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Synthesis, Structure, and Reactivity of the Remarkably Stable Early-Late Binuclear Metal Hydride Cp$_2$Ta(μ-CH$_2$)$_2$Ir(Cp*)(H). A Warning Concerning Catalyst Identification in Homogeneous Catalytic Reactions

Matthew D. Butts and Robert G. Bergman*

Department of Chemistry, University of California, Berkeley, California 94720

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The early-late heterobimetallic complex Cp$_2$Ta(μ-CH$_2$)$_2$Ir(Cp*)(Cl) (1) was isolated in 68% yield from the reaction of 0.5 equiv of [Cp*IrCl$_2$]$_2$ with LiN(SiMe$_3$)$_2$ and Cp$_2$Ta(CH$_2$)(CH$_3$). The complex mechanism of this reaction, investigated by low-temperature NMR and ESR spectroscopy, involves paramagnetic intermediates. Treatment of 1 with LiBH$_4$ led to the isolation of Cp$_2$Ta(μ-CH$_2$)$_2$Ir(Cp*)(H) (2), which was characterized by X-ray crystallography (monoclinic space group $P2_1/n$ ($Z = 4$) with $a = 9.034(2)$ Å, $b = 13.603(4)$ Å, $c = 15.974(2)$ Å, and $\beta = 101.287(16)°$). The deuterium analogue of 2, Cp$_2$Ta(μ-CH$_2$)$_2$Ir(Cp*)(D) (3), was prepared by treating 1 with LiAlD$_4$. Complex 2 could be converted back to the chloride 1 upon reaction with CCl$_4$. Surprisingly, the thermally stable 2 was unreactive toward phosphines and D$_2$, as well as several other reagents, but reacted slowly with an excess of CO at 135 °C to form Cp$_2$Ta(μ-CH$_2$)$_2$Ir(CO)$_2$ (5) and 1 equiv of Cp*H. Treatment of 2 with MeI at 105 °C led to the slow formation of Cp$_2$Ta(μ-CH$_2$)$_2$Ir(Cp*)(I) (6) (which exhibited temperature dependent NMR spectra in solution) together with 1 equiv of CH$_4$. Despite the marked stability of 2, we found that ethylene was readily hydrogenated in the presence of 2 and H$_2$ at room temperature. Although this at first appeared to be a well-behaved homogeneous reaction, further investigation of this reaction revealed that 2 itself cannot be the hydrogenation catalyst.

Introduction

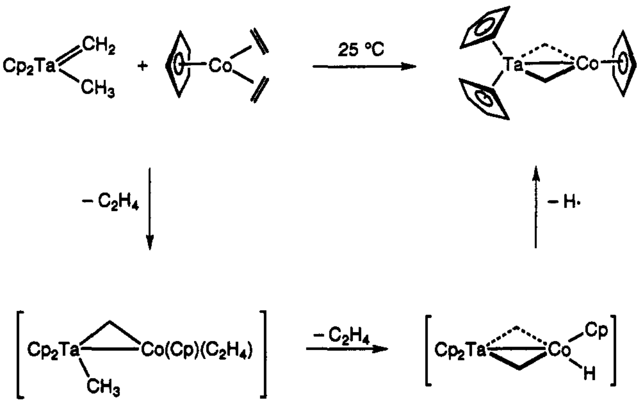
Our interest in the chemistry of early-late heterobimetallic (ELHB) complexes is due in part to the possibility of observing unique reactivity resulting from cooperative interactions between two metals with different properties.[1,2] As part of our early efforts directed toward preparing such compounds, Goldberg and Bergman reported that the reaction of Cp$_2$Ta(CH$_2$)(CH$_3$) with CpCo(C$_2$H$_4$)$_2$ at 25 °C yielded the ELHB complex Cp$_2$Ta(μ-CH$_2$)$_2$CoCp (Scheme 1).[3] The Ta-Co complex, which was characterized by X-ray crystallography, is a radical species with the unpaired electron localized on one metal center (probably cobalt). The reaction in Scheme 1 is believed to proceed through the intermediate Cp$_2$Ta(μ-CH$_2$)$_2$Co(Cp)(H), which gives the paramagnetic complex upon hydrogen abstraction or homolytic cleavage of the kinetically labile Co-H bond, although this species was not observed.

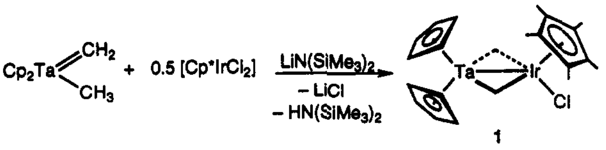
In order to test the validity of these conclusions directly, a stable analogue of the proposed cobalt hydride was sought. This paper reports the synthesis of the ELHB complex Cp$_2$Ta(μ-CH$_2$)$_2$Ir(Cp*)(Cl) (1) and its conversion upon reaction with LiBH$_4$ to the corresponding hydride Cp$_2$Ta(μ-CH$_2$)$_2$Ir(Cp*)(H) (2). The X-ray characterization and the chemistry of this remarkably stable metal hydride complex are also described.

Results

Synthesis and Characterization of Cp$_2$Ta(μ-CH$_2$)$_2$Ir(Cp*)(Cl). The reaction of 0.5 equiv of [Cp*IrCl$_2$]$_2$ with LiN(SiMe$_3$)$_2$ and Cp$_2$Ta(CH$_2$)(CH$_3$)[4] in THF at -25 °C led to the isolation of Cp$_2$Ta(μ-CH$_2$)$_2$Ir(Cp*)(Cl) (1) in 68% yield as an orange crystalline solid (eq 1). On the basis of NMR data, the Ir center of 1 appears to be coordinated in a three-legged piano-stool geometry while the Ta center is pseudotetrahedral. The ^{1}H NMR (C$_6$D$_6$) spectrum of 1 contains resonances for inequivalent Cp rings at 5.28 and 4.48 ppm. The geminal hydrogens of the methylene bridges are also inequivalent, appearing at 6.11 and 5.61 ppm; they are coupled to each other (J = 7.7 Hz). The Cp* methyl resonance is at 1.52 ppm.

Scheme 1





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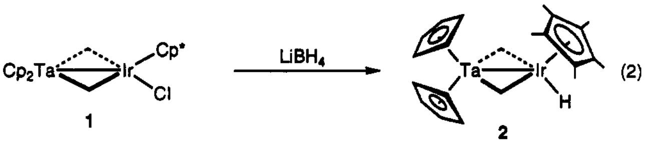
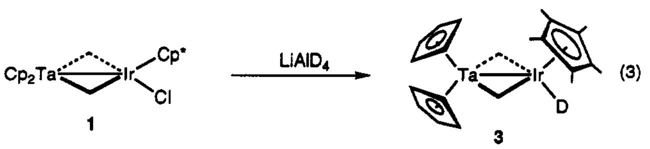
The mechanism of the reaction of 0.5 equiv of $[Cp^*IrCl_2]_2$ with $LiN(SiMe_3)_2$ and $Cp_2Ta(CH_2)(CH_3)$ to form **1** is not straightforward. The reaction between $[Cp^*IrCl_2]_2$ and 2 equiv of $LiN(SiMe_3)_2$ was monitored at low temperature by ^1H NMR spectroscopy in the absence of $Cp_2Ta(CH_2)(CH_3)$ and was found to be quite complex. An intense transient singlet at −0.2 ppm was observed at −64 °C in the ^1H NMR spectrum; this signal disappears on reaction with the tantalum complex. ESR experiments carried out on similar mixtures at low temperatures in the presence and absence of $Cp_2Ta(CH_2)(CH_3)$ revealed the presence of at least two transient paramagnetic species. Unfortunately, we have not been able to isolate or establish the identity of these intermediates.

Synthesis and Characterization of $Cp_2Ta(\mu\text{-}CH_2)_2Ir(Cp^*)(H)$. Treatment of **1** with an excess of $LiBH_4$ in THF at room temperature afforded the hydride $Cp_2Ta(\mu\text{-}CH_2)_2Ir(Cp^*)(H)$ (**2**; eq 2), isolated in 47% yield as a dark yellow crystalline solid. The ^1H and $^{13}C\{^1H\}$ NMR spectra of **2** are similar in splitting patterns to those of **1**, and therefore the same coordination geometry is assigned. In the ^1H NMR (C_6D_6) spectrum of **2** the Cp* methyl resonance and one set of chemically equivalent methylene hydrogens show coupling to the hydride ligand (J = 0.6 and 3.1 Hz, respectively), although the hydride itself appears as a broad singlet at −22.0 ppm. These couplings collapsed when the hydride frequency was irradiated in a homonuclear decoupling experiment. The C–H coupling constants for the inequivalent methylene hydrogens were found to be 133 and 140 Hz. The infrared spectrum (KBr) includes a strong peak at 2155 cm^{-1}, which is assigned to the Ir–H stretch.



