evolution of the reaction system depends upon which Bronsted base intercepts $[H_3IrP_3^{\bullet +}]$ most rapidly:

(1) Nitrogen bases accept a proton (a formal two-electron *reduction* of Ir(IV)), yielding the neutral radical $[H_2IrP_3^{\bullet}]$, which then suffers one-electron oxidation more rapidly than does H_3IrP_3. The resultant 16-electron species $H_2IrP_3^+$ then adds Lewis base (acetone, MeCN, pyridine, or even CH_2Cl_2) to give the observed product.

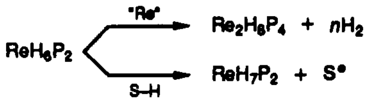
(2) In the absence of such conventional bases and because H_3IrP_3 is also a Bronsted base, proton transfer to unoxidized H_3IrP_3 effects consumption of 50% of the iridium reactant in a procedure which is a formal two-electron oxidation, but does not consume the Fe(III) oxidant. The resulting $H_4IrP_3^+$ has been detected directly in CH_2Cl_2. By a final quirk of the system, $H_4IrP_3^+$ reacts with donor solvents MeCN or acetone to give the *same* product, $H_2Ir(S)P_3^+$, formed by an EC process from $[H_2IrP_3^{\bullet}]$ or $H_2Ir(S)P_3^{\bullet}$. Curiously, however, while the overall reaction in eq 3 is properly characterized as intermolecular hydrogen transfer, it ends with a unimolecular H_2 dissociation (eq 14).

$$IrH_4P_3^+ + S \rightarrow H_2Ir(S)P_3^+ + H_2 \qquad (14)$$

In all solvents except CH_2Cl_2, then, the iridium has undergone no net oxidation at the completion of the reaction. The oxidation is localized in the hydrogen, which is transformed from H^- to either H_2 (in the absence of Bronsted bases) or H^+ (when a nitrogen base is added). This study, then, reveals in some detail the process of oxidatively induced reductive elimination upon which our method of ligand assay is based[1] and which has been seen before for $MoH_4(PR_3)_4$.[21]

Finally, this study disproves our initial supposition that the dihydrogen elimination of eq 1 is unimolecular. The intermediate detected here, $H_2Ir(S)P_3^+$, has been shown to form by an intermolecular (hydrogen-transfer) step, and further oxidation of this dihydride (see Experimental Section) yields *cis*,*mer*-$HIr(MeCN)_2P_3^{2+}$ to complete eq 1.

Scheme I



This study also permits comparison of the reactivity of the neutral radical $ReH_6(PMePh)_2^{\bullet}$ with the cation radical $[IrH_3P_3^{\bullet +}]$. The fate of the former in THF or MeCN is summarized in Scheme I.[3] Here "Re" is either ReH_6P_2 or $ReH_6P_2^-$ and S–H is any of the hydrogen atom donors THF, CH_3CN, or 1,4-cyclohexadiene. The key difference is that the rhenium system yields no monometallic *reductive* elimination products, while such are the exclusive products from $[H_3IrP_3^{\bullet +}]$. Since reductive H_2 elimination is effected by proton (H^+) transfer in the iridium case, it is the Bronsted acidity of $[H_3IrP_3^{\bullet +}]$ that underlies this disparate reactivity. $ReH_6P_2^{\bullet}$ is not a Bronsted acid, but instead exhibits typical radical behavior: H atom abstractions (and dimerization). This disparity may be due to the unfavorable charge separation required to split $ReH_6P_2^{\bullet}$ into $ReH_5P_2^{\bullet -}$ and H^+.

A recent report by Ryan, Parker, and Tilset on the electrooxidation of $CpM(CO)_3H$ (M = Cr, Mo, W) shows remarkable similarity to the ECE network reported here in eqs 5–7 for our polyhydride substrates.[22] In addition, the quantitative acidities of $CpM(CO)_3H^+$ were shown by Ryan, Parker, and Tilset to be some 20 powers of 10 higher than their neutral precursors, and this is certainly sufficient to account for our results. However, the polyhydride character of our compounds, together with the evidence[23] that the H_2 ligand is more Bronsted acidic than an analogous dihydride, leads us to suggest that the radical $[H_3IrP_3^{\bullet +}]$ may not be an Ir(IV) species but rather the more acidic $(H_2)HIr^{II}P_3^{\bullet +}$. This would make it a close analogue of the recently reported 16-electron dihydrogen complex $Ru(H_2)H(I)(PCy_3)_2$.[24]

