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Comparative Study of the Oxidation Chemistry of the Iridium Dihydride, Hydridomethyl, and Dimethyl Complexes $\mathrm{Cp^*Ir(PPh_3)(R)(R')}$ ($\mathrm{R/R'}$ = H/H, H/Me, Me/Me)

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The oxidative behaviors of the dihydride, hydridomethyl, and dimethyl complexes $\mathrm{Cp^*Ir(PPh_3)H_2}$ (**1**), $\mathrm{Cp^*Ir(PPh_3)(H)(CH_3)}$ (**2**), and $\mathrm{Cp^*Ir(PPh_3)(CH_3)_2}$ (**3**) have been compared ($\mathrm{Cp^*} = \eta^5\text{-}\mathrm{C_5Me_5}$). Cyclic voltammetry studies show that $\mathbf{1}^{\bullet+}$ and $\mathbf{2}^{\bullet+}$ undergo rapid homogeneous follow-up reactions, whereas $\mathbf{3}^{\bullet+}$ is persistent on the voltammetry time scale. The oxidation of **1** results in products characteristic of proton-transfer reactions. In acetonitrile, the one-electron oxidation results in equimolar quantities of $\mathrm{Cp^*Ir(PPh_3)(H)_3^+}$ and $\mathrm{Cp^*Ir(PPh_3)(NCMe)H^+}$; in dichloromethane, the fluxional dinuclear complex $\mathrm{[Cp^*Ir(PPh_3)(H)]_2(\mu\text{-}H)^+}$ and $\mathrm{Cp^*Ir(PPh_3)(H)_3^+}$ are formed in equimolar amounts. The two-electron oxidation of **2** resulted in spontaneous intramolecular reductive elimination of methane and produced $\mathrm{Cp^*Ir(PPh_3)(NCMe)_2^{2+}}$ as the only Ir-containing product. The one-electron oxidation of **3** proceeded to slowly give mostly $\mathrm{Cp^*Ir(PPh_3)(NCMe)(CH_3)^+}$ and methane. The anticipated reductive elimination of ethane occurred only to a minor extent. The results suggest that reductive elimination of $\mathrm{CH_4}$ from the 17-electron hydridoalkyl species $\mathrm{Cp^*Ir(PPh_3)(CH_3)H^{\bullet+}}$ is kinetically favored relative to the elimination of $\mathrm{C_2H_6}$ from the dimethyl complex $\mathrm{Cp^*Ir(PPh_3)(CH_3)_2^{\bullet+}}$, a trend which is also commonly seen when the reactivities of 18-electron hydridoalkyl and dialkyl complexes are compared.

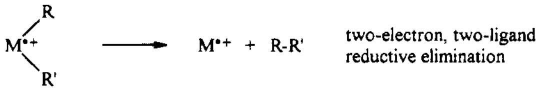
Introduction

The liberation of organic products from catalytic or stoichiometric reactions that are mediated by transition-metal complexes usually occurs by reductive elimination. Consequently, reductive elimination reactions constitute one of the most important reaction types in organotransition-metal chemistry.[2] As is intuitively expected, high-oxidation state metals usually undergo reductive elimination more readily than low-oxidation state metals. Thus, an oxidation (whether by electron transfer or by reactions with electrophiles) of organotransition-metal complexes containing σ-bonded ligands frequently leads to an enhanced tendency toward reductive elimination by the loss of one or two ligands via a variety of reaction mechanisms.

The thermodynamic acidities of 17-electron metal−hydride cation radicals are 20−25 pK_a units lower than those of their neutral 18-electron parents.[3] Accordingly, metal−hydride cation radicals commonly act as Brønsted acids and undergo proton transfer to suitable bases.[3a,b,4,5] These processes represent a special case of what may be termed a two-electron, one-ligand reductive elimination (eq 1). Metal—ligand bond homolysis reactions represent formal one-electron, one-ligand reductive eliminations (eq 2) and are frequently accelerated by one-electron oxidations.[6] Finally, two-electron, two-ligand reductive eliminations (eq 3) are also induced by a one-electron oxidation.[7]

$$\mathrm{M^{\bullet+}{-}R} \longrightarrow \mathrm{M^{\bullet}} + \mathrm{R^+} \qquad \text{two-electron, one-ligand reductive elimination} \tag{1}$$

$$\mathrm{M^{\bullet+}{-}R} \longrightarrow \mathrm{M^{+}} + \mathrm{R^{\bullet}} \qquad \text{one-electron, one-ligand reductive elimination} \tag{2}$$



$$\mathrm{M^{\bullet+}(R)(R')} \longrightarrow \mathrm{M^{\bullet+}} + \mathrm{R\text{-}R'} \qquad \text{two-electron, two-ligand reductive elimination} \tag{3}$$

We recently reported that oxidation of the dimethyl complex $\mathrm{Cp^*Rh(PPh_3)(CH_3)_2}$ ($\mathrm{Cp^*} = \eta^5\text{-}\mathrm{C_5Me_5}$) led to reductive elimination of ethane by an ECE mechanism and yielded $\mathrm{Cp^*Rh(PPh_3)(NCMe)_2^{2+}}$ as the organome-

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Table 1. Electrochemical Data for the Oxidation of 1−3

	E_{ox}, V vs Fc[a]		n_{ox}, faraday/mol	
compound	acetonitrile[b]	dichloromethane[c]	acetonitrile	dichloromethane
$Cp^*Ir(PPh_3)(H)_2$ (**1**)	0.184[d]	0.181[d]	0.84[b,e]	0.77[c,e]
$Cp^*Ir(PPh_3)(CH_3)(H)$ (**2**)	−0.014[d]	−0.035[d]	1.46[e]	0.99[e]
$Cp^*Ir(PPh_3)(CH_3)_2$ (**3**)	0.035[f]	−0.014[f]	1.0[g]	1[h]

[a] Measured by cyclic voltammetry (0.6 mm Pt disk electrode, 20 °C, v = 1.0 V/s). [b] 0.1 M $Bu_4N^+PF_6^-$. [c] 0.2 M $Bu_4N^+PF_6^-$. [d] Anodic peak potential. [e] Measured by constant-current coulometry with derivative cyclic voltammetry monitoring of substrate consumption.[19] Average of three measurements. [f] Reversible potential, taken as the midpoint between the anodic and cathodic peaks. [g] By oxidation with $Cp_2Fe^+PF_6^-$. [h] Constant potential electrolysis.[8b]

tallic product.[7f] The two-electron, two-ligand elimination took place in a first-order, intramolecular reaction of the cation radical at rates that were not very dependent on the nature of the solvent, and therefore it was concluded that a 19-electron intermediate or transition state was not involved in the reductive elimination step. The rate enhancement for the reductive elimination was at least 3 × 10^9 when $Cp^*Rh(PPh_3)(CH_3)_2$ was oxidized by one electron.

The isoelectronic iridium complexes $Cp^*Ir(PPh_3)(H)_2$ (**1**), $Cp^*Ir(PPh_3)(CH_3)H$ (**2**), and $Cp^*Ir(PPh_3)(CH_3)_2$ (**3**) are all readily synthesized and stable and offer the opportunity to compare the oxidative behavior of a dihydride, an alkyl hydride, and a dialkyl complex in which the metal and ancillary ligands remain the same. On the basis of previous work, we were particularly intrigued by the following questions: (a) Will oxidation of the dihydride **1** lead to proton-transfer reactions or to direct elimination of H_2? (b) Will oxidation of the alkyl hydride **2** result in a proton-transfer reaction typical of many metal hydrides[3a,4,5] or to a two-electron, two-ligand reductive elimination reaction analogous to the oxidative behavior of $Cp^*Rh(PPh_3)(CH_3)_2$? (c) How does the reactivity of $\mathbf{3}^{\bullet+}$ compare with that of the rhodium analogue, as recently[7f] reported by us? The oxidation chemistry of compounds **1**−**3** in acetonitrile and dichloromethane is the subject of this paper.[8a]

Results

Cyclic Voltammetry Investigation of $Cp^*Ir(PPh_3)(H)_2$ (1), $Cp^*Ir(PPh_3)(CH_3)H$ (2), and $Cp^*Ir(PPh_3)(CH_3)_2$ (3). The oxidation chemistry of **1**−**3** was investigated by cyclic voltammetry (CV). Electrode potentials, referenced against the Cp_2Fe/Cp_2Fe^+ (Fc) couple, and coulometry data are summarized in Table 1. Figure 1 shows cyclic voltammograms for the oxidations of **1**−**3** in acetonitrile/0.1 M $Bu_4N^+PF_6^-$ (Pt disk electrode, d = 0.4 mm, 20 °C, voltage sweep rate v = 1.0 V/s).

