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Synthesis and Reactivity of Ethyliridium Complexes. Reductive Elimination of C–H and H–H Bonds from an Ethyldihydridoiridium Complex

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Abstract: The reaction of $IrH_3(CO)(dppe)$ with C_2H_4 leads to the formation of C_2H_6 and $Ir(Et)(\eta^2\text{-}C_2H_4)(CO)(dppe)$. This unusual complex reacts with H_2 to form $IrH_2(Et)(CO)(dppe)$, in which the ethyl ligand and two hydride ligands are mutually cis. The kinetics of the competitive reductive eliminations of C_2H_6 and H_2 from $IrH_2(Et)(CO)(dppe)$ have been studied, and both reactions follow simple first-order kinetics. For the reductive elimination of C_2H_6, $E_{act} = 20.8 \pm 0.4$ kcal/mol, $\Delta H^* = 20.2 \pm 0.4$ kcal/mol, $\Delta S^* = -10.9 \pm 1.3$ cal/deg mol, and $\Delta G^*(298) = 23.4 \pm 0.8$ kcal/mol. For the reductive elimination of H_2, $E_{act} = 16.1 \pm 0.8$ kcal/mol, $\Delta H^* = 15.5 \pm 1.1$ kcal/mol, $\Delta S^* = -23.7 \pm 3.5$ cal/deg mol, and $\Delta G^*(298) = 22.6 \pm 2.1$ kcal/mol. The kinetic studies indicate that both reactions proceed through a simple unimolecular reductive elimination process, which has a highly ordered transition state. In the course of going through the conversions from $IrH_3(CO)(dppe)$ to $Ir(\eta^2\text{-}C_2H_4)(Et)(CO)(dppe)$, $IrH_2(Et)(CO)(dppe)$, and back to $IrH_3(CO)(dppe)$, C_2H_4 is hydrogenated. This is verified by a catalytic study under 150 Torr of C_2H_4 and 300 Torr of H_2 at 80 °C. The complex $IrH_2(Et)(CO)(dppe)$ is thus a rare example of an alkyldihydridometal complex that is directly involved in olefin hydrogenation.

There is currently a great deal of interest in the interactions of H–H and C–H bonds with transition-metal complexes, both in the activation of these bonds by oxidative addition and in their formation by reductive elimination from metal complexes.[1] These processes are of fundamental importance in homogeneous hydrogenation, hydroformylation, and other metal complex catalyzed transformations of organic compounds.[1]

While many advances have been made in understanding the mechanisms and factors controlling the activation of C–H and H–H bonds, much less is known about their reductive elimination from metal complexes, despite current activity in this area. In particular, little is known about the *relative* tendency for H–H and C–H reductive elimination from closely related systems, even though the ultimate success or failure of a catalytic hydrogenation or hydroformylation may rest upon these very processes. In order to gain information about this relative tendency, either (a) the reductive elimination of R–H and H–H from L_nMRH and L_nMH_2, respectively, to yield the same L_nM fragment must be studied or (b) the reductive elimination of H–H and R–H from the same MRH_2 complex must be studied. However, while good kinetic and mechanistic studies of H–H and C–H reductive elimination from metal complexes have appeared in the literature,[2-13] both reactions have not been studied for the same system.

The reductive elimination of H_2 from Vaska's dihydride complex, $IrH_2Cl(CO)(PPh_3)_2$, and its analogues has been fairly well documented,[2] but there are no reports of C–H reductive elimination from similar alkyl hydride species. The few reports of C–H reductive elimination from the related alkyl dihydride complexes, $IrH_2R(CO)(PMe_3)_2$ and $IrH_2R(CO)(PPh_3)_2$ (R = Me, Ph), do not include kinetic studies.[3]

Halpern[4] has discussed the kinetics of CH_4 and C_2H_6 reductive elimination from *cis*-$PtHR(PPh_3)_2$ where R = Me or Et, and Michelin et al. have reported on the elimination of CF_3CH_3 from *cis*-$PtH(CF_3CH_2)(PPh_3)_2$.[5] However, the elimination of H_2 from "*cis*-$PtH_2(PPh_3)_2$" has not been documented although Trogler has studied the analogous tertiary phosphine complexes, *cis*-$PtH_2(PR_3)_2$ where R = Me, Et.[6]

In important investigations of C–H activation, Bergman and Jones have independently studied the reductive elimination of C–H bonds from $Cp^*MHR(PMe_3)$ complexes (M = Ir, Rh; $Cp^* = \eta^5\text{-}C_5Me_5$; R = Me, Pr, C_6H_{11}, C_6H_5, etc.), but the thermal elimination of H_2 from the corresponding $Cp^*MH_2(PMe_3)$ complexes has not been reported to date.[7,8] In a study by Norton and co-workers, the reductive elimination of methane from $Cp_2WH(CH_3)$, $Cp = \eta^5\text{-}C_5H_5$, was studied kinetically between 70 and 96 °C,[9] but all that is stated about the related and well-known dihydride is that Cp_2WH_2 is stable toward H_2 loss up to 120 °C.[10]

In some cases, the reductive elimination of C–H bonds takes place by complex mechanisms. For example, the elimination of acetone from $RhH(CH_2C(O)CH_3)Cl(PMe_3)_3$ is preceeded by PMe_3 loss,[11] while involvement of the methyl groups of Cp^* is implicated in the reductive elimination of isobutane from $Cp^*_2ZrH(CH_2CHMe_2)$.[12] Studies by Norton have addressed the question of H–H vs C–H reductive elimination in the related complexes $OsH(CH_3)(CO)_4$ and $OsH_2(CO)_4$, but the systems were found to be mechanistically more complicated, proceeding by bimolecular processes.[13]

Previous reports from this laboratory have dealt with the chemistry of iridium complexes containing a single dppe ligand (dppe = $Ph_2PCH_2CH_2PPh_2$). These studies have dealt with the oxidative addition of H_2, HX, and R_3SiH to the complexes $IrX(CO)(dppe)$ where X = Cl, Br, I, H, and CN and the reaction chemistry of $IrH_3(CO)(dppe)$ leading to the photochemical carbonylation of benzene.[14] In this paper, we describe the chemistry of iridium ethyl complexes containing dppe including

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Table I. Selected ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR Spectroscopic Data[a]

complex	δ (H$^-$)	J_{H-P}	J_{H-C}[b]	δ (P)	J_{P-P}	J_{P-C}[c]	δ (C)[d]	J_{C-P}[e]
$IrH_3(CO)(dppe)$[f] (**1**)	−9.474	124, −12	5	30.85		3	178.24	4, 4
	−10.855	19, 19	36					
$IrEt(C_2H_4)(CO)(dppe)$ (**2**)				29.07	5	17	186.27	17, 6
				26.96		6		
$IrH_2(Et)(CO)(dppe)$ (**3**)	−8.663	140, 13	4	28.30	7	3	180.37	3, 3
	−9.422	20, 20	40	27.28		3		
$IrH(CO)_2(dppe)$[f]	−10.343	41, 41	6	33.82		13	183.46[g]	13
$IrBr(CO)(dppe)$[f]				48.01	14	122	184.93	122, 10
				43.79		10		
$IrH_2Br(CO)(dppe)$[f]	−7.857	152, 14	4	35.82	6	3	174.2	4, 4
(kinetic)	−8.928	19, 19	47	12.88		5		
$IrH_2Br(CO)(dppe)$[f]	−8.332[h]	133, 17	6	33.84	6	122	174.39[i]	121, 6
(thermodynamic)	−17.475	17, 9	6	26.66		6		

[a] ^1H, ^{31}P, and ^{13}C NMR spectra recorded at 400, 162, and 75 MHz, respectively, in C_6D_6. ^1H and ^{13}C chemical shifts reported in ppm downfield from Me_4Si, measured relative to C_6D_6 at δ 7.15 and 128, respectively. ^{31}P chemical shifts reported in ppm downfield from external H_3PO_4. Coupling constants are in hertz. [b] Observed in ^1H NMR spectra of ^{13}CO-labeled complexes. [c] Observed in ^{31}P NMR spectra of ^{13}CO-labeled complexes. [d] ^{13}C NMR of ^{13}CO-labeled complexes. [e] Observed in ^{13}C NMR spectra of labeled complexes. [f] Some data from ref 20a–c. [g] $J_{C-H} = 6$ Hz observed in the hydride-coupled ^{13}C NMR spectrum. [h] $^2J_{H-H} = 5$ Hz. [i] $^2J_{C-H} = 6.6$ Hz observed in hydride-coupled ^{13}C NMR spectrum.

the formation of an ethyl dihydride complex, which permits competitive H–H and C–H reductive eliminations to be studied.[15]