In order to confirm the structure of **2**, an X-ray crystallographic study was performed by Dr. F. J. Hollander on a yellow, blocklike crystal obtained by cooling a 3:1 pentane–benzene solution of **2** to −30 °C. ORTEP diagrams are shown in Figure 1. Crystal and data collection parameters, selected bond distances and bond angles, and positional parameters can be found in Tables 1–4. Significant features of the structure include a planar four-membered metallacycle with average $Ta\text{–}CH_2$ and $Ir\text{–}CH_2$ distances of 2.152(6) and 2.079(5) Å, respectively. The Ta–Ir distance is 2.776(1) Å, and the Ir–H bond length is 1.45(6) Å.

The deuterium analogue of **2**, $Cp_2Ta(\mu\text{-}CH_2)_2Ir(Cp^*)(D)$ (**3**), was synthesized in the reaction of **1** with $LiAlD_4$ in THF (eq 3) and isolated in 49% yield. The ^1H NMR spectrum of **3** in C_6D_6 is identical to that of **2** except that the hydride resonance and all coupling to it are absent. The deuteride ligand appears in the ^2H NMR (C_6H_6) spectrum at −22.0 ppm. The IR (KBr) spectrum of **3** indicated that the Ir-H stretch at 2155 cm^{-1} in **2** is shifted to 1550 cm^{-1} upon deuterium substitution. Other than this, the IR spectra of these two compounds are indistinguishable. Heating **3** in C_6D_6 at 105 °C resulted in the slow growth of a hydride resonance at −22.0 ppm in the ^1H NMR spectrum with the concomitant conversion of the methylene hydrogen resonances from doublets to multiplets. This indicates that exchange of deuterium into the bridging methylene positions occurred at high temperatures (eq 4). Exchange into each of the two chemically inequivalent methylene positions took place at approximately the same rate.



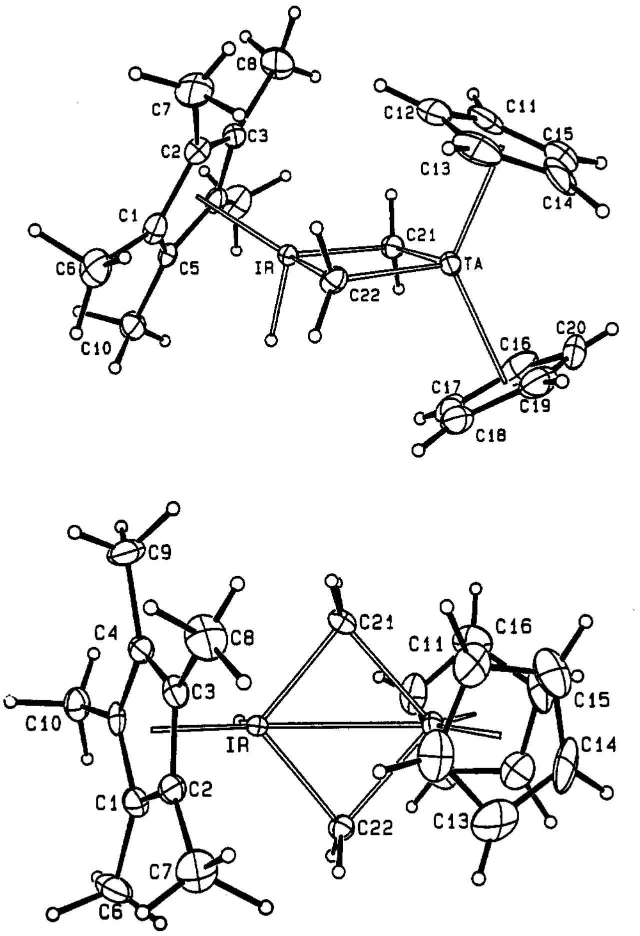
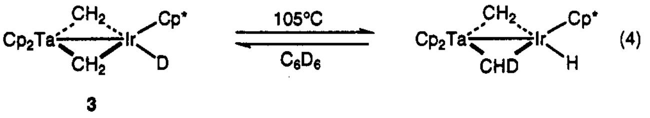


Figure 1. ORTEP diagrams of **2**: two views of the molecule.



Reactivity of $Cp_2Ta(\mu\text{-}CH_2)_2Ir(Cp^*)(H)$. The complex $Cp_2Ta(\mu\text{-}CH_2)_2Ir(Cp^*)(H)$ (**2**) is a remarkably stable metal hydride. It did not react with phosphines (PMe_3, PPh_3, $Me_2P(CH_2)_2PMe_2$, or $Ph_2P(CH_2)_2PPh_2$) or D_2 even under harsh conditions (several days at 140 °C). It was not deprotonated by *tert*-butyllithium at 25 °C. No reaction was observed when **2** was treated with ethylene, dimethyl fumarate, benzaldehyde, triethylsilane, 2-hexyne, or triphenylmethyl tetrafluoroborate. Only decomposition was observed when **2** was allowed to react with diethyl acetylenedicarboxylate. Furthermore, no reaction was observed when **2** was photolyzed in C_6D_6 even in the presence of di-*tert*-butyl peroxide. The complex $Cp_2Ta(\mu\text{-}CH_2)_2Ir(Cp^*)(Me)$ (**4**), prepared as shown in eq 5 and

Table 1. Crystal and Data Collection Parameters for $Cp_2Ta(\mu\text{-}CH_2)_2Ir(Cp^*)(H)$ (2)

(A) Crystal Parameters at $T = -105$ °C[a,b]

$a = 9.034(2)$ Å
$b = 13.603(4)$ Å
$c = 15.974(2)$ Å
$\alpha = 90.0°$
$\beta = 101.287(16)°$
$\gamma = 90.0°$
$V = 1925.2(13)$ Å^3
size: 0.17 × 0.28 × 0.60 mm
space group: $P2_1/n$
fw = 667.6
$Z = 4$
d(calc) = 2.30 g cm^{-3}
μ(calc) = 125.0 cm^{-1}

(B) Data Measurement Parameters

radiation: Mo Kα (λ = 0.710 73 Å)
monochromator: highly oriented graphite (2θ = 12.2°)
detector: cryst scintillation counter, with PHA
rflns meas: $\pm h,+k,\pm l$
2θ range: 3–55°
scan type: θ–2θ
scan width: $\Delta\theta = 0.65 + 0.35 \tan\theta$
scan speed: 5.49 (θ, deg/min)
bkgd: meas over 0.25($\Delta\theta$) added to each end of the scan
vert aperture: 4.0 mm
horiz aperture: 2.0 + 1.0 tan θ mm
no. of rflns collected: 5084
no. of unique rflns: 4407
intensity stds: measured every 1 h of X-ray exposure time; over the data collection period no decrease in intensity observed
orientation: 3 reflections checked after every 200 measurements; crystal orientation redetermined if any of the reflections were offset by more than 0.10° from their predicted positions; reorientation not performed during data collection

[a] Unit cell parameters and their esd's were derived by a least-squares fit to the setting angles of the unresolved Mo Kα components of 24 reflections with 2θ between 28 and 34°. [b] In this and all subsequent tables the esd's of all parameters are given in parentheses, right-justified to the least significant digit(s) of the reported value.

Table 2. Intramolecular Distances (Å) for 2

Ir–Ta	2.776(1)	Ta–Cp1	2.114
Ir–C21	2.083(5)	Ta–Cp2	2.117
Ir–C22	2.075(5)	C21–H21A	1.04(7)
Ir–H(Ir)	1.45(6)	C21–H21B	1.03(6)
Ir–Cp*	1.905	C22–H22A	0.94(7)
Ta–C21	2.145(6)	C22–H22B	1.03(6)
Ta–C22	2.158(6)		

Table 3. Intramolecular Angles (deg) for 2

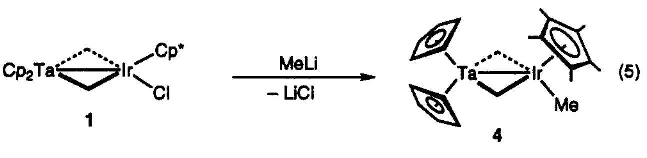
Ta–Ir–H(Ir)	101.5(21)	H21A–C21–H21B	105.4(49)
Ta–Ir–Cp*	150.4	Ir–C22–H22A	113.2(39)
H(Ir)–Ir–Cp*	108.1	Ir–C22–H22B	108.5(33)
C21–Ir–Cp*	124.2	Ta–C22–H22A	123.1(39)
C22–Ir–Cp*	125.5	Ta–C22–H22B	115.0(33)
C21–Ir–H(Ir)	97.0(21)	H22A–C22–H22B	111.0(51)
C22–Ir–H(Ir)	94.5(20)	Cp2–Ta–Cp2	130.1
C21–Ir–C22	100.19(22)	C21–Ta–Cp1	107.0
Ir–C21–H21A	108.2(40)	C21–Ta–Cp2	105.5
Ir–C21–H21B	115.8(31)	C22–Ta–Cp1	106.7
Ta–C21–H21A	124.0(38)	C22–Ta–Cp2	106.5
Ta–C21–H21B	119.2(29)	C21–Ta–C22	95.67(20)

Table 4. Positional Parameters of 2 and Their Estimated Standard Deviations[a]

atom	x	y	z	B (Å^2)
Ir	0.24139(1)	0.18030(1)	0.02520(1)	0.878(3)
Ta	0.38131(1)	0.23325(1)	–0.10810(1)	1.143(4)
C1	0.2543(6)	0.1748(4)	0.1668(3)	1.7(1)
C2	0.2454(6)	0.2766(4)	0.1429(3)	1.5(1)
C3	0.1064(6)	0.2935(4)	0.0865(3)	1.5(1)
C4	0.0258(6)	0.2017(4)	0.0732(3)	1.5(1)
C5	0.1182(6)	0.1300(4)	0.1249(3)	1.40(9)
C6	0.3763(7)	0.1299(5)	0.2323(4)	2.4(1)
C7	0.3610(8)	0.3519(5)	0.1797(4)	2.7(1)
C8	0.0438(7)	0.3903(5)	0.0508(4)	2.8(1)
C9	–0.1315(7)	0.1880(5)	0.0238(4)	2.5(1)
C10	0.0720(7)	0.0246(4)	0.1354(4)	1.9(1)
C11	0.2830(7)	0.4004(4)	–0.1278(4)	2.5(1)
C12	0.3811(8)	0.3979(4)	–0.0493(4)	2.7(1)
C13	0.5284(8)	0.3787(5)	–0.0631(5)	3.1(1)
C14	0.5138(7)	0.3710(5)	–0.1523(4)	3.2(1)
C15	0.3646(8)	0.3846(5)	–0.1910(4)	3.0(1)
C16	0.3135(8)	0.1232(5)	–0.2283(4)	2.9(1)
C17	0.3582(7)	0.0631(5)	–0.1563(4)	2.3(1)
C18	0.5092(7)	0.0774(5)	–0.1243(4)	2.5(1)
C19	0.5611(7)	0.1482(5)	–0.1759(4)	2.5(1)
C20	0.4422(8)	0.1754(5)	–0.2403(4)	2.8(1)
C21	0.1486(6)	0.2110(4)	–0.1020(3)	1.3(1)
C22	0.4695(6)	0.1922(4)	0.0227(3)	1.3(1)

[a] The thermal parameter given for anisotropically refined atoms is the isotropic equivalent thermal parameter defined as $[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$, where a, b, and c are real cell parameters and $\beta(i,j)$ are anisotropic β's.

isolated in 46% yield as a brown crystalline solid, was also unreactive toward photolysis in C_6D_6 or THF-d_8.



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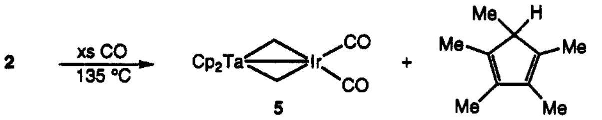
Even reactions that 2 did undergo typically required harsh conditions, as illustrated in the reaction of 2 with carbon monoxide. Heating a benzene solution of 2 in the presence of 10.5 equiv of CO caused no change until a temperature of 135 °C was reached. After 50 h at this temperature, the elimination of Cp*H was observed along with the formation of the previously reported $Cp_2Ta(\mu\text{-}CH_2)_2Ir(CO)_2$ (5; eq 6).[5] Complex 5 was isolated as a dark

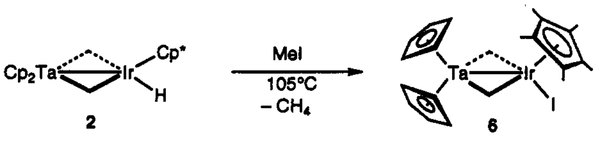


(6)

yellow crystalline solid in 46% yield and was identified by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy. The identity of the coproduct Cp*H was confirmed by ^1H NMR spectroscopy, GC, and GCMS by comparison with an authentic sample. When the reaction was performed in C_6D_6, there was no deuterium incorporation into the eliminated Cp*H, as determined by ^1H NMR spectroscopy.

The slow elimination of Cp*H was also observed when the hydride 2 was allowed to react with 2 equiv of $P(OMe)_3$ at 135 °C in C_6D_6, although no metal-containing species was produced cleanly. Only slow decomposition at 140 °C was observed when 2 equiv of *tert*-butyl isocyanide was added to 2. Heating 2 in C_6D_6 alone does not result in the loss of Cp*H. For example, no decomposition could be detected by ^1H NMR spectroscopy when 2 was heated to 135 °C for 4 days.

The complex $Cp_2Ta(\mu\text{-}CH_2)_2Ir(Cp^*)(H)$ (2) reacted slowly with MeI at 105 °C to produce $Cp_2Ta(\mu\text{-}CH_2)_2Ir(Cp^*)(I)$ (6) with loss of 1 equiv of CH_4 (eq 7). Compound



(7)

6 was isolated in 59% yield as a dark orange crystalline solid. Methane was identified by ^1H NMR spectroscopy. This reaction proceeded smoothly in 1,4-cyclohexadiene

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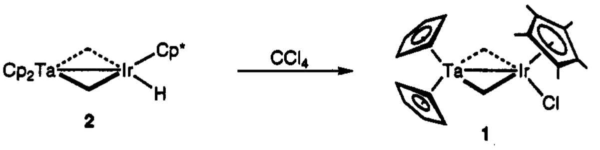
(5) Hostetler, M. J.; Butts, M. D.; Bergman, R. G. *Inorg. Chim. Acta* **1992**, *198–200*, 377.

solvent and also in C_6D_6 solvent in the presence of 9,10-dihydroanthracene-d_4.[6]

Unlike the chloride 1, the iodide 6 displayed temperature-dependent behavior in solution (C_6D_6 or THF-d_8). At −45.3 °C the ^{1}H NMR spectrum of 6 in THF-d_8 contained two doublets at 6.16 and 5.47 ppm for the inequivalent geminal hydrogens of the methylene bridges (they are coupled to each other with J = 7.7 Hz). The inequivalent Cp rings appeared as singlets at 5.54 and 5.06 ppm, while the Cp* methyl resonance was found at 1.76 ppm. As the solution was warmed, the two resonances for the bridging methylene hydrogens broadened, coalescing at approximately 45 °C, as did the two Cp ring resonances. At 62.4 °C the resonances for the methylene hydrogens and the Cp rings were each broad singlets at 5.9 and 5.2 ppm, respectively. The Cp* methyl peak remained sharp and stationary over the entire temperature range.

As expected, $Cp_2Ta(\mu\text{-}CH_2)_2Ir(Cp^*)(H)$ (2) was converted back to the chloride 1 by treatment with carbon tetrachloride (eq 8). The addition of excess CCl_4 (20 equiv)



(8)

to a benzene solution of 2 led over the course of several hours to the formation of 1, isolated in 28% yield. This reaction, as anticipated for a radical chain mechanism, was inhibited when performed in 1,4-cyclohexadiene solvent.[6]

Catalytic Hydrogenation. In light of the exceptional stability of $Cp_2Ta(\mu\text{-}CH_2)_2Ir(Cp^*)(H)$ (2), we were surprised to find that ethylene was readily hydrogenated under H_2 in the presence of 2 at room temperature. The addition of 21.5 equiv of ethylene and 54 equiv of H_2 to a 8.6 mM C_6D_6 solution of 2 resulted in the clean production of ethane at a rate of 1 turnover/h in the first 5% of reaction. Monitoring the reaction by ^{1}H NMR spectroscopy for several days confirmed that the hydrogenation went to completion. The observed rate of hydrogenation under these conditions was quite reproducible and was not changed by recrystallizing 2 multiple times. The synthesis of 2 from separate supplies of $IrCl_3 \cdot xH_2O$ and $TaCl_5$ also resulted in an active catalyst. Further studies indicated that the hydrogenation reaction was not affected by the addition of Hg (10 μL) to the experiment; mercury would be expected to spoil a heterogeneous catalyst.[7] Furthermore, no loss of 2 could be detected by integration against an internal standard (1,3,5-trimethoxybenzene) in the ^{1}H NMR spectrum in any hydrogenation experiment over the course of the reaction, nor was any induction period observed.

