with the empty orbital on the metal. Rehybridization of the ligating oxygen from $sp^3$ to $sp^2 + p$ would direct a lone pair toward the metal, but this seems inconsistent with the normal C–O–C angle for the coordinated THF.

## Conclusion

The essentially planar configuration of the tricoordinate oxygen in bound $H_2O$ often seen in coordination complexes is now found in an 18-e organometallic aqua complex (**2**), where the $H_2O$ is a 2-e donor. Planar tricoordinate oxygen is also found for the coordinated THF. It may be that the H-bonds enforce planarity for water, especially where a long Ir–O bond is present, as here, but the same cannot be true for THF, which is also planar. Arguments about $\pi$-bonding and 2-e vs 4-e donor character for ligands of the $R_2O$ type should therefore not be based solely on the distinction between planar and pyramidal geometries. The great lengthening of the Ir–O bonds found in **2**·THF due to the trans influence of the hydride ligands is consistent with the lability of the O-donor ligands and the unusual activity of the complex in a number of stoichiometric and catalytic reactions.

## Experimental Section

All manipulations were performed under an atmosphere of purified nitrogen with use of standard Schlenk-tube techniques. $^1H$ NMR spectra were recorded on a Bruker WM 250 spectrometer, and IR spectra, on a Nicolet 5-SX FT-IR spectrometer. THF and hexane were distilled from $Na/Ph_2CO$ and stored under nitrogen over 4-Å molecular sieves $[(cod)Ir(PPh_3)_2]SbF_6$ was synthesized by a method similar to that for the $BF_4^-$ salt[29] and recrystallized before use.

**Dihydridobis(tetrahydrofuran)bis(triphenylphosphine)iridium(III) Hexafluoroantimonate (1).** A red solution of $[(cod)Ir(PPh_3)_2]SbF_6$ (1.0 g) in THF (10 mL) was cooled to 0 °C. Hydrogen was bubbled gently through the solution for 10–15 min until the solution turned pale yellow. The volume of the solution was then reduced to ca. 4 mL in vacuo. Hexane (40 mL) was added carefully to form a separate layer on top of the THF solution. After 24 h in a refrigerator, the resulting white crystalline product was filtered out, washed with hexane (4 × 10 mL), and dried in vacuo. Yield: 0.79 g (76%). Anal. Calcd for $C_{44}H_{48}F_6IrO_2P_2Sb$: C, 48.10; H, 4.40. Found: C, 47.92; H, 4.29. IR (Nujol): $\nu_{Ir-H}$ 2290 $cm^{-1}$. $^1H$ NMR ($CD_2Cl_2$, 298 K): $\delta$ 7.1–7.4 (c, 30 H, Ph), 3.4 (br s, 8 H, $CH_2$), 1.5 (br s, 8 H, $CH_2$), −28.6 (br s, 2 H, Ir–H).

**Preparation of $[IrH_2(THF)(H_2O)(PPh_3)_2]SbF_6$·THF (2·THF) for Crystallography.** $[IrH_2(THF)_2(PPh_3)_2]SbF_6$ (**1**) (70 mg) was dissolved in 2 mL of slightly moist THF in a small vial that was then submerged in 30 mL of hexane in a Schlenk tube. After several days in a cold room (4 °C), white crystals of **2**·THF were formed.

**X-ray Crystallography of 2·THF.** A suitable crystal (0.50 mm × 0.25 mm × 0.20 mm) of **2**·THF was sealed in a thin-walled glass capillary that was mounted on an Enraf-Nonius CAD-4 fully automated diffractometer using graphite-monochromated Mo $K\alpha$ radiation ($\lambda$ = 0.71069 Å) and variable scan speed (2.5–10°/min). The unit cell (see Table I) was determined and refined from 25 randomly selected reflections. The space group, based on the systematic absences observed in the data, was uniquely assigned as $P2_1/n$, with one molecule of $C_{44}H_{50}IrP_2O_3SbF_6$ forming the asymmetric unit. The absorption coefficient was $\mu$(Mo $K\alpha$) = 36.78 $cm^{-1}$ and an empirical absorption correction, based on azimuthal scans of three reflections (−2,−7,−2; −2,−7,−1; −2,−7,−3), was applied. The data were also corrected for Lorentz and polarization effects.