Experimental Section

General Information. All manipulations were performed under an N_2 atmosphere by using standard Schlenk techniques or in a Vacuum Atmospheres glovebox. Acetonitrile was dried and distilled from CaH_2. Reagent grade acetone was dried over K_2CO_3, vacuum-transferred to a flask containing K_2CO_3, and subjected to three freeze–pump–thaw degassing cycles. Dichloromethane was dried and distilled from P_2O_5. Reagent grade 2-propanol was degassed by three freeze–pump–thaw cycles. Triethylamine and pyridine were dried over 3-Å molecular sieves. $HBF_4 \cdot Et_2O$ (Aldrich) and Ph_3CPF_6 (Aldrich) were used as received. Cumene was passed down a column of alumina and freeze–pump–thaw-degassed three times. Deuterated solvents were dried over the appropriate reagent, vacuum-transferred, degassed, and stored in a glovebox. ^1H NMR spectra were recorded at 23 °C (unless otherwise indicated) on a Nicolet NT360 spectrometer at 360 MHz. Chemical shifts (δ, in ppm) were referenced to TMS by using residual solvent proton chemical shifts. $^{31}P\{^1H\}$ NMR spectra were recorded at 40.5 MHz on a Varian Associates XL-100 spectrometer operating in FT mode at ambient temperature. Chemical shifts (δ, in ppm) are referenced to external 85% H_3PO_4 (positive chemical shifts downfield of H_3PO_4). Cp_2FeBF_4, *fac*-$H_3Ir(PMe_2Ph)_3$ (1), $Fe(bpy)_3(PF_6)_3$, and *mer*-$H_3Ir(PPh_3)_3$ were synthesized by literature methods.[1,25] Electrochemical experiments were conducted as previously described.[26] Solutions of H_3IrP_3 were generally in the concentration range 5×10^{-5} to 7×10^{-4} M. Peak potential shifts with scan rate were measured against decamethylferrocene as an internal standard to eliminate effects of uncompensated resistance. The electrochemical behavior was independent of concentration. In all cases, the supporting electrolyte was 0.1 M Bu_4NPF_6 and Pt was the working electrode.

---

(20) Saveant, J. M. *Acc. Chem. Res.* **1980**, *13*, 323.

(21) Rhodes, L. F.; Zubkowski, J. D.; Folting, K.; Huffman, J. C.; Caulton, K. G. *Inorg. Chem.* **1982**, *21*, 4185.

(22) Ryan, O. B.; Tilset, M.; Parker, V. D. *J. Am. Chem. Soc.* **1990**, *112*, 2618.

(23) Chinn, M. S.; Heinekey, D. M. *J. Am. Chem. Soc.* **1990**, *112*, 5166.

(24) Chaudret, B.; Chung, G.; Eisenstein, O.; Jackson, S. A.; Lahoz, F. J.; Lopez, J. A. *J. Am. Chem. Soc.*, in press.

(25) Hendrickson, D. N.; Sohn, Y. S.; Gray, H. B. *Inorg. Chem.* **1971**, *10*, 1559.

(26) Geiger, W. E.; Gennett, T.; McVicer, W. K.; Herrmann, W. A. *Organometallics* **1987**, *6*, 1634.

Oxidation of 1 in MeCN: Synthesis of $H_2Ir(MeCN)(PMe_2Ph)_3^+$ (4a). A Schlenk flask containing a stir bar, 50 mg (0.082 mmol) of **1**, and 22.4 mg (0.083 mmol) of Cp_2FeBF_4 was evacuated and cooled to −196 °C. MeCN (~5 mL) was vacuum-transferred to the flask, and the contents were allowed to warm slowly by using an ice bath. When the solvent melted, the blue color of ferrocenium began to fade and was completely replaced by the yellow color of Cp_2Fe after 10 min. Removal of the solvent in vacuo left a yellow residue. Dissolution of the residue in C_6D_6 indicated that, in addition to Cp_2Fe, **4a** was the only product by NMR spectroscopy. Spectral data have been reported.[7]