The oxidation peak potentials of the complexes increase in the order **2** < **3** < **1**. Because the oxidations of **1** and **2** are chemically irreversible even at high voltage sweep rates (vide infra), their waves are subjected to kinetic potential shifts that preclude an assessment about the thermodynamic significance of the oxidation potential differences. The reversible oxidation potential for **3**, taken as the midpoint between the anodic and cathodic peaks, was 0.035 V vs Fc in acetonitrile, and −0.014 V vs Fc in dichloromethane. A recent account of the oxidation of **3** reported an oxidation potential of −0.03 V vs Fc in dichloromethane,[8b] in excellent agreement with our data.

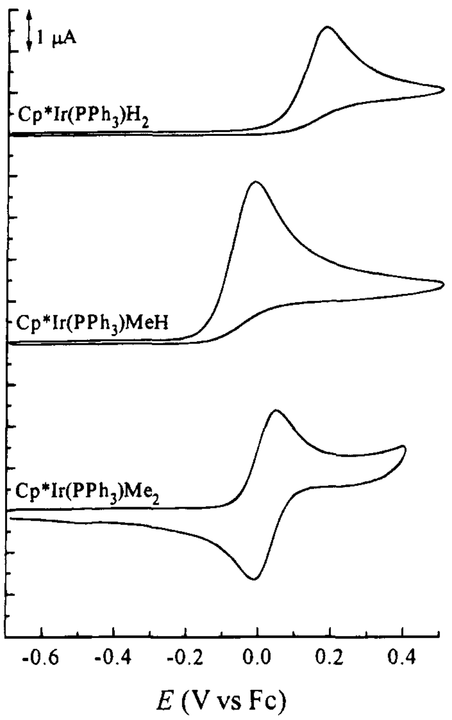

Figure 1. Cyclic voltammograms for the oxidation of compounds **1**−**3**. Conditions: 1.0 mM substrate in acetonitrile/0.1 M $Bu_4N^+PF_6^-$, Pt disk electrode (d = 0.4 mm), voltage sweep rate v = 1.0 V/s, 20 °C.

The oxidations of **1** and **2** were chemically irreversible on the time scale of the CV measurements, indicative of rapid follow-up chemical reactions that consumed the electrode-generated cations. For both species, the irreversibility pertained at voltage sweep rates as high as 2000 V/s, establishing an upper limit to the half-lives of $\mathbf{1}^{\bullet+}$ and $\mathbf{2}^{\bullet+}$ of about 10^{-4} s. On the other hand, the oxidation of **3** was chemically reversible on the CV time scale. Essentially full reversibility was seen even at v = 0.020 V/s at a temperature of 40 °C (d = 2.0 mm, Pt disk electrode). The stability of $\mathbf{3}^{\bullet+}$ is in contrast to the instability of the Rh analogue, which underwent extensive reductive elimination of ethane on the time scale of experiments performed at 1.0 V/s at 20 °C.[7f]

Interestingly, a CV analysis of the oxidation of **3** to more positive potentials than those employed for Figure 1 revealed a second, broad wave located at 0.54 V vs Fc in Figure 2. This wave is chemically irreversible but is coupled to a well-defined reduction wave at −0.48 V vs Fc. The exact position of the second oxidation wave was rather variable and shifted to more positive values when repeated scans were performed. The thermodynamic significance of this potential value should be deemphasized because of the adsorption phenomena that appear to influence the second wave. We attribute the wave to the oxidation of the persistent radical cation $\mathbf{3}^{\bullet+}$ to the 16-electron dication $\mathbf{3}^{2+}$ which is presumably captured by a solvent molecule to give a species tentatively assumed to be $Cp^*Ir(PPh_3)(NCMe)(CH_3)_2^{2+}$ (vide

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(8) (a) After initiation of this work, the interesting electron-transfer chemistry of **3** in nonpolar solvents (benzene, dichloromethane) was reported.[8b] Surprisingly, **3** underwent elimination of methane to give the orthometalated complex $Cp^*\overline{Ir(C_6H_4P}Ph_2)(CH_3)$ in a reaction that was *catalyzed* by one-electron oxidizing agents such as Cp_2Fe^+ or Ag^+. The orthometalated product underwent a slow reaction with arene C−H bonds; for example, the reaction with benzene resulted in $Cp^*Ir(PPh_3)(CH_3)Ph$. (b) Diversi, P.; Iacoponi, S.; Ingrosso, G.; Laschi, F.; Lucherini, A.; Zanello, P. *J. Chem. Soc., Dalton Trans.* **1993**, 351.

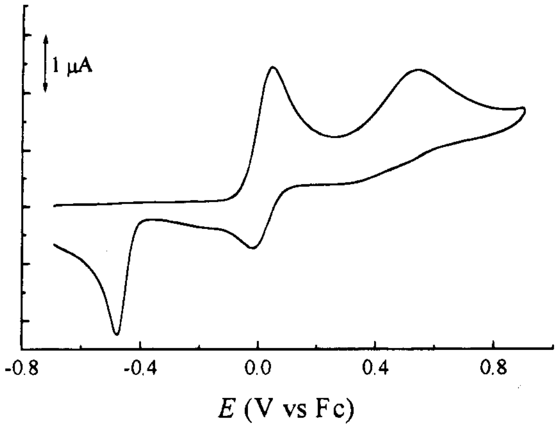
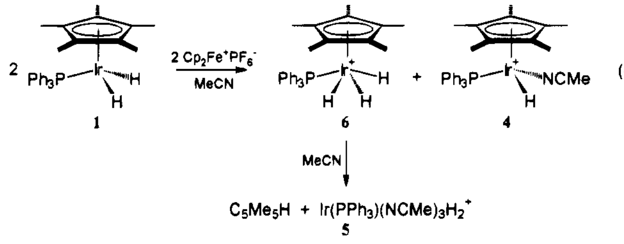


Figure 2. Cyclic voltammogram for the oxidation of **3**. Experimental conditions are as in the caption to Figure 1.

infra). It is this Ir(V) 18-electron dication which is reduced at −0.48 V vs Fc during the reverse scan. In comparison, the Ir(III) cations $Cp^*Ir(PPh_3)(NCMe)CH_3^+$ and $Cp^*Ir(PPh_3)(NCMe)_2^{2+}$ (vide infra) are reduced at −2.5 and −1.4 V vs Fc, respectively. The CV behavior of **3** is reminiscent of that reported for the oxidation of $CpCr(CO)_3^-$ and substituted derivatives,[3c] and for $TpM(CO)_3^-$ (Tp = η^3-hydridotris(pyrazolyl)borate; M = Mo, W)[3d] which underwent two successive one-electron oxidations to yield cationic products with coordinated acetonitrile.

Bulk Electrolysis Oxidation of $Cp^*Ir(PPh_3)(H)_2$ (1). The constant-current electrolysis of **1** in acetonitrile and dichloromethane required the passage of 0.84 and 0.77 faraday/mol of charge, respectively (average of three experiments each), for the complete consumption of the substrate. Workup of the resulting solution from an exhaustive electrolysis in acetonitrile followed by immediate analysis of the product mixture by ^1H NMR spectroscopy showed the presence of $Cp^*Ir(PPh_3)(NCMe)H^+$ (**4**) and $Ir(PPh_3)(NCMe)_3(H)_2^+$ (**5**) in a ca. 4:1 ratio. We have previously shown that **5** is produced by the acetonitrile-assisted elimination of pentamethylcyclopentadiene (Cp*H) from $Cp^*Ir(PPh_3)(H)_3^+$ (**6**).[9] The product **4**(PF_6^-) has been independently prepared and characterized (vide infra), whereas **5**(BF_4^-) and **6**(BF_4^-) have been previously described.[7f] Compound **5**(BF_4^-) underwent partial decomposition on the time scale of these experiments, and losses during workup may have occurred. On the basis of chemistry to be described in the next paragraph, we believe that the true **4**:**5** ratio caused by the reaction should be unity. When an excess (3 equiv) of quinuclidine was added to the electrolyte, 2.0 faraday/mol was required for the complete consumption of **1**. In this case, **4** was the only Ir-containing product that could be detected by ^1H NMR spectroscopy.