The structure was solved by a combination of Patterson and difference Fourier syntheses.[30] The position of the iridium atom was obtained from the Patterson synthesis. The remaining non-hydrogen atoms were obtained by iterative use of the WFOURIER option in DIRDIF.[31] All hydrogen atoms were calculated and input at their idealized positions. The full-matrix refinement of the non-hydrogen atoms and input of the hydrogen scattering factors resulted in convergence of the crystallographic reliability factor to an unweighted residual of 0.039 and a weighted residual of 0.045. The (101) reflection, having a $\Delta(F)/\sigma(F)$ value of 10.18 was ignored in the refinement. The final difference Fourier showed two electron density maxima close to the Ir atom at 0.2994, 0.1995, 0.7769, and 0.5099, 0.1989, 0.7653 with electron densities of 1.9 and 1.8 e/Å$^3$, respectively.

**Acknowledgment.** We thank the National Science Foundation for support, Professor J. W. Faller and a referee for crystallographic suggestions, and Dr. Marc Zimmer for discussions.

**Supplementary Material Available:** Tables of further bond distances and angles, torsion angles, calculated H atom positions, and thermal parameters for **2**·THF (10 pages); a listing of $F_o$ vs $F_c$ values for **2**·THF (25 pages). Ordering information is given on any current masthead page.

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(29) Haines, L. M.; Singelton, E. *J. Chem. Soc., Dalton Trans.* **1972**, 1891.

(30) *TEXSAN-TEXRAY Structure Analysis Package*; Molecular Structure Corp: Woodlands, TX, 1985.

(31) Beurskens, P. T. DIRDIF: Direct Methods for Difference Structure—an automatic procedure for phase extension and refinement of difference structure factors. Technical Report 1984/1; Crystallography Laboratory: Toernooiveld, 6525 Ed, Nijmegen, The Netherlands.

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# Hydride Abstraction. The Reaction of IrX(CO)(dppe) with $Cp_2TaH_3$

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The reaction of IrX(CO)(dppe) (X = Br, I; dppe = 1,2-bis(diphenylphosphino)ethane) with $Cp_2TaH_3$ (Cp = $\eta^5$-cyclopentadienyl) is extremely rapid and leads to clean formation of *fac*-$IrH_3$(CO)(dppe) and $Cp_2TaX$, or $Cp_2TaXL$ (L = CO, $C_2H_4$, $C_3H_7C{\equiv}CC_3H_7$) in the presence of added ligand. Trapping and isotope-labeling experiments indicate that the reaction does not proceed through production of free $IrH_2X$(CO)(dppe), [IrH(CO)(dppe)], or [$Cp_2TaH$]. the results are consistent with formation of unstable hydride and halide-bridged binuclear intermediates, in which transfer of all hydride and halide ligands occurs before fragmentation into mononuclear species.

## Introduction

It has been shown that the reaction of $H_2$ with IrX(CO)(dppe) (**1**) (**1a**, X = Br; **1b**, X = I; dppe = 1,2-bis(diphenylphosphino)ethane) leads to rapid and reversible formation of an isomer of $IrH_2X$(CO)(dppe) (**2**) as the kinetically favored reaction product (eq 1).[1] With time, **2** disappears and another isomer of $IrH_2X$(CO)(dppe) (**3**) grows in as the thermodynamically favored product. A detailed kinetic study of the conversion of **2a** into **3a** by Kunin et al.[2] showed that the rate of conversion was

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(1) (a) Johnson, C. E.; Fisher, B. J.; Eisenberg, R. *J. Am. Chem. Soc.* **1983**, *105*, 7772. (b) Johnson, C. E.; Eisenberg, R. *J. Am. Chem. Soc.* **1985**, *107*, 3148.