Oxidation of 1 in Acetone: Synthesis of $H_2Ir(OCMe_2)(PMe_2Ph)_3^+$ (4b). A mixture of 100 mg (0.164 mmol) of **1** and 44.8 mg (0.164 mmol) of Cp_2FeBF_4 in a Schlenk flask was cooled to 0 °C by using an ice bath. Acetone (10 mL) precooled to 0 °C was added to the flask. The reaction was over in 5 min, as judged by the absence of the blue color of the ferrocenium ion. NMR analysis (acetone-d_6) of a 0.5-mL aliquot of the reaction solution showed complete conversion to Cp_2Fe and **4b**. Addition of Me_2CO-d_6 (0.3 mL) at room temperature to 25 mg (0.041 mmol) of **1** and 11.2 mg (0.041 mmol) of Cp_2FeBF_4 in an NMR tube led to vigorous gas evolution and production of Cp_2Fe and the Me_2CO-d_6 analogue of **4b**. ^1H NMR (25 °C, acetone-d_6): 2.06 (Me_2CO), 1.82 (v t, J = 3 Hz, PMe), 1.76 (v t, 3 Hz, PMe), 1.47 (d, 8 Hz, PMe), −10.5 (d × t × d, 130, 22, 6 Hz), −28.3 (t × d × d, 16, 10, 6 Hz).

Oxidation of *mer*-$H_3Ir(PPh_3)_3$ in MeCN. Acetonitrile (5 mL) was condensed onto 100 mg (0.102 mmol) of *mer*-$H_3Ir(PPh_3)$ and 27.8 mg (0.102 mmol) of Cp_2FeBF_4. Upon warming to room temperature, the blue color disappeared as the solvent melted and the resulting yellow solution was taken to dryness in vacuum. The ^1H NMR spectrum of a $CDCl_3$ solution of the yellow residue showed the products to be *cis*,-*mer*-$H_2(MeCN)Ir(PPh_3)_3^+$ and Cp_2Fe.

Oxidation of 1 in CH_2Cl_2. (a) Deuteriodichloromethane (0.3 mL) was condensed (−196 °C) into an NMR tube containing 11.2 mg (0.018 mmol) of **1** and 5 mg (0.018 mmol) of Cp_2FeBF_4, and the tube was sealed under vacuum. The tube was then warmed to −90 °C to allow the solvent to melt and dissolve the reactants. At −70 °C, the color slowly changed from blue to yellow over a 10-min period. The tube was then warmed to room temperature. ^1H NMR spectroscopy revealed the products to be **5**, **4c**, and **6** (21%, 53%, 26%, respectively), in addition to Cp_2Fe. For $[IrH_2(CH_2Cl_2)P_3]BF_4$, ^1H NMR (25 °C, CD_2Cl_2): 1.97 (v t), 1.82 (v t), 1.25 (d), all PMe; −10.27 (d × t × d, J = 134, 22, 6 Hz, IrH); −26.27 (d × t × d, 20, 11, 6 Hz, IrH). $^{31}P\{^1H\}$ NMR (25 °C, CD_2Cl_2): −26.0 (d, 20 Hz, 2 P), −34.8 (t, 20 Hz, 1 P).

(b) A Schlenk flask containing 50 mg (0.082 mmol) of **1** and 22.4 mg (0.082 mmol) of Cp_2FeBF_4 was cooled to −196 °C. Dichloromethane (3 mL) was then condensed into the flask, which was then allowed to warm to room temperature. As the solvent melted, the blue color of ferrocenium disappeared, resulting in a yellow solution. Removal of the solvent in vacuo left a yellow residue. NMR (CD_2Cl_2) spectroscopy showed the products to be **5**, **4c**, and **6** (32%, 26%, 42%, respectively) as above. In a similar manner, the oxidation was carried out in CD_2Cl_2. ^2D NMR analysis of the residue in C_6H_6 showed no $H_xD_{4-x}IrP_3^+$ species, although $H_4IrP_3^+$ was evident by $^{31}P\{^1H\}$ NMR spectroscopy.