Chemical Oxidation of $Cp^*Ir(PPh_3)(H)_2$ in Acetonitrile. Synthesis and Characterization of $Cp^*Ir(PPh_3)(NCMe)H^+BF_4^-$. The complete oxidation of **1** in acetonitrile required the use of 1.0 equiv of $Cp_2Fe^+PF_6^-$, using the "ferrocenium titration" technique.[4a] Treatment of a solution of **1** in acetonitrile-d_3 with 1 equiv of $Cp_2Fe^+PF_6^-$ immediately (^1H NMR) led to the formation of a near 1:1 ratio of $Cp^*Ir(PPh_3)(NCCD_3)H^+$ (**4**-d_3; δ 1.94 (d, J_{Cp^*-P} = 2.0 Hz, Cp*), −13.93 (d, $^2J_{P-H}$ = 34.3 Hz, Ir—H)) and $Cp^*Ir(PPh_3)(H)_3^+$ (**6**; δ 1.64 (d, J_{Cp^*-P} = 2.3 Hz, Cp*), −12.65 (br s, Ir—H)). The variable-temperature ^1H NMR spectra and fluxional behavior of **6** have been previously described, and it was concluded that **6** is best viewed as a classical trihydride.[7f] Traces of $Ir(PPh_3)(NCCD_3)_3(H)_2^+$ (**5**-d_9; δ −21.89 (d, $^2J_{P-H}$ = 21.9 Hz, Ir—H)) and Cp*H (δ 0.8–1.9) were present. When the solution was left at ambient temperature for several hours, the signals due to **6** decreased in intensity with a concomitant increase in the intensities of signals from **5**-d_9 and Cp*H. In the presence of a small excess (2 equiv) of quinuclidine, 2.0 equiv of $Cp_2Fe^+PF_6^-$ was needed to effect the complete consumption of **1**. The results are summarized in eqs 4 and 5. The combined results of the electrochemical and chemical oxidation experiments suggest that the primary reaction of $1^{•+}$ is the transfer of a proton to **1** (eq 4) or to quinuclidine (eq 5). The resulting radical $Cp^*Ir(PPh_3)H^•$ undergoes a second oxidation to yield **4**, presumably via a readily oxidizable 19-electron acetonitrile adduct $Cp^*Ir(PPh_3)(NCMe)H^•$.[10] The mechanism of the apparent H^+ transfer cannot be established on the basis of the available data. In view of recent results from our laboratories, it is possible that the mechanism of the reaction between **1** and $1^{•+}$ is considerably more complex than the direct transfer of a proton.[4c]



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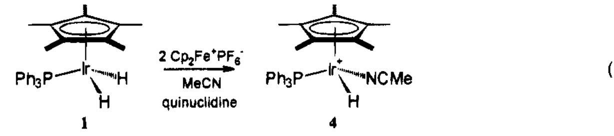
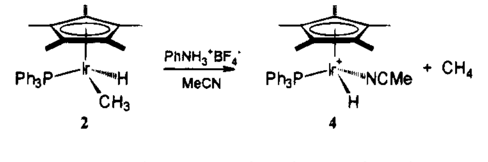


(5)

4(BF_4^-) was independently synthesized in good yields by the treatment of $Cp^*Ir(PPh_3)(CH_3)H$ with $PhNH_3^+BF_4^-$ in acetonitrile at −35 °C (eq 6).[11] The presumed, but unobserved, intermediate $Cp^*Ir(PPh_3)(CH_3)(H)_2^+$, as anticipated, underwent the desired reductive elimination of methane. Complete spectroscopic data for **4** are given in the Experimental Section.



(6)

Chemical Oxidation of 1 in Dichloromethane. Treatment of **1** with 0.67 equiv of $Cp_2Fe^+PF_6^-$ in dichloromethane-d_2 led to the complete consumption of **1**. The ^1H NMR spectrum of the reaction mixture showed the presence of two Cp* resonances at δ 1.94 and 1.45 in a 1:2 ratio, along with two hydride reso-

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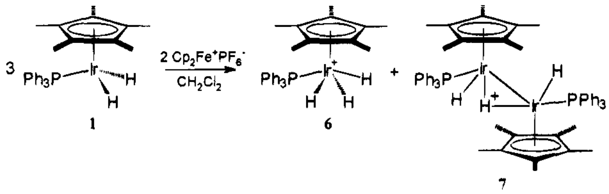
[9] Pedersen, A.; Tilset, M. *Organometallics* **1993**, *12*, 3064.

[10] 19-electron species can be potent reducing agents: (a) Tyler, D. R. *Acc. Chem. Res.* **1991**, *24*, 325. (b) Trogler, W. C. In *Organometallic Radical Processes*; Trogler, W. C., Ed.; Elsevier: Amsterdam, 1990; p 306. (c) Tyler, D. R. In *Organometallic Radical Processes*; Trogler, W. C., Ed.; Elsevier: Amsterdam, 1990; p 338.

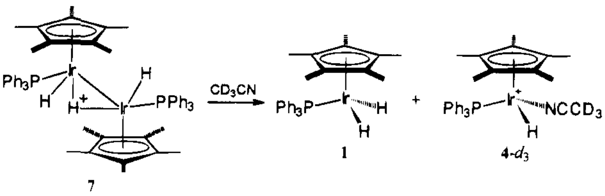
[11] Anilinium salts have been previously used for mild protonolysis of metal–carbon bonds. For related examples, see: (a) Buchanan, J. M.; Stryker, J. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 1537. (b) Glueck, D. S.; Bergman, R. G. *Organometallics* **1991**, *10*, 1479.

nances of equal intensities at δ −12.65 (br s, 1 H) and −20.37 (t, J = 16.7 Hz, 3 H). The first product was readily identified as **6** (δ 1.94 (Cp*) and δ −12.65 (Ir—H)). The second product has been tentatively assigned the structure of the hydride-bridged dimer $[Cp^*Ir(PPh_3)H]_2(\mu\text{-}H)^+$ (**7**; ^{1}H NMR δ −20.37 (t, $^2J_{P-H}$ = 16.7 Hz, Ir—H), 1.45 (d, J_{Cp^*-P} = 2.1 Hz, Cp*). Other alternatives which conform with the 18-electron rule cannot be ruled out, however. For example, a species with only terminal hydrides and a dative Ir—Ir bond,[12] i.e. $Cp^*(PPh_3)(H)_2Ir{\rightarrow}Ir^+(H)(PPh_3)Cp^*$, is an equally conceivable structure that will be in agreement with available spectroscopic data and observed chemical reactions (vide infra).



(7)

The single hydride signal that was seen in the ^{1}H NMR spectrum for **7** is readily explained by a rapid fluxional process that exchanges terminal and bridging hydrides. The ambient-temperature spectrum shows a weighted average of the chemical shifts and couplings of the two terminal and the bridging hydride. When a dichloromethane-d_2 solution of almost pure **7** (prepared as described in the next paragraph) was cooled, the hydride triplet changed to a broad signal with no observable couplings at ca. −50 °C. At −91 °C, the broad signal had almost merged with the baseline. A limiting low-temperature spectrum with separate signals for the bridging and terminal hydrides could not be obtained. When $7(BF_4^-)$ was dissolved in acetonitrile-d_3, the complex underwent spontaneous fragmentation to quantitatively yield a 1:1 mixture of **1** and **4**-d_3 in less than 5 min (eq 8).



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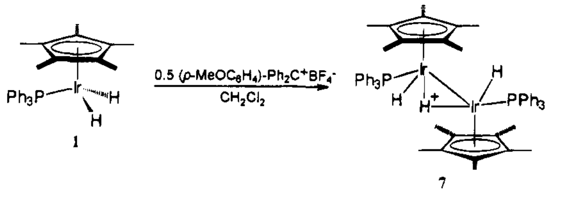


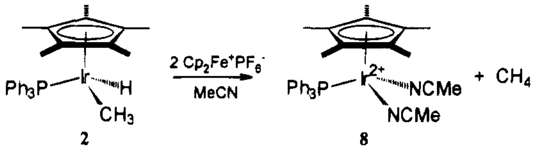
(9)

The preparation of pure **7** was attempted by the treatment of **1** with 0.5 equiv[13] of the substituted trityl reagent $(p\text{-}MeOC_6H_4)Ph_2C^+BF_4^-$ according to eq 9. This approach resulted in a product mixture containing $7(BF_4^-)$ contaminated by small quantities (ca. 5−15%) of **6**. We never succeeded in obtaining pure **7**. The **7**:**6** ratio in these reactions was always higher when the reaction was performed at ambient temperature than at low temperature (−90 °C). The formation of **7** and **6** is well rationalized in terms of competing hydride abstraction (leading to **7**) and electron-transfer (yielding **7** and **6** in a 1:1 ratio, as in the reaction with $Cp_2Fe^+PF_6^-$) pathways in the reaction between **1** and the trityl reagent. This interpretation implies a non-electron-transfer pathway for the hydride abstraction.[14] An alternate possibility is that even the hydride abstraction proceeds by electron transfer, in which case the product distribution reflects a partition into an in-cage reaction between the trityl radical and $1^{\bullet+}$ (yielding **7**) and a cage escape process (ultimately yielding **6** and **7** by proton transfer).

The generation of **4** and **7** in a 1:1 ratio during the oxidation requires the consumption of $^2/_3$ equiv of oxidant, which is in agreement with experimental observations. This reaction is strikingly similar to the "$^2/_3$-electron oxidation" of $CpRu(CO)(PMe_3)H$, which yielded a 1:1 mixture of $CpRu(CO)(PMe_3)(H_2)^+$ and $[CpRu(CO)(PMe_3)]_2(\mu\text{-}H)^+$ in dichloromethane. For this reaction, it was suggested that the dimer was produced by a radical−radical coupling of $CpRu(CO)(PMe_3)H^{\bullet+}$ with $CpRu(CO)(PMe_3)^{\bullet}$.[4a]

Oxidation of $Cp^*Ir(PPh_3)(CH_3)H$ (2) by Bulk Electrolysis. The consumption of 1.5 faraday/mol was required for the constant-current electrolysis of **2** in acetonitrile. Workup of the electrolyte yielded mostly $Cp^*Ir(PPh_3)(NCMe)_2{}^{2+}(BF_4^-)_2$ ($8(BF_4^-)_2$), identified by comparison of its ^{1}H NMR spectrum with that of an authentic sample of $8(PF_6^-)_2$ (vide infra). The product **8** was generated rapidly, even on the cyclic voltammetry time scale: a wide sweep cyclic voltammogram of **2** showed a reduction wave at −1.42 V vs Fc on the reverse sweep. This reduction peak gained intensity when $8(PF_6^-)_2$ was added to the solution.

Chemical Oxidation of $Cp^*Ir(PPh_3)(CH_3)H$. Synthesis and Characterization of $Cp^*Ir(PPh_3)(NCMe)_2{}^{2+}(PF_6^-)_2$ ($8(PF_6^-)_2$). A total of 2 equiv of $Cp_2Fe^+PF_6^-$ was required for the oxidation of **2** in acetonitrile-d_3. The reaction proceeded quantitatively (^{1}H NMR, internal standard) to yield $Cp^*Ir(PPh_3)(NCCD_3)_2{}^{2+}$ and methane (eq 10). The salt $Cp^*Ir(PPh_3)(NCMe)_2{}^{2+}(PF_6^-)_2$ ($8(PF_6^-)_2$) was isolated from an oxidation in acetonitrile and was readily identified from its ^{1}H NMR spectrum which was identical to that of an authentic sample that was prepared by chloride abstraction from $Cp^*Ir(PPh_3)Cl_2$ with 2 equiv of $Ag^+PF_6^-$ in acetonitrile[15] (δ 1.50 (d, 15 H, Cp*), 2.40 (d, 6 H,



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(12) (a) Batchelor, R. J.; Einstein, F. W. B.; Pomeroy, R. K.; Shipley, J. A. *Inorg. Chem.* **1992**, *31*, 3155. (b) Antonelli, D. M.; Cowie, M. *Organometallics* **1991**, *10*, 2550.

(13) Cationic, bridging hydride complexes have been previously prepared by the addition of 0.5 equiv of trityl reagents to mononuclear precursors in poorly coordinating solvents. See ref 4a and: (a) Beck, W.; Schloter, K. *Z. Naturforsch. B* **1978**, *33B*, 1214. (b) Markham, J.; Cutler, A. *Organometallics* **1984**, *3*, 736.

(14) The possible involvement of electron-transfer mechanisms in hydride abstraction from transition-metal hydrides have been previously addressed. See refs 3a, 4b, and: Smith, K.-T.; Tilset, M. *J. Organomet. Chem.* **1992**, *431*, 55.

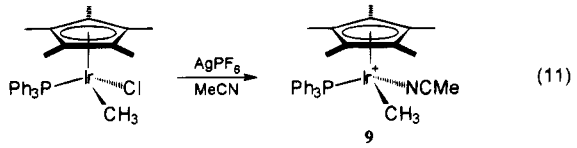
(15) The triflate salt $Cp^*Ir(PMe_3)(NCMe)_2{}^{2+}(CF_3SO_3^-)_2$ was prepared from $Cp^*Ir(PMe_3)Cl_2$ and 2 equiv of $AgSO_3CF_3$ in dichloromethane, followed by anion displacement by acetontrile: Stang, P. J.; Huang, Y.-H.; Arif, A. M. *Organometallics* **1992**, *11*, 231.

(16) Low, J. J.; Goddard, W. A., III. *J. Am. Chem. Soc.* **1984**, *106*, 6928, 8321.

MeCN), 7.4–7.8 (m, 15 H, Ph). The δ 2.40 resonance gradually vanished in acetonitrile-d_3 as a consequence of exchange of coordinated acetonitrile with the solvent. GLC and MS analysis of the volatiles from the oxidation verified the presence of methane. The reductive elimination of methane took place intramolecularly, as evidenced by the formation of CD_4 and CH_4, and no detectable CD_3H or CDH_3, when a 1:1 mixture of Cp*Ir(PPh_3)(CH_3)H and Cp*Ir(PPh_3)(CD_3)D was treated with 2 equiv of $Cp_2Fe^+PF_6^-$.

The oxidation of **2** with $Cp_2Fe^+PF_6^-$ in dichloromethane required only 1 equiv of oxidant. A ^{1}H NMR spectrum was recorded immediately after an oxidation that was performed in dichloromethane-d_2 and revealed the presence of methane (δ 0.18) and a cluster of peaks at δ 1–2. None of the peaks matched the Cp* resonance of the dichloride Cp*Ir(PPh_3)Cl_2, which could be perceived as a likely product from halide abstraction reactions or from the decomposition of complexes containing coordinated dichloromethane. Immediately after the oxidation, the solution was clear and yellow, but it gradually darkened and was virtually black after 30 min.

Bulk Electrolysis and Chemical Oxidation of Cp*Ir(PPh₃)(CH₃)₂ (3). It has been previously communicated that the oxidation of **3** requires 1 faraday/mol at ambient temperature and that the cation radical $\mathbf{3}^{\bullet+}$ is quite persistent at −20 °C, giving a red-violet solution in dichloromethane.[8b] Our observations agree with these. Also in acetonitrile/0.05 M $Me_4N^+BF_4^-$, a dark violet color developed during a one-electron electrolysis, but faded during a 10-min period at ambient temperature. Therefore, $\mathbf{3}^{\bullet+}$ is kinetically unstable under these conditions. Analysis of the reaction mixture in the faded solution by ^{31}P{^{1}H} NMR spectroscopy revealed that Cp*Ir(PPh_3)(NCMe)$CH_3^+BF_4^-$ (**9**(BF_4^-)) was the major (ca. 60% of total signal intensity) organometallic product (δ 8.2). Other signals were seen at δ −2.9 (30%) and −12.2 (10%). The identity of **9** was verified by comparison of the ^{1}H and ^{31}P{^{1}H} NMR spectra with those of an authentic sample of **9**(PF_6^-), prepared by chloride abstraction from Cp*Ir(PPh_3)(CH_3)Cl with 1 equiv of $Ag^+PF_6^-$ in acetonitrile (eq 11).



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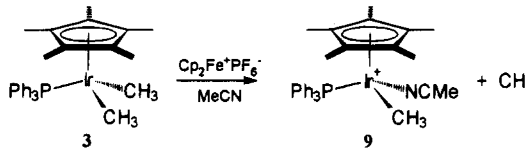
A two-electron electrolysis was performed at 0 °C in order to increase the lifetime of $\mathbf{3}^{\bullet+}$. A ^{31}P{^{1}H} NMR spectrum of the products of a two-electron electrolysis showed the same three products but now in a 30:10:60 ratio. It appears that **9** and the unknown species giving rise to the δ −2.9 signal are due to chemical reactions of $\mathbf{3}^{\bullet+}$, whereas the species resonating at δ −12.2 is generated by the two-electron oxidation.

The chemical oxidation of **3** was also effected with oxidizing agents of quite different oxidizing powers: $Cp_2Fe^+PF_6^-$, (η^5-C_5H_4COMe)(Cp)$Fe^+BF_4^-$ (**10**(BF_4^-); E_{red} = 0.25 V vs Fc), and $(phen)_3Fe^{3+}(PF_6^-)_3$ (**11**$(PF_6^-)_3$; E_{red} = 0.70 V vs Fc; phen = 9,10-phenanthroline).

Treatment of **3** with 1 equiv of **10**(BF_4^-) in acetonitrile-d_3 caused a slow reaction to take place (eq 12), eventually leading to complete consumption of the substrate. The ^{1}H NMR spectrum showed the presence of methane (δ 0.18) and smaller quantities of ethane (δ 0.85). Furthermore, Cp*Ir(PPh_3)($NCCD_3$)CH_3^+ (**9**-d_3) was present as the dominant organometallic product (ca. 60%; δ 0.63 (d, J = 5.7 Hz, 3 H), 1.46 (d, J = 2.2 Hz, 15 H). Signals of unknown origin were seen at δ 0.52 (d, J = 3.0 Hz), 0.69 (s), and 1.7–1.8 (m). Finally, a minor product (<5%) showed signals at δ 1.22 (d, J = 2.8 Hz, 6 H) and 1.69 (d, J = 2.8 Hz, 15 H). The same products, with **9**-d_3 as the dominating organometallic species, and in relatively similar yields, were obtained when $Cp_2Fe^+PF_6^-$ was used as the oxidizing agent. However, when 2 equiv of **11**$(PF_6^-)_3$ was used to effect the oxidation, the amount of ethane had increased and although **9**-d_3 was still the major product (ca. 50%), the compound that gave rise to the signals at δ 1.22 and 1.69 was now second-most important (ca. 30%). The ^{31}P NMR spectra gave signals at δ +8.2 and −12.2 in the same ratio.



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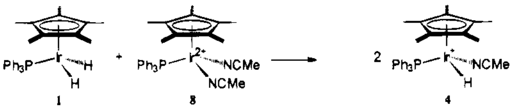
These data along with the results from the two-electron electrolysis experiment and the cyclic voltammetry investigation led us to tentatively assign this product the structure Cp*Ir(PPh_3)($NCCD_3$)$(CH_3)_2^{2+}$. Evidence for coordinated acetonitrile in this species was found when **3** was oxidized with 2 equiv of **11**$(PF_6^-)_3$ in acetonitrile, followed by removal of solvent and recording of the ^{1}H NMR spectrum in acetonitrile-d_3. A signal at δ 2.57 (d, J = 1.0 Hz, 3 H) of half the intensity of the signal at δ 1.22 is attributed to coordinated acetonitrile. Once generated, the presumed dication was rather stable in solution and did *not* produce **8** or ethane during a period of 8 h at ambient temperature.

Interestingly, the oxidation of **3** did *not* produce Cp*Ir(PPh_3)$(NCMe)_2^{2+}$ (**8**) which, on the basis of the chemistry of the Rh analogue of **3**, would be the expected product from reductive elimination of ethane from $\mathbf{3}^{\bullet+}$. We can rule out that the failure to see **8** is due to a rapid comproportionation of **3** and **8** to yield **9** under the reaction conditions. Although the comproportionation of **3** and **8** to yield **9** *does* occur, this reaction takes days (vide infra) and is therefore much too slow to account for the production of **9** on the time scale of the oxidation experiments.

A labeling experiment was performed to investigate the source of the fourth hydrogen atom in the methane product. Oxidation of **3** and **3**-d_6 in acetonitrile-d_3 gave CH_4 and CD_3H, respectively (mass spectrometry analysis). This result alone can be understood in terms of the orthometalation reaction that was communicated recently.[8b] However, a ^{2}H NMR spectrum of the reaction mixture after completion of the reaction revealed that D had been incorporated into the Cp* methyl resonance of the product. There was no evidence for D incorporation into the Ir-bonded methyl group or into the phenyl rings of PPh_3.

Thus far, we suggest that the major mode of reaction of $\mathbf{3}^{\bullet+}$ appears to be elimination of methane and generation of **9**. An extensive investigation of the mechanisms of reactions of $\mathbf{3}^{\bullet+}$ and $\mathbf{3}^{2+}$ is underway. Further details about the one- vs two-electron oxidation chemistry of **3**, the methane- and ethane-producing reactions, and the apparent Cp* C—H activation process will be separately reported.

Comproportionation of $Cp^*Ir(PPh_3)(NCMe)_2^{2+}$ (8) with $Cp^*Ir(PPh_3)(H)_2$ (1), $Cp^*Ir(PPh_3)(CH_3)H$ (2), and $Cp^*Ir(PPh_3)(CH_3)_2$ (3). When **1** and **8**$(PF_6^-)_2$ were mixed in acetonitrile-d_3, a slow reaction ensued to give **4**(PF_6^-) as the only product (^1H NMR) (eq 13). A similar reaction occurred between **2** and **8**$(PF_6^-)_2$ in acetonitrile-d_3. The reaction was quantitative and resulted in a 1:1 mixture of **9**(PF_6^-) and **4**(PF_6^-) (eq 14). The reaction was complete in about 4 days at 40 °C. Finally, in analogy with the behavior of the related Rh complex, a 1:1 mixture of **3** and **8**$(PF_6^-)_2$ in acetonitrile-d_3 underwent a quantitative reaction to provide **9**(PF_6^-) as the only product (eq 15). The reaction was rather slow and more than 1 week was required for it to go to completion. No attempts were made at establishing the mechanisms of these reactions.



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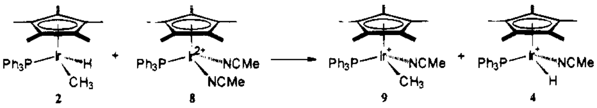

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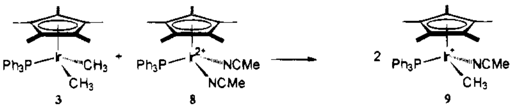

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Concluding Remarks. The first comparison of the oxidative behavior of dihydride, hydridomethyl, and dimethyl complexes has shown very different behavior among these species. The oxidation of the dihydride **1** led to proton-transfer reactions of the type that have been established as typical for numerous metal hydrides. For the hydridomethyl compound **2**, oxidatively induced reductive elimination of methane was the exclusive reaction. The rate of thermal elimination of methane from **2** is very slow (we find ca. 10% reaction after 72 h in benzene-d_6 at 110 °C; $Cp^*Ir(PMe_3)(CH_3)H$ undergoes elimination at 130 °C[11b]), and the one-electron oxidation leads to a tremendous rate enhancement for the reductive elimination. The cation radical $Cp^*Ir(PPh_3)(CH_3)H^{\bullet+}$ obviously undergoes reductive elimination of methane at a rate much greater than that at which $Cp^*Ir(PPh_3)(CH_3)_2^{\bullet+}$ expels ethane. This reactivity trend parallels that of 18-electron hydridoalkyl vs dialkyl species.[2a,11b,17] The dimethyl complex $\mathbf{3}^{\bullet+}$, unlike the Rh analogue $Cp^*Rh(PPh_3)(CH_3)_2^{\bullet+}$, did not undergo reductive elimination of ethane as the major reaction. The major reaction involved production of methane by an as yet unresolved mechanism. Two factors may contribute to disfavor ethane elimination from $\mathbf{3}^{\bullet+}$ when compared with the Rh analogue. First, the tendency to undergo reductive elimination is reduced as a consequence of stronger M—C bonds for Ir than for Rh. Second, Cp* C—H activation at the 17-electron center may be favored for Ir over Rh due to the formation of stronger M—C and M—H bonds for M = Ir than for M = Rh.

Experimental Section

General Procedures. All manipulations involving organometallic compounds were carried out with the use of vacuum line, Schlenk, syringe, or drybox techniques. Acetonitrile was distilled from P_2O_5, and acetonitrile-d_3, dichloromethane, and dichloromethane-d_2 were distilled from CaH_2. Acetonitrile and dichloromethane containing the supporting electrolyte were passed through a column of active neutral alumina prior to use to remove water and protic impurities before electrochemical measurements. The electrolyte was freed of air by purging with purified solvent-saturated argon, and all measurements and electrolyses were carried out under a blanket of argon.