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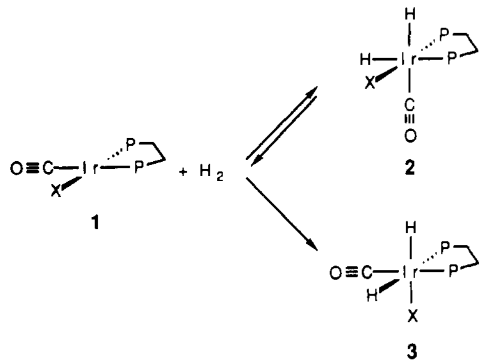
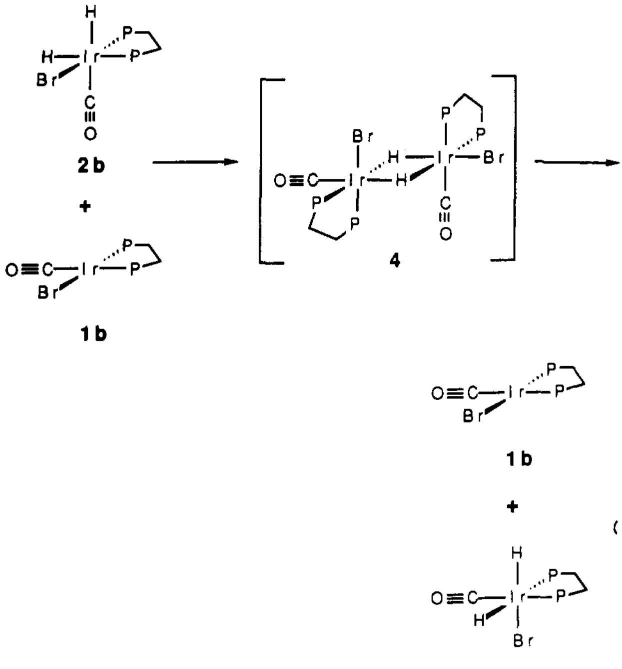


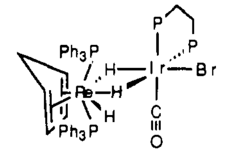
**1** **2** **3** (1)

slow in the presence of excess $H_2$ but was substantially faster with less than 1 equiv of $H_2$. While a reductive elimination/oxidative addition sequence appeared to be operative under high $H_2$ pressure, a bimolecular pathway proposed to involve hydrogen transfer via a dihydride-bridged binuclear species, **4**, was operative in the low $H_2$ pressure regime (eq 2).



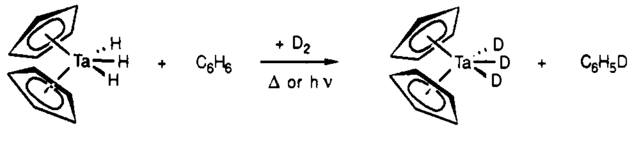
**2b** **1b** **4** **1b** **3b** (2)

Formation of stable hydride-bridged binuclear complexes is well-known,[3] and similar dihydride-bridged binuclear intermediates have been proposed in closely related studies.[1b,4] Of particular interest is the reaction of $(\eta^4\text{-}C_5H_6)Re(PPh_3)_2H_3$ with **1a**, which resulted in the formation of $(\eta^5\text{-}C_5H_5)Re(PPh_3)_2H_2$ and the thermodynamic isomer of $IrH_2Br(CO)(dppe)$ (**3a**).[4b] Experimental evidence showed that reductive elimination of $H_2$ from $(\eta^4\text{-}C_5H_6)Re(PPh_3)_2H_3$ followed by oxidative addition to **1a** forming **2a** or **3a** was *not* occurring, and indicated that **3a** was formed by direct dihydride transfer from the rhenium atom of $(\eta^4\text{-}C_5H_6)Re(PPh_3)_2H_3$ to the iridium center of **1a** via a dihydride-bridged binuclear intermediate, A.