Results

Reaction of $IrH_3(CO)(dppe)$ with C_2H_4. The trihydride complex $IrH_3(CO)(dppe)$ (**1**) was found to react with excess C_2H_4 in benzene to form C_2H_6 and very pale yellow solutions of a new complex, **2**. On the basis of the spectroscopic characterization outlined below and of the identity and characterization of related complexes to be reported separately,[15] complex **2** is the ethyl ethylene complex $Ir(Et)(\eta^2\text{-}C_2H_4)(CO)(dppe)$, Et = $\sigma\text{-}C_2H_5$. Spectroscopic data for **2** and other complexes are listed in Table I. The reaction of **1** with C_2H_4, eq 1, is complete in 30–60 min at 70 °C and appears essentially quantitative based upon ^1H NMR spectroscopy. The same reaction also occurs over a period of days at 25 °C in the dark.

$$\underset{\mathbf{1}}{IrH_3(CO)(dppe)} \xrightarrow[\Delta,\ C_6D_6]{C_2H_4} \underset{\mathbf{2}}{Ir(Et)(\eta^2\text{-}C_2H_4)(CO)(dppe)} + C_2H_6 \quad (1)$$

The aromatic region of the ^1H NMR spectrum of **2** contains three distinct resonances downfield from residual C_6D_5H in the C_6D_6 solvent (δ 7.15). The cleanliness of this region, usually containing the *o*-phenyl protons of the dppe ligand,[14a–d] indicates that the reaction, eq 1, produces a single iridium complex with inequivalent phenyl groups on the dppe ligand. The aliphatic region of the ^1H NMR spectrum is somewhat complex, containing a number of overlapping resonances and a few broad resonances belonging to the ethylene bridge of dppe, the ethyl group, and the $\eta^2\text{-}C_2H_4$ ligand. The broad resonances (δ 1.73, 1.526, 0.901, 0.462, and 0.082) integrate as 1 H each whereas the three *o*-phenyl resonances integrate as 2 H each. These results support the proposal that only a single new iridium complex is formed in eq 1, but they provide little additional information about the exact nature of the complex.

A series of isotope labeling studies using C_2H_4 and C_2D_4 was performed in order to analyze more thoroughly the assignment of the resonances between δ 2.5 and 0.0 for **2**; see Figure 1. When a solution of **1** was heated with C_2D_4 (70 °C, $^1/_2$ h), only four broad multiplets remained in the methylene region of the ^1H NMR spectrum, Figure 1a, and they are assigned to the ethylene bridge of the dppe ligand. It should be noted that no methyl proton from a C_2HD_4 ligand was observed in this complex, **2**-d_9. When excess C_2D_4 was removed from this solution by two freeze/pump/thaw cycles at −78 °C and the sample exposed to C_2H_4, four more broad resonances (1 H each) appeared within 4 min to give **2**-d_5, Figure 1b. These four resonances (δ 2.117, 2.01, 0.901, and 0.462) are therefore assigned to a $\eta^2\text{-}C_2H_4$ ligand, while the remaining three

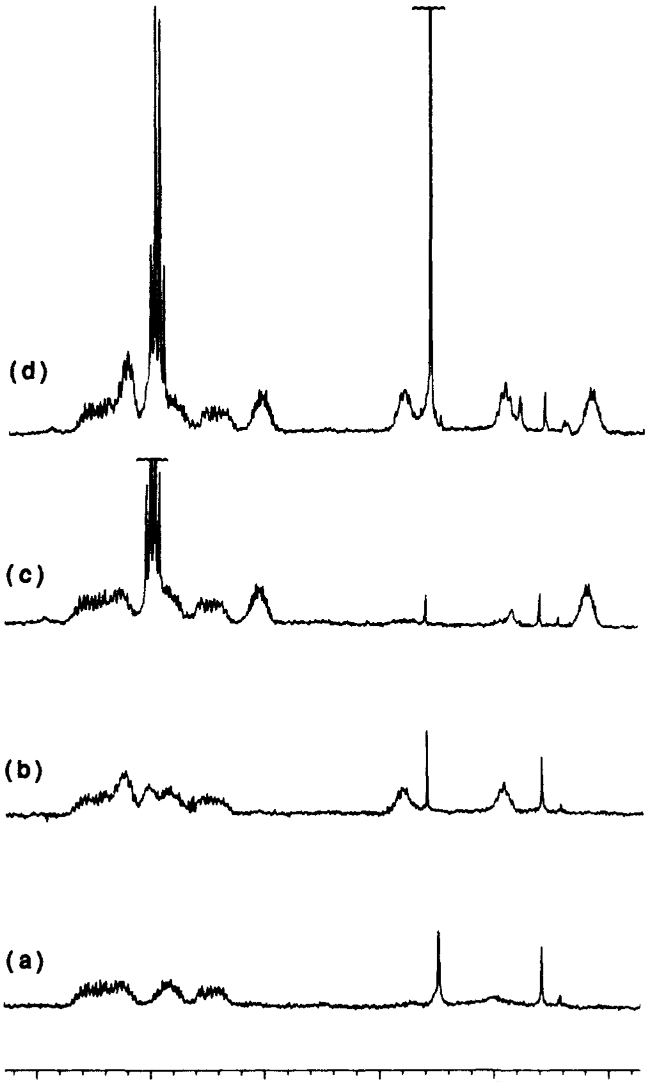

Figure 1. ^1H NMR spectrum (400 MHz) of aliphatic region of $Ir(\sigma\text{-}C_2H_5)(\eta^2\text{-}C_2H_4)(CO)(dppe)$-$d_n$ complexes, **2**-d_n, containing $\sigma\text{-}C_2D_5$ and/or $\pi\text{-}C_2D_4$ groups. (a) **2**-d_9 produced from the reaction of $IrH_3(CO)(dppe)$ (**1**) with C_2D_4. (b) **2**-d_5 produced from exposure of **2**-d_9 to C_2H_4 for 5 min. (c) **2**-d_4 produced from exposure of **2**-d_0 to C_2D_4 for 5 min. (d) **2**-d_0 produced from the reaction of **1** with C_2H_4.

resonances (δ 1.985, 1.526, and 0.82; 3 H, 1 H, and 1 H, respectively) are assigned to a σ-ethyl ligand. The converse reaction, removal of excess C_2H_4 from a sample of **2**-d_0 (Figure 1d) followed by exposure of the solution to C_2D_4, supported these assignments.

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(15) Related reactions that form propionyl and propionyldihydride complexes will be reported separately.

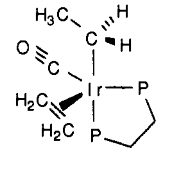
The observation of four distinct resonances for the η^2-C_2H_4 ligand of **2** indicates that this ligand is not undergoing any type of rapid rotation or exchange process.[16] In addition, the methylene protons of the ethyl group, σ-CH_2CH_3, are diastereotopic and resonate at significantly different frequencies.[17] Over a period of days the intensity of all of the resonances assigned to the η^2-C_2H_4 and Et ligands reached an equilibrium value based upon the relative amounts of C_2H_4 and C_2D_4 present in the NMR tube. Throughout all of these C_2H_4/C_2D_4 exchange studies, the phenyl region of the ^1H NMR spectrum remained unchanged.

A similar correlation of the resonances attributed to the η^2-C_2H_4 and Et groups was observed through selective decoupling experiments. When either the δ 0.082 or 1.526 resonances were irradiated, the quartet at δ 1.985 collapsed into a triplet, while irradiation of the resonance at δ 1.985 produced some sharpening of the former two multiplets. Similar decoupling experiments showed that the resonances at δ 2.117, 0.901, and 0.462 were coupled to one another. Continuous irradiation of the resonance due to free C_2H_4 (δ 5.24) caused a decrease in the intensity of the δ 2.117, 0.901, and 0.462 resonances.

Because the CH_3 resonances of the ethyl group of **2** appeared as a quartet at δ 1.985 rather than the expected triplet, a $^1H\{^{31}P\}$ NMR study was done to identify the extra coupling. In the $^{31}P\{^1H\}$ NMR spectrum of **2**, two sharp doublets were observed at δ 29.069 and 26.958 (J_{P-P} = 5 Hz). When the $^1H\{^{31}P\}$ NMR spectrum was recorded with selective decoupling of the δ 29.069 resonance, the two *o*-phenyl resonances at δ 7.857 and 7.357, which normally appear as unresolved doublets of doublets, collapsed into simple doublets, while the region from δ 2.5 to 0.0 appeared essentially unchanged. Likewise, when the $^1H\{^{31}P\}$ NMR spectrum was recorded with selective decoupling of the δ 26.958 resonance, the *o*-phenyl resonance at δ 7.652 collapsed into a doublet and the quartet at δ 1.985 collapsed into a triplet. These results demonstrate conclusively that the extra coupling observed in the CH_3 resonance of **2** is due to long-range coupling, $^4J_{P-H}$.[18]

The NMR and IR spectroscopic data for **2** not only indicate the presence of the Et, η^2-C_2H_4, CO, and dppe ligands but also give insight into the stereochemistry and solution structure of the complex. Ir(Et)(η^2-C_2H_4)(CO)(dppe) can be considered a five-coordinate d^8 Ir^I species, most likely adopting a trigonal-bipyramidal geometry.[19] The dppe ligand cannot easily span two equatorial positions and must therefore occupy one axial site and one equatorial site.[20] The $^2J_{P-C}$ couplings observed in the ^{31}P and ^{13}C NMR spectra of ^{13}CO-enriched **2** help to determine the relative disposition of phosphine and carbonyl ligands since $^2J_{P-M-C}$(trans) is usually greater than $^2J_{P-M-C}$(cis).[21] This is especially applicable when $^2J_{P-C}$ is known for similar, characterized complexes (Table I). In **2**, the smaller coupling (6 Hz to phosphorus at δ 26.958) is in the range for cis coupling in octahedral complexes, whereas the larger coupling (17 Hz to phosphorous at δ 29.069) is comparable to that observed in the fluxional complex $IrH(CO)_2$(dppe), 13 Hz. Trans coupling in similar square-planar Ir^I or octahedral Ir^{III} complexes is much larger, >120 Hz.