Oxidation in CH_2Cl_2 with $Fe(bpy)_3(PF_6)_3$. To a mixture of 50 mg (0.082 mmol) of **1** and 78.7 mg (0.082 mmol) of $Fe(bpy)_3(PF_6)_3$ in a Schlenk flask was added 5 mL of CH_2Cl_2 at room temperature. Immediately upon addition, the blue color of $Fe(bpy)_3^{3+}$ discharged to the red color of $Fe(bpy)_3^{2+}$. Removal of the volatiles in vacuo deposited a red residue. ^1H NMR spectroscopy in CD_2Cl_2 indicated the production of **5**-PF_6, **4c**-PF_6, and **6**-$(PF_6)_2$ (identical with the BF_4^- salts). In addition, a small amount of **4a**-PF_6 was produced due to MeCN contamination of $Fe(bpy)_3(PF_6)_3^1$.

Reaction of 4c with D_2O. A solution of **4c** was generated from a CH_2Cl_2 (10 mL) solution of **5** [from 161 mg (0.264 mmol) of **1** treated with 26 μL (0.264 mmol) of $HBF_4{\cdot}Et_2O$] by purging with a stream of Ar (presaturated with CH_2Cl_2) for 5 h. The volatiles were removed in vacuo, resulting in a pale yellow residue. The residue was then dissolved in CD_2Cl_2 for NMR analysis. Addition of 50 μL of D_2O produced *cis*,*mer*-$H_2Ir(D_2O)(PMe_2Ph)_3^+$ (66%) and unreacted **4c**.

Dimerization of 4c in C_6H_6. A solution of **4c** was generated as above from 157.2 mg (0.258 mmol) of **1** and 25 μL (0.268 mmol) of $HBF_4{\cdot}Et_2O$ in 15 mL of CH_2Cl_2 followed by a 2-h purge with Ar. One portion of the solution was stripped and dissolved in CD_2Cl_2 for ^1H NMR analysis. The other portion was stripped and dissolved in C_6H_6 (50 mL) at 50 °C for 15 min and the resulting solution stripped again. This benzene extraction procedure was repeated two more times. The resulting light yellow residue was then dissolved in C_6D_6 for ^1H NMR analysis. **6** is produced, along with several other unidentified products. The hydride signals of **6** in C_6D_6 are shifted downfield 0.4 and 0.7 ppm, when compared to their values in CD_2Cl_2.

Oxidation in the Presence of NEt_3. A flask containing **1** (52 mg, 0.085 mmol), Cp_2FeBF_4 (46.5 mg, 0.170 mmol), and NEt_3 (300 μL, 2.15 mmol) was cooled to 0 °C with an ice bath. Acetone (10 mL, at 0 °C) was then added. After 5 min the blue solution turned yellow. The solution was then warmed to room temperature, and the volatiles were removed in vacuo. The remaining yellow residue was dissolved in acetone-d_6 for NMR analysis. ^1H and $^{31}P\{^1H\}$ NMR spectroscopy showed the products to be **4b**, Cp_2Fe, and $HNEt_3BF_4$.

Oxidation in the Presence of Pyridine. A flask containing **1** (100 mg, 0.164 mmol), Cp_2FeBF (89.6 mg, 0.328 mmol), and pyridine (100 μL, 1.23 mmol) was cooled to −196 °C and evacuated. Acetone (5 mL) was condensed into the flask, which was then warmed to room temperature. As the solvent melted, the reaction was complete within 5 min. The yellow solution was stripped of solvent and extracted with $CDCl_3$. A small amount of white precipitate ($[C_5H_5NH]BF_4$) remained. By ^1H and $^{31}P\{^1H\}$ NMR spectroscopy the products were **4d** and Cp_2Fe. For **4d**, ^1H NMR (25 °C, $CDCl_3$): 8.64 (d, py), 7.79 (m, py), 7.06 (t, py), 1.80 (v t, PMe), 1.53 (v t, PMe), 1.43 (d, J = 7 Hz, PMe), −10.83 (d × t × d, 129, 22, 4 Hz, IrH), −22.86 (q × d, 16, 5 Hz, IrH). $^{31}P\{^1H\}$ NMR (25 °C, $CDCl_3$): −30.17 (d, 19 Hz, 2 P), −38.1 (br t, 1 P).