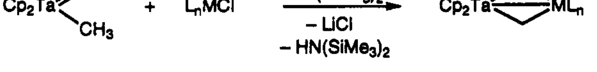
In spite of this apparently straightforward behavior, continued studies led us to suspect that we were not observing a process catalyzed directly by 2. For example, we carried out the hydrogenation experiment using D_2. Significantly, the addition of ethylene and D_2 to a C_6D_6 solution of 2 *resulted in the incorporation of deuterium into the ethane product but not into 2.* Analysis of the head gas in this reaction by mass spectrometry indicated the presence of molecules with molecular weights ranging from 28 (residual ethylene) to 36 (ethane-d_6) inclusive.

A crucial test of the true catalytic activity of 2 was performed by carrying out the hydrogenation of ethylene in the presence of 2, H_2 or D_2, and added PMe_3. When 6 equiv of PMe_3 was added to a hydrogenation experiment, the reaction was completely stopped; no product could be detected by ^{1}H NMR spectroscopy. After 11.5 h at room temperature the volatile materials were removed from the reaction mixture under vacuum, and a second hydrogenation experiment was set up with the residual solid identical with the first, except that PMe_3 was not added. Once again, no hydrogenation was observed. No loss of 2 could be detected by ^{1}H NMR spectroscopy over the course of these reactions, nor was a PMe_3 adduct observed by ^{31}P{^{1}H} NMR spectroscopy. However, when the PMe_3-inactivated solid was isolated, purified by recrystallization, and resubjected to the hydrogenation conditions in the absence of PMe_3, the hydrogenation activity was restored: the hydrogenation of ethylene was found to occur at a rate of 1 turnover/h in the first 10% of reaction. Thus, recrystallization of the PMe_3-spoiled material resulted in the full restoration of catalytic activity, whereas merely subjecting it to a dynamic vacuum did not.

In a similar test, hydrogenation was found to be inhibited in the presence of added CO, but not quite as effectively. Trace amounts of ethane were detected after 11.5 h at room temperature when a C_6D_6 solution of 2 was charged with ethylene and a 3:1 mixture of H_2 and CO. No hydroformylation products were observed. As in the PMe_3 inhibition reaction, the volatile materials were removed under vacuum and a second experiment set up with the residual solid without added CO. The formation of small amounts of ethane (1 turnover in 7 h at 15% reaction) at room temperature indicated that partial activity had been restored. An infrared spectrum (KBr) of the residual solid obtained by removing the volatiles *in vacuo* following these experiments did not contain any peaks which could be readily attributed to a CO adduct.

Discussion

Synthesis of $Cp_2Ta(\mu\text{-}CH_2)_2Ir(Cp^*)(Cl)$ and $Cp_2Ta(\mu\text{-}CH_2)_2Ir(Cp^*)(H)$. We have previously reported the syntheses of tantalum/late-metal ELHB complexes using the general base-assisted pathway shown in eq 9.[5,8] This route has been extended to include the preparation of $Cp_2Ta(\mu\text{-}CH_2)_2Ir(Cp^*)(Cl)$ (1), isolated from the reaction of 0.5 equiv of $[Cp^*IrCl_2]_2$ with $LiN(SiMe_3)_2$ and $Cp_2Ta(CH_2)(CH_3)$ at −25 °C (eq 1). The mechanism of this reaction proved to be quite complicated. As described in the Results, intermediates could be observed by both NMR and ESR spectroscopy, but we were unable to isolate and/or characterize them.



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The complex $Cp_2Ta(\mu\text{-}CH_2)_2Ir(Cp^*)(Cl)$ (1) was converted to the corresponding hydride 2 on treatment with $LiBH_4$ at room temperature (eq 2). Complex 2 can also

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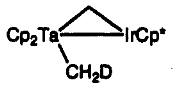
be prepared by treating 1 with $LiAlH_4$ or potassium isopropoxide, but only the reaction of 1 with $LiBH_4$ was performed on a large scale. The reaction of 1 with $LiB(Et)_3H$ ("Super-Hydride") led to a mixture of products resulting from both hydride and ethyl group transfer.

An X-ray crystallographic study of $Cp_2Ta(\mu\text{-}CH_2)_2Ir(Cp^*)(H)$ (**2**) revealed that the four-membered metallacycle is completely planar, a structural feature that is quite common in bis(methylene)-bridged bimetallic complexes,[9-11] although exceptions are known.[12] The observation of acute M–CH_2–M angles in $M(\mu\text{-}CH_2)_2M$ complexes is typical (usually 80–82°), regardless of whether the ring is planar or not, and M–M bonding interactions are invariably invoked.[9-12] Consistent with this, the Ta–CH_2–Ir angles of 2 were found to be 82.0(2) and 81.9(2)°. The Ta–Ir distance of 2.776(1) Å is also consistent with Ta–late-metal distances observed in related bis(methylene)-bridged Ta–late-metal complexes.[3,5,13,14] Some M–M bonding interaction in 2 is implicated in these data, although it is not possible to assign a dominant resonance structure to the four-membered ring on the basis of structural considerations alone.[15] The average Ta–CH_2 distance of 2.152(6) Å is consistent with a bond order of 1.5, equidistant between the Ta–CH_2 (2.039(1) Å) and the Ta–CH_3 distances (2.268(1) Å) of $Cp_2Ta(CH_2)(CH_3)$.[16] The Ir–H distance of 1.45(6) Å is slightly shorter than those found for $Cp^*Ir(PMe_3)(C_6H_{11})(H)$, which crystallizes with two molecules in the unit cell having Ir–H bond lengths of 1.55(6) and 1.62(5) Å.[17]

Reactivity of $Cp_2Ta(\mu\text{-}CH_2)_2Ir(Cp^*)(H)$. The compound $Cp_2Ta(\mu\text{-}CH_2)_2Ir(Cp^*)(H)$ (2) represents a stable analogue of the proposed cobalt hydride intermediate shown in Scheme 1 which could not be isolated. It was thought that perhaps photolysis of 2 or the methyl derivative 4 might lead to extrusion of a hydride or methyl radical and formation of the paramagnetic species $Cp_2Ta(\mu\text{-}CH_2)_2IrCp^*$ as an analogue of $Cp_2Ta(\mu\text{-}CH_2)_2CoCp$. Unfortunately, both iridium compounds exhibited stability in marked contrast to that of the proposed cobalt hydride intermediate and were unreactive toward photolysis. In addition, thermal decomposition of 2 and 4 did not lead to a stable paramagnetic species.

In previous studies we found that the reductive elimination of a methylene bridge and a late-metal-bound hydride (or deuteride) is a facile process when the complexes $Cp_2Ta(\mu\text{-}CH_2)_2M(CO)(L)$ (M = Ir, Rh; L = CO, PPh_3) were allowed to react with H_2 (or D_2) at 45 °C in benzene.[8] Thus, we were surprised to find that the exchange of the deuteride and the bridging methylene hydrogens of $Cp_2Ta(\mu\text{-}CH_2)_2Ir(Cp^*)(D)$ (3) was observed only at 105 °C, as shown in eq 4, and even then it was rather slow. The deuterium exhibited no preference for migration to either of the two inequivalent C–H positions (cis to Cp* or cis to M–H). The reason for the slower rate of deuterium exchange in 3 is not clear. If this reaction were to occur by the initial reductive elimination of the deuteride and a methylene bridge, as we found in our previous studies, then an intermediate species such as 7



7

might be formed, perhaps stabilized by a M–M bond.[8] Although a consideration of the molecular orbitals of the Cp^*IrL fragment suggests the existence of a high-energy metal-based orbital of the correct symmetry for overlap with the Ta center,[18,19] we have not succeeded in trapping species such as 7 (or analogous intermediates in related Ta/Ir systems[5,8]) using phosphines or other dative ligands. Interestingly, in previous studies the reaction of $Cp_2Ta(CH_2)(CH_3)$ with $(PMe_3)_2Pt(C_2H_4)$ led to the isolation of $(Cp)_2(CH_3)Ta(\mu\text{-}CH_2)Pt(PMe_3)_2$, which is similar in structure to 7.[13] This complex slowly decomposed at 25 °C to the bis(methylene)-bridged compound $Cp_2Ta(\mu\text{-}CH_2)_2Pt(PMe_3)(H)$ among other species. It is well-known that reductive elimination results in a decrease in charge at the metal center.[20] The Ir center of 3 is presumably too electron rich for reductive elimination to be facile, and sufficient stabilization is not provided by the M–M bond.

The strength of the M–Cp* interaction is a practical feature of organometallic Cp* complexes that has allowed the extensive study of the chemistry of such compounds. However, a few examples of Cp* loss under certain conditions have been reported.[21-23] For example, the reaction of $Cp^*Rh(H)_3(SiEt_3)$ with an excess of PMe_3 at 25 °C led to the production of $HRh(PMe_3)_4$ together with Cp^*H and $HSiEt_3$.[24] The reductive elimination of Cp*H was proposed to occur via an η^1-Cp* intermediate. We have observed the elimination of Cp*H in the reaction of $Cp_2Ta(\mu\text{-}CH_2)_2Ir(Cp^*)(H)$ (2) with CO under rather harsh conditions (50 h at 135 °C) to form $Cp_2Ta(\mu\text{-}CH_2)_2Ir(CO)_2$ (5; eq 6). The low yield of 5 (46% isolated) is due to the slow decomposition of the product under the reaction conditions.

Although no intermediates were observed in this reaction, Cp* ring slip ($\eta^5 \rightleftharpoons \eta^3 \rightleftharpoons \eta^1$) followed by reductive elimination of an η^1-Cp* group and the hydride ligand is a likely route, with the ring-slipped species stabilized by CO. It was not possible to determine whether the reductive elimination of a methylene bridge and the hydride followed by attack of CO is involved in the reaction mechanism. Activation of the C–H bond in the benzene solvent as an intermediate step is unlikely, since no deuterium was incorporated into the Cp*H product when the reaction was performed in C_6D_6. The reverse of the reaction shown in eq 6 was not observed when 5 was allowed to react with

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Cp*H (37 equiv) at 105 °C. As with CO, the reaction of **2** with P(OMe)$_3$ led to the production of Cp*H, although the Ta–Ir phosphite product was not stable to the reaction conditions. Interestingly, it appears that π acceptors are required to promote the loss of Cp*H from **2**, an elimination that is not induced thermally under the same reaction conditions or in the presence of phosphines.

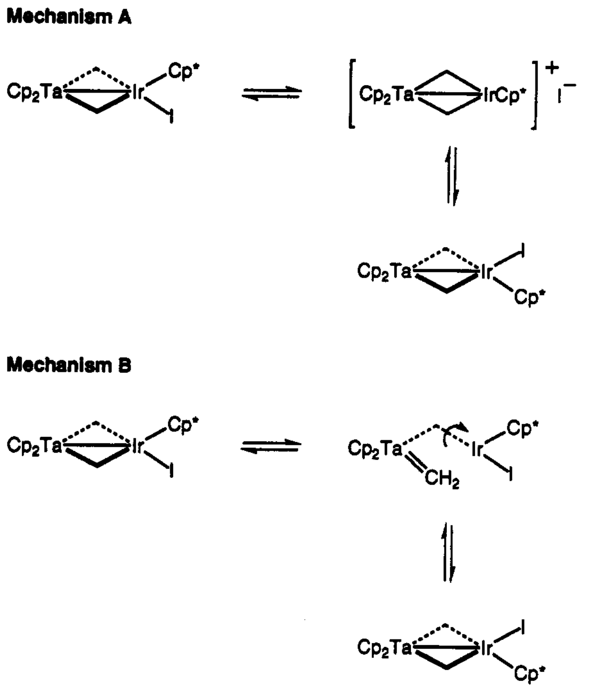
Treatment of $Cp_2Ta(\mu\text{-}CH_2)_2Ir(Cp^*)(H)$ (**2**) with CCl_4 in benzene resulted in its conversion to the chloride **1** (eq 8). As expected, no reaction was observed when this experiment was performed in 1,4-cyclohexadiene solvent.[6] This result indicates the operation of a radical chain mechanism in the formation of **1**. Thus, it is possible that the radical species $Cp_2Ta(\mu\text{-}CH_2)_2IrCp^*$ (analogous to the Ta–Co species in Scheme 1) is formed in this reaction, which is then trapped by chloride.

The overall exchange of the hydride for an iodide occurred when **2** was allowed to react with MeI at 105 °C, forming the iodide **6** and 1 equiv of methane (eq 7). It is possible that this reaction occurs by the nucleophilic attack of **2** on MeI, forming $[Cp_2Ta(\mu\text{-}CH_2)_2Ir(Cp^*)(Me)(H)]I$, which would generate **6** upon the elimination of methane. However, **2** does not react with methyl tosylate under the same reaction conditions as might have been expected if this were the reaction pathway. Despite the fact that the reaction was unaffected when performed in 1,4-cyclohexadiene solvent or in the presence of 9,10-dihydroanthracene-d_4, it probably also proceeds through a radical chain pathway analogous to the reaction of **2** with CCl_4. The participation of short radical chains (very little propagation) would be consistent with our results.

A variable-temperature NMR spectroscopic study of the iodide **6** in THF-d_8 indicated that a fluxional process exists whereby the geminal bridging methylene hydrogens, which are inequivalent at low temperature, are exchanged on warming. The same behavior was observed for the Cp rings, also inequivalent at low temperature, and the coalescence temperature for both processes was the same. We believe that this temperature-dependent behavior is a result of the facile loss of I$^-$, which generates a symmetrical cationic Ta—Ir species as shown in mechanism A of Scheme 2. Alternatively, the dissociation of a Ta=CH$_2$ group from the iridium center followed by rotation about the Ir—CH$_2$ bond as shown in mechanism B of Scheme 2 would result in the same observations. This pathway seems less likely than that shown in mechanism A in consideration of the observed reactivity of the hydride **2**. Although the hydride ligand of **2** would be expected to have a stronger trans effect than the iodide ligand of **6**,[25] no evidence exists for the dissociation of a Ta=CH$_2$ group in **2**. It is not a fluxional molecule in benzene or THF, and no such intermediate as shown in mechanism B could be trapped by reactions with small molecules (see Results). Furthermore, in agreement with mechanism A, the methylene and Cp resonances of the iodide **6** were much less broadened at 25 °C in C_6D_6 than in the more polar solvent THF-d_8. THF would be expected to stabilize the cationic intermediate better than benzene.

Catalytic Hydrogenation. The hydrogenation of alkenes catalyzed by transition metal complexes has been studied for many years,[26–28] although the exact nature of the catalysts has often not been well described. In recent years various tests have been reported in the literature to determine whether or not a catalyst is truly homogeneous.[7,29–31] Still, assumptions are often made concerning the structure of the catalyst when investigating a catalytic reaction or proposing reaction mechanisms.

Scheme 2



When we studied the hydrogenation of ethylene in the presence of $Cp_2Ta(\mu\text{-}CH_2)_2Ir(Cp^*)(H)$ (**2**), we found several initial indications that **2** was the catalyst precursor. For example, the reaction was not inhibited by added Hg, indicating that the catalyst was homogeneous. The catalytic activity was not affected by recrystallizing **2** (analytically pure) multiple times, and no decomposition of **2** could be detected over the course of the reaction. No induction period could be detected.

Further studies, however, led us to doubt that **2** was truly a well-behaved catalyst. For example, when the hydrogenation experiment was carried out in the presence of **2**, D_2, and ethylene, deuterium was incorporated into the ethane product but not into **2**. Although reaction mechanisms involving catalysis by **2** can be drawn to account for this result (such as the migration of the hydride ligand to the Cp* ring followed by a complete hydrogenation cycle), it is somewhat suspicious.

In the most revealing experiment, we found that the hydrogenation of ethylene in the presence of **2** was completely inhibited by added PMe$_3$. This significant result demonstrates unequivocally that **2** is not the catalyst precursor in this reaction, because PMe$_3$ does not react with **2**.

We propose that **2** decomposes irreversibly to a small extent under hydrogenation conditions to what must be a very active catalyst, which is undetectable by NMR

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spectroscopy. The fact that the rate of hydrogenation was reproducible as described in the Results suggests that the same extent of decomposition was achieved each time the reaction was carried out. This unidentified catalyst is spoiled irreversibly by PMe_3. Thus, exposing the PMe_3-spoiled material to a dynamic vacuum does not restore catalytic activity (the PMe_3 that binds the active species remains in sufficient quantities to spoil freshly generated catalyst in subsequent hydrogenation experiments). However, completely purging the solid of phosphine by recrystallization does lead once again to the formation of a catalytically active species when it is subsequently subjected to hydrogenation conditions.

We do not believe that the catalytic activity observed in these hydrogenation reactions can be attributed to the activity of small amounts of rhodium (as $RhCl_3$) that may possibly contaminate the $IrCl_3 \cdot xH_2O$ used in preparing the $[Cp^*IrCl_2]_2$ starting material. Attempts to synthesize the rhodium analogues of 1 and 2 resulted in the formation of a green paramagnetic species (perhaps analogous to $Cp_2Ta(\mu\text{-}CH_2)_2CoCp$) that could not be purified by recrystallization or column chromatography, nor could it be cleanly oxidized with Cp_2FeBF_4. This Rh complex is highly soluble, even in pentane, and separation from 2 should have been facile by recrystallization.

Overall, this study has shown that a seemingly simple and straightforward catalytic system was demonstrated to be far more complicated only when subjected to careful scrutiny. We offer these results in part as a warning that care must be taken when describing a proposed homogeneous catalytic system.

Experimental Section

General Considerations. Unless otherwise noted, all reactions and manipulations were performed in dry glassware under a nitrogen atmosphere in a Vacuum Atmospheres DC-882 drybox equipped with a MO-40-2 Dri-train or using standard Schlenk techniques. "Glass bomb" refers to a cylindrical, medium-walled Pyrex vessel joined to a Kontes K-826510 high-vacuum Teflon stopcock.

All ^1H, ^2H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded on 300- or 400-MHz instruments at the University of California, Berkeley, NMR facility. One of the 300-MHz instruments was constructed by Mr. Rudi Nunlist and interfaced with a Nicolet 1280 computer. The other 300-MHz and the 400-MHz machines were commercial Bruker AM or AMX series spectrometers. IR spectra were obtained on a Mattson Galaxy Series FTIR 3000 spectrometer. Mass spectrometry (MS) analyses were obtained at the UCB mass spectrometry facility on AEI MS-12 and Kratos MS-50 mass spectrometers. GC analyses were performed on a HP 5890A gas chromatograph equipped with a 95:5 dimethylsilicone–phenylmethylsilicone column. An HP 5970 Series mass selective detector attached to an HP 5890A GC instrument was used in GCMS analyses. Elemental analyses were obtained from the UCB Microanalytical Laboratory or Oneida Research Services, Inc. The photolysis apparatus consisted of a 450-W medium-pressure Conrad-Hanovia mercury lamp in an Ace 7874B-38 immersion well. The immersion well was secured in a stainless steel beaker filled with water cooled to 12 °C by a Forma Scientific Model 2095 refrigerated bath circulator. The photolysis experiments were carried out in sealed NMR tubes (505PS Wilmad).

Benzene, toluene, pentane, Et_2O, and THF were distilled from sodium/benzophenone. High-purity H_2 (>99.999%) and ethylene (>99.99%) were purchased from Matheson. $LiN(SiMe_3)_2$ was recrystallized from toluene and dried under high vacuum. $LiAlD_4$ was extracted with Et_2O prior to use. Methyl iodide was dried over $CaCl_2$ and stored in the dark over copper metal. Carbon tetrachloride was dried over P_2O_5, and 1,3,5-trimethoxybenzene was recrystallized from hexane and dried under high vacuum. Cyclohexadiene was distilled and dried over 4-Å molecular sieves. 9,10-Dihydroanthracene-d_4 was prepared according to the literature.[32] All other reagents were obtained from commercial suppliers and used without further purification.

Reactions with gases (other than H_2 or D_2) or transferable liquids involved condensation of a calculated pressure (ideal gas law) of gas from a bulb of known volume into the reaction vessel at 77 K utilizing an MKS Baratron gauge attached to a high-vacuum line. Because H_2 and D_2 are gases at this temperature, these were added directly into the reaction vessel held at 77 K; when the vessel was an NMR tube (505-PS Wilmad), it was flame-sealed 1 cm above the level of the liquid nitrogen. Sealed NMR tubes were prepared by connecting an NMR tube to a Kontes vacuum adapter via a Cajon joint, freezing and degassing the sample once (unless otherwise stated), and flame-sealing the tube with an oxygen/propane torch.

$Cp_2Ta(\mu\text{-}CH_2)_2Ir(Cp^*)(Cl)$ (1). Method a. In the drybox $[Cp^*IrCl_2]_2$[33] (241 mg, 0.303 mmol), $Cp_2Ta(CH_2)(CH_3)$[4] (212 mg, 0.622 mmol), and $LiN(SiMe_3)_2$ (106 mg, 0.635 mmol) were added as solids to a 50-mL glass bomb equipped with a stirbar. To a separate bomb was added 10 mL of THF. On a vacuum line the THF was degassed by three freeze–pump–thaw cycles and added by vacuum transfer to the evacuated bomb containing the solids at 77 K. The flask was transferred immediately to a −25 °C bath (ethylene glycol–CO_2). The reaction mixture was stirred at −25 °C for 1 h, after which it was warmed slowly to room temperature. The volatile materials were removed under vacuum, leaving a dark orange powder. Inside the drybox the solid was washed with pentane (4 × 8 mL) and extracted with hot benzene (2 × 6 mL). The two dark orange benzene solutions were filtered through Celite and reduced in volume to 4 mL each under vacuum with heating. Orange crystalline 1 precipitated as the solutions were cooled to room temperature, and a second crop was obtained from each solution by vapor diffusion of pentane into the benzene solutions at room temperature, giving a total yield of 68% (289 mg).

Method b. Carbon tetrachloride (540 μL, 4.66 mmol, 20 equiv) was added by syringe with stirring to 3 mL of a brown benzene solution of 2 (154 mg, 0.231 mmol). The reaction mixture was stirred at room temperature for 6.5 h, after which the volatile materials were removed under vacuum. Trituration of the residue two times with pentane afforded an orange-brown powder that was washed with pentane (2 × 5 mL) and extracted with 5 mL of hot benzene; this extract was filtered through Celite. Complex 1 was isolated by vapor diffusion of pentane into the benzene solution at room temperature, and a second crop was obtained by cooling the decanted benzene–pentane (1:3) solution to −35 °C, giving a total yield of 45 mg (28%): ^1H NMR (C_6D_6) δ 6.11 (d, J = 7.7 Hz, 2H, CH_2), 5.61 (d, J = 7.7 Hz, 2H, CH_2), 5.28 (s, 5H, Cp), 4.48 (s, 5H, Cp), 1.52 (s, 15H, Cp*); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 100.8 (s, Cp), 97.7 (s, CH_2), 96.2 (s, Cp), 91.8 (s, C_5Me_5), 9.1 (s, $C_5\mathit{Me}_5$); IR (KBr) 3104 (m), 2974 (m), 2949 (s), 2904 (s), 2858 (m), 1439 (s), 1402 (m), 1375 (s), 1022 (s), 928 (m), 835 (s), 794 (s) cm^{-1}. A small amount of the combined product from method a was recrystallized a second time for elemental analysis by vapor diffusion of pentane into a saturated benzene solution at room temperature. Anal. Calcd for $C_{22}H_{29}ClIrTa$: C, 37.64; H, 4.16. Found: C, 37.45; H, 4.18.

Electron Spin Resonance Spectroscopy Measurements. 1. $[Cp^*IrCl_2]_2$ (6.7 mg, 8.41×10^{-6} mol) and $LiN(SiMe_3)_2$ (3.0 mg, 1.78×10^{-5} mol) were added as solids to an ESR tube. On a vacuum line 0.35 mL of THF was added by vacuum transfer to the evacuated tube at −78 °C (acetone–CO_2). The tube was sealed under vacuum at 77 K, warmed to −78 °C, where it was held for 5 min (with continuous shaking), and then frozen at 77 K until the ESR spectrum was obtained.

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2. A THF (0.35 mL) solution of $[Cp^*IrCl_2]_2$ (6.2 mg, 7.78 × 10^{-6} mol) and $LiN(SiMe_3)_2$ (2.6 mg, 1.57 × 10^{-5} mol) was prepared as described above for (1). After the tube was sealed at 77 K, the solution was warmed to −35 °C for 15 min, over which time the solution became deep red and homogeneous. The tube was then kept frozen at 77 K until the ESR spectrum was recorded.

3. A solution of $[Cp^*IrCl_2]_2$ (7.1 mg, 8.91 × 10^{-6} mol), $LiN(SiMe_3)_2$ (3.0 mg, 1.78 × 10^{-5} mol), and $Cp_2Ta(CH_2)(CH_3)$ (6.3 mg, 1.85 × 10^{-5} mol) in 0.35 mL of THF was prepared as described above for (1). The reaction mixture was warmed to 25 °C after sealing, shaken for 3 min, and then frozen at 77 K, where it was held until the ESR spectrum was obtained.

The ESR spectra were each recorded at 8 K using a Varian E-LINE Century Series ESR spectrometer (9.215 GHz) equipped with a Varian E102 microwave bridge and an R. G. Hansen & Associates Series 7000 temperature indicator and controller. No signal was observed ($g = 0$ to $g = 4$) for sample 1. Sample 2 had an intense anisotropic signal where $g_x = 2.476$, $g_y = 2.126$, and $g_z = 1.938$. For sample 3, an intense complicated 10-line spectrum centered at $g = 1.997$ was observed which decreased in intensity by 70% when the solution was warmed to 25 °C for an additional 3 min.

$Cp_2Ta(\mu\text{-}CH_2)_2Ir(Cp^*)(H)$ (2). To a slurry of 1 (1.10 g, 1.57 mmol) in 20 mL of THF was added $LiBH_4$ (95%, 104 mg, 4.54 mmol) in small portions with stirring in the drybox. The orange mixture quickly turned brown and homogeneous. The solution was stirred at room temperature for 17 h, followed by removal of the volatile materials under vacuum. The remaining sticky tan solid was converted to a powder by two pentane triturations. Extraction with hot benzene (2 × 10 mL) followed by filtration through Celite afforded a brown solution from which dark yellow crystals were isolated by vapor diffusion of pentane at room temperature. A second crop was obtained by cooling the C_6H_6–pentane (1:3) solution to −35 °C to give a total yield of 495 mg (47%): ^1H NMR (C_6D_6) δ 4.84 (dd, J = 6.7, 3.1 Hz, 2H, CH_2), 4.78 (s, 5H, Cp), 4.53 (s, 5H, Cp), 3.96 (d, J = 6.7 Hz, 2H, CH_2), 1.97 (d, J = 0.6 Hz, 15H, Cp*), −22.0 (br s, 1H, Ir–H); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 99.4 (s, Cp), 94.7 (s, Cp), 92.4 (s, C_5Me$_5$), 74.5 (s, CH_2), 10.6 (s, C$_5$$Me_5$); IR (KBr) 2965 (m), 2938 (s), 2891 (s), 2876 (s), 2155 (s), 1437 (m), 1375 (m), 1016 (m), 931 (m), 824 (s), 795 (s), 486 (m) cm^{-1}. Anal. Calcd for $C_{22}H_{30}IrTa$: C, 39.57; H, 4.54. Found: C, 39.27; H, 4.49 (obtained on the combined crops).

Reaction of 2 with CCl_4 in 1,4-Cyclohexadiene. Complex 2 (12.1 mg, 1.81 × 10^{-5} mol) was dissolved in 2 mL of 1,4-cyclohexadiene in the drybox. Carbon tetrachloride (35 μL, 0.363 mmol, 20 equiv) was added by syringe to the yellow solution; no color change was observed. The solution was allowed to stand at room temperature for 6.5 h. The volatile materials were then removed under vacuum, leaving a yellow-brown powder. A ^1H NMR spectrum (C_6D_6) of the powder indicated that no reaction had occurred.

$Cp_2Ta(\mu\text{-}CH_2)_2Ir(Cp^*)(D)$ (3). A 1-mL THF solution of $LiAlD_4$ (6.8 mg, 0.162 mmol) was added slowly to 4 mL of an orange THF solution of 1 (87.9 mg, 0.125 mmol) with stirring in the drybox. The solution turned orange-yellow and was stirred at room temperature for 30 min. The volatile materials were then removed under vacuum, and the remaining yellow powder was washed with pentane (2 × 4 mL). Extraction with toluene followed by filtration through Celite and concentration to 2 mL under vacuum afforded a dark yellow solution, which was layered with 2 mL of pentane. Yellow crystalline 3 was isolated in 49% yield (41.4 mg) by cooling the toluene–pentane solution to −35 °C: ^1H NMR (C_6D_6) δ 4.82 (d, J = 6.7 Hz, 2H, CH_2), 4.78 (s, 5H, Cp), 4.53 (s, 5H, Cp), 3.95 (d, J = 6.7 Hz, 2H, CH_2), 1.97 (s, 15H, Cp*); ^2H NMR (C_6H_6) δ −22.0 (br s, Ir–D). The IR (KBr) spectrum is identical with that of 2, except that the Ir–H stretch at 2155 cm^{-1} is replaced by an Ir–D stretch at 1550 cm^{-1}.

$Cp_2Ta(\mu\text{-}CH_2)_2Ir(Cp^*)(Me)$ (4). Methyllithium (1.4 M in Et_2O, 170 μL, 0.238 mmol) was added by syringe with stirring to 5 mL of a THF solution of 1 (162 mg, 0.232 mmol) in the drybox. The solution immediately turned from orange to brown and was stirred at room temperature for 1 h 45 min. The volatile materials were removed under vacuum, and the remaining brown powder was extracted with hot pentane (2 × 10 mL). The extracts were combined and reduced to 15 mL under vacuum. Brown crystalline 4 was isolated after cooling the solution to −35 °C. A second crop was obtained by concentrating the decanted pentane solution *in vacuo* to 5 mL followed by cooling once more to give a total yield of 72.4 mg (46%): ^1H NMR (C_6D_6) δ 4.83 (d, J = 7.3 Hz, 2H, CH_2), 4.95 (s, 5H, Cp), 4.53 (s, 5H, Cp), 4.37 (d, J = 7.3 Hz, 2H, CH_2), 1.66 (s, 15H, Cp*), −0.20 (s, 3H, Me); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 98.2 (s, Cp), 95.4 (s, Cp), 93.3 (s, C_5Me$_5$), 88.7 (s, CH_2), 9.0 (s, C$_5$$Me_5$), −14.5 (s, Me); IR (KBr) 2964 (m), 2910 (s), 2875 (s), 2870 (s), 2810 (m), 1439 (m), 1375 (m), 1022 (s), 931 (m), 908 (m), 810 (s), 480 (m) cm^{-1}. Anal. Calcd for $C_{23}H_{32}IrTa$: C, 40.52; H, 4.73. Found: C, 41.20; H, 4.85. The carbon percentage was consistently off despite repeated attempts at analysis; mass spectral analysis (FAB) was unsuccessful due to excessive fragmentation.

Conversion of $Cp_2Ta(\mu\text{-}CH_2)_2Ir(Cp^*)(H)$ (2) to Cp*H and $Cp_2Ta(\mu\text{-}CH_2)_2Ir(CO)_2$ (5). In the drybox a brown solution of 2 (194 mg, 0.291 mmol) dissolved in 13 mL of benzene was added to a 50-mL thick-walled glass bomb. On a vacuum line the solution was degassed by three freeze–pump–thaw cycles at 77 K and CO was condensed into the flask (402 Torr, 77 K, 37 mL, 3.1 mmol, approximately 10.5 equiv). The flask was closed and heated to 135 °C for 50 h, after which time the solution was yellow-brown and contained a brown precipitate. The volatile materials were removed under vacuum, and the remaining brown powder was washed with pentane (3 × 5 mL) and extracted with hot benzene (2 × 3 mL) in the drybox. The extracts were filtered through Celite. Dark yellow crystalline 5 was obtained by vapor diffusion of pentane into the separate benzene solutions at room temperature, with a second crop acquired by cooling the decanted benzene–pentane solutions to −35 °C, giving a total yield of 78.2 mg (46%). The previously reported complex 5 was identified by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy.[5] Analysis of the first pentane washing by GC and GCMS confirmed the identity of Cp*H as a reaction coproduct, as compared to an authentic sample. In a small-scale reaction the production of Cp*H was found to be quantitative by ^1H NMR spectroscopy.

$Cp_2Ta(\mu\text{-}CH_2)_2Ir(Cp^*)(I)$ (6). A 19-mL glass bomb was charged with 10 mL of a benzene solution of 2 (196 mg, 0.294 mmol) in the drybox, after which MeI (22 μL, 0.35 mmol) was added by syringe. The reaction mixture was heated to 105 °C for 24 h, during which time the brown solution turned brown-red with the formation of a small amount of a brown precipitate. The volatile materials were then removed under vacuum, and a single pentane trituration afforded a brown powder. The solid was washed with pentane (3 × 15 mL) and extracted with hot benzene (2 × 5 mL). A 59% total yield (137.7 mg) of dark orange crystalline 6 was isolated by vapor diffusion of pentane into each benzene solution at room temperature: ^1H NMR (THF-d_8, −45 °C) δ 6.16 (d, J = 7.7 Hz, 2H, CH_2), 5.54 (s, 5H, Cp), 5.47 (d, J = 7.7 Hz, 2H, CH_2), 5.06 (s, 5H, Cp), 1.76 (s, 15H, Cp*); $^{13}C\{^1H\}$ NMR (THF-d_8, −51 °C) δ 101.9 (s, Cp), 97.6 (s, Cp), 93.0 (s, CH_2), 92.3 (s, C_5Me$_5$), 10.2 (s, C$_5$$Me_5$); IR (KBr) 3086 (m), 3072 (m), 2947 (m), 2931 (m), 2897 (s), 1475 (m), 1439 (s), 1375 (s), 1018 (s), 933 (m), 926 (m), 839 (s), 827 (s), 812 (s), 791 (s); HRMS (FAB) *m/c* calcd for $C_{22}H_{30}IIrTa(MH^+)$ 793.0478, found 793.0457.

Hydrogenation Experiments. All experiments were performed as in the following example. In the drybox 0.54 mL of a yellow 8.6 mM C_6D_6 solution of 2 containing 1,3,5-trimethoxybenzene (2.7 mg, 1.6 × 10^{-5} mol) as an internal standard was added to an NMR tube. Ethylene (60 Torr, 29.7 mL, 298 K, 9.6 × 10^{-5} mol, 21.5 equiv) was added on a vacuum line followed by H_2 (555 Torr, 77 K, 2.17 mL, 2.50 × 10^{-4} mol, 54 equiv). The NMR tube was flame-sealed and held at room temperature (23 ± 1 °C) for the duration of the experiment while being mechanically rotated end over end continuously to ensure good mixing. The production of ethane and loss of ethylene were monitored by ^1H NMR spectroscopy by integrating against the internal standard. The hydrogenation rate of 1 turnover/h is that which took place during the first 5% of reaction, i.e., when the rate is essentially linear. All reactions were monitored well beyond this point at consistent time intervals.

PMe_3 Inhibition Experiment. In the drybox 0.5 mL of a yellow 4.97 mM C_6D_6 solution of 2 containing 2.5 mg of Cp_2Fe (internal standard) was added to an NMR tube. On a vacuum line the solution was degassed by two freeze–pump–thaw cycles. The tube was then charged with PMe_3 (1.60×10^{-5} mol, 6.4 equiv), ethylene (9.61×10^{-5} mol, 38 equiv), and H_2 (2.56×10^{-4} mol, 103 equiv) and flame-sealed. The experiment was monitored as described above for the general hydrogenation reaction; no reaction was observed by ^1H NMR spectroscopy. After 11.5 h at room temperature the volatile materials were removed under vacuum in the drybox. The yellow residue was transferred to another NMR tube, and a second hydrogenation reaction was set up under conditions identical with the first except that PMe_3 was not added. Once again, no reaction was observed by ^1H NMR spectroscopy after 11.5 h at room temperature.

PMe_3 Inhibition/Catalyst Regeneration Experiment. In the drybox 2 (82.0 mg, 0.123 mmol) was dissolved in 12 mL of benzene. The yellow-brown solution was added to a 157-mL thick-walled bomb together with a stirbar. On a vacuum line the solution was degassed once at 77 K and charged with PMe_3 (0.638 mmol, 5.2 equiv), ethylene (2.46 mmol, 20 equiv), and H_2 (13.6 mmol, 111 equiv). The reaction mixture was then stirred at room temperature (23 ± 1 °C) for 15.5 h; no color change was evident. The volatile materials were then removed under vacuum. The remaining tan powder was dissolved in 4 mL of benzene, which was reduced to 2 mL under vacuum. Yellow-brown crystals of 2 were isolated from the yellow-brown benzene solution by vapor diffusion of pentane at room temperature. A second crop was obtained by cooling the decanted 1:3 benzene–pentane solution to −35 °C, giving a total yield of 47.8 mg (58%).

In the drybox 0.52 mL of a 10.9 mM C_6D_6 solution of the recrystallized 2 (from the first crop) was added to an NMR tube. The solution was degassed on a vacuum line, and ethylene (9.98×10^{-5} mol, 17.5 equiv) and H_2 (2.55×10^{-4} mol, 45 equiv) were added by vacuum transfer. The NMR tube was then flame-sealed. The reaction was monitored as described above for the general hydrogenation reaction. The hydrogenation of ethylene was found to occur at an initial rate (10% reaction) of 1 turnover/h.

CO Inhibition Experiment. In the drybox 0.5 mL of a 21.8 mM C_6D_6 solution of 2 containing Cp_2Fe (2.5 mg) as an internal standard was added to an NMR tube. The solution was degassed by two freeze–pump–thaw cycles on a vacuum line. To the tube was then added ethylene (1.28×10^{-4} mol, 12 equiv) and synthesis gas (3:1 H_2–CO; H_2, 1.87×10^{-4} mol, 17 equiv; CO, 6.22×10^{-5} mol, 6 equiv). The tube was flame-sealed. The reaction was monitored as described above for the general hydrogenation reaction. Trace amounts of ethane were detected in the ^1H NMR spectrum after 11.5 h at room temperature. Inside the drybox the volatile materials were removed under vacuum and a second hydrogenation experiment was set up with the remaining powder under identical conditions, except that CO was not added. The reaction was again monitored in the same way. The hydrogenation of ethylene was found to occur at a rate of 1 turnover/7 h in the first 15% of the reaction, as determined by ^1H NMR spectroscopy. After 11.5 h at room temperature the volatile materials were removed from the reaction mixture under vacuum in the drybox. An infrared spectrum (KBr) of the remaining powder contained no peaks which could be assigned to metal–carbonyl stretching absorptions.

X-ray Structure Determination of 2. Pale yellow blocklike crystals were obtained by crystallization from a pentane–benzene solution of 2 at −30 °C. An X-ray crystallographic study of 2 was then performed by Dr. F. J. Hollander. Fragments cleaved from some of the crystals were mounted on glass fibers using Paratone N hydrocarbon oil. The crystals were then transferred to an Enraf-Nonius CAD-4 diffractometer, centered in the beam, and cooled to −105 °C by a nitrogen-flow low-temperature apparatus which had been previously calibrated by a thermocouple placed at the sample position. These crystals were tested for quality by peak scans, and one was selected. Automatic peak search and indexing procedures yielded a monoclinic reduced primitive cell. Inspection of the Niggli values revealed no conventional cell of higher symmetry. The final cell parameters and specific data collection parameters for this data set are given in Table 1. Data collection was interrupted midway through collection of the second asymmetric unit due to misorientation and was not continued from that point.

The 5084 raw intensity data were converted to structure factor amplitudes and their esd's by correction for scan speed, background, and Lorentz and polarization effects. No correction for crystal decomposition was necessary. Inspection of the azimuthal scan data showed the variation $I_{min}/I_{max} = 0.54$ for the average curve; however, the azimuthal scans were performed after the significant reorientation of the crystal and thus had a different orientation matrix than did the collected data. Data were corrected for absorption using the empirical method described by Walker and Stuart ($T_{max} = 1.28$, $T_{min} = 0.87$).[34] Inspection of the systematic absences indicated uniquely space group $P2_1/n$. Removal of systematically absent data and averaging of redundant data ($R_I = 2.4\%$) left 4407 unique data in the final data set.

The structure was solved by Patterson methods and refined via standard least-squares and Fourier techniques. Hydrogen atom positions were predicted and used to calculate structure factors prior to the empirical correction for absorption. Following the averaging of the redundant data, the hydrogen positions and isotropic thermal parameters were refined. The Ir hydride was then located and refined as well. It was necessary to restrain the thermal parameter of the hydride, since it was continually refined to a negative value. Before the final cycles of refinement five strong reflections were given zero weight because they appeared to be critically affected by secondary extinction, and 24 reflections with low values of F were removed for apparent affects of multiple diffraction.

The final residuals for 337 variables refined against the 3663 accepted data for which $F^2 > 3\sigma(F^2)$ were $R = 2.40\%$, $R_w = 2.73\%$, and GOF = 1.16. The R value for all 4407 data was 3.40%. In the final cycles of refinement a secondary extinction parameter was included (maximum correction 8.5% on F for included data and 35% for the very highest intensity data removed from the refinement).[34]

The quantity minimized by the least-squares program was $\sum w(|F_o| - |F_c|)^2$, where w is the weight of a given observation. The p factor, used to reduce the weight of intense reflections, was set to 0.03 throughout the refinement. The analytical forms of the scattering factor tables for the neutral atoms were used, and all scattering factors were corrected for both the real and imaginary components of anomalous dispersion.

Inspection of the residuals ordered in ranges of $(\sin \theta)/\lambda$, $|F_o|$, and parity and value of the individual indexes showed no unusual features or trends. The largest peak in the final difference Fourier map had an electron density of 1.22 e/Å^3 and the lowest excursion −0.34 e/Å^3. The largest peaks were located near the Ta and Ir atoms.

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Supplementary Material Available: X-ray diffraction data (complete tables of intramolecular bond distances and angles, anisotropic thermal parameters, and positional and isotropic thermal parameters for hydrogen atoms) for 2 (4 pages). This material is provided with the archival edition of this journal, available in many libraries. Alternatively, ordering information is given on any current masthead page.

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