As noted above, the CH_3 protons of the ethyl ligand exhibit an extra coupling due to $^4J_{P-H}$, suggesting that the Et ligand is trans to a phosphine. This analysis would then place the η^2-C_2H_4 ligand in an equatorial position, and yield the proposed static structure for **2** in solution shown as A. Theoretical studies suggest



A

that good σ-donor ligands prefer to occupy axial sites in d^8 trigonal-bipyramidal complexes whereas strong π-acceptor ligands prefer equatorial positions.[22] These studies further suggest that the C–C bond of olefins would prefer to lie in the equatorial plane, maximizing back-bonding from the metal. The structure for **2** is drawn as a regular trigonal bipyramid with a simple Dewar–Chatt–Duncanson η^2-C_2H_4 ligand.[22a] An alternative description, which is less appealing based on the reaction chemistry and spectroscopic data, is that of an Ir^{III} octahedral complex with the η^2-C_2H_4 ligand having metallocyclopropane character.[22a]

Slow decomposition of **2** took place when samples of **2** in C_6D_6 were put through a series of freeze/pump/thaw cycles at −10 °C. A small amount of **1** was identified among the decomposition products.

When the reaction of **1** with C_2H_4 was examined at early reaction times, t = 5 or 10 min, the ^1H NMR spectrum showed the presence of **2**, unreacted **1**, and another complex **3** containing two hydride resonances at δ −8.663 (dd; J_{P-H} = 140, 13 Hz) and δ −9.422 (t; J_{P-H} = 20 Hz). The nature of this complex is discussed below.

Reaction of 2 with H_2. Benzene solutions of Ir(Et)(η^2-C_2H_4)(CO)(dppe) (**2**) undergo a rapid reaction with H_2 to liberate ethylene and produce a new species in solution, **3**, which is proposed to be IrH_2(Et)(CO)(dppe) on the basis of spectroscopic characterization. This complex, **3**, forms from **2** in less than 5 min and is identical with the species observed at early times in the reaction of **1** with C_2H_4. Formation of IrH_3(CO)(dppe) also occurs to some extent in this reaction, shown as eq 2.

$$\underset{\mathbf{2}}{\mathrm{Ir(Et)}(\eta^2\text{-}\mathrm{C_2H_4})\mathrm{(CO)(dppe)}} + \mathrm{H_2} \rightarrow \underset{\mathbf{3}}{\mathrm{IrH_2(Et)(CO)(dppe)}} + \mathrm{C_2H_4} \quad (2)$$

The ^1H NMR spectrum of **3** contains two hydride resonances, δ −8.663 (dd; J_{P-H} = 140, 13 Hz) and δ −9.422 (t; J_{P-H} = 20 Hz). The coupling patterns observed in these hydrides indicate that one hydride (δ −8.663) is trans to one phosphorus nucleus while the other hydride (δ −9.422) is cis to two phosphines.[21,23,24] In addition to the two hydride resonances, the ^1H NMR spectrum of **3** shows four distinct *o*-phenyl resonances (2 H each), a broad resonance at δ 2.45 (4 H), and two broad multiplets at δ 2.2 and 1.9 (5 H total). In order to assign these aliphatic resonances, deuterium labeling was again used. When **2**-d_9 was reacted with H_2, the δ 2.45 resonance was absent and the two multiplets were somewhat cleaner and integrated to 4 H. The two multiplets in the spectrum of **2**-d_9 therefore arise from the ethylene bridge of the dppe ligand. The δ 2.45 resonance appears to arise from the terminal methyl group of the Et ligand and from one of the two diastereotopic methylene protons also from this ligand. The other methylene proton resonance was situated under the dppe $-CH_2-$ proton resonances, judging from the integration difference.

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[18] We are aware of no other transition-metal complexes in which $^4J_{P-H}$ has been documented. However, such long-range coupling has been observed in some organophosphorus compounds. See: Bentrude, W. G.; Setzer, W. N. In *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*; Verkade, J. G., Quin, L. D., Eds.; VCH Publishers: Deerfield, FL, 1987; Chapter 11.

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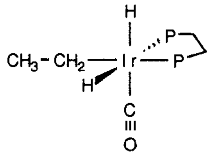
A colorless benzene-d_6 solution of **3** contained two infrared absorptions between 2200 and 1500 cm^{-1}, ν_{CO} = 1964 cm^{-1} and ν_{Ir-H} = 2071 cm^{-1}, whereas a solution of **3**-d_2 formed by the reaction of **2** with D_2 showed only one resonance in the same region, ν_{C-O} = 2000 cm^{-1} (ν_{Ir-D} were not located). The coupling observed between ν_{C-O} and ν_{Ir-H} in **3** indicates that these two groups are trans to one another.[23,25,26] The coupling patterns observed in the ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectra of **3**–^{13}CO, prepared from the reaction of **2**–^{13}CO with H_2, support the notion that the carbonyl ligand is trans to a hydride and cis to both phosphines.[21,24]

The structure of $IrH_2(Et)(CO)(dppe)$ (**3**), determined from the aforementioned spectroscopic data, is shown as B and contains



B

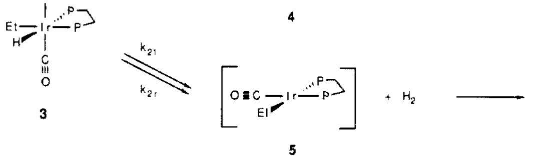
a facial arrangement of the ethyl and two hydride ligands. The stereochemistry about the metal center is thus the same as that observed in the kinetic products of H_2 oxidative addition to other $IrX(CO)(dppe)$ complexes.[14]

$IrH_2(Et)(CO)(dppe)$ (**3**) was not stable in solution and slowly decomposed under excess H_2 to produce $IrH_3(CO)(dppe)$ and C_2H_6, eq 3.[27] When the same reaction was performed using D_2,

$$\underset{\mathbf{3}}{IrH_2(Et)(CO)(dppe)} \xrightarrow[C_6D_6,\ RT]{H_2} \underset{\mathbf{1}}{IrH_3(CO)(dppe)} + C_2H_6 \quad (3)$$

it was observed that some incorporation of D_2 into **3** occurred *prior* to reductive elimination of ethane, suggesting competitive elimination of H_2. Moreover, the formation of some H/D was also observed. These two reductive elimination pathways from **3** leading to ethane and H_2 proved to be amenable for kinetic and mechanistic studies.

Kinetics of Reductive Elimination of H_2 and C_2H_6 from $IrH_2(Et)(CO)(dppe)$. Two different reductive eliminations from $IrH_2(Et)(CO)(dppe)$ are possible due to the mutually cis disposition of the ethyl and two hydride ligands in the complex. These reductive elimination reactions can give rise to either H_2 or C_2H_6, eq 4. Because of the relatively rarity of alkyldihydride complexes,[3,28-30] and the opportunity that the present system offers regarding relative tendency for reaction, the competitive ethane and H_2 reductive elimination reactions were studied in detail.



The overall rate equation for eq 4 is shown in eq 5.[31] To obtain the rate constant for the reductive elimination of C_2H_6, k_1, reactions were performed under an excess of H_2. Under these reaction conditions, no complex such as **5** or a secondary product arising from **5** is observed and a steady-state approximation for [**5**] can be used. This leads to eq 6 and the integrated rate law, eq 7.

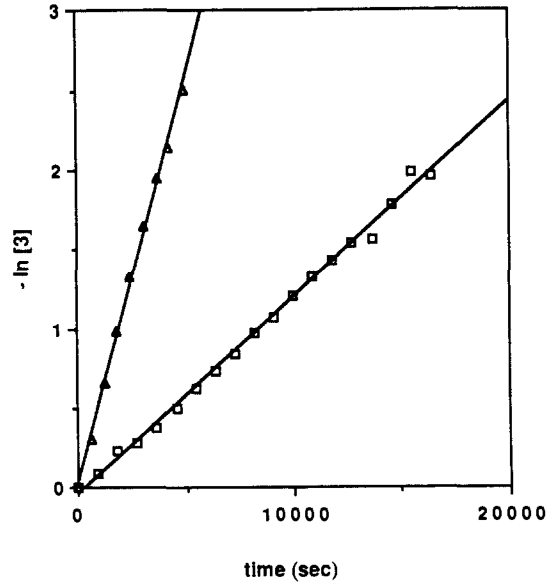


Figure 2. Kinetic data for reductive elimination of C_2H_6 (□) and C_2H_6 + H_2 (△) from **3** at 307.8 K.