Substoichiometric Oxidation in CD_2Cl_2. Deuteriodichloromethane (0.5 mL) was condensed into an NMR tube containing 22.4 mg (0.036 mmol) of **1** and 5 mg (0.018 mmol) of Cp_2FeBF_4 at −196 °C. The tube was then sealed under vacuum and warmed to −90 °C to dissolve the reactants. At −70 °C, the blue solution turned yellow over a period of 10 min. The tube was then warmed to room temperature for NMR analysis. The products were **1**, **5**, **4c**, **10**, and **11** (7%, 17%, 56%, 17%, 3%, respectively). ^1H NMR data for **10**, *cis*,*mer*-IrH_2ClP_3 (25 °C, CD_2Cl_2): 1.89 (v t, PMe), 1.78 (v t, PMe), 1.17 (d, PMe), −10.86 (d × t × d, J = 133, 22, 5 Hz, IrH), −22.91 (d × t × d, 17, 11, 5 Hz, IrH). $^{31}P\{^1H\}$ NMR: −28.25 (d, 22 Hz, 2 P), −36.89 (t, 22 Hz, 1 P).

Oxidation by Ph_3CPF_6 in CH_2Cl_2. The oxidation of **1** (50 mg, 0.082 mmol) by Ph_3CPF_6 (31.8 mg, 0.082 mmol) was carried out in CH_2Cl_2 (5 mL) in a manner analogous to the Cp_2FeBF_4 oxidations. By NMR (CD_2Cl_2) spectroscopy the products are **5**, **4c**, and **6** (31%, 46%, 23%, respectively) and Ph_3CH. The integral of IrH and Ph_3CH resonances remains 3:1, indicating CH_2Cl_2 as the source of $H^{\bullet}$ for $[Ph_3C^{\bullet}]$.

Oxidation in 2-Propanol. (a) To a flask containing **1** (25 mg, 0.041 mmol) and Cp_2FeBF_4 (11.2 mg, 0.041 mmol) was added 7 mL of ^iPrOH at room temperature. The Cp_2FeBF_4 slowly dissolved and was consumed after 45 min. After removal of the solvent in vacuo, the resulting yellow residue was dissolved in C_6D_6 for NMR analysis. The only products were **4e** and Cp_2Fe. For $IrH_2(^iPrOH)P_3^+$, ^1H NMR (25 °C, C_6D_6): 5.0 (br s, C*H*), 3.68 (br, S, OH), 1.86 (br, PMe), 1.81 (br, PMe), 1.17 (d, J = 5 Hz, PMe), 1.04 (br, *Me*$_2$CHOH), −9.29 (d × t × m, 129, 21, 1 Hz, IrH), −28.6 (br m, IrH). $^{31}P\{^1H\}$ NMR (25 °C, C_6D_6): −24.6 (d, 17 Hz, 2 P), −30.0 (br m, 1 P).

(b) A Schlenk flask containing 152.5 mg (0.25 mmol) of **1** and 68.2 mg (0.25 mmol) of Cp_2FeBF_4 was evacuated for 30 min and cooled to −196 °C. Thoroughly degassed ^iPrOH (10 mL) was then condensed onto the reactants. After 1 h at room temperature, the Cp_2FeBF_4 was completely consumed. The liberated hydrogen was measured by connecting the flask to a vacuum system containing a Toepler pump. The yield of noncondensable gases was 0.124 ± 0.001 mmol (99.2% yield of theoretical 0.125 mmol for evolution of $^1/_2$ mol of H_2/Ir).

Oxidation of 4a to 3. A solution of **4a** was generated in situ by adding MeCN (10 ML) to a solution of **5** [from 100 mg (0.164 mmol) of **1** and 16 μL (0.164 mmol) of $HBF_4{\cdot}Et_2O$] in 5 mL of CH_2Cl_2. Production of **4a** was established by ^{31}P NMR spectroscopy. A slight excess of $Fe(bpy)_3(PF_6)_3$ (160 mg, 0.167 mmol) was then added to the solution of **4a** at room temperature. The blue color of $Fe(bpy)_3(PF_6)_3$ disappeared immediately and was replaced by the red color of $Fe(bpy)_3(PF_6)_2$. The solution was stirred for an additional 30 min, and the volatiles were removed in vacuo. The red precipitate was extracted with CH_2Cl_2 (0.5 mL) for $^{31}P\{^1H\}$ NMR analysis. This showed ~50% conversion of **4a** to **3**. The low yield was due to the low solubility of $Fe(bpy)_3(PF_6)_3$ in CH_2Cl_2/MeCN and the short reaction time. Spectral data for **3** have been reported.[7]

Oxidation in the Presence of Cumene. A Schlenk flask containing 50 mg (0.082 mmol) of **1**, 22.4 mg (0.082 mmol) of Cp_2FeBF_4, and cumene (250 μL, 1.80 mmol) was cooled to −196 °C. Dichloromethane (10 mL) was then condensed into the flask, which was then allowed to warm to room temperature. As the solvent melted, the blue color of ferrocenium disappeared, resulting in a yellow solution. After removal of the solvent in vacuo, NMR (CD_2Cl_2) spectroscopy showed the products to be **5**, **4c** and **6** (27%, 42%, 31%, respectively).