**A**

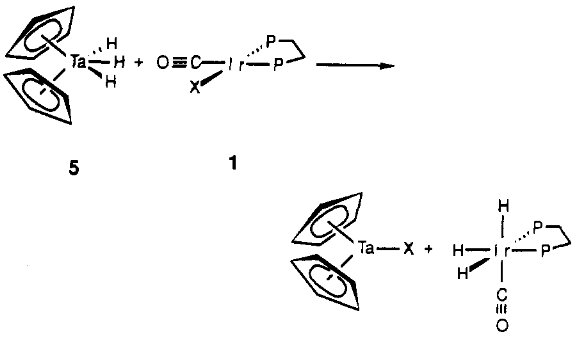
The high affinity of the iridium(I) system IrX(CO)(dppe) for formal $H_2$ oxidative addition, as indicated by the formation of **3** via the dihydride-bridged binuclear intermediates described above, led to the proposal that **1** might be capable of abstracting $H_2$ from other transition-metal polyhydrides, $L_nMH_x$, yielding $IrH_2X(CO)(dppe)$ (**3**) and reactive, coordinatively unsaturated species, $L_nMH_{x-2}$. Whereas reductive elimination of $H_2$ from metal polyhydrides to give coordinatively unsaturated species frequently involves somewhat extreme thermal or photochemical conditions, we reasoned that $H_2$ loss from $L_nMH_x$ could be effected under mild conditions by dihydride transfer using **1** with the driving force being the formation of an iridium(III) dihydride complex containing strong Ir–H bonds. The first transition-metal polyhydride chosen for this study was $Cp_2TaH_3$ (Cp = $\eta^5$-cyclopentadienyl) because of its known $D_2$ exchange and activation of aromatic C–H bonds[5] (eq 3). In this paper, we wish to report on the results of this investigation.



**5** **5**-$d_3$ (3)

## Results

The reaction of IrX(CO)(dppe) (**1**) with $Cp_2TaH_3$ (**5**) in benzene-$d_6$ at 25 °C was very rapid and led to the clean formation of $IrH_3(CO)(dppe)$ (**6**)[6] and an insoluble precipitate of "$Cp_2TaX$" (**7**) (eq 4). The reaction occurs rapidly as solutions of **1** and **5** are mixed, such that the reaction is complete within 3 min when the first NMR spectrum is accumulated. Compounds **1** and **5** react in a 1:1 ratio to produce 1 equiv of **6**. No evidence for any other $Cp_2Ta$ species or $IrH_2X(CO)(dppe)$, **2** or **3**, was observed by $^1H$ NMR spectroscopy.



**5** **1** **7** **6** (4)

When the reaction was performed at low temperature, similar results were obtained. In toluene-$d_8$ at −60 °C, only **6** and excess **5** were observed in the $^1H$ NMR spectrum, and the same species were observed in dichloromethane-$d_2$ at −70 °C. The reaction was rapid even at these temperatures. No intermediates or other species (including unreacted **1**) were observed in either of these low-temperature reactions.

The reaction of **1a** with $Cp_2TaD_3$ in the presence of $H_2$ was slowed somewhat due to the reversible formation of **2a**, as shown in eq 5. The products of this reaction were the "$Cp_2TaBr$" precipitate and **6**-$d_3$. Analysis of the hydride region of the $^1H$ NMR spectrum indicated that no incorporation of $H_2$ into the $Cp_2TaD_3$ reactant or **6**-$d_3$ product had occurred. The reaction of **1a** with $Cp_2TaH_3$ in the presence of $D_2$ gave similar results, with essentially no deuterium incorporation into the $IrH_3(CO)(dppe)$ product. This result is based upon NMR integration of hydrides vs methylene and phenyl ortho protons and upon analysis of the coupling pattern in the iridium–hydride resonance

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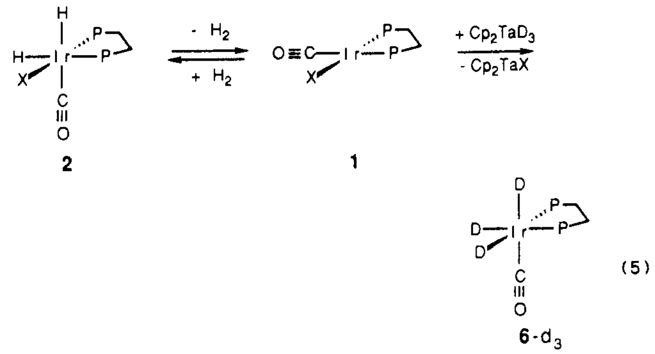
(2) Kunin, A. J.; Johnson, C. E.; Maguire, J. A.; Jones, W. D.; