ability than S_B ($K_{ex\ A} > K_{ex\ B}$) then the concentration of S_A in the receiving phase will always be greater than that of S_B.

Concluding Remarks. Apart from being a novel development within the area of host guest chemistry, the observation that certain metal complexes can be transported intact across bulk liquid membranes has implications for other areas of chemistry (as well as biochemistry).[30] For example, the technique clearly shows potential for the separation of mixtures of metal complexes and their isomers. In this regard, the present study demonstrates the use of the procedure for the partial resolution of suitable optically active complexes—the latter remains a classical requirement in coordination chemistry which is not always readily met by conventional methods.

(30) Although the respective mechanisms are not yet fully understood, particular microbial iron transport systems have been demonstrated to involve the active transport of intact Fe(III) complexes of natural ligands (siderophores) from outside to inside the cell through the outer cell membrane. For example, this occurs in the case of the Fe(III) complex of enterobactin which forms part of the iron transport system of *Escherichia coli*. See: Raymond, K. N.; Carrano, C. J. *Acc. Chem. Res.* **1979**, *12*, 183. Ecker, D. J.; Matzanke, B. F.; Raymond, K. N. *J. Bacteriol.* **1986**, *167*, 666. Similarly, the active transport of the cobalt complex, vitamin B_{12}, across the outer cell membrane of *Escherichia coli* has also been documented. See: Reynolds, P. R.; Mottur, G. P.; Bradbeer, C. *J. Biol. Chem.* **1980**, *255*, 431.

Acknowledgment. We thank the Australian Research Council for support and Associate Professor F. R. Keene and Mr. A. J. Leong for assistance. G.W.E. is grateful for the hospitality extended to him at James Cook University during a recent sabbatical leave.

Registry No. 1, 25999-31-9; $[Co(NH_3)_6]^{3+}$, 14695-95-5; $[Co(NH_3)_5Cl]^{2+}$, 14970-14-0; $[Pt(NH_3)_6]^{4+}$, 18536-12-4; $[Co(en)_3]^{3+}$, 14878-41-2; μ-*cis*-$[Co(dien)_2]^{3+}$, 38318-05-7; $[Co(sep)]^{3+}$, 72496-77-6; $[Co(sep)](LAS)_3$, 131656-80-9; $CHCl_3$, 67-66-3; NH_4^+, 14798-03-9.

Calorimetric Determination of the Heats of Protonation of the Metal in (Methyl-substituted cyclopentadienyl)iridium Complexes, Cp'Ir(1,5-COD)

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Received August 13, 1990

Abstract: Titration calorimetry has been used to determine the enthalpies of protonation (ΔH_{HM}) of the iridium in the Cp'Ir(1,5-COD) (Cp' = $C_5Me_xH_{5-x}$, x = 0, 1, 3-5) complexes according to the following reactions: Cp'Ir(1,5-COD) + CF_3SO_3H (0.1 M) → $[Cp'Ir(H)(1,5\text{-}COD)]^+CF_3SO_3^-$, at 25.0 °C in 1,2-dichloroethane. The ΔH_{HM} values become more exothermic from −22.8 ± 0.2 kcal mol^{-1} for Cp' = C_5H_5 to −28.5 ± 0.2 kcal mol^{-1} for Cp' = C_5Me_5. A plot of ΔH_{HM} versus the number of Me groups on Cp' is linear; this result has been interpreted to indicate that the bulkiness of the Me group, even in the C_5Me_5 ligand, probably does not affect the ΔH_{HM} values. Each Me group contributes −1.1 kcal mol^{-1} to ΔH_{HM}. Correlations between ΔH_{HM} and the COD olefin ^1H NMR chemical shift of the Cp'Ir(1,5-COD) compounds and the Ir−H ^1H NMR chemical shift of the protonated species are also made. Equilibrium studies for the protonation of Cp'Ir(1,5-COD) show that the effect of each added Me group on $\Delta G^\ominus$ is −0.89 kcal mol^{-1} and on $\Delta S^\ominus$ is −0.7 eu. Thus, $\Delta S^\ominus$ contributes little to the differences in equilibrium constants for protonation of the Cp'Ir(1,5-COD) complexes. A comparison of the common C_5H_5 and C_5Me_5 ligands shows that the replacement of C_5H_5 by C_5Me_5 increases the equilibrium constant for the protonation of Cp'Ir(1,5-COD) by 1900, makes $\Delta G^\ominus$ more favorable by −4.5 kcal mol^{-1}, causes ΔH_{HM} to be more exothermic by −5.7 kcal mol^{-1}, and reduces $\Delta S^\ominus$ slightly by ca. −4 eu.

Introduction

Currently there is much interest in quantitative measures of the basicities of metals in transition-metal complexes.[1] Yet few data are available for neutral complexes in which the ligands are systematically varied.[1d,f] In this paper, we report the first of a series of such determinations by titration calorimetry in which the basicity is given as the enthalpy of protonation of the transition-metal complex (ΔH_{HM}) with triflic acid (CF_3SO_3H) in 1,2-dichloroethane (DCE) solution at 25.0 °C (eq 1). Previously, we reported enthalpies of protonation (ΔH_{HP}) of several organophosphines using this method.[2]

$$ML_x + CF_3SO_3H \xrightarrow[25.0\ °C]{DCE} HML_x^+CF_3SO_3^-,\ \Delta H_{HM} \quad (1)$$

Among the types of ligands that are of special interest in organotransition-metal chemistry are the cyclopentadienyl ligand (C_5H_5) and its methyl-substituted analogues ($C_5Me_xH_{5-x}$, x = 1-5). Elschenbroich and Salzer[3] summarized some special properties of the pentamethylcyclopentadienyl ligand (C_5Me_5) as compared with C_5H_5. Properties that may affect the basicity of C_5Me_5 complexes relative to their C_5H_5 analogues are "stronger π-donor, weaker π-acceptor properties, increased covalent character of the cyclopentadienyl–metal bond, and kinetic stabilization effected by steric shielding of the metal center." Equilibrium acidities[4] of uncoordinated C_5Me_5H and C_5H_6 in dimethyl sulf-

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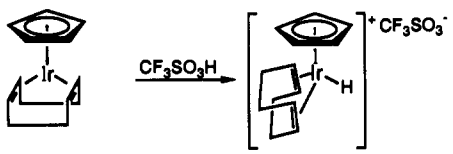
oxide solution show C_5Me_5H (pK_{HA} = 26.1) to be considerably less acidic than C_5H_6 (pK_{HA} = 18.0). Differences in the donor abilities of coordinated C_5H_5 and C_5Me_5 ligands have been explored by a variety of techniques.[1f,5,6] Gassman and co-workers[5a] showed by ESCA studies that the substitution of C_5H_5 by C_5Me_5 results in a "dramatic" lowering of the binding energies of the inner-shell electrons of the metal. They found that the substitution of two C_5H_5 ligands by two C_5Me_5 ligands results in an effective one-electron reduction of the metal.[5b] Lowering of the core and valence ionization energies of the metal's electrons is attributed to an increase in electron density at the metal center caused primarily by the inductive effect of the methyl group on the Cp′ ring.[5c] Brill and co-workers,[5d] however, studied the effect of C_5H_5 vs C_5Me_5 by ^{59}Co nuclear quadrupole resonance spectroscopy and concluded that the inductive effect of the permethylated ligand was small.

Perhaps the best available comparison of the effect of C_5H_5 vs C_5Me_5 on the basicity of a metal center is provided by Norton and co-workers.[5e] They determined pK_a's of $Cp'Mo(CO)_3H$ and $Cp'Fe(CO)_2H$ (Cp′ = C_5H_5, C_5Me_5) by deprotonation with organic bases of known pK_a in acetonitrile solution. For the $Cp'Mo(CO)_3H$ complexes, the C_5Me_5 derivative was less acidic by 3.2 pK_a units than the C_5H_5 analogue. In the iron series $(C_5Me_5)Fe(CO)_2H$ was 6.9 pK_a units less acidic than $(C_5H_5)Fe(CO)_2H$.

No studies which investigate systematically the effect of methyl substitution in the cyclopentadienyl ligand on the proton basicity of a neutral metal center have been reported. In this paper we describe an investigation of the effects of methyl-substituted cyclopentadienyl ligands on the basicity of the iridium center in Cp′Ir(1,5-COD) complexes (Cp′ = C_5H_5, C_5MeH_4, 1,2,3-$C_5Me_3H_2$, C_5Me_4H, C_5Me_5) by measuring heats of protonation (ΔH_{HM}) of the reactions shown in eq 2. Also, competitive equilibrium studies for proton transfer between methyl-substituted



1, Cp′ = C_5H_5
2, Cp′ = C_5MeH_4
3, Cp′ = 1,2,3-$C_5Me_3H_2$
4, Cp′ = C_5Me_4H
5, Cp′ = C_5Me_5

1H+, Cp′ = C_5H_5
2H+, Cp′ = C_5MeH_4
3H+, Cp′ = 1,2,3-$C_5Me_3H_2$
4H+, Cp′ = C_5Me_4H
5H+, Cp′ = C_5Me_5 (2)

Cp′Ir(1,5-COD) complexes have yielded values of K_{eq}, $\Delta G^{\ominus}$, and $\Delta S^{\ominus}$ for the reaction in eq 3. Comparisons of these thermodynamic quantities for the C_5H_5 and C_5Me_5 complexes permit a detailed discussion of their ligand properties as they affect the basicity of the metal. In addition, protonation reactions of (indenyl)Ir(1,5-COD) (6), $(HBPz^*_3)Ir(1,5\text{-COD})$ (7) (Pz* = 3,5-dimethyl-1-pyrazolyl), and $(Me_3SiC_5H_4)Ir(1,5\text{-COD})$ are reported.

$$Cp'Ir(H)(COD)^+ + Cp''Ir(COD) \underset{25.0\ ^\circ C}{\overset{K_{eq}}{\rightleftharpoons}} Cp'Ir(COD) + Cp''Ir(H)(COD)^+ \quad (3)$$

(a) Cp′ = C_5H_5 (**1H+**), Cp″ = C_5MeH_4 (**2**)

(b) Cp′ = $C_5Me_3H_2$ (**3H+**), Cp″ = C_5Me_4H (**4**)

(c) Cp′ = C_5Me_5 (**5H+**), Cp″ = C_5Me_4H (**4**)

(d) Cp′ = C_5H_5 (**1H+**), Cp″ = C_5Me_5 (**5**)

Experimental Section

Argon and nitrogen gases were purified by passing them through a deoxygenation column containing a supported, activated Cu metal catalyst (R3-11, Chemical Dynamics Corp.) thermostated at 100 °C.[7] This column was followed by a drying column (45 × 4.5 cm) packed with molecular sieves (Davison Type 4A, Fisher Scientific) which were treated at 350 °C at 10^{-2} mmHg for 12 h prior to loading.[8] All preparative reactions and manipulations (except as stated otherwise) were carried out under an atmosphere of nitrogen following Schlenk techniques similar to those described by Cooper and co-workers.[9] Hexanes and petroleum ether "A" (bp 28 °C) were refluxed over CaH_2 and then distilled.[10] The petroleum ether was stored over molecular sieves. Tetrahydrofuran (THF) and diethyl ether were distilled from sodium benzophenone. Deuteriochloroform was stored over molecular sieves in air or distilled from P_2O_5 under nitrogen. Neutral Al_2O_3 (Brockmann, activity I) used for chromatography was deoxygenated at room temperature under high vacuum for 9 h, deactivated with 5% (w/w) N_2-saturated water, and stored under N_2.

The ^1H, 2-D COSY ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Nicolet-NT 300-MHz spectrometer (except as stated otherwise) with TMS (δ = 0.00 ppm) and $CDCl_3$ (δ = 77.0 ppm), respectively, as the internal references. Elemental microanalyses were performed by Galbraith Laboratories Inc., Knoxville, TN.

The preparations of $(C_5Me_5)Ir(1,5\text{-COD})$[11] (**5**) and (indenyl)Ir(1,5-COD)[12] (**6**) have been described previously. Even though the synthesis of $(C_5H_5)Ir(1,5\text{-COD})$ (**1**) has been described elsewhere[13] the route given below resulted in higher yields. The preparation is given in detail and serves as an example of the procedure for the synthesis of related new Cp′Ir(1,5-COD) compounds, $(HBPz^*_3)Ir(1,5\text{-COD})$ (**7**) (Pz* = 3,5-dimethyl-1-pyrazolyl) and $(Me_3SiC_5H_4)Ir(1,5\text{-COD})$ (**8**).

Preparation of $(C_5H_5)Ir(1,5\text{-COD})$ (1). Freshly cracked cyclopentadiene[14] (0.22 mL, 2.7 mmol) was added to a suspension of freshly cut potassium metal (~0.1 g, 2.6 mmol) in 30 mL of THF. The mixture was heated to reflux until all of the potassium reacted (~1 h). After the mixture was cooled to room temperature $[ClIr(1,5\text{-COD})]_2$[15] (0.53 g, 0.79 mmol) was added, and the solution was heated to reflux for 1 h. The THF was then evaporated under vacuum, and the residue was extracted with 2 × 10 mL of hexanes. The hexanes solution was then passed through a 15 × 1.5 cm column of neutral alumina by eluting with hexanes. The colorless eluent was evaporated and the residue was dissolved in 10 mL of petroleum ether. After the solution was cooled to −40 °C (dry ice/acetonitrile) for 2 h, the resulting white precipitate was filtered and washed twice with 2 mL of petroleum ether (at −40 °C) and dried under vacuum for 10 min. The filtrate was evaporated further and

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cooled to −40 °C to give a second crop of the product **1**; yield 0.38 g, 66%. The compound was further purified by recrystallization from petroleum ether at −40 °C or sublimation at 60–80 °C (10^{-2} mmHg). ^{1}H NMR:[13b] δ 3.78 (br s, 4 H, =CH, COD), 2.03 (m, 4 H, *exo*-CH_2, COD), 1.78 (pseudo-q, 4 H, *endo*-CH_2, COD), 5.18 (s, 5 H, Cp). ^{13}C{H} NMR: δ 45.51 (=CH, COD), 33.85 (CH_2, COD), 81.56 (Cp).

Preparations of 2–4, 7, and 8. These previously unreported compounds were prepared by the stated modifications of the above procedure. Compounds **2–4** and **8** are white, but **7** is orange. They are all air-stable as solids and in solution.

(C_5MeH_4)Ir(1,5-COD) (2). Methylcyclopentadiene was obtained by cracking the dimer.[16] Sublimation of **2** was performed at 30 °C (10^{-2} mmHg); yield 84%. Anal. Calcd for $C_{14}H_{19}Ir$: C, 44.31; H, 5.05. Found: C, 44.04; H, 5.09. ^{1}H NMR:[17] δ 3.56 (br s, 4 H, =CH, COD), 2.05 (m, 4 H, *exo*-CH_2, COD), 1.80 (pseudo-q, 4 H, *endo*-CH_2, COD), 5.18 (m, 2 H, H2, H5, Cp), 4.97 (t, $^2J = {}^3J$ = 1.9 Hz, 2 H, H3, H4, Cp), 1.90 (s, 3 H, MeCp).

(1,2,3-$C_5Me_3H_2$)Ir(1,5-COD) (3). The synthesis of 1,2,3-trimethylcyclopentadiene (**9**) involved a modification of a previously reported procedure.[18a] The products of the reactions were determined by GC, IR, and ^{1}H NMR spectroscopy and their spectra can be found in the references cited. Oxidative coupling of methyl ethyl ketone to form 3,4-dimethylhexane-2,5-dione (**10**) was performed as previously described.[18b] The formation of 2,3,4-trimethylcyclopent-2-enone (**11**)[18a] by intramolecular aldol condensation of **10** was performed with use of the same conditions employed in the preparation of 3-methylcyclopent-2-enone.[18c] Finally, reduction of **11** with $LiAlH_4$ in Et_2O by the procedure described for the reduction of cyclopent-2-enone[18d] (excess $LiAlH_4$ was quenched by careful, dropwise addition of saturated, aqueous Na_2SO_4) followed by treatment with I_2 (see, for example, ref 18e) gave **9**. It was isolated by vacuum transfer at room temperature, 10^{-2} mmHg, with a liquid-N_2-cooled receiver in 9% overall yield. The organometallic product **3** was sublimed at 60–80 °C (10^{-2} mmHg); yield 60%. Anal. Calcd for $C_{16}H_{23}Ir$: C, 47.15; H, 5.68. Found: C, 47.19; H, 5.80. ^{1}H NMR: δ 3.16 (br s, 4 H, =CH, COD), 2.03 (m, 4 H, *exo*-CH_2, COD), 1.80 (pseudo-q, 4 H, *endo*-CH_2, COD), 4.87 (s, 2 H, H4, H5, Cp), 1.91 (s, 3 H, 2-MeCp), 1.84 (s, 6 H, 1,3-Me_2Cp). ^{13}C{H} NMR: δ 50.44 (=CH, COD), 34.07 (CH_2, COD), 96.76 (C2, Cp ring), 9.18 (2-MeCp), 95.14 (C1, C3, Cp ring), 10.84 (1,3-Me_2Cp), 78.18 (C4, C5, Cp ring).

(C_5Me_4H)Ir(1,5-COD) (4). The tetramethylcyclopentadiene was prepared from 2,3,4,5-tetramethylcyclopent-2-enone (Aldrich), as previously described.[19] It was metalated with 1 equiv of *n*-BuLi in THF. Sublimation of **4** at 60–80 °C (10^{-2} mmHg) gave a 45% yield. Anal. Calcd for $C_{17}H_{25}Ir$: C, 48.43; H, 5.98. Found: C, 48.20; H, 5.99. ^{1}H NMR: δ 2.90 (br s, 4 H, =CH, COD), 2.10 (m, 4 H, *exo*-CH_2, COD), 1.81 (pseudo-q, 4 H, *endo*-CH_2, COD), 5.06 (s, 1 H, Cp), 1.88 (s, 6 H, Me_2Cp), 1.73 (s, 6 H, Me_2Cp).

(C_5Me_5)Ir(1,5-COD) (5). ^{1}H NMR:[11] δ 2.73 (m, 4 H, =CH, COD), 2.04 (m, 4 H, *exo*-CH_2, COD), 1.76 (pseudo-q, 4 H, *endo*-CH_2, COD), 1.83 (s, 15 H, Me_5Cp). ^{13}C{H} NMR: δ 53.09 (=CH, COD), 34.16 (CH_2, COD), 92.10 (Cp ring), 9.20 (Me_5Cp).

(HBPz*$_3$)Ir(1,5-COD) (7). Potassium hydrotris(3,5-dimethyl-1-pyrazolyl)borate, K(HBPz*$_3$), was purchased from Columbia Organic Chemical. Compound **7** was obtained by chromatography on neutral alumina (15 × 1.5 cm) as an orange band eluting with Et_2O/hexanes (1:5). It was recrystallized from CH_2Cl_2/hexanes (1:10) at −40 °C; yield 60%. ^{1}H NMR:[20] δ 3.83 (br s, 4 H, =CH, COD), 1.95 (m, 4 H, *exo*-CH_2, COD), 1.35 (pseudo-q, 4 H, *endo*-CH_2, COD), 5.82 (s, 3 H, Pz*H), 2.35 (s, 9 H, 3-MePz*), 2.14 (s, 9 H, 5-MePz*).

($Me_3SiC_5H_4$)Ir(1,5-COD) (8). (Trimethylsilyl)cyclopentadiene was prepared following a literature procedure[21] and was metalated with *n*-BuLi in THF.[22] Yield of **8**: 58%. ^{1}H NMR: δ 3.74 (br s, 4 H, =CH, COD), 2.01 (m, 4 H, *exo*-CH_2, COD), 1.76 (pseudo-q, 4 H, *endo*-CH_2, COD), 5.43 (t, $^2J = {}^3J$ = 1.8 Hz, 2 H, Cp), 4.74 (t, $^2J = {}^3J$ = 1.8 Hz, 2 H, Cp), 0.50 (s, 9 H, Me_3Si).

Protonation Reactions. Compounds **1–5** were protonated by dissolving approximately 50 mg of each compound in Et_2O (0 °C) and adding 1 equiv of CF_3SO_3H; a white precipitate formed immediately. Filtering the white precipitate and washing once with Et_2O (2 mL) and once with petroleum ether (2 mL) gave **1H$^+$–5H$^+$** as the $CF_3SO_3^-$ salts. Only complex **1H$^+$**PF_6^- was reported previously.[23] The white powders can be handled in the air for short periods except for **4H$^+$**$CF_3SO_3^-$ which decomposes readily. Samples were stored under nitrogen or preferably under vacuum. Solutions of the salts in undried, non-deaerated solvents discolored after ~1 h; therefore, all solvents used with the protonated complexes were deaerated and dried. The compounds were characterized by NMR spectroscopy (refer to text for explanation of assignments for **1H$^+$–5H$^+$**). A 3–5 s pulse delay was used while obtaining proton spectra in order to ensure complete relaxation of all protons and accurate integrations. An elemental analysis was performed on **1H$^+$**$CF_3SO_3^-$. The data for each of these complexes are as follows:

[(C_5H_5)Ir(H)(1,5-COD)](CF_3SO_3) (1H$^+$$CF_3SO_3^-$). Yield: 78%. Anal. Calcd for $C_{14}H_{18}F_3IrO_3S$: C, 32.59; H, 3.52. Found: C, 32.63; H, 3.42. ^{1}H NMR: δ 5.43 (m, 2 H, H_B, COD), 4.52 (m, 2 H, H_A, COD), 2.5 (m, 4 H, H_Y, H_X, COD), 2.39 (m, 2 H, $H_{X'}$, COD), 2.27 (pseudo-q, 2 H, $H_{Y'}$, COD), 6.02 (s, 5 H, Cp), −11.79 (s, 1 H, Ir-H). ^{13}C{H} NMR: δ 71.27 (=CH, COD), 69.17 (=CH, COD), 32.85 (CH_2, COD), 31.61 (CH_2, COD), 88.35 (Cp).

[(C_5MeH_4)Ir(H)(1,5-COD)](CF_3SO_3) (2H$^+$$CF_3SO_3^-$). Yield: 86%. ^{1}H NMR:[17] δ 5.01 (m, 2 H, H_B, COD), 4.43 (m, 2 H, H_A, COD), 2.50 (m, 6 H, H_Y, H_X, $H_{X'}$, COD), 2.26 (pseudo-q, 2 H, $H_{Y'}$, COD), 5.81 (s, 2 H, H2, H5, Cp), 5.73 (s, 2 H, H3, H4, Cp), 2.21 (s, 3 H, MeCp), −11.89 (s, 1 H, Ir-H). ^{13}C NMR (proton coupled):[24] δ 73.32 (d, J_{CH} = 159 Hz, =CH, COD), 69.66 (d, J_{CH} = 166 Hz, =CH, COD), 32.60 (t, J_{CH} = 132 Hz, CH_2, COD), 31.80 (t, J_{CH} = 134 Hz, CH_2, COD), 109.46 (s, C1, Cp ring), 12.47 (q, J_{CH} = 129 Hz, MeCp), 87.71 (dm, $^1J_{CH}$ = 186 Hz, C2, C5, Cp ring), 86.44 (dd, $^1J_{CH}$ = 186 Hz, $^2J_{CH}$ = 6.5 Hz, C3, C4, Cp ring).

[(1,2,3-$C_5Me_3H_2$)Ir(H)(1,5-COD)](CF_3SO_3) (3H$^+$$CF_3SO_3^-$). Yield: 58%. ^{1}H NMR: δ 4.47 (m, 2 H, H_B, COD), 4.32 (m, 2 H, H_A, COD), 2.55 (m, 2 H, H_Y, COD), 2.41 (m, 4 H, $H_{Y'}$, H_X, COD), 2.21 (pseudo-q, 2 H, $H_{X'}$, COD), 5.76 (s, 2 H, H4, H5, Cp), 2.17 (s, 6 H, 1,3-Me_2Cp), 2.07 (s, 3 H, 2-MeCp), −12.04 (s, 1 H, Ir-H).

[(C_5Me_4H)Ir(H)(1,5-COD)](CF_3SO_3) (4H$^+$$CF_3SO_3^-$). Yield: 86%. ^{1}H NMR: δ 4.27 (m, 2 H, H_B, COD), 4.16 (m, 2 H, H_A, COD), 2.55 (m, 2 H, H_Y, COD), 2.41 (m, 4 H, $H_{Y'}$, H_X, COD), 2.20 (pseudo-q, 2 H, $H_{X'}$, COD), 5.88 (s, 1 H, Cp), 2.11 (s, 6 H, Me_2Cp), 2.07 (s, 6 H, Me_2Cp), −12.02 (s, 1 H, Ir-H).

[(C_5Me_5)Ir(H)(1,5-COD)](CF_3SO_3) (5H$^+$$CF_3SO_3^-$). Yield: 66%. ^{1}H NMR: δ 4.04 (br m, 4 H, H_B, H_A, COD), 2.54 (m, 2 H, H_Y, COD), 2.36 (m, 4 H, $H_{Y'}$, H_X, COD), 2.17 (pseudo-q, 2 H, $H_{X'}$, COD), 2.02 (s, 15 H, Me_5Cp), −12.09 (s, 1 H, Ir-H). ^{13}C{H} NMR: δ 78.34 (=CH, COD), 71.28 (=CH, COD), 32.14 (CH_2, COD), 31.49 (CH_2, COD), 100.87 (Cp ring), 9.48 (Me_5Cp).

The following protonation reactions proceeded differently than those for compounds **1–5**.

Reaction of 6 with CF_3SO_3H. An excess of triflic acid (~2 equiv) was added to a solution of **6** (4.7 mg) in 0.5 mL of $CDCl_3$ or CD_2Cl_2 yielding a bright red solution. The ^{1}H NMR spectrum revealed a transient Ir–H resonance (−13.3 ppm in $CDCl_3$) which disappeared after 15 min. The final product, [(η^6-indene)Ir(1,5-COD)](CF_3SO_3), was characterized spectroscopically; however, no attempt was made to isolate it. Assignments of the η^6-indene resonances are based on those made for [(η^6-indene)Rh(C_2H_4)$_2$]BF_4[25a] (see eq 5 for numbering scheme). ^{1}H NMR (CD_2Cl_2): η^6-indene; δ 6.73 (d, J_{1-2} = 5.2 Hz, 1 H, H1), 7.03 (br s, 1 H, H2), 3.21 (d, $J_{3-3'}$ = 24.3 Hz, 1 H, H3), 2.64 (d, 1 H, H3′), 7.32 (d, J_{4-5} = 6 Hz, 1 H, H4), 6.24 (t, $J_{5-4} = J_{5-6}$ = 6 Hz, 1 H, H5), 6.50 (t, $J_{5-6} = J_{6-7}$ = 6 Hz, 1 H, H6), 7.23 (d, 1 H, H7), 4.18 (m, 2 H, =CH, COD), 3.95 (m, 2 H, =CH, COD), 2.21–1.99 (br m, 8 H, CH_2, COD).

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Reaction of 7 with CF_3SO_3H. The protonation was performed in $CDCl_3$ but no hydride resonance was detected; however, a resonance at 12.92 ppm was attributed to protonation of a pyrazolyl nitrogen to give $\{[(\eta^2\text{-HBPz*}_2)(\text{Pz*H})]\text{Ir}(1,5\text{-COD})\}(CF_3SO_3)$. ^{1}H NMR:[20a] δ 12.92 (s, 1 H, Pz*H), 6.19 (s, 1 H, Pz*, H4), 5.96 (s, 2 H, η^2-Pz*, H4), 2.54 (s, 3 H, 3-Pz*Me), 2.47 (s, 3 H, 5-Pz*Me), 2.41 (s, 6 H, η^2-3-Pz*Me), 2.36 (s, 6 H, η^2-5-Pz*Me), 4.31 (m, 2 H, =CH, COD), 3.62 (m, 2 H, =CH, COD), 2.2–1.9 (br m, 8 H, CH_2, COD).

Reaction of 8 with CF_3SO_3H. The protonation was done in Et_2O as described for compounds **1–5**. The product was identified by ^{1}H NMR as $\mathbf{1H^+}CF_3SO_3^-$ (40% yield) by comparison with an authentic sample.

Calorimetry Studies. The determinations of the heats of protonation of the Cp'Ir(1,5-COD) compounds were performed with use of a Tronac Model 458 isoperibol calorimeter as previously described.[2] The only modifications of the procedure were that triflic acid was purchased from 3M Co. and both triflic acid and 1,2-dichloroethane (DCE) were distilled under argon instead of nitrogen. The preparation and standardization of the acid solution were also performed under an argon atmosphere.

Typically a run consisted of three sections:[26] initial heat capacity calibration, titration (at 25.0 °C), and final heat capacity calibration. Each section was preceded by a baseline acquisition period. The titration period involved the addition of 1.2 mL of a standardized 0.1 M CF_3SO_3H solution in DCE at a constant rate over 3 min to 50 mL of a 2.6 mM solution of Cp'Ir(1,5-COD) (~10% excess) in DCE. The Cp'Ir(1,5-COD) solutions were prepared by adding solid compound to an argon-filled Dewar flask. The flask was then attached to the calorimeter's insert assembly and flushed with argon, and 50 mL of DCE was added by syringe. The reaction enthalpies were corrected for the heat of dilution (ΔH_{dil}) of the acid in DCE (–0.2 kcal mol^{-1}), see below. Readers interested in further experimental details and data analysis should refer to our previous publication.[2]

The value for ΔH_{dil} has been redetermined. The previous measurement of this quantity[2] was complicated by traces of H_2O in the reaction vessel. This was remedied by turning the buret on for 1 min prior to data collection, in effect, neutralizing the adventitious H_2O base. The time of the titration period was reduced to 2 min instead of 3 min. Three determinations with two different acid solutions (0.1059 and 0.1047 M) were done giving an average ΔH_{dil} value of –0.24 ± 0.02 kcal mol^{-1} which compares with –0.32 kcal mol^{-1} reported earlier. Note that this value is very close to the experimental error in the titrations.

To ensure reproducibility of the determined ΔH_{HM} values, at least two different standardized acid solutions were used for titrations of each compound. The ΔH_{HM} values are reported as the average of at least four titrations, and as many as eight, for each compound. The error is reported as the average deviation from the mean of all the determinations.

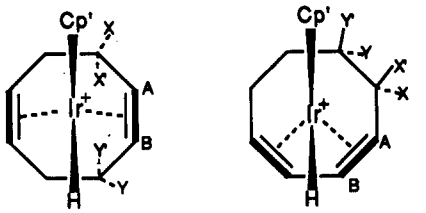
The accuracy of the calorimeter was monitored periodically by titration of 1,3-diphenylguanidine (GFS Chemicals) with CF_3SO_3H in DCE (–36.9 ± 0.2 kcal mol^{-1}, 24 measurements; literature value,[2] –37.2 ± 0.4 kcal mol^{-1}) or tris(hydroxymethyl)aminomethane (THAM, Fisher Scientific) with HCl in water (–11.6 ± 0.1 kcal mol^{-1}; literature value,[26] –11.33 kcal mol^{-1}).

Equilibrium Studies. In a typical experiment, 21.4 mg (0.0384 mmol) of $\mathbf{3H^+}CF_3SO_3^-$, 11.3 mg (0.0268 mmol) of **4** (eq 3b), and 10.4 mg (0.0426 mmol) of the internal standard Ph_3CH were added to an NMR tube. Deuteriochloroform (~0.6 mL) was condensed into the tube with use of a liquid N_2 trap, and the tube was flame sealed under vacuum. The ^{1}H NMR spectrum was taken at 298 K with a Bruker WM 200 NMR spectrometer with the methyl proton of Ph_3CH (5.55 ppm) as the internal reference. We observed that no changes in the spectrum occurred with time indicating that equilibrium was readily achieved, at least within 5 min. A 10 s pulse delay was used to ensure complete relaxation of all the protons and 128 scans were taken.

The expression (eq 4) used for the calculation of the equilibrium constant, K_{eq}, is based on the reactions given in eq 3. The relative concentrations of the species present at equilibrium were calculated on

$$K_{eq} = \frac{[\text{Cp'Ir(COD)}][\text{Cp''Ir(H)(COD)}^+]}{[\text{Cp'Ir(H)(COD)}^+][\text{Cp''Ir(COD)}]} \quad (4)$$

the basis of integrations of the COD olefin, Ir–H, and the Cp' ring proton NMR resonances of each particular species. Proton transfer is sufficiently slow that ^{1}H NMR signals for all four complexes are present in the spectrum. Only those resonances that were well separated from other resonances were integrated. When more than one resonance attributable to a single species was integrated, the calculated concentrations were averaged. For each experiment the mass balance was checked against the internal reference. We estimate that there is a possible 10% error in the equilibrium constants.



1A 1B

Figure 1. (A) 1,5-COD coordination to $Cp'IrH^+$ or (B) 1,3-COD coordination. Protons X and Y are exo; protons X' and Y' are endo.

The equilibrium for eq 3b ($\mathbf{3H^+}CF_3SO_3^-$, 20.9 mg, 0.0375 mmol; **4**, 11.7 mg, 0.0278 mmol) was also performed in d_4-DCE (MSD Isotopes) but because of changes in the chemical shifts of the species present Ph_3CH was an ineffective standard. Therefore, the relative concentrations of the species present could be calculated but the mass balance could not be checked. For the equilibrium in eq 3a ($\mathbf{1H^+}CF_3SO_3^-$, 25.1 mg, 0.0487 mmol; **2**, 13.8 mg, 0.0364 mmol) the standard used was ferrocene (4.14 ppm, 2.3 mg, 0.012 mmol). For eq 3c the equilibrium experiment was performed by mixing known quantities of $\mathbf{5H^+}CF_3SO_3^-$ (29.1 mg, 0.0497 mmol) and **4** (15.6 mg, 0.0370 mmol) with the Ph_3CH (11.7 mg, 0.0479 mmol) standard.

Results

Characterization of Reactants and Products in Equation 2. Several preparations of **1** have been reported[13] previously including the synthesis from NaC_5H_5 and $[\text{ClIr}(1,5\text{-COD})]_2$.[13a] No experimental details, however, for the latter preparation are given. We describe the synthesis of **1** from KC_5H_5 and $[\text{ClIr}(1,5\text{-COD})]_2$ in 66% yield which is higher than yields (<50%) previously reported.[13b,c] Analogous Cp'Ir(1,5-COD) complexes, **2–4**, **7**, and **8**, are also prepared in 45–84% yields by reaction of $[\text{ClIr}(1,5\text{-COD})]_2$ with the respective cyclopentadienide salt in refluxing THF. The use of potassium metal or *n*-BuLi as the metalating agent (see Experimental Section) circumvents the inconvenience of preparing finely dispersed sodium metal.[27] (Note, potassium melts in refluxing THF; therefore, a clean reaction surface is constantly obtained.) The products are characterized by their ^{1}H NMR and in some cases ^{13}C NMR spectra (see Experimental Section). The assignments of the 1,5-COD ligand resonances are based on assignments made for $[\text{Rh}(1,5\text{-COD})(CH_2(\text{Pz})_2)]ClO_4$ (Pz = pyrazolyl).[28a] In particular, it is shown for the methylene backbone of the ligand that the downfield multiplet corresponds to the exo methylene protons (shown as X and Y, Figure 1A for the related $[\text{Cp'Ir(H)}(1,5\text{-COD})]^+$ derivative) and the upfield pseudo-quartet corresponds to the endo methylene protons (X' and Y' in Figure 1A).

The reaction of **1–5** with CF_3SO_3H in diethyl ether results in precipitation of the white protonated products $\mathbf{1H^+}CF_3SO_3^-$–$\mathbf{5H^+}CF_3SO_3^-$. Resonances are observed in the ^{1}H NMR spectra between –11.79 ppm for $\mathbf{1H^+}$ and –12.09 ppm for $\mathbf{5H^+}$, typical of a metal hydride.[29] The protonated species are isolated in 58–86% yields; however, when the protonation reactions are carried out in $CDCl_3$ solution (~0.5 mL) by addition of 1 equiv of CF_3SO_3H to the neutral complexes, quantitative formation of $\mathbf{1H^+}$–$\mathbf{5H^+}$ is observed by ^{1}H NMR. When the $CDCl_3$ solutions are air-free no changes in the ^{1}H NMR spectra of the protonated species are observed over a period of at least 24 h. Quantitative deprotonation of $\mathbf{1H^+}$–$\mathbf{5H^+}$ to form neutral compounds **1–5**, respectively, is observed by ^{1}H NMR when 1 equiv of 1,3-diphenylguanidine base is added to the above $CDCl_3$ solutions.

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It was important to establish that these complexes undergo protonation at the metal center forming Ir–H bonds with no subsequent proton transfer to the 1,5-COD ligand, formation of agostic C–H interactions, or isomerization of the 1,5-COD diene ligand. The structures of the protonated products **1H⁺–5H⁺** were investigated by various NMR methods. The Ir–H resonance integrates as 1H for each species. Previously,[23] the protonated product **1H⁺** was formulated with an isomerized 1,3-COD diene ligand. Our ^{1}H NMR data for **1H⁺**$CF_3SO_3^-$ are nearly identical with those previously reported; however, further consideration of the ^{1}H, ^{13}C NMR and a 2-D COSY ^{1}H NMR experiment indicates that the formulation is more likely $[(C_5H_5)Ir(H)(1,5\text{-COD})]CF_3SO_3$, without an isomerized diene. Attempts to grow crystals of **1H⁺**$CF_3SO_3^-$ suitable for X-ray diffraction studies were unsuccessful.

Distinction between the two types of COD coordination is not trivial because both coordinated ligands have a σ_v plane of symmetry (Figure 1). Each type should exhibit six signals corresponding to H_A, H_B, H_X, $H_{X'}$, H_Y, and $H_{Y'}$ in the ^{1}H NMR spectrum and four signals for C_A, C_B, C_X, and C_Y in the ^{13}C NMR spectrum. The previous authors[23] made the 1,3-COD structural assignment on the basis of double irradiation experiments which in our hands led to ambiguous results. The authors also claimed that "the isomerization of the octadiene ligand must occur without incorporation of D⁺" when protonation was done with CF_3COOD.[30] We find this hard to believe because if such an isomerization were to occur, it is likely that it would involve migration of D⁺ to an olefinic carbon;[31] consequently, incorporation of deuterium should occur (for example, the protonation of $(C_5H_5)Rh(1,5\text{-COD})$ gives $[(C_5H_5)Rh(1,3,4\text{-}\eta^3\text{-}C_8H_{13})]PF_6$[23]). Furthermore, protonation of Cp'Ir(1,3-diene)[32] (Cp' = C_5H_5, C_5Me_5; 1,3-diene = butadiene, 2,3-dimethylbutadiene, 1,3-cyclohexadiene) at room temperature gives products with fluxional NMR spectra consistent with the formation of η^3-allyl intermediates which are stabilized by an agostic C–H bond. Only upon cooling are the classical hydride structures seen in the NMR spectra.[32a] In view of this reactivity it is unlikely that a species such as $[C_5H_5Ir(H)(1,3\text{-COD})]^+$ would have a stable Ir–H bond at room temperature.

An examination of the differences in chemical shifts between ^{1}H and ^{13}C NMR resonances at positions A and B (see Figure 1), given as $|\Delta^1H_{AB}|$ and $|\Delta^{13}C_{AB}|$, usually shows greater Δ values for 1,3-COD complexes than for asymmetric 1,5-COD complexes. Four 1,3-COD complexes found in the literature[33] give $|\Delta^1H_{AB}|$ values from 1.43 to 2.02, and three of these complexes give $|\Delta^{13}C_{AB}|$ values which range from 28.6 to 35.5. Takats[34] has also noted a significant difference between the ^{13}C chemical shifts of outer carbons (Figure 1B, C_A) and inner carbons (Figure 1B, C_B) of conjugated diene complexes of iron. Consideration of a total of 33 asymmetric 1,5-COD complexes[28b,c,35] gives $|\Delta^1H_{AB}|$ values in the range 0.2–1.7 (average = 0.77) and $|\Delta^{13}C_{AB}|$ values in the range 0.6–28.2 (average = 4.5). The $|\Delta^1H_{AB}|$ and $|\Delta^{13}C_{AB}|$ values for **1H⁺** are 0.91 and 2.1, respectively. In fact, for compounds **2H⁺–5H⁺** the $|\Delta^1H_{AB}|$ values are found between 0.58 and ~0. The $|\Delta^{13}C_{AB}|$ values for **2H⁺** and **5H⁺** are 3.66 and 7.06, respectively. Furthermore, $(C_5H_5)Ru(H)(1,5\text{-COD})$,[35e] which is isoelectronic with **1H⁺** and is known to have 1,5-COD coordination, has a $|\Delta^1H_{AB}|$ value of 0.6 and a $|\Delta^{13}C_{AB}|$ value of 1.4. The crystal structure of $(C_5Me_5)Ru(H)(1,5\text{-COD})$ has been reported recently;[35g] the $|\Delta^1H_{AB}|$ and $|\Delta^{13}C_{AB}|$ values are 0.3 and 8, respectively. The Δ values for the ruthenium complexes are within the range for 1,5-COD complexes. Our results also suggest that **1H⁺** as well as **2H⁺–5H⁺** are 1,5-COD complexes because the Δ values clearly fall within the asymmetric 1,5-COD complex ranges but not in the higher ranges for 1,3-COD complexes.

Also the 2-D COSY ^{1}H NMR spectrum[36] of **1H⁺** shows ^{1}H–^{1}H coupling more indicative of a 1,5-COD structure. One cross peak connects the 5.43-ppm (H_B) resonance to the left side of the broad multiplet at 2.5 ppm, and another cross peak connects the 4.52-ppm (H_A) resonance to the right side of the 2.5-ppm multiplet. This indicates that the multiplet at 2.5 ppm consists of two different types of protons coincidently overlapped. There is also a weak cross peak connecting 5.43 and 2.27 ppm. The pattern is typical for coordinated 1,5-COD;[28a] in particular, it has been shown[28a] that the olefin protons in 1,5-COD ligands couple strongly to the cis, exo methylene protons (assigned as H_Y to the left side and H_X to the right side of the resonance at 2.5 ppm) and weakly, if at all, to the trans, endo methylene protons (assigned as $H_{Y'}$ and $H_{X'}$ to 2.27 and 2.39 ppm, respectively). We note that 2.27 and 2.39 ppm share cross peaks with 2.5 ppm but they do not share a cross peak between themselves. This supports their assignment as $H_{Y'}$ and $H_{X'}$ because they are separated by five bonds. We find these assignments for the 1,5-COD coordination more consistent than any probable assignments for the 1,3-COD coordination type. The CH_2 COD resonances of **2H⁺** have been assigned analogously because of their similarity to **1H⁺**.

The ^{1}H NMR resonances of the CH_2 COD protons of **5H⁺** are slightly different than those in **1H⁺**; therefore, a similar 2-D COSY experiment was performed with **5H⁺**. The broad multiplet at 4.04 ppm is assigned to olefin protons H_B (left side) and H_A (right side), see Figure 1A. The resonance at 2.54 ppm is connected to the left side of 4.04 (H_B) by a cross peak and thus assigned to H_Y. The multiplet at 2.36 ppm which integrates as 4 H shares a cross peak between its right side and the right side of 4.04 ppm (H_A) and thus 2 H's of the 4 H's are assigned to H_X. A cross peak between 2.54 and 2.36 ppm permits $H_{Y'}$ to be assigned to the remaining 2H's of 2.36 ppm. And the 2.17-ppm resonance is assigned to $H_{X'}$ because there is a cross peak connecting that resonance with 2.36 ppm. However, there is no cross peak between the 2.17- and 2.54-ppm signals. Again, we find these assignments for 1,5-COD coordination more consistent than any probable assignments for 1,3-COD coordination. Furthermore, because of the similarity between the CH_2 COD proton resonances of **5H⁺** to those of **3H⁺** and **4H⁺** analogous assignments have been made.

We note that we cannot unequivocally assign the resonances of the olefin protons H_A (and therefore, H_X, $H_{X'}$) or H_B (and therefore, H_Y, $H_{Y'}$) to those up toward the cyclopentadienyl ring

(30) We repeated the deuteration experiment discussed in ref 23 by reacting **1** with 1 equiv of CF_3SO_3D in CH_2Cl_2 solution at room temperature. The reaction was monitored by ^{2}H NMR spectroscopy (Bruker WM 300 MHz spectrometer, CD_2Cl_2 internal standard, δ 5.32 ppm); we observed initial deuteration at the iridium center (δ −11.6 ppm, Ir–D) followed by slow incorporation of deuterium into the 1,5-COD ligand (δ 2.5 ppm, *exo*-CH_2 COD). These changes correspond to those reported in ref 23; however, because we assign a 1,5-COD geometry to **1H⁺**$CF_3SO_3^-$ these data indicate that the deuterium exchange is with the *exo*-1,5-COD protons rather than the *endo*-1,3-COD protons previously reported. It was not noted in ref 23, but deuterium is also incorporated into the Cp ring (δ 6.0 ppm) after 3 days.

(31) Proton transfer from a M–H to the vinylic carbon of 1,5-COD has been shown to give η^3-cyclooctadienyl complexes. (a) Liles, D. C.; Oosthuizen, H. E.; Shaver, A.; Singleton, E.; Wiege, M. B. *Organometallics* **1986**, *5*, 591–593 and references therein. (b) Speckman, D. M.; Knobler, C. B.; Hawthorne, M. F. *Organometallics* **1985**, *4*, 426–428.

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(33) Unfortunately η^4-1,3-COD complexes are rare. (a) (η^6-toluene)Fe(1,3-COD): Ittel, S. D.; Tolman, C. A. *Organometallics* **1982**, *1*, 1432–1436. (b) $[P(OMe)_3]_3Fe(1,3\text{-COD})$: Ittel, S. D.; Van-Catledge, F. A.; Jesson, J. P. *J. Am. Chem. Soc.* **1979**, *101*, 3874–3884. (c) $(CO)_3Fe(1,3\text{-COD})$: Cable, R. A.; Green, M.; Mackenzie, R. E.; Timms, P. L.; Turney, T. W. *J. Chem. Soc., Chem. Commun.* **1976**, 270–271 and references therein. (d) $(PF_3)_3Fe(1,3\text{-COD})$: Kruck, T.; Knoll, L.; Laufenberg, J. *Chem. Ber.* **1973**, *106*, 697–706. (e) The following references report 1,3-COD complexes but do not give supporting spectral data: (i) Tayim, H. A.; Mahmoud, F. T. *J. Organomet. Chem.* **1975**, *92*, 107–115, (ii) Moraczewski, J.; Geiger, W. E., Jr. *J. Am. Chem. Soc.* **1981**, *103*, 4779–4787.

(34) Kruczynski, L.; Takats, J. *Inorg. Chem.* **1976**, *15*, 3140–3147.

(35) The range listed does not cover a comprehensive search of all asymmetric 1,5-COD complexes. (a) Derome, A. E.; Green, M. L. H.; O'Hare, D. *J. Chem. Soc., Dalton Trans.* **1986**, 343–346. (b) Albers, M. O.; Robinson, D. J.; Shaver, A.; Singleton, E. *Organometallics* **1986**, *5*, 2199–2205. (c) Ashworth, T. V.; Chalmers, A. A.; Meintjies, E.; Oosthuizen, H. E.; Singleton, E. *Organometallics* **1984**, *3*, 1485–1491. (d) Crabtree, R. H.; Quirk, J. M.; Fillebeen-Khan, T.; Morris, G. E. *J. Organomet. Chem.* **1979**, *181*, 203–212. (e) Albers, M. D.; Crosby, S. F. A.; Liles, D. C.; Robinson, D. J.; Shaver, A.; Singleton, E. *Organometallics* **1987**, *6*, 2014–2017. (f) Oshima, N.; Suzuki, H.; Moro-Oka, Y. *Chem. Lett.* **1984**, 1161–1164. (g) Kölle, U.; Kang, B.-S.; Raabe, G.; Krüger, C. *J. Organomet. Chem.* **1990**, *386*, 261–266.

(36) Derome, A. E. *Modern NMR Techniques for Chemistry Research*; Pergamon: New York, 1987; Chapter 8.

Table I. Heats of Protonation (ΔH_{HM}) of Cp'Ir(1,5-COD) Complexes[a]

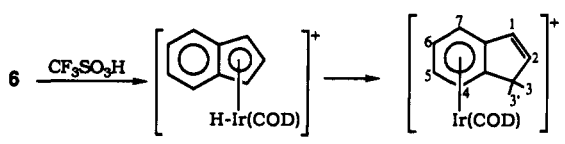
Cp'Ir(1,5-COD)	$-\Delta H_{HM}$, kcal mol^{-1}
(C_5H_5)Ir(COD) (**1**)	22.8 (±0.2)[b]
(C_5MeH_4)Ir(COD) (**2**)	24.1 (±0.1)
(1,2,3-$C_5Me_3H_2$)Ir(COD) (**3**)	26.4 (±0.2)
(C_5Me_4H)Ir(COD) (**4**)	27.5 (±0.2)
(C_5Me_5)Ir(COD) (**5**)	28.5 (±0.2)

[a] For protonation with CF_3SO_3H (0.1 M) in DCE solvent at 25.0 °C. [b] Numbers in parentheses are average deviations.

or those down and close to the hydride ligand as they are drawn in Figure 1A.

No evidence was found for the formation of an agostic type C–H interaction with the metal which may have resulted from protonation of the COD olefin.[37] Normal chemical shifts are observed for the COD olefin and methylene groups in the ^{1}H NMR spectra of **1H$^+$**–**5H$^+$** and in the ^{13}C NMR spectra of **2H$^+$** and **5H$^+$**. In addition, the proton-coupled ^{13}C NMR spectrum of **2H$^+$** was investigated as low values for J_{CH} are diagnostic of agostic CH interactions.[38] However, normal coupling constants for the COD sp^2 carbons (J_{CH} = 159 and 166 Hz) and the sp^3 carbons (J_{CH} = 132 and 134 Hz) were found.[39]

The protonation reactions of **6**–**8** proceed differently than those of compounds **1**–**5**. Protonation of (indenyl)Ir(1,5-COD) (**6**) in $CDCl_3$ gives a transient Ir–H resonance at −13.3 ppm probably due to [(η^5-indenyl)Ir(H)(1,5-COD)]CF_3SO_3 (see eq 5), but this resonance disappears within 15 min. The resulting product has ^{1}H resonances which are indicative of an η^6-indene complex[25] (see Experimental Section). A very similar reaction is reported by McGlinchey and co-workers[25a] for the protonation of (η^5-indenyl)Rh(C_2H_4)$_2$ with HBF_4·Et_2O. Our data suggest that the proton is transferred from the metal to the indenyl ligand resulting in an η^5 to η^6 haptotropic rearrangement forming [(η^6-indene)-Ir(1,5-COD)]CF_3SO_3 (eq 5).



(5)

Protonation of (HBPz*$_3$)Ir(1,5-COD) (**7**) does not give a detectable Ir–H resonance in the ^{1}H NMR spectrum; however, a resonance which integrates as 1 H is found at 12.92 ppm. This is attributed to protonation of a pyrazolyl nitrogen yielding {[(η^2-HBPz*$_2$)(Pz*H)]Ir(1,5-COD)}CF_3SO_3. Graham and co-workers[20a] have obtained a similar rhodium complex by protonation of (η^3-HBPz*$_3$)Rh(CO)$_2$ with HBF_4·Et_2O. Surprisingly, they also observed that protonation of (η^3-HBPz*$_3$)Ir(CO)$_2$ occurs at the Ir.[20a]

Reaction of ($Me_3SiC_5H_4$)Ir(1,5-COD) (**8**) with CF_3SO_3H in Et_2O gives a white precipitate, but the product is identified to be **1H$^+$**$CF_3SO_3^-$ (40% yield) by ^{1}H NMR. Apparently, the reaction occurs by protodesilylation[40] followed by protonation of iridium (or vice versa), which requires overall 2 equiv of acid per 1 equiv of **8**.

Compounds **6**–**8** were not studied calorimetrically because clean protonation at the metal center does not occur.

Calorimetric and Equilibrium Studies. Heats of protonation determined by calorimetric titration of the Cp'Ir(1,5-COD) complexes with CF_3SO_3H in 1,2-dichloroethane (DCE) at 25.0 °C according to eq 2 are presented in Table I. The titrations of the organometallic compounds went cleanly. We observed no side reactions prior to the start of the titration or after the titration was completed as evidenced by normal baseline slopes in these periods. As expected, the titrations displayed a linear increase in temperature with acid addition indicating stoichiometric reaction of the compounds with the acid. There was also an immediate temperature response upon addition of the acid indicating that the kinetics of the protonation reactions were fast. Usually the final titrated solutions of the iridium complexes were colorless; however, occasionally a slight tinge of brown or yellow was detected. The ΔH_{HM} values were the same within experimental error whether or not the product solution was slightly colored. Analysis of the resultant titrate solutions by ^{1}H NMR spectroscopy after removal of the DCE solvent revealed only the protonated species, and a trace of the unprotonated species due to the presence of a slight excess of the starting material in the reaction.

Table II. Results of Equilibrium Studies (at 25.0 °C) for the Reactions in Eq 3

reactants	K_{eq}[a]	$-\Delta G^\ominus$,[a] kcal mol^{-1}	$\Delta S^\ominus$,[b] eu
1H$^+$/2[c]	4.4	−0.88	−0.74
3H$^+$/4[c]	5.0	−0.95	−0.50
3H$^+$/4[d]	4.8	−0.93	−0.57
4H$^+$/5[c]	3.9	−0.81	−0.97
1H$^+$/5[e]	1900	−4.5	~−4

[a] Estimated error in K_{eq} is 10% and ±0.06 for $\Delta G^\ominus$. [b] Calculated with $\delta\Delta H_{HM}$ = −1.1 kcal mol^{-1} for eq 3. Estimated error is ±0.7 eu. [c] In $CDCl_3$. [d] In d_4-DCE. [e] Values for this unmeasured equilibrium were calculated from the average K_{eq} value of 4.5 per methyl group. $\Delta G^\ominus$ was calculated ($\Delta G^\ominus = -RT \ln K_{eq}$) from K_{eq}, and $\Delta S^\ominus$ was calculated ($\delta\Delta H_{HM} = \Delta G^\ominus + T\Delta S^\ominus$) with $\delta\Delta H_{HM}$ = −5.7 kcal mol^{-1}.

Because DCE has a low dielectric constant (ϵ = 10.36)[41] the products formed in eq 2 probably occur as ion pairs. Dissociation of these ion pairs and autoprotolysis and dimerization of the acid are other reactions that may occur in nonpolar solvents such as DCE. An analysis of these factors was presented in the phosphine basicity study;[2] it was concluded that they contribute less than 2% to the total ΔH_{HP} value. Presumably, these reactions also contribute negligibly to ΔH_{HM} values in the current study.

The results of the competitive equilibrium studies at 25.0 °C between two methyl-substituted Cp'Ir(1,5-COD) complexes (eq 3) are given in Table II. The equilibria between **1H$^+$** and **2** (eq 3a) and **5H$^+$** and **4** (eq 3c) were studied in $CDCl_3$, while the **3H$^+$/4** equilibrium (eq 3b) was studied in both $CDCl_3$ and d_4-DCE. An error of 10% is estimated for each K_{eq}; therefore, the K_{eq} values in all four studies, including that in d_4-DCE, are within experimental error approximately the same. Values of $\Delta G^\ominus$ were calculated ($\Delta G^\ominus = -RT \ln K_{eq}$)[42] from the K_{eq} values. Because of the similarity of the K_{eq} values for the **3H$^+$/4** equilibrium (eq 3b) in $CDCl_3$ and d_4-DCE, we combined ($\delta\Delta H_{HM} = \Delta G^\ominus + T\Delta S^\ominus$) relative ΔH_{HM} values ($\delta\Delta H_{HM}$ = −1.1 kcal mol^{-1}) in DCE and $\Delta G^\ominus$ values in $CDCl_3$ to obtain the $\Delta S^\ominus$ of each reaction. An error of ±0.06 kcal mol^{-1} in $\Delta G^\ominus$ is obtained from the corresponding estimated error in K_{eq}, and the error in $\delta\Delta H_{HM}$ is estimated to be ±0.2 kcal mol^{-1}. Although the estimated error (±0.7 eu) in $\Delta S^\ominus$ is as large as $\Delta S^\ominus$ itself, values for the four reactions (Table II) are consistently negative. Thermodynamic constants for the equilibrium between **1H$^+$**$CF_3SO_3^-$ and **5** (eq 3d) are calculated from the average K_{eq} values in Table II and ΔH_{HM} values in Table I. This allows the effect of C_5Me_5 vs C_5H_5 on the basicity of iridium to be discussed in terms of ΔH_{HM}, $\Delta G^\ominus$, and $\Delta S^\ominus$; the data are summarized in Table II.

Discussion

The data presented in Table I show an excellent correlation between the number of methyl groups on the Cp' ring (N_{Me}) and

(37) Reaction of (C_5Me_5)Ir(η^4-dicyclopentadiene) with HPF_6 gives a product where the olefin ligand is protonated but the metal is stabilized by an agostic C–H interaction. Bennett, M. A.; McMahon, I. J.; Pelling, S.; Robertson, G. B.; Wickramasinghe, W. A. *Organometallics* **1985**, *4*, 754–761.

(38) Brookhart, M.; Green, M. L. H.; Wong, L.-L. *Prog. Inorg. Chem.* **1988**, *36*, 1–124.

(39) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectroscopic Identification of Organic Compounds*, 4th ed.; John Wiley and Sons: New York, 1981; p 273.

(40) Elschenbroich, C.; Hurley, J.; Metz, B.; Massa, W.; Baum, G. *Organometallics* **1990**, *9*, 889–897.

(41) *Lange's Handbook of Chemistry*, 13th ed.; Dean, J. A., Ed.; McGraw-Hill: New York, 1985.

(42) We follow Henry's law convention for the standard state of reactions in dilute solution. See for example: Tyrrell, H. J. V.; Beezer, A. E. *Thermometric Titrimetry*; Chapman and Hall: London, 1968; Chapter 1.

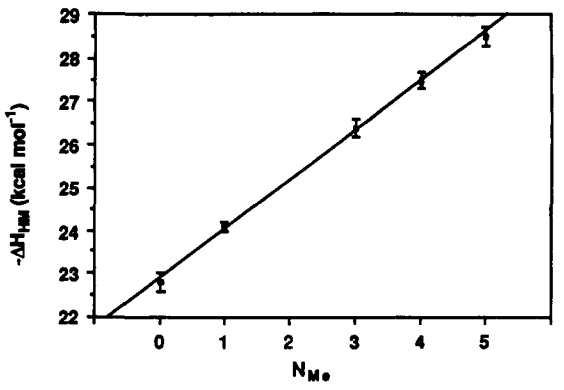


Figure 2. Plot of ΔH_{HM} (kcal mol^{-1}) for the protonation (eq 2) of Cp'Ir(1,5-COD) (Cp' = $C_5Me_xH_{5-x}$, x = 0, 1, 3–5) vs the number of methyl groups on Cp' (N_{Me}).

the basicity of the iridium metal center, as measured by ΔH_{HM}. The ΔH_{HM} values are exothermic and become more negative as the number of methyl groups in the cyclopentadienyl ring increases. A linear correlation is obtained when ΔH_{HM} is plotted against N_{Me} as shown in Figure 2. The line fits eq 6 (correlation coefficient (r) = 0.999) as determined by linear least-squares regression analysis. Each methyl effectively increases the basicity

$$-\Delta H_{HM} = 22.9 + 1.1N_{Me} \text{ (kcal mol}^{-1}\text{)} \quad (6)$$

of the metal center by −1.1 kcal mol^{-1}. The results are consistent with an increase of electron density at the metal center caused by the electron-donating effect of the methyl groups.[5c]

As protonation occurs at the Ir, the Cp' and COD ligands are forced closer to each other (see, for example, the crystal structure of $(C_5Me_5)Ru(H)(1,5\text{-}COD)$[35g]) to make room for the hydride ligand. It is conceivable that steric repulsion between the COD and a highly methylated Cp' would cause ΔH_{HM} for the reaction to be less exothermic than otherwise expected. The linearity of the plot (Figure 2), however, suggests that either there is no steric effect of the methyl groups or the steric effect of each Me group is the same. The latter possibility seems less likely because the Cp' ligand with, for example, only one Me could rotate out of the way in order to avoid steric repulsion with the COD, whereas a Me group in C_5Me_5 would definitely contribute to steric repulsion. Thus, one would expect the steric effect of added methyl groups to be most important in the more highly methylated complexes. The observation that each Me has the same effect (−1.1 kcal mol^{-1}) suggests that there is no measurable steric effect on ΔH_{HM} even in $(C_5Me_5)Ir(1,5\text{-}COD)$.

It is useful to correlate the ΔH_{HM} values with spectroscopic properties of the complexes, especially NMR data. As the basicity of the iridium increases, an increase in shielding of the 1,5-COD olefin ^{1}H NMR resonances is observed. In fact, there is a linear correlation (r = −0.999) between ΔH_{HM} and the olefin proton chemical shift (x) of the 1,5-COD ligand in complexes **1–5**, eq 7. The results can be interpreted in terms of the Dewar–

$$-\Delta H_{HM} = 43.2 - 5.4x \text{ (kcal mol}^{-1}\text{)} \quad (7)$$

Chatt–Duncanson model for π-olefin bonding to a metal.[43] Increasing N_{Me} increases the electron density on the metal center thereby enhancing M → olefin dπ–pπ* backbonding and decreasing olefin-to-metal σ bonding. There is, consequently, an increase of electron density on the olefin resulting in an upfield shift of the olefin resonance.

We observe a systematic upfield shift of the Ir–H resonance of the protonated products with increasing N_{Me}. Deviating from this trend is **3H**$^+$ whose hydride resonance is found at slightly higher field (−12.04 ppm) than that of **4H**$^+$ (−12.02 ppm). Perhaps the asymmetry in the 1,2,3-$Me_3C_5H_2$ ring and an unusual distribution of rotamers[44] contribute to the surprising Ir–H resonance of **3H**$^+$. Although Ir–H chemical shifts appear to follow the trend in ΔH_{HM} values in this series of compounds, it seems unlikely to be a general trend for a broader range of metal hydrides.[45]

In order to determine equilibrium constants (and therefore $\Delta G^\ominus$) which measure the relative basicities of the Cp'Ir(1,5-COD) complexes, we studied the reactions in eq 3. The K_{eq} studies support the calorimetry results; K_{eq} values (Table II) consistently show that protonation of the more highly methyl-substituted complex is favored. For the reactions in Table II and eq 3, K_{eq} ranges from 3.9 to 5.0; however, with an experimental error of ~10%, all four K_{eq} values are approximately the same (4.5 average). Thus each Me increases the equilibrium constant by a factor of 4.5. This average value gives an average $\Delta G^\ominus$ of −0.89 ± 0.06 kcal mol^{-1} per methyl group. There is only a relatively small difference between $\Delta G^\ominus$ (−0.89 ± 0.06 kcal mol^{-1}) and $\delta\Delta H_{HM}$ (−1.1 ± 0.2 kcal mol^{-1}), especially considering the estimated errors. It is likely, however, that there is a small decrease in $\Delta S^\ominus$ (−0.7 ± 0.7 eu average per methyl group, Table II) when a proton is transferred to a complex with more Me groups. Other thermochemical studies[46] suggest that the effect of Me on the entropy associated with substitution of C_6H_6 in $(\eta^6\text{-}C_6H_6)Mo(CO)_3$ with methyl-substituted arenes is also small. This small decrease in entropy in the present system may be interpreted as arising from more restricted rotation of the more highly methylated Cp'' ring in Cp''Ir(H)(COD)$^+$ as compared with rotation in the less methyl-substituted ring in Cp'Ir(H)(COD)$^+$ in eq 3. The effect appears to be relatively constant for each Me group.

The results of the above experiments permit one to compare the effects of C_5H_5 and C_5Me_5 on ΔH_{HM}, $\Delta G^\ominus$, and $\Delta S^\ominus$ values for the proton transfer reaction between compounds **1** and **5** (eq 3d). From Table I it is found that ΔH_{HM} of **5** is −5.7 kcal mol^{-1} more exothermic than ΔH_{HM} of **1**. The estimated value of K_{eq} for reaction 3d is 1900 (Table II) which means that $\Delta G^\ominus$ for this reaction is −4.5 kcal mol^{-1}. From these ΔH_{HM} and $\Delta G^\ominus$ values, $\Delta S^\ominus$ is estimated to be ~−4 eu. The small value of $\Delta S^\ominus$ clearly indicates that K_{eq} for reaction 3d is largely determined by the ΔH_{HM} values of **1** and **5**.

For comparison with the $\Delta G^\ominus$ difference (−4.5 kcal mol^{-1}) between $(C_5H_5)Ir(COD)$ (**1**) and $(C_5Me_5)Ir(COD)$ (**5**), one can choose other pairs of complexes containing C_5H_5 and C_5Me_5 ligands. Norton and co-workers[5e] determined K_{eq} values for the protonation of $Cp'Mo(CO)_3^-$ and $Cp'Fe(CO)_2^-$, where Cp' is C_5H_5 or C_5Me_5, in acetonitrile solution. After converting their K_{eq} values to $\Delta G^\ominus$'s, one finds that the $\Delta G^\ominus$ for protonation of the C_5Me_5 molybdenum complex is −4.4 kcal mol^{-1} more favorable than that for the corresponding C_5H_5 complex. Thus, replacing C_5H_5 by C_5Me_5 in either Cp'Ir(COD) or $Cp'Mo(CO)_3^-$ causes essentially the same increase in metal basicity ($\Delta G^\ominus$ = ~−4.5 kcal mol^{-1}). On the other hand, $\Delta G^\ominus$ for the protonation of $(C_5Me_5)Fe(CO)_2^-$ is −9.4 kcal mol^{-1} more favorable than that for $(C_5H_5)Fe(CO)_2^-$. Thus, in the iron system, the replacement of C_5H_5 by C_5Me_5 produces a much larger increase in metal basicity than in the Ir and Mo complexes. So it is evident that the substitution of C_5Me_5 for C_5H_5 does not cause the same increase in metal basicity in all metal-complex systems.

Summary

These studies of methyl-substituted Cp'Ir(1,5-COD) complexes show that protonation with CF_3SO_3H definitely occurs at the metal center to form products formulated as $[Cp'Ir(H)(1,5\text{-}COD)]\text{-}CF_3SO_3$. The basicity of the iridium center as determined by the heats of protonation (ΔH_{HM}) of the complexes in 1,2-dichloro-

(43) Lukehart, C. M. *Fundamental Transition Metal Organometallic Chemistry*; Brooks/Cole: Monterey, CA, 1985; pp 148–149.

(44) For example, a novel temperature dependence of the chemical shift of the Cp' ring protons in $(XC_5H_4)RhL_2$ complexes has been attributed "to preferential population of a particular rotamer state" at low temperature. See ref 17.

(45) (a) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed.; John Wiley & Sons: New York, 1980; p 1115. (b) Miyamoto, T. *J. Organomet. Chem.* **1977**, *134*, 335–362.

(46) Hoff, C. D. *J. Organomet. Chem.* **1985**, *282*, 201–214 and references therein.

ethane increases linearly with the number of methyl groups in Cp′ (N_{Me}) from C_5H_5 to C_5Me_5. For each methyl group ΔH_{HM} changes by −1.1 kcal mol^{-1} ($\delta\Delta H_{HM}$). The ΔH_{HM} values correlate with the chemical shift of the olefin ^{1}H NMR resonance in the 1,5-COD ligand of the neutral complexes and the Ir−H ^{1}H NMR resonance of the protonated products.

Equilibrium studies of the proton transfer reactions (eq 3) show that the successive addition of methyl groups to the Cp′ ring changes $\Delta G^\ominus$ by −0.89 ± 0.06 kcal mol^{-1} per methyl group and $\Delta S^\ominus$ by −0.7 ± 0.7 eu per methyl. Thus, the differences in basicities (K_{eq} or $\Delta G^\ominus$) of the various methyl-substituted Cp′Ir-(1,5-COD) complexes are largely determined by ΔH_{HM} values of the complexes, and $\Delta S^\ominus$ makes a relatively small contribution. Comparing the common C_5H_5 and C_5Me_5 ligands, one finds that replacing C_5H_5 in (C_5H_5)Ir(1,5-COD) by C_5Me_5 increases the equilibrium constant, K_{eq}, for the protonation of the complex by 1900; $\Delta G^\ominus$ becomes more favorable by −4.5 kcal mol^{-1}; ΔH_{HM} becomes more favorable by −5.7 kcal mol^{-1}, while $\Delta S^\ominus$ becomes slightly less favorable by ∼−4 eu.

Acknowledgment. We thank the National Science Foundation (Grant CHE-8719744) for their support of this research. The loan of $IrCl_3 \cdot xH_2O$ from Johnson Matthey is greatly appreciated. We are also grateful to Dr. Vinko Rutar and Dr. Dave Scott of the Iowa State University Chemical Instrument Services for their assistance with the NMR experiments.

Reactions of Cp*Ir(2,5-dimethylthiophene) with Iron Carbonyls: A New Mechanism for Thiophene Hydrodesulfurization

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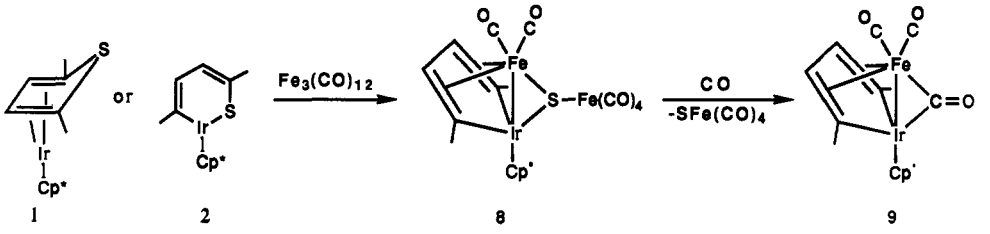
Contribution from Ames Laboratory[1] and the Department of Chemistry, Iowa State University, Ames, Iowa 50011. *Received September 4, 1990*

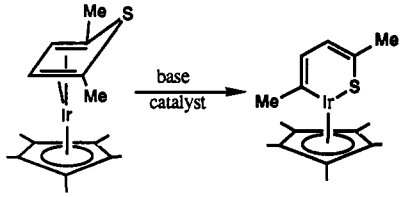
Abstract: Reactions of the isomers Cp*Ir(η^4-2,5-Me_2T) (**1**) and Cp*Ir(*C,S*-2,5-Me_2T) (**2**), where Cp* = η^5-C_5Me_5 and 2,5-Me_2T = 2,5-dimethylthiophene, with iron carbonyls ($Fe(CO)_5$, $Fe_2(CO)_9$, and $Fe_3(CO)_{12}$) give eight different products, **3**–**10**. Two of them, Cp*Ir(η^4-2,5-Me_2T·$Fe(CO)_4$) (**3**) and Cp*Ir(η^4-2,5-Me_2T·$Fe_2(CO)_7$) (**7**), retain the η^4-2,5-Me_2T coordination to the Ir but are also bonded through the sulfur to the Fe atom(s). Both **1** and **2** react with $Fe_3(CO)_{12}$ to give **8** in which all of the elements of 2,5-Me_2T are present but the sulfur has been removed from the thiophene ring. Reaction of **8** with CO (1 atm)



1 2 8 9

gives the totally desulfurized **9**. A new mechanism is proposed for thiophene hydrodesulfurization (HDS) based on the C–S bond cleavage reactions which occur when **1** rearranges to **2** and **2** is converted to **8**. Structures of **3**, **7**, **8**, and **9** were established by X-ray diffraction studies.

On the basis of organometallic model compound and catalytic reactor studies, a mechanism (Scheme I) was proposed[2,3] in these laboratories for the transition-metal-catalyzed hydrodesulfurization (HDS) of thiophene to give H_2S and C_4 hydrocarbons. The actual desulfurization step (Scheme I), which involves C–S bond cleavage, occurs after thiophene is partially hydrogenated to dihydrothiophene. Very recently[4] we observed another type of C–S bond cleavage (eq 1) in thiophene itself. In this base-catalyzed rearrangement, the iridium in Cp*Ir(η^4-2,5-Me_2T) (**1**) inserts into

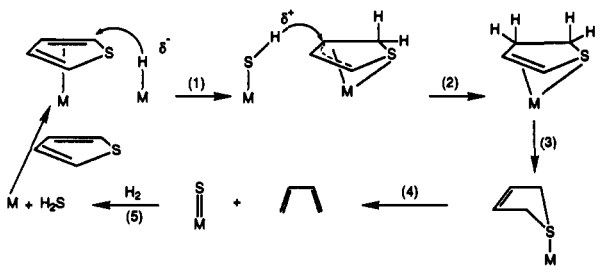


(1)

1 2

† Iowa State University Molecular Structure Laboratory.

Scheme I. Hydrogenation Mechanism for Thiophene HDS[2,3]



a C–S bond of the η^4-thiophene to give the ring-opened iridathiabenzene Cp*Ir(*C,S*-2,5-Me_2T)[5] (**2**), where Cp* is η^5-C_5Me_5 and

(1) Ames Laboratory is operated by the U.S. Department of Energy by Iowa State University under Contract W-7405-Eng-82. This research was supported by the Office of Basic Energy Sciences, Chemical Sciences Division.
(2) (a) Sauer, N. N.; Markel, E. J.; Schrader, G. L.; Angelici, R. J. *J. Catal.* **1989**, *117*, 295. (b) Markel, E. J.; Schrader, G. L.; Sauer, N. N.; Angelici, R. J. *J. Catal.* **1989**, *116*, 11.

0002-7863/91/1513-2544$02.50/0