$[Ir_2H_x(PMe_2Ph)_6]BF_4$. Addition of $HBF_4{\cdot}Et_2O$ (3.5 mg, 0.020 mmol, 2 μL) to a solution of $H_3Ir(PMe_2Ph)_3$ (25.9 mg, 0.041 mmol) in 0.4 mL of CD_2Cl_2 gave immediate conversion to a solution exhibiting the following resonances of $Ir_2H_x(PMe_2Ph)_6^+$. ^1H NMR: +1.66 (d, J_{PH} = 5

Hz), −15.6 (septet, J_{PH} = 14 Hz). $^{31}P\{^1H\}$ NMR: −44.8 (s). The solution also contains unreacted *fac*-$H_3Ir(PMe_2Ph)_3$ (33%) and $IrH_4(PMe_2Ph)_3^+$ (33%). The mole percentage composition quoted is based on integration of the PMe proton resonances.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research and to Johnson Matthey, Inc., for a generous loan of iridium salts. W.E.G. also acknowledges the National Science Foundation for support under Grant CHE 86-03728. We thank Mats Tilset for useful suggestions.

Contribution from the Institut de Chimie Minérale et Analytique,
Université de Lausanne, 3, Place du Château, CH-1005 Lausanne, Switzerland

Solvent-Exchange Mechanisms of Nonaqueous Square-Planar Tetrasolvates: A High-Pressure ^1H NMR Investigation[1]

Noel Hallinan, Valérie Besançon, Marc Forster, Gilles Elbaze, Yves Ducommun,
and André E. Merbach*

Received August 15, 1990

Solvent exchange of square-planar PdS_4^{2+} complexes, where S = DMA, DMF, MeCN, MeNC, Me_2S, Et_2S, and $Pt(MeNC)_4^{2+}$, has been studied as a function of temperature (average temperature range of 40 K) and pressure (0.1–200 MPa) by ^1H NMR line-broadening studies in diluents CD_3NO_2 and CD_3CN. The exchange rates span several orders of magnitude—from k_2^{298} = 5 m^{-1} s^{-1} for $Pd(Et_2S)_4^{2+}$ to 1.06 × 10^6 m^{-1} s^{-1} for $Pd(MeNC)_4^{2+}$—as a result of large changes in ligand nucleophilicity and of differing encumbrance of ligand and complex. Nevertheless, the volume of activation remains consistently negative with values ranging from −0.1 to −11.6 cm^3 mol^{-1} for $Pd(MeCN)_4^{2+}$ to $Pd(Et_2S)_4^{2+}$, respectively. In combination with the negative activation entropies obtained, these results indicate that regardless of the nature of the ligand the mechanism of exchange remains associative in nature.

Introduction

Ligand substitution reactions occurring at transition-metal centers have been probed largely by examining concentration and temperature dependence of the reaction rate, substituent effects in the complex, changes of solvent and medium, and changes of the nature of the entering ligands. The study of the pressure dependence of the exchange rate has increasingly found use,[2,3] and it is now firmly established that volumes of activation obtained from pressure dependence studies can make a significant contribution in deciphering the intimate nature of substitution mechanisms.[4] A large quantity of activation volume data exists for solvent exchange reactions of hexasolvento octahedral metal complexes,[5] but exchange reactions of square-planar[6,7] and particularly tetrasolvento square-planar[8,9] complexes have been much less extensively probed by high-pressure techniques. Studies of water exchange on $Pt(H_2O)_4^{2+}$ and $Pd(H_2O)_4^{2+}$, previously performed in this laboratory, give rise to negative entropies and volumes of activation.[8,9] These results supported an associative activation mode. The size of the volumes of activation were, however, small, −4.6 and −2.2 cm^3 mol^{-1}, respectively, and it was not possible therefore to discriminate between an associative interchange I_a and an associative A mechanism. We were thus prompted to extend these studies to nonaqueous solvents where the use of organic diluent would also allow rate laws to be established. A detailed kinetic study of the pressure and temperature effects on the rates of ligand exchange of various MS_4^{2+} complexes was carried out according to eq 1, where S = DMA, DMF, MeCN, MeNC, Me_2S, and Et_2S.

$$MS_4^{2+} + 4S^* \rightleftarrows MS_4^{*2+} + 4S \qquad (1)$$

Palladium was chosen as the metal of preference because of the generally observed lability of Pd(II) complexes compared to Pt(II) complexes. For comparison purposes, both metal ions were studied with methyl isocyanide as ligand.

Experimental Section

Materials and Preparation of Solutions. $[Pd(MeCN)_4](BF_4)_2$ was prepared according to the method described in the literature[10] or was obtained commercially (Fluka, purum). The new complexes, $[Pd(DMA)_4](BF_4)_2$, $[Pd(DMF)_4](BF_4)_2$, $[Pd(Me_2S)_4](BF_4)_2$, and $[Pd(Et_2S)_4](BF_4)_2$, were prepared by dissolution of $[Pd(MeCN)_4](BF_4)_2$ in an excess of dimethylacetamide (DMA) (Fluka, p.a.), dimethylformamide (DMF) (Fluka, p.a.), dimethyl sulfide (Me_2S) (Fluka, purum), and diethyl sulfide (Et_2S) (Fluka, purum), respectively, followed by precipitation with ether. $[Pd(MeNC)_4](BF_4)_2$ was prepared by adding a slight excess of MeNC (methyl isocyanide)[11] to a solution of $[Pd(MeCN)_4](BF_4)_2$ in acetonitrile; after the solvent and excess ligand were pumped off, the residue was redissolved in a small volume of acetonitrile, the solution was filtered, and $[Pd(MeNC)_4](BF_4)_2$ was obtained as white crystals on cooling. $[Pt(MeNC)_4](PF_6)_2$ was prepared by the literature method.[12]

The complexes were dried under vacuum for several hours, and the purity was checked by ^1H NMR spectroscopy. The coordination number, n_c, was obtained by integration of the free and bound NMR signals, except in the case of MeNC in which fast exchange precluded this me-

---

(1) Part 47 of the series High-Pressure NMR Kinetics. For part 46, see: Luginbühl, W.; Zbinden, P.; Pittet, P.-A.; Armbruster, T.; Bürgi, H.-B.; Merbach, A. E.; Ludi, A. *Inorg. Chem.*, submitted for publication.

(2) van Eldik, R., Ed. *Inorganic High Pressure Chemistry: Kinetics and Mechanism*; Elsevier: Amsterdam, 1986.

(3) Kotowski, M.; van Eldik, R. *Coord. Chem. Rev.* **1989**, *93*, 19.

(4) Merbach, A. E. *Pure Appl. Chem.* **1989**, *59*, 161.

(5) Ducommun, Y.; Merbach, A. E. In *Inorganic High Pressure Chemistry: Kinetics and Mechanism*; van Eldik, R., Ed. Elsevier: Amsterdam, 1986; Chapter 2.

(6) Tubino, M.; Merbach, A. E. *Inorg. Chim. Acta* **1983**, *71*, 149.

(7) Ducommun, Y.; Helm, L.; Merbach, A. E.; Hellquist, B.; Elding, L. I. *Inorg. Chem.* **1989**, *28*, 377.

(8) Helm, L.; Elding, L. I.; Merbach, A. E. *Helv. Chim. Acta* **1984**, *67*, 1453.

(9) Helm, L.; Elding, L. I.; Merbach, A. E. *Inorg. Chem.* **1985**, *24*, 1719.

(10) Wayland, B.; Schramm, R. F. *Inorg. Chem.* **1969**, *8*, 971.

(11) Schuster, R. E.; Scott, J. E.; Casanova, J., Jr. *Organic Syntheses*; John Wiley: New York, 1966; Collect. Vol. 5, p 772.

(12) Miller, J. S.; Balch, A. L. *Inorg. Chem.* **1972**, *11*, 2069.

0020-1669/91/1330-1112$02.50/0 © 1991 American Chemical Society