Table II. Rate Constants for the Reductive Elimination of C_2H_6 and H_2 from $IrH_2(Et)(CO)(dppe)$ (**3**)[a]

temp, K	$k_1 \times 10^4$, s^{-1}	$k_{obs} \times 10^4$, s^{-1}	$k_{2f} \times 10^4$, s^{-1}
290.9	0.177 ± 0.002	1.09 ± 0.03	0.91 ± 0.03
298.8	0.431 ± 0.005	2.40 ± 0.09[b]	1.97 ± 0.10[c]
307.8	1.239 ± 0.019[d]	5.10 ± 0.10[e]	3.86 ± 0.12
316.7	3.328 ± 0.086	12.69 ± 0.16	9.36 ± 0.25

[a] Reaction conditions: [**3**] = 10 mM in C_6D_6, and 700 Torr of H_2 or D_2 added at 77 K. Values are least-squares fits of lines from plots of ln [**1**] vs time.[31,32] Errors (1 standard deviation) according to ref 32. [b] Using CO instead of D_2 gives k_{obs} = (2.58 ± 0.07) × 10^{-4} s^{-1}. [c] From CO reaction, k_{2f} = (2.15 ± 0.08) × 10^{-4} s^{-1}. [d] With [**3**] = 2.5 mM, k_1 = (1.269 ± 0.065) × 10^{-4} s^{-1}. Using only 175 Torr of H_2 added at 77 K, k_1 = (1.117 ± 0.034) × 10^{-4} s^{-1}. At 309.2 K, k_1 = (1.355 ± 0.013) × 10^{-4} s^{-1}.

$$-d[\mathbf{3}]/dt = (k_1 + k_{2f})[\mathbf{3}] - k_{2r}[H_2][\mathbf{5}] \quad (5)$$

$$-d[\mathbf{3}]/dt = k_1[\mathbf{3}] \quad (6)$$

$$-\ln([\mathbf{3}]/[\mathbf{3}]_0) = k_1 t \quad (7)$$

The reductive elimination of C_2H_6 from $IrH_2(Et)(CO)(dppe)$ (**3**) under an excess of H_2 was followed by ^1H NMR spectroscopy over a 26 °C temperature range, T = 17.8–43.6 °C. The decay of the hydride resonances from **3** and the growth of hydride resonances from the **1** product follow simple first-order kinetics.[31] Plots of $-\ln([\mathbf{3}]/[\mathbf{3}]_0)$ vs time are linear for at least 2 and up to 4 half-lives. Some of the kinetic data are shown in Figure 2, and the observed rate constants, k_1, are listed in Table II.[32] The rate constant for C_2H_5–H elimination from **3**, k_1, at 307.8 K is (1.239 ± 0.019) × 10^{-4} s^{-1} for a 10 mM C_6H_6 solution of **3** under 700 Torr of H_2 at 77 K. The rate constant was not significantly affected by changing the concentration of **3** or the pressure of H_2. The reductive elimination of C_2H_5–D from $IrD_2(Et)(CO)(dppe)$ (**3**-d_2) occurs with a k_1 of (0.516 ± 0.005) × 10^{-4} s^{-1}, giving k_H/k_D = 2.4 ± 0.1 for ethane elimination from **3**.

The reaction was performed under D_2 in order to obtain the rate constant for H_2 elimination, k_{2f}. Under the conditions used, any **5** that formed would react with D_2 to give **3**-d_2, thereby eliminating the reverse reaction to regenerate **3**-d_0 via the k_{2r} path.

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(26) Vaska, L. *J. Am. Chem. Soc.* **1966**, *88*, 4100–1.

(27) The hydrogenation of C_2H_4 by **1** was confirmed by a catalytic study under 150 Torr of C_2H_4 and 300 Torr of H_2 at 80 °C in a sealed tube containing 0.4 mL of a 5-mmol C_6D_6 solution of **1**. NMR spectroscopy revealed an initial reaction rate of ~2 mmol/h of C_2H_6 per mmol of **1**, with a total of 10 turnovers in 18 h and regeneration of **1**. Deutsch and Eisenberg, unpublished results.

(28) Hirsekorn, F. J.; Rakowski, R. C.; Muetterties, E. L. *J. Am. Chem. Soc.* **1975**, *97*, 237–8.

(29) Strope, D.; Shriver, D. F. *J. Am. Chem. Soc.* **1973**, *95*, 8197–8.

(30) Longato, B.; Bresadola, S. *Inorg. Chem.* **1982**, *21*, 168–73.

(31) Atwood, J. D. *Inorganic and Organometallic Reaction Mechanisms*; Brooks/Cole: Monterey, CA, 1985.

(32) Unweighted least-squares fit of straight line with error analysis (1 standard deviation) from algorithms in: Bevington, P. R. *Data Reduction and Error Analysis for the Physical Sciences*; McGraw-Hill: New York, 1969; Chapter 6, pp 117–8.

Table III. Activation Parameters for Reductive Elimination of C_2H_6 and H_2 from **3**[a]

activation param	C_2H_5–H elimination	H–H elimination
E_{act}, kcal/mol	20.8 ± 0.4	16.1 ± 0.8
$\Delta H^{\ddagger}$, kcal/mol	20.2 ± 0.4	15.5 ± 1.1
$\Delta S^{\ddagger}$, cal/deg mol	−10.9 ± 1.3	−23.7 ± 3.5
$\Delta G^{\ddagger}_{(298)}$, kcal/mol	23.4 ± 0.8	22.5 ± 2.1

[a] Using data from reactions with [**3**] = 10 mM in C_6D_6, and 700 Torr of H_2 or D_2 added at 77 K. Values are from least-squares fits of Arrhenius and Eyring plots according to ref 31 and 32. Errors are 1 standard deviation.[32]

The rate equation for the disappearance of **3** under D_2 is shown in eq 8, and the integrated law is given by eq 9. Since k_1 was obtained directly from the previous experiments under H_2, k_{2f} can be calculated.

$$-d[\mathbf{3}]/dt = (k_1 + k_{2f})[\mathbf{3}] \qquad (8)$$

$$-\ln [\mathbf{3}]/[\mathbf{3}]_0 = (k_1 + k_{2f})t \qquad (9)$$

The reductive elimination of H_2 from **3** under D_2 was monitored by ^1H NMR spectroscopy over the same 26 °C temperature range as before. The decay of the hydride resonances of $IrH_2(Et)(CO)(dppe)$ under D_2 followed first-order kinetics. Plots of $-\ln([\mathbf{3}]/[\mathbf{3}]_0)$ vs time were again found to be linear for at least 2 half-lives, provided that the sample was shaken regularly to prevent a buildup of H_2 in solution. Some of these kinetic data are shown in Figure 2, and the observed rate constants, k_{obs}, are listed in Table II. The observed rate constant in these experiments, k_{obs}, is equal to the sum of the individual rate constants k_1 and k_{2f}. The values for k_{obs} and k_{2f} for H_2 elimination from **3** at 307.8 K are (5.10 ± 0.10) × 10^{-4} and (3.86 ± 0.12) × 10^{-4} s^{-1}, respectively, whereas k_{obs} and k_{2f} for D_2 elimination from $IrD_2(Et)(CO)(dppe)$ are (2.89 ± 0.17) × 10^{-4} and (2.37 ± 0.29) × 10^{-4} s^{-1}, respectively (determined from the reaction of $IrD_2(Et)(CO)(dppe)$ with H_2). These values give k_H/k_D = 1.6 ± 0.2 for H_2 elimination from **3**.

A reaction was performed under a CO atmosphere in order to double check the reductive elimination of H_2 from **3**. The decay of the hydride resonances of **3** again followed first-order kinetics, with k_{obs} under CO similar to k_{obs} observed under D_2. The reaction was also performed under a ^{13}CO atmosphere, and it was observed that no incorporation of ^{13}CO into **3** occurred *prior* to H_2 or C_2H_6 elimination.

Activation parameters for the reductive elimination of C_2H_6 and H_2 from **3** were determined from the temperature dependence of the rate constants k_1 and k_{2f}, respectively.[31] Arrhenius plots (ln *k* vs 1/*T*) were linear and gave values for E_{act} listed in Table III. Eyring plots (ln (*k*/*T*) vs 1/*T*) were also linear, with values for $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ shown in Table III. While E_{act} and $\Delta H^{\ddagger}$ are in the expected range for this type of reaction, $\Delta S^{\ddagger}$ is more negative for both of the reductive elimination reactions than might have been expected (see Discussion).