Electrochemical measurements were performed with an EG&G-PAR Model 273 potentiostat/galvanostat driven by an external HP 3314A sweep generator. The signals were fed to a Nicolet 310 digital oscilloscope and processed by an on-line personal computer. The working electrode was a Pt disk electrode (d = 0.4 mm), the counter electrode was a Pt wire, and the Ag wire reference electrode assembly[17] was filled with acetonitrile/0.01 M $AgNO_3$/0.1 M $Bu_4N^+PF_6^-$. The reference electrode was calibrated against Cp_2Fe which is also used as the reference in this work. The positive-feedback iR compensation circuitry of the potentiostat was employed; the separation of anodic and cathodic peaks for the Cp_2Fe oxidation was 59–61 mV in acetonitrile.

^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on Varian XL-300 or Varian Gemini-200 instruments. Chemical shifts are reported in ppm relative to tetramethylsilane, with the residual solvent proton resonance as the internal standard. $^{31}P\{^1H\}$ NMR spectra were recorded on the Varian XL-300 instrument operating at 121 MHz. Chemical shifts are reported in ppm relative to 85% H_3PO_4, using a capillary tube containing a solution of PPh_3 in the appropriate solvent, calibrated against H_3PO_4, as an external standard. Pulse delays of 8 s were used when $^{31}P\{^1H\}$ NMR spectra were to be integrated. ^2H NMR spectra were recorded on the Varian XL-300 instrument operating at 55 MHz. Chemical shifts are referenced against acetonitrile-d_3 at δ 1.93. Infrared spectra were obtained on a Perkin-Elmer 1310 infrared spectrophotometer. Melting points were measured on a Büchi melting point apparatus in capillary tubes sealed under vacuum. Elemental analyses were performed by Ilse Beetz Mikroanalytisches Laboratorium, Kronach, Germany.

The compounds $Cp_2Fe^+PF_6^-$,[18a] $(\eta^5\text{-}C_5H_4COMe)CpFe^+BF_4^-$ (**10**(BF_4^-)),[18b] $(p\text{-}MeOC_6H_4)Ph_2C^+BF_4^-$,[18c] $Cp^*Ir(PPh_3)Cl_2$,[18d] $Cp^*Ir(PPh_3)(CH_3)Cl$,[11b] $Cp^*Ir(PPh_3)(CH_3)H$ (**2**),[11b] $Cp^*Ir(PPh_3)(H)_2$ (**1**),[9] $Cp^*Ir(PPh_3)(H)_3^+BF_4^-$ (**6**(BF_4^-)),[9] and $(phen)_3Fe^{3+}(PF_6^-)_3$ (**11**$(PF_6^-)_3$)[18e] were prepared according to published procedures. $PhNH_3^+BF_4^-$ was prepared from aniline and $HBF_4{\cdot}Et_2O$ in ether. All other compounds were used as received from commercial suppliers.

$Cp^*Ir(PPh_3)(CH_3)_2$ (3). The following procedure in our hands gave better yields than the previously reported procedure.[11b] A solution of CH_3MgI (4.6 mL of a 1 M solution, 4.6 mmol) was added slowly to a stirred solution of $Cp^*Ir(PPh_3)Cl_2$ (400 mg, 0.606 mmol) in benzene (8 mL). During the addition of the Grignard reagent, the solution changed from an orange slurry to a clear, homogeneous red solution. On further stirring, the color changed to yellow. After 24 h the solution was transferred through a double-ended needle onto an ice-cooled, rapidly stirred, saturated aqueous ammonium chloride solution (7 mL). The resulting mixture was stirred vigorously to ensure complete hydrolysis of the excess Grignard reagent. The organic phase was separated and washed with water (10 mL). The aqueous phase was washed with ether (3 × 5 mL), and the combined organic extracts were

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dried ($MgSO_4$) for 15 min. The solution was filtered, and the solvents were removed in vacuo. The resulting solid was purified by column chromatography (grade II alumina, benzene) under N_2. The yellow product was recrystallized from benzene/heptane (2/1) by slowly removing the benzene by rotary evaporation to give yellow crystals of **3** (289 mg, 77%). ^1H NMR (300 MHz, benzene-d_6) δ 0.57 (d, J = 4.9 Hz, 6 H, Ir—CH_3), 1.90 (d, J = 1.7 Hz, 15 H, Cp*), 6.9–7.2 and 7.4–7.6 (m, 15 H, Ph).

$Cp^*Ir(PPh_3)(NCMe)H^+BF_4^-$ (4(BF_4^-)). A slurry of $Cp^*Ir(PPh_3)(CH_3)H$ (83 mg, 0.137 mmol) and $PhNH_3^+BF_4^-$ (25 mg, 0.137 mmol) in acetonitrile (3 mL) was stirred in a −50 °C cooling bath. The temperature was gradually allowed to increse, and at −35 °C the solution was homogeneous. Stirring was continued until the temperature reached 0 °C over a 2 h period. The solution was concentrated in vacuo, and the product (64 mg, 65%) was precipitated by the addition of ether: white powder, mp 188–190 °C slow dec; ^1H NMR (300 MHz, acetonitrile-d_3) δ −13.93 (d, J = 34.3 Hz, 1 H, Ir—H), 1.64 (d, J = 2.0 Hz, 15 H, Cp*), 2.01 (s, 3 H, MeCN), 7.4–7.6 (m, 15 H, Ph); $^{13}C\{^1H\}$ NMR (75 MHz, acetonitrile-d_3) δ 1.8, 9.6, 96.6, 129.7 (d), 132.0 (d), 134.7 (d). Anal. Calcd for $C_{30}H_{34}BF_4IrNP$: C, 50.14; H, 4.77; N, 1.95. Found: C, 50.09; H, 4.72; N, 2.04.

$[(Cp^*Ir(PPh_3)H)_2(\mu\text{-}H)]^+BF_4^-$ (7(BF_4^-)). $Cp^*Ir(PPh_3)(H)_2$ (52 mg, 0.088 mmol) and $(p\text{-}MeOC_6H_4)Ph_2C^+BF_4^-$ (15 mg, 0.042 mmol) were dissolved in dichloromethane (5 mL) at ambient temperature. The reaction mixture was stirred for 5 min, and the solution was concentrated in vacuo. The product was obtained as a pale red powder by rapid addition of ether. The ^1H NMR analysis showed that the product contained traces of **6**(BF_4^-). Extensive decomposition was experienced during attempted recrystallization of the material. ^1H NMR (200 MHz, dichloromethane-d_2): δ −20.37 (t, J = 16.7 Hz, 3 H, Ir—H), 1.45 (d, J = 2.1 Hz, 30 H, Cp*), 7.2–7.6 (m, 30 H, Ph). Lowering of the temperature caused the hydride resonance (δ −20.37) to broaden. At −50 °C, the signal was a broad singlet, at −90 °C the broad signal had almost merged with the baseline. No other changes in the spectrum were observed.

The reaction was repeated at −90 °C. This procedure gave considerably more **6** (25–30%) than the ambient-temperature experiment.

Fragmentation of $[(Cp^*Ir(PPh_3)H)_2(\mu\text{-}H)]^+BF_4^-$ in Acetonitrile-d_3. When **7**(BF_4^-) was dissolved in acetonitrile-d_3 at ambient temperature, the complex underwent a spontaneous (complete in 5 min) fragmentation to yield $Cp^*Ir(PPh_3)(H)_2$ and $Cp^*Ir(PPh_3)(NCMe)H^+BF_4^-$ in a 1:1 ratio, as seen by ^1H NMR spectroscopy.

$Cp^*Ir(PPh_3)(NCMe)_2{}^{2+}(PF_6^-)_2$ (8(PF_6^-)$_2$). A solution of $Cp^*Ir(PPh_3)Cl_2$ (300 mg, 0.454 mmol) and $Ag^+PF_6^-$ (230 mg, 0.908 mmol) in acetonitrile (3 mL) was stirred for 5 min and filtered through Celite. The solution was concentrated in vacuo, and the product (251 mg, 57%) was obtained by the addition of ether at −40 °C: yellow crystals, mp 185–190 °C slow dec; ^1H NMR (300 MHz, acetonitrile-d_3) δ 1.50 (d, J = 2.5 Hz, 15 H, Cp*), 2.40 (d, J = 1.2 Hz, 6 H, MeCN), 7.4–7.5 and 7.6–7.8 (m, 15 H, Ph); $^{13}C\{^1H\}$ NMR (75 MHz, acetonitrile-d_3) δ 9.1, 99.5 (d), 130.4 (d), 133.6, 135.0 (d); $^{31}P\{^1H\}$ NMR (121 MHz, acetonitrile-d_3) δ 6.0 (s). Anal. Calcd for $C_{32}H_{36}F_{12}IrN_2P_3$: C, 39.96; H, 3.77; N, 2.91. Found: C, 40.19; H, 3.79; N, 3.36. The acetonitrile ν_{CN} absorption was not detected by IR spectroscopy.

$Cp^*Ir(PPh_3)(NCMe)(CH_3)^+PF_6^-$ (9(PF_6^-)). An acetonitrile solution (3 mL) of $Cp^*Ir(PPh_3)(CH_3)Cl$ (200 mg, 0.312 mmol) and $Ag^+PF_6^-$ (79 mg, 0.312 mmol) was stirred for 5 min and filtered through Celite. The solution was concentrated in vacuo, and the product was obtained by the addition of ether (141 mg, 57%): yellow powder, mp 198–200 °C slow dec; ^1H NMR (300 MHz, acetonitrile-d_3) δ 0.63 (d, J = 5.7 Hz, 3 H, Ir—CH_3), 1.46 (d, J = 2.2 Hz, 15 H, Cp*), 7.3–7.6 (m, 15 H, Ph); $^{13}C\{^1H\}$ NMR (75 MHz, acetonitrile-d_3) δ −17.1 (d), 8.5, 95.0 (d), 128.0 (d), 130.5 (d), 133.3 (d); $^{31}P\{^1H\}$ NMR (acetonitrile-d_3) δ 8.15 (s). Anal. Calcd for $C_{31}H_{36}F_6IrNP_2$: C, 47.08; H, 4.59; N, 1.77. Found: C, 47.51; H, 4.70; N, 1.98. The acetonitrile ν_{CN} IR absorption was not detected.

Oxidation of $Cp^*Ir(PPh_3)(H)_2$ with $Cp_2Fe^+PF_6^-$ in Acetonitrile-d_3. $Cp^*Ir(PPh_3)(H)_2$ (5.0 mg, 0.008 mmol) and $Cp_2Fe^+PF_6^-$ (2.8 mg, 0.008 mmol) were added to an NMR tube equipped with a ground-glass joint. Acetonitrile-d_3 (0.7 mL) was added by vacuum transfer, and the tube was sealed under vacuum. An immediate reaction occurred, as judged by the instant fading of the dark blue color of Cp_2Fe^+ to give a yellow solution. The ^1H NMR spectrum of the reaction mixture showed complete consumption of the substrate and the presence of Cp_2Fe (δ 4.15 (s)) and a near 1:1 mixture of $Cp^*Ir(PPh_3)(H)_3^+$ (**6**; δ −12.65 (br s, Ir—H), 1.94 (d, Cp*)) and $Cp^*Ir(PPh_3)(NCCD_3)H^+$ (**4**-d_3; δ −13.93 (d, Ir—H), 1.64 (d, Cp*)). Traces of *fac*-$Ir(PPh_3)(NCCD_3)(H)_2^+$ (**5**-d_9; δ −21.89 (d, Ir—H)) and Cp*H were seen. When the solution was left at ambient temperature for 8 h, the signals due to **6** disappeared with a concomitant increase in the intensities of the resonances arising from **5**-d_9 and Cp*H.

A separate experiment was performed with hexamethylbenzene (HMB) as an internal standard for quantification purposes. The instant yields of **4**-d_3 and **6** were ca. 40% of each (80% Ir mass balance).

Oxidation of $Cp^*Ir(PPh_3)(H)_2$ with $Cp_2Fe^+PF_6^-$ in Acetonitrile in the Presence of Quinuclidine. The above experiment was repeated in the presence of quinuclidine (3.7 mg, 2.0 equiv). This resulted in only 50% consumption of the starting material, as judged by inspection of the ^1H NMR spectrum. The use of 2 equiv of $Cp_2Fe^+PF_6^-$ (5.6 mg, 0.016 mmol) effected full consumption of the substrate. The ^1H NMR spectrum showed $Cp^*Ir(PPh_3)(NCCD_3)H^+$ to be the only detectable Cp*-containing product.

Oxidation of $Cp^*Ir(PPh_3)(H)_2$ with $Cp_2Fe^+PF_6^-$ in Dichloromethane-d_2. $Cp^*Ir(PPh_3)(H)_2$ (5.0 mg, 0.008 mmol) and $Cp_2Fe^+PF_6^-$ (1.9 mg, 0.005 mmol) were added to an NMR tube equipped with a ground-glass joint. Dichloromethane-d_2 (0.7 mL) was added by vacuum transfer, and the tube was sealed under vacuum. A color change from blue to yellow signaled an immediate reaction. The ^1H NMR spectrum showed the presence of $Cp^*Ir(PPh_3)(H)_3^+$ and $[Cp^*Ir(PPh_3)(H)]_2(\mu\text{-}H)^+$ in a 1:1 molar ratio. The mass balance was found to be at least 95% when hexamethylbenzene was used as an internal standard.

Oxidation of $Cp^*Ir(PPh_3)(CH_3)H$ with $Cp_2Fe^+PF_6^-$ in Acetonitrile-d_3. $Cp^*Ir(PPh_3)(CH_3)H$ (5.0 mg, 0.008 mmol) and $Cp_2Fe^+PF_6^-$ (5.4 mg, 0.016 mmol) were added to an NMR tube equipped with a ground-glass joint. Acetonitrile-d_3 (0.7 mL) was added by vacuum transfer, and the tube was sealed under vacuum. The color of the solution changed from blue to yellow immediately. The ^1H NMR spectrum showed methane (δ 0.18) and $Cp^*Ir(PPh_3)(NCCD_3)_2{}^{2+}$ (δ 1.50 (d, Cp*)) to be the only products. A mass balance of at least 95% was established by the use of hexamethylbenzene as an internal standard.

Oxidation of $Cp^*Ir(PPh_3)(CH_3)H$ with $Cp_2Fe^+PF_6^-$ in Dichloromethane-d_2. $Cp^*Ir(PPh_3)(CH_3)H$ (5.0 mg, 0.008 mmol) and $Cp_2Fe^+PF_6^-$ (2.7 mg, 0.008 mmol) were added to an NMR tube equipped with a ground-glass joint. Dichloromethane-d_2 (0.7 mL) was added by vacuum transfer, and the tube was sealed under vacuum. The ^1H NMR spectrum showed a cluster of peaks in the region δ 1–2, none of which have been identified, and methane (δ 0.18).

Oxidation of $Cp^*Ir(PPh_3)(CH_3)_2$ with 10(BF_4^-) in Acetonitrile-d_3. $Cp^*Ir(PPh_3)(CH_3)_2$ (7.4 mg, 0.012 mmol) and **10**(BF_4^-) (3.7 mg, 0.011 mmol) were added to an NMR tube equipped with a ground-glass joint. Acetonitrile-d_3 (0.7 mL) was added by vacuum transfer, and the tube was sealed under vacuum. A relatively slow fading of the blue color of the solution occurred. The ^1H NMR spectrum showed the presence of methane (δ 0.18) and smaller quantities of ethane (δ 0.85). $Cp^*Ir(PPh_3)(NCCD_3)CH_3^+$ (**9**-d_3) was the major Cp*-containing product (ca. 60% of combined Cp* signal intensity). Signals of unknown origin were located at δ 0.52 (d, J = 3.0 Hz), 0.69 (s), and 1.7−1.8 (m). Traces (<5%) of the compound which is tentatively assumed to be $Cp^*Ir(PPh_3)(NCCD_3)(CH_3)_2^{2+}$ gave signals at δ 1.22 (d, Ir−CH_3) and 1.69 (d, Cp*) (see next experiment). The same products, also with **9**-d_3 as the dominating organometallic species, were obtained in an even slower reaction when $Cp_2Fe^+PF_6^-$ was used as the oxidant.

Oxidation of $Cp^*Ir(PPh_3)(CH_3)_2$ with 11(BF_6^-)$_3$ in Acetonitrile-d_3. $Cp^*Ir(PPh_3)(CH_3)_2$ (10.0 mg, 0.016 mmol) and **11**(PF_6^-)$_3$ (30.6 mg, 0.030 mmol) were added to an NMR tube equipped with a ground-glass joint. Acetonitrile-d_3 (0.7 mL) was added by vacuum transfer, and the tube was sealed under vacuum. The ^{1}H NMR spectrum showed that **9**-d_3 was the major product (ca. 50%). Another product, assumed to be the dication $Cp^*Ir(PPh_3)(NCCD_3)(CH_3)_2^{2+}$, was also quite dominant (ca. 30%; δ 1.22 (d, J = 2.8 Hz, 6 H, Ir−CH_3), 1.69 (d, J = 2.8 Hz, 15 H, Cp*)). The $^{31}P\{^1H\}$ NMR spectra displayed signals at δ +8.2 (**9**-d_3) and −12.2 in the same ratio.

A similar experiment was performed in an NMR tube using acetonitrile as the solvent. After the reaction, the solvent was removed by vacuum transfer and acetonitrile-d_3 (0.7 mL) was added. The ^{1}H NMR spectrum was recorded immediately and showed a ^{1}H NMR spectrum essentially identical to that above except that signals due to coordinated acetonitrile in $Cp^*Ir(PPh_3)(NCCH_3)(CH_3)_2^{2+}$ were seen at δ 2.57 (d, J = 1.0 Hz, 3 H).

Comproportionation of $Cp^*Ir(PPh_3)(NCMe)_2^{2+}(PF_6^-)_2$ with $Cp^*Ir(PPh_3)(H)_2$, $Cp^*Ir(PPh_3)(CH_3)H$, and $Cp^*Ir(PPh_3)(CH_3)_2$. An NMR tube equipped with ground-glass joint was loaded with $Cp^*Ir(PPh_3)(NCMe)_2^{2+}(PF_6^-)_2$ (7.4 mg, 0.008 mmol) and $Cp^*Ir(PPh_3)(H)_2$ (5.0 mg, 0.008 mmol) in acetonitrile-d_3 (0.7 mL) in the drybox. The tube was attached to the vacuum line via an adapter, cooled in a dry ice/acetone bath, evacuated, and sealed. A very slow reaction (15−20% by ^{1}H NMR spectroscopy in 6 days) between the two components was observed at ambient temperature, yielding $Cp^*Ir(PPh_3)(NCMe)H^+$ as the only observable product.

A similar experiment with $Cp^*Ir(PPh_3)(NCMe)_2^{2+}(PF_6^-)_2$ (7.4 mg, 0.008 mmol), $Cp^*Ir(PPh_3)(CH_3)H$ (5.0 mg, 0.008 mmol) and hexamethylbenzene (1.1 mg, 0.007 mmol) internal standard in acetonitrile-d_3 (0.7 mL) was performed. The comproportionation resulted in the quantitative (^{1}H NMR) formation of a 1:1 mixture of $Cp^*Ir(PPh_3)(NCMe)CH_3^+PF_6^-$ and $Cp^*Ir(PPh_3)(NCMe)H^+PF_6^-$. The reaction was complete after 4 days at 40 °C.

$Cp^*Ir(PPh_3)(NCMe)_2^{2+}(PF_6^-)_2$ (7.4 mg, 0.008 mmol), $Cp^*Ir(PPh_3)(CH_3)_2$ (5.0 mg, 0.008 mmol), and hexamethylbenzene (1.1 mg, 0.007 mmol) were dissolved in acetonitrile-d_3 (0.7 mL). The reaction quantitatively (^{1}H NMR) yielded $Cp^*Ir(PPh_3)(NCMe)CH_3^+PF_6^-$ after 8−9 days at ambient temperature.

Constant-Current Coulometry and Preparative Electrolysis Experiments of $Cp^*Ir(PPh_3)(H)_2$, $Cp^*Ir(PPh_3)(CH_3)H$, and $Cp^*Ir(PPh_3)(CH_3)_2$. Constant-current coulometry measurements and preparative electrolyses were performed in an H-shaped cell, the compartments of which were separated by a medium-frit glass junction. A platinum-gauze working electrode was used. Solutions of 10−20 mg of substrate in 20 mL of acetonitrile/0.1 M $Bu_4N^+PF_6^-$ or dichloromethane/0.2 M $Bu_4N^+PF_6^-$ were electrolyzed with a constant current of 10 mA, while the consumption of the substrate was monitored by derivative cyclic voltammetry.[19] Monitoring of the potential of the working Pt-gauze electrode under experimental conditions showed that electrode potential was lower than the cyclic voltammetry oxidation peak potential for ca. 90% of the electrolysis time. For coulometry, three separate measurements were made for each compound in each solvent. The results are given in Table 1.

The preparative constant-current electrolysis experiments were similarly done in acetonitrile/0.05 M $Me_4N^+BF_4^-$ for **1**−**3**. The solution from the anode compartment was concentrated by vacuum transfer. For $^{31}P\{^1H\}$ NMR analysis, the concentrated solution was directly characterized spectroscopically. For analysis by ^{1}H NMR spectroscopy, the solvent was completely removed, and the solid residue was extracted with dichloromethane (10 mL). The extract was filtered, the solvent was removed in vacuo, and the isolated product mixture was spectroscopically characterized.

Analysis of the Volatiles from the Oxidation of $Cp^*Ir(PPh_3)(CH_3)H$ with $Cp_2Fe^+PF_6^-$ in Acetonitrile and Dichloromethane. A 5-mL round bottom flask was loaded with **2** (5.0 mg, 0.0083 mmol) and **10**(BF_4^-) (5.5 mg, 0.0165 mmol). The flask was attached to the vacuum line via a vacuum adapter, the solvent (1 mL) was added by vacuum transfer, the vessel was closed, and the reaction mixture was stirred until the reaction appeared complete. The volatiles were transferred to another flask by vacuum transfer and analyzed by GLC. Methane was detected as a product from the reactions in both acetonitrile and dichloromethane, and its identity was further authenticated by mass spectrometry.

The volatiles from a crossover experiment in which **2** and **2**-d_4 (15 mg of each, 0.050 mmol combined) were oxidized with **10**(BF_4^-) (33 mg, 0.10 mmol) in acetonitrile (1 mL) were analyzed by attaching the closed reaction vessel directly to the mass spectrometer. The volatiles were observed to contain CH_4 and CD_4 and less than 10% of the crossover products CH_3D and CD_3H.

Analysis of the Volatiles from the Oxidation of $Cp^*Ir(PPh_3)(CH_3)_2$ with 10(BF_4^-) in Acetonitrile and Dichloromethane. The experiments were conducted the same way as described above for the oxidation of **2**. In both solvents, both ethane and methane were observed. In acetonitrile, the GLC analysis showed that ethane and methane were present in a 1:9 ratio, whereas in dichloromethane the ratio varied between 1:9 and 1:4.

A mixture of **3** and **3**-d_6 (15.0 mg of each, 0.048 mmol combined) was oxidized with **10**(BF_4^-) (14.5 mg, 0.048 mmol) in acetonitrile (1 mL). The volatiles were found to contain ethane, CH_4, and CD_3H. Low yields of ethane precluded an accurate determination of its isotope pattern.

The volatiles from the oxidation of **3** (20.0 mg, 0.032 mmol) with **10**(BF_4^-) (9.7 mg, 0.032 mmol) in acetonitrile-d_3 (1 mL) were analyzed by attaching the closed reaction vessel directly to the mass spectrometer. The volatiles were found to contain CH_4. No CH_3D was detected.

^{2}H NMR Investigation of the Oxidation of $Cp^*Ir(PPh_3)(CH_3)_2$ in Acetonitrile-d_3. $Cp^*Ir(PPh_3)(CH_3)_2$ (10.0 mg, 0.016 mmol) was oxidized with **10**(BF_4^-) (4.8 mg, 0.016 mmol) in acetonitrile-d_3 (1 mL) in the drybox. The formation of **9**(BF_4^-) was verified by ^{1}H NMR spectroscopy. The solvent was removed, and the residue was dissolved in nondeuterated acetonitrile. A ^{2}H NMR spectrum of the resulting solution showed only two resonances (δ 1.93 and 1.46). These are attributed to uncoordinated acetonitrile-d_3 and to D incorporated in the Cp* ligand of **9**(BF_4^-), respectively.

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