Discussion

Reaction of $IrH_3(CO)(dppe)$ with C_2H_4. Formation of $Ir(Et)(\eta^2\text{-}C_2H_4)(CO)(dppe)$ (2). A reaction occurs between $IrH_3(CO)(dppe)$ (**1**) and C_2H_4 in solution to produce ethane and $Ir(Et)(\eta^2\text{-}C_2H_4)(CO)(dppe)$ (**2**). This reaction occurs over 1 h at 70 °C or over a few days at room temperature and produces **2** essentially quantitatively, based upon NMR spectroscopy. While the reaction can be scaled up, attempts to isolate the complex have been unsuccessful. Support for the formulation of **2** comes from both spectroscopic characterization and subsequent reaction chemistry.

The ^1H NMR spectra of **2** and its deuterated analogues provide the strongest spectroscopic evidence for the formulation as $Ir(Et)(\eta^2\text{-}C_2H_4)(CO)(dppe)$. In reactions of **2** with C_2H_4 or C_2D_4, four ^1H NMR spectral resonances, which integrate as 1 H each, under rapid exchange with free C_2H_4 or C_2D_4, leading to their assignment as part of a η^2-olefin type ligand. The fact that there are four separate and distinct resonances indicates that the ligand is not undergoing rapid rotation or exchange with free ethylene on the ^1H NMR time scale. The exchange with free olefin, which occurs over the course of minutes, is likely what causes the difficulty in isolation of this complex. Three other resonances integrating as 3 H, 1 H, and 1 H appear in the ^1H NMR spectrum of **2**, and their coupling to one another leads to their assignment as an Et group. The diastereotopic nature of the methylene protons of this ethyl ligand and the $^4J_{P-H}$ coupling observed in the methyl protons of the ethyl group add to the interesting nature of the complex. The ^{13}C and ^{31}P NMR spectra of **2** aided in determining the stereochemistry of the ligands about the metal center, and with the ^1H NMR data, indicate that $Ir(Et)(\eta^2\text{-}C_2H_4)(CO)(dppe)$ adopts a fairly rigid solution structure. Some metallocyclopropane character in the coordination of the $\eta^2\text{-}C_2H_4$ ligand may be the reason why **2** maintains a rigid solution structure. The spectroscopic data are best accommodated by a trigonal-bipyramidal arrangement of ligands about an Ir^I center, shown earlier as A.

The formation of $Ir(\eta^2\text{-}C_2H_4)(Et)(CO)(dppe)$ from $IrH_3(CO)(dppe)$ and C_2H_4 undoubtedly occurs via a multistep sequence, eq 10–13, involving reductive elimination of H_2, ethylene

$$IrH_3(CO)(dppe) \underset{}{\overset{H_2}{\rightleftharpoons}} [IrH(CO)(dppe)] \qquad (10)$$

$$[IrH(CO)(dppe)] \overset{C_2H_4}{\rightleftharpoons} [IrH(\eta^2\text{-}C_2H_4)(CO)(dppe)] \qquad (11)$$

$$[IrH(\eta^2\text{-}C_2H_4)(CO)(dppe)] \rightleftharpoons [Ir(Et)(CO)(dppe)] \qquad (12)$$

$$[Ir(Et)(CO)(dppe)] \overset{C_2H_4}{\rightleftharpoons} Ir(\eta^2\text{-}C_2H_4)(Et)(CO)(dppe) \qquad (13)$$

addition and insertion, and addition of a second ethylene molecule. The fact that **2** forms only slowly at room temperature but rapidly at elevated temperatures (>50 °C) is consistent with the fact that $IrH_3(CO)(dppe)$ undergoes H_2 exchange rapidly at elevated temperatures and only slowly at room temperature. While none of the intermediates in eq 10–13 are observed, precedents for each species exist.

For example, a number of stable unsaturated monohydride complexes similar to the proposed [IrH(CO)(dppe)] are known, including $RhH(PPh_3)_3$,[33] $PdHX(PR_2)_2$, and $PtHX(PR_2)_2$ (X = halogen, alkyl, or aryl group, etc.; R = alkyl or aryl groups).[34] Indeed, monohydride complexes of this type are frequently proposed as intermediates in catalytic hydrogenation, hydroformylation, and hydrosilation reactions.[35] These intermediates are proposed to form in situ from MHL_nL' complexes by thermal or photochemically induced ligand dissociation to give unsaturated $[MHL_n]$ species.

While the hydrido–olefin intermediate, $[IrH(\eta^2\text{-}C_2H_4)(CO)(dppe)]$, is also not observed, precedent for this species is given by numerous hydrido–olefin complexes in the literature. Perhaps the closest analogues are the olefin complexes of the type $IrH(RCH{=}CHR')(CO)(PPh_3)_2$, (R = H, R′ = Ph, CN, COOMe; R = Ph, R′ = CN, COOH; R = R′ = CN, COOMe, COOH; etc.).[36] A single-crystal X-ray structure determination of $IrH(\textit{trans}\text{-}NCCH{=}CHCN)(CO)(PPh_3)_2$ shows the complex to be trigonal bipyramidal, with the hydride and carbonyl ligands in axial positions and the C=C bond of the fumaronitrile ligand in the equatorial plane.[36e] Spectroscopic data for the other $IrH(olefin)(CO)(PPh_3)_2$ complexes indicate that they have a similar geometry.[36a–d] Some related platinum complexes, $PtH(SnCl_3)(C_3H_7CH{=}CHC_3H_7)(PPh_3)_2$ and $PtH(CN)((NC)_2C{=}C(CN)_2)(PEt_3)_2$, also adopt the same geometry.[37]

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(33) Dewhirst, K. C.; Keim, W.; Reilly, C. A. *Inorg. Chem.* **1968**, *7*, 546–61.

(34) See: Moore, D. S.; Robinson, S. D. *Chem. Soc. Rev.* **1983**, *12*, 415–52, and references therein.

(35) See discussions of involvement of M–H in catalytic reactions in: Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, J. R. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; Chapters 10–12.

(36) (a) Drouin, M.; Harrod, J. F. *Inorg. Chem.* **1983**, *22*, 999–1001. (b) Drouin, M.; Harrod, J. F. *Can. J. Chem.* **1985**, *63*, 353–60. (c) Baddley, W. H.; Fraser, M. S. *J. Am. Chem. Soc.* **1969**, *91*, 3661–3. (d) Baddley, W. H.; Fraser, M. S. *J. Organomet. Chem.* **1972**, *36*, 377–87. (e) Muir, K. W.; Ibers, J. A. *J. Organomet. Chem.* **1969**, *18*, 175–87.

(37) (a) Tayim, H. A.; Bailar, J. C., Jr. *J. Am. Chem. Soc.* **1967**, *89*, 4330–8. (b) Uguagliati, P.; Baddley, W. H. *J. Am. Chem. Soc.* **1968**, *90*, 5446–52.

The rapid ethylene insertion into the Ir–H bond of [IrH(η^2-C_2H_4)(CO)(dppe)] to give [Ir(Et)(CO)(dppe)] is also well precedented in olefin insertions into M–H bonds, and a number of ethyl complexes resulting from ethylene insertion are known. Most relevant to the present work are the formation of *trans*-Pt(Et)X-$(PEt_3)_2$ (X = Cl, Br, CN)[38] and Rh(C_2F_4H)(CO)$(PH_3)_2$[39] and the spectroscopic observation of IrEt(CO)$(PPh_3)_2$,[40] RhEtCl_2-$(PPh_3)_2$,[40] and RuEtCl$(PPh_3)_3$.[38a] Analogous complexes such as IrR(CO)$(PR'_3)_2$ (R = Me, Ph; R' = Me, Ph) that cannot undergo the reverse reaction, β-elimination, have also been prepared.[41]

In the present system, the [Ir(Et)(CO)(dppe)] species is not stable under the reaction conditions and quantitatively forms the ethylene adduct Ir(η^2-C_2H_4)(Et)(CO)(dppe) (**2**). This complex is somewhat unusual, but other alkyl–olefin complexes are known, including Ir(CH_3CHCN)($CH_2{=}CHCN$)(CO)$(PPh_3)_2$,[36b] Rh-(MeC$(CH_2PPh_2)_3$)(η^2-C_2H_4)(Et),[42] Cp_2M(η^2-C_2H_4)(Et) [M = Nb, Ta],[43] (η^5-C_5Me_5)Nb(η^2-C_2H_4)(Et),[44] and CpRh-(PMe_3)(η^2-C_2H_4)(Et).[45] Some of the most interesting examples of this type of complex are the alkyl–olefin complexes of Brookhart and others, which contain agostic protons.[46]

There is experimental evidence that supports the reversibility of all of the reaction steps in eq 10–13. Both the reactions of **2** with H_2 and C_2D_4 indicates that the formation of the ethylene adduct is rapidly reversible. Since **2** is a coordinatively saturated complex, this most likely happens by a dissociative mechanism involving [Ir(Et)(CO)(dppe)]. The slow decay of the ethyl resonances of **2** when exposed to C_2D_4 also indicates that the reaction is reversible all the way back to [IrH(CO)(dppe)].

When the reaction of IrH_3(CO)(dppe) with C_2H_4 was stopped early, it was noticed that some of **3** was present in solution in addition to **2** and unreacted **1**. The observation of **3** at this early reaction time does not mean that it is an intermediate on the path to formation of **2**. Since the first step in the formation of **2** is reductive elimination of H_2 from **1**, some free H_2 is initially present in solution, which can compete effectively with free C_2H_4 to trap out [Ir(Et)(CO)(dppe)], thereby forming **3**. The ethane observed in solution is the result of reductive elimination from **3**. This reductive elimination also produces [IrH(CO)(dppe)], which then goes on to form **2**. The formation of **3** therefore occurs to remove the H_2 produced in the initial step of the reaction sequence and leads to stoichiometric hydrogenation of ethylene as part of eq 1.

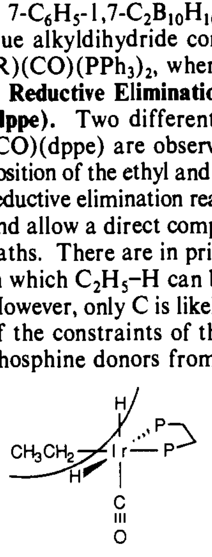
Formation of IrH_2(Et)(CO)(dppe) (3). A rapid reaction occurs when solutions of **2** are exposed to hydrogen, this reaction resulting in the liberation of free C_2H_4 and the formation of a new complex **3**. This new complex is identified as IrH_2(Et)(CO)(dppe) on the basis of the spectroscopic characterization outlined above. The formulation of **3** is also supported by the formation of C_2H_6 and IrH_3(CO)(dppe) in subsequent reaction.

The stereochemistry of IrH_2(Et)(CO)(dppe) was deduced solely from the spectroscopic data, with J_{P-H} coupling constants indicating the relative positions of the two hydride and two phosphine groups. The coupling between ν_{C-O} and ν_{Ir-H} in the infrared spectrum also shows that the carbonyl group is trans to a hydride ligand. This is further supported by $^2J_{C-H}$ and $^2J_{C-P}$ in the ^1H, ^{31}P, and ^{13}C NMR spectra of the labeled complex IrH_2(Et)(^{13}CO)(dppe). The structure of IrH_2(Et)(CO)(dppe) has one hydride trans to phosphine, one hydride trans to carbonyl, and the ethyl group trans to the remaining phosphine ligand.

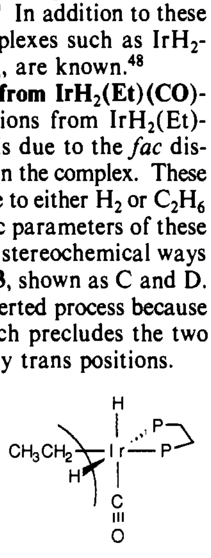
This complex, IrH_2(Et)(CO)(dppe), as a well-characterized alkyldihydridometal complex is quite rare. While a number of alkyl- and arylhydrido complexes are reported in the literature, there are relatively few alkyldihydridometal complexes known,[3,28–30] although they are postulated in hydrogenation reactions catalyzed by monohydride transition-metal complexes.[47]

Crabtree has recently reported on the reaction of H_2 with some methyliridium complexes, IrMe(CO)$(PR_3)_2$ (R = Ph, Me) giving rise to methyldihydridoiridium(III) complexes.[3] In an earlier study of olefin hydrogenation using (η^3-C_3H_5)Co$(P(OMe)_3)_3$, Muetterties observed a "complex metal hydride" in a low-temperature ^1H NMR spectrum that was attributed to the species (η^1-C_3H_5)Co$H_2$$(P(OMe)_3)_3$.[28] Shriver has also reported on the formation of $(Cp_2MoH_2Me)^+$,[29] while Longato and Bresadola have reported on the stereochemistry of H_2 oxidative addition to the carboranyl complex Ir(σ-carb)(CO)(RCN)(PPh_3) where σ-carb = 7-C_6H_5-1,7-$C_2B_{10}H_{10}$ and R = Me, Ph.[30] In addition to these true alkyldihydride complexes, other complexes such as IrH_2-(R)(CO)$(PPh_3)_2$, where R = SiR'_3, SnR'_3, are known.[48]

Reductive Elimination of H_2 and C_2H_6 from IrH_2(Et)(CO)(dppe). Two different reductive eliminations from IrH_2(Et)-(CO)(dppe) are observed to occur. This is due to the *fac* disposition of the ethyl and two hydride ligands in the complex. These reductive elimination reactions, eq 4, give rise to either H_2 or C_2H_6 and allow a direct comparison of the kinetic parameters of these paths. There are in principle two different stereochemical ways in which C_2H_5–H can be eliminated from **3**, shown as C and D. However, only C is likely to occur as a concerted process because of the constraints of the dppe ligand, which precludes the two phosphine donors from moving to mutually trans positions.



C



D

The reductive elimination of H_2 from **3** is a facile, reversible reaction while the elimination of C_2H_6 occurs more slowly and is irreversible. Both the reductive elimination of C_2H_6 and H_2 exhibit normal primary isotope effects (k_H/k_D = 2.2 and 1.6, respectively), indicating only minimal formation of the strong C–H or H–H bonds in the transition state. Activation parameters for the reductive elimination of C_2H_6 and H_2 from **3** were determined from kinetic studies. For the elimination of H_2 $\Delta H^{\ddagger} = 15.5 \pm 1.1$ kcal/mol and $\Delta S^{\ddagger} = -23.7 \pm 3.5$ cal/deg mol, whereas for the elimination of C_2H_6 $\Delta H^{\ddagger} = 20.2 \pm 0.4$ kcal/mol and $\Delta S^{\ddagger} = -10.9 \pm 1.3$ cal/deg mol. While large negative entropies of activation indicate an ordered transition state and are frequently used to propose associative reaction mechanisms,[31] other observations rule against such a mechanism. Specific observations that argue strongly against an associative reaction include the following: (a) The rate of C–H reductive elimination is independent of the concentration of **3** and H_2. (b) The reductive elimination of H_2 takes place at the same rate under D_2 or CO. (c) ^{13}CO is not incorporated into **3** prior to H_2 or C_2H_6 reductive elimination.

Studies of the reductive elimination of R–H and H–H from other transition-metal complexes have been reported in the literature.[2–13,49–52] However, there are very few cases in which both

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[42] Bianchini, C.; Meli, A.; Peruzzini, M.; Vizza, F.; Fujiwara, Y.; Jintoku, T.; Taniguchi, H. *J. Chem. Soc., Chem. Commun.* **1988**, 299–301.

[43] Tebbe, F. N.; Parshall, G. W. *J. Am. Chem. Soc.* **1971**, *93*, 3793–5.

[44] Burger, B. J.; Santarsiero, B. D.; Trimmer, M. S.; Bercaw, J. E. *J. Am. Chem. Soc.* **1988**, *110*, 3134–46.

[45] Werner, H.; Feser, R. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 157–8.

[46] See, for example: Brookhart, M.; Lincoln, D. M. *J. Am. Chem. Soc.* **1988**, *110*, 8719–20, and references therein.

[47] (a) James, B. R. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed.; Pergamon: Oxford, 1982; Vol. 8; Chapter 51. (b) Jardine, F. H. In *The Chemistry of the Metal–Carbon Bond*; Hartley, F. R., Patai, S., Eds.; Wiley-Interscience: New York, 1987; Vol. 4, Chapter 12, pp 1049–71.

[48] See, for example: (a) Rappoli, B. J.; Janik, T. S.; Churchill, M. R.; Thompson, J. S.; Atwood, J. D. *Organometallics* **1988**, *7*, 1939–44. (b) Arnold, D. P.; Bennet, M. A. *Inorg. Chem.* **1984**, *23*, 2110–6.

H–H and R–H elimination have been observed to occur cleanly from the same complex or occur to give the same resulting metal fragment.

The kinetics of H_2 reductive elimination from $IrH_2X(CO)(PR_3)_2$ complexes were studied independently by Vaska and Strohmeier as a function of X, P, and solvent.[2] Crabtree has observed $IrMeH_2(CO)(PR_3)_2$ complexes but has not studied their elimination of methane kinetically.[3] A number of intramolecular reductive elimination reactions of C–H bonds from *cis*-alkylhydride complexes have been reported. Halpern, for example, reported methane reductive elimination from *cis*-$PtHMe(PPh_3)_2$ with a rate constant of $(4.5 \pm 0.5) \times 10^{-4}\ s^{-1}$ at -25 °C, and $k_H/k_D = 3.3 \pm 0.3$.[4] However, reductive elimination of H_2 from the corresponding *cis*-dihydride complex has not been reported. The reductive elimination of CF_3CH_2–H from *cis*-$PtH(CF_3CH_2)(PPh_3)_2$ has also been reported to occur through a concerted unimolecular process following first-order kinetics, with $\Delta H^* = 24.6 \pm 0.6$ kcal/mol, $\Delta S^* = 4.9 \pm 2$ eu, and $k_H/k_D = 2.2$.[5] The reductive elimination of H_2 from the related PMe_3 complex, $PtH_2(PMe_3)_2$, has been studied by Trogler.[6] This process occurs with $\Delta H^* = 20.0 \pm 0.5$ kcal/mol and $\Delta S^* = -1 \pm 2$ cal/deg mol. In tetrahydrofuran, the reductive elimination occurs with very different parameters, $\Delta H^* = 9.4 \pm 1$ kcal/mol and $\Delta S^* = -41 \pm 3$ cal/deg mol, due to reorganization of solvent in the transition state. For this reaction, an inverse isotope effect was found, $k_H/k_D = 0.45 \pm 0.1$. The reductive elimination of CH_3–H, H–H, and CH_3–CH_3 from cis platinum and palladium complexes has also been studied theoretically.[49]

Bergman and co-workers have reported on the reductive elimination of cyclohexane from $Cp^*Ir(PMe_3)(C_6H_{11})H$.[50] This reaction was studied from 100 to 140 °C, and values for activation parameters were determined, $\Delta H^* = 35.6 \pm 0.5$ kcal/mol and $\Delta S^* = 10 \pm 2$ cal/deg mol. In this case, k_H/k_D is 0.7 ± 0.1. Reductive elimination of methane from the analogous complex $Cp^*Ir(PMe_3)MeH$ occurred at 125 °C but was not cleanly unimolecular, and elimination of benzene from $Cp^*Ir(PMe_3)PhH$ did not occur up to 190 °C. The thermally induced reductive elimination of H_2 from known $Cp^*Ir(PMe_3)H_2$ has not been reported, but it is likely that this elimination will occur only at extremely high temperatures if at all.

Reductive elimination from analogous rhodium complexes appears to be more facile.[51] The reductive elimination of Me–H from $Cp^*Rh(PMe_3)MeH$ is a clean process with $\Delta G^*(256\ K) = 19.8 \pm 0.1$ kcal/mol.[51a] The reductive elimination of other alkanes from $Cp^*Rh(PMe_3)RH$ appears to be similar, with many reactions occurring readily below 0 °C.[51a,c] A comparison of the rates of C_2H_5–H and C_2D_2–D elimination from $Cp^*Rh(PMe_3)EtH$-d_0 and -d_6 complexes gave $k_H/k_D = 0.5$.[51c] While the R–H reductive eliminations are all simple, unimolecular processes, the reductive elimination of H_2 from $Cp^*Rh(PMe_3)H_2$ may be complicated mechanistically. The dihydride complex is stable up to 65 °C under argon in benzene[51b] but appears to undergo H/D exchange in the hydrides with formation of HD, when placed under D_2 at 25 °C in benzene.[51d]

The reductive elimination of methane from Cp_2WMeH takes place by a clean first-order process with $\Delta H^* = 25.1 \pm 3$ kcal/mol and $\Delta S^* = -4 \pm 1$ cal/deg mol.[9] However, the dihydride analogue, Cp_2WH_2, was found not to eliminate H_2 thermally, at least up to 120 °C.[10]

An interesting and germane observation was made by Chan and Halpern on the hydrogenation of methyl (*Z*)-α-acetamidocinnamate (MAC) catalyzed by $Rh(dppe)^+$.[52] A monohydridoalkylrhodium complex, resulting from H_2 addition to $Rh(dppe)(MAC)^+$ followed by olefin insertion, was observed by NMR spectroscopy at low temperature. Activation parameters for reductive elimination from this complex were determined, $\Delta H^* = 17.0$ kcal/mol and $\Delta S^* = 6.0$ cal/deg mol, by studying the decay of the hydride at -56.4 and -43.4 °C. This work is especially important because of the implications in asymmetric hydrogenation reactions.[53] However, the corresponding dihydride complex was not studied in a similar way.

The elimination of R–H from *cis*-alkylhydride complexes does not always proceed by a simple process. The reductive elimination of methane from $OsHMe(CO)_4$, for example, happens via a bimolecular mechanism.[13a] The reductive elimination of H_2 from the corresponding dihydride $OsH_2(CO)_4$ also occurs by a dinuclear process.[13b] Milstein has found that the rate-determining step in the reductive elimination of H–$CH_2C(O)CH_3$ from $RhH(CH_3C(O)CH_2)(PMe_3)_3Cl$ is dissociation of PMe_3 to give a 5-coordinate 16-electron rhodium(III) species.[11] This unsaturated rhodium(III) complex then reductive eliminates H–$CH_2C(O)CH_3$ rapidly.

The complex $IrH_2(Et)(CO)(dppe)$ is interesting because it can undergo two different reductive elimination reactions. Another complex that theoretically has two possible C–H reductive eliminations is *fac*-$IrH(Me)(C(O)H)(PMe_3)_3$, prepared by the oxidative addition of formaldehyde to $IrMe(PMe_3)_4$.[54] Reductive elimination of methane to form $IrH(CO)(PMe_3)_3$ can be made to be the predominant path. Otherwise, the reductive elimination of H_2 to produce $IrMe(CO)(PMe_3)_3$ is observed.

With the reductive elimination of C_2H_6 from $IrH_2(Et)(CO)(dppe)$ and regeneration of $IrH_3(CO)(dppe)$, we have completed a catalytic hydrogenation cycle. The cycle, Scheme I, is similar to that proposed for other monohydride complexes such as $RhH(CO)(PPh_3)_3$.[39,55] The main feature in this study, however, is the observation of the alkyldihydride complex. Such a species has been proposed in catalytic hydrogenation cycles of monohydride complexes for many years, but this is the first such complex that is actually observed. The few other reported dihydridoalkyl complexes in the literature are not involved in hydrogenation reactions.

Concluding Remarks

In this work, we have observed and characterized two new complexes relevant to homogeneous hydrogenation, $Ir(Et)(\eta^2\text{-}C_2H_4)(CO)(dppe)$ and $IrH_2(Et)(CO)(dppe)$. The kinetics and mechanism of both H_2 and C_2H_6 reductive elimination from the latter complex were studied. Further investigations are under way involving both the interactions of olefins other than C_2H_4 with $[IrH(CO)(dppe)]$ and the reaction of other substrates such as silanes with these complexes.

Experimental Section

Procedures and Materials. All procedures were performed in a nitrogen-filled glovebox, under nitrogen or other appropriate gas on a Schlenk-type vacuum line or on a high-vacuum line. All solvents were reagent grade or better and were dried and degassed before use by accepted techniques.[56] Most gases were used as received, including hydrogen (Air Products, 99.9%), deuterium (Air Products, 99.99%), carbon monoxide (Air Products, CP 99.3%), ethylene (Matheson, CP 99.5%), ethylene-d_4 Cambridge Isotope Laboratories, 99%), and carbon monoxide-^{13}C (Monsanto Research Corp., 99%).

^1H and ^{31}P NMR spectra were recorded at 400.13 and 161.98 MHz, respectively, on a Bruker WH-400 spectrometer. A Bruker BVT-1000 temperature control unit was used in the regulation of temperature when needed and was calibrated against standard methanol (low-temperature) or ethylene glycol (high-temperature) samples. $^1H\{^{31}P\}$ NMR spectra were recorded on a Varian VXR-500 spectrometer at 499.84 MHz, and ^{13}C NMR were recorded on a Nicolet QE-300 NMR at 75.48 MHz. ^1H

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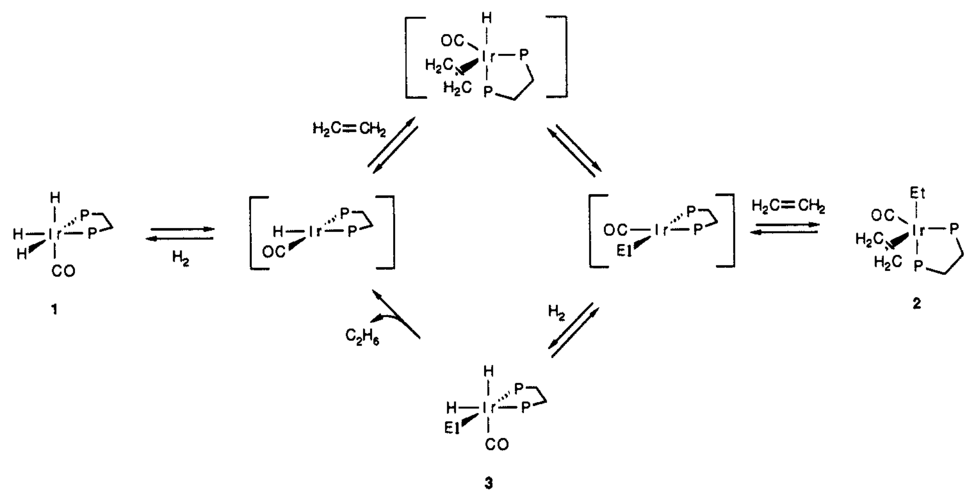
Scheme I



chemical shifts are reported in ppm downfield from tetramethylsilane but were measured relative to residual ^1H resonances in the deuterated solvents, C_6D_5H (δ 7.150) and $C_6D_5CD_2H$ (δ 2.100). ^{31}P chemical shifts are reported in ppm downfield from phosphoric acid and were referenced to external 85% H_3PO_4. ^{13}C chemical shifts are reported in ppm downfield from tetramethylsilane and were referenced to benzene-d_6 solvent (δ 127.6). Benzene-d_6 (MSD, 99.6% D) and toluene-d_8 (Aldrich, 99+% D) were vacuum distilled from sodium benzophenone ketyl. Infrared spectra were recorded on a Mattson Sirius 100 FT-IR.

The complex IrBr(CO)(dppe)[14b] was prepared according to the literature procedure.

Preparation of $IrH_3(CO)(dppe)$ (1). This complex was prepared according to the literature procedure,[14a] except for substitution of IrBr(CO)(dppe) for IrI(CO)(dppe). $IrH_3(^{13}CO)(dppe)$, **1**-*CO*, was prepared in a similar fashion from $IrBr(^{13}CO)(dppe)$.

Preparation of $IrBr(^{13}CO)(dppe)$. This complex was prepared by ^{13}CO exchange into IrBr(CO)(dppe). A 250-mL flask containing a benzene solution (60 mL) of IrBr(CO)(dppe) (185 mg, 0.43 mmol) was connected to a high-vacuum line and subjected to one freeze/pump/thaw cycle at −78 °C. After the flask was filled with 250 Torr of ^{13}CO (approximately 10 equiv), the solution was thawed and stirred at room temperature overnight. Following two freeze/pump/thaw cycles at −78 °C, the flask was attached to a Schlenk line and filled with nitrogen. Ethanol (50 mL) was then added, followed by slow vacuum removal of solvent until the orange product precipitated. The solid was collected on a frit, washed with ethanol and pentane, and dried in vacuo; yield 150 mg (80%). The product was ~90% ^{13}CO enriched, as evidenced by ^{13}C and ^{31}P NMR of this product and by ^1H, ^{13}C, and ^{31}P NMR of subsequent products.

Reaction of $IrH_3(CO)(dppe)$ with C_2H_4. Formation of 2. In a typical reaction, 0.4 mL of a 10 mM solution of $IrH_3(CO)(dppe)$ in benzene-d_6 in an NMR tube under C_2H_4 (400–760 Torr) was heated for $^1/_2$ h at 70 °C. The product, $Ir(\eta^2\text{-}C_2H_4)(Et)(CO)(dppe)$ (**2**) was formed in essentially quantitative amounts (by NMR spectroscopy) along with free C_2H_6. ^1H NMR (C_6D_6): δ 7.857 (dd, $J = 10, 8$ Hz, 2 H, dppe), 7.652 (dd, $J = 10, 8$ Hz, 2 H, dppe), 7.357 (dd, $J = 10, 8$ Hz, 2 H, dppe), 2.25 (m, 1 H, dppe), 2.12 (m, 1 H, dppe), 1.91 (m, 1 H, dppe), 1.73 (m, 1 H, dppe), 1.985 (q, $J = 8$, 3 H, CH_3CH_2), 1.526 (m, 1 H, CH_3CH_2), 0.082 (m, 1 H, CH_3CH_2), 2.117 (m, 1 H, $\eta^2\text{-}C_2H_4$), 2.10 (m, 1 H, $\eta^2\text{-}C_2H_4$), 0.901 (m, 1 H, $\eta^2\text{-}C_2H_4$), 0.462 (m, 1 H, $\eta^2\text{-}C_2H_4$). IR: $\nu_{C-O} = 1938\ cm^{-1}$, $\nu_{*C-O} = 1893\ cm^{-1}$.

The above procedure can be scaled up. In this case, $IrH_3(CO)(dppe)$ (100 mg, 0.16 mmol) in 10 mL of benzene or toluene under 1 atm of C_2H_4 was vigorously stirred and heated to 70 °C for 1 h. This resulted in essentially quantitative formation of **2** as a very pale yellow solution. Precipitation of analytically pure **2** by solvent evaporation, even under passage of a stream of C_2H_4, has been unsuccessful to date.

Reaction of $Ir(\eta^2\text{-}C_2H_4)(Et)(CO)(dppe)$ with H_2. Formation of 3. In a typical reaction, 0.4 mL of a 10 mM solution of $Ir(\eta^2\text{-}C_2H_4)(Et)(CO)(dppe)$ in benzene-d_6, prepared as described above, was placed in a resealable NMR tube (J. Young, available from Wilmad Glass Co.). After two freeze/pump/thaw cycles at −78 °C, the solution was frozen and pumped on at −78 °C, and the frozen solution placed under 400–700 Torr of H_2. The reaction was then followed by NMR spectroscopy. ^1H NMR of $IrH_2(Et)(CO)(dppe)$ (C_6D_6): δ 7.950 (dd, $J = 11, 8$ Hz, 2 H, dppe), 7.641 (dd, $J = 10, 8$ Hz, 2 H, dppe), 7.553 (dd, $J = 10, 8$ Hz, 2 H, dppe), 7.458 (dd, $J = 11, 7$ Hz, 2 H, dppe), 2.451 (m, 4 H, CH_3CH_2 and one of CH_3CH_2), −8.663 (dd, $J = 140, 13$ Hz, 1 H, Ir–H), −9.422 (t, $J = 20$ Hz, 1 H, Ir–H). IR: $\nu_{C-O} = 1964\ cm^{-1}$, $\nu_{Ir-H} = 2071\ cm^{-1}$. IR for $IrD_2(Et)(CO)(dppe)$: $\nu_{C-O} = 2000\ cm^{-1}$, ν_{Ir-D} not found.

Kinetic Studies of Reductive Elimination of C_2H_6 from 3. Working in a nitrogen-filled glovebox, 0.40 mL of a ~10 mM stock solution of **2** in benzene-d_6 (prepared as described above) was placed in a resealable NMR tube. The tube was sealed, removed from the glovebox, and attached to a high-vacuum line. After two freeze/pump/thaw cycles at −78 °C, 700 Torr of H_2 was added to the frozen (−78 °C) tube. The solution was thawed, the tube shaken vigorously for 30 s, and the sample allowed to sit for 2 min, forming the desired complex, $IrH_2(Et)(CO)(dppe)$. The solution was subsequently put through two more freeze/pump/thaw cycles at −78 °C, after which the NMR tube was immersed in liquid nitrogen to just below the valve and 700 Torr of H_2 added. This procedure placed ~80 equiv of H_2 in the NMR tube.[57]

The NMR tube was thawed, vigorously shaken for 30 s, and placed into the temperature-equilibrated NMR probe, and the reaction was monitored by ^1H NMR spectroscopy by following the decay of the hydride resonances of **3**. The growth of the hydride resonances due to $IrH_3(CO)(dppe)$ was also followed. To ensure mass transfer of H_2 between the gas phase and solution, the tubes were periodically removed from the NMR probe and shaken vigorously. The reactions were monitored for at least 2 half-lives. The reaction temperature ranged from 17.8 to 43.6 °C, ±0.3 °C.

Kinetic Studies of Reductive Elimination of H_2 from 3. Solutions of $IrH_2(Et)(CO)(dppe)$ (**3**) in C_6D_6 were prepared in situ in an NMR tube as described above for studies of C_2H_6 elimination. After the solution of **3** (under 700 Torr of H_2) was put through two freeze/pump/thaw cycles at −78 °C, 700 Torr of D_2 was added to the tube. The solution was thawed, the tube shaken vigorously for 30 s, and the sample then put through two additional freeze/pump/thaw cycles at −196 °C. Following this, 700 Torr of D_2 was added to the NMR tube, which was immersed in liquid nitrogen to just below the valve.[57]

The NMR tube was thawed, vigorously shaken for 30 s, and placed into the temperature-equilibrated NMR probe, and the reaction was monitored by ^1H NMR spectroscopy by following the decay of the hydride resonances of **3**. The tube was removed from the NMR probe after every NMR accumulation (every 10 min) and shaken vigorously to ensure that D_2 was brought into solution and that H_2 was removed from solution. The reactions were again monitored for at least 2 half-lives, with the reaction temperature ranging from 17.8 to 43.6 °C, ±0.3 °C.

A similar procedure was followed for the reactions performed under CO and ^{13}CO. After preparing $IrH_2(Et)(CO)(dppe)$ in situ and removing excess H_2 by two freeze/pump/thaw cycles at −78 °C, 700 Torr of CO was added to the NMR tube, which was submersed in a −78 °C bath. The tube was then immersed in liquid nitrogen and opened to the ~5-mL space above the NMR tube, which contained 700 Torr of CO. This procedure placed ~75 equiv of CO in the NMR tube.

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(57) The total internal volume of the J. Young NMR tubes was ~2.6 mL. Using the ideal gas law with 2.2 mL of gas volume (0.4 mL of solution), 700 mmHg, and 77 K, there was ~320 mmol of gas in the NMR tube or ~80 equiv. The amount of gas in solution was however much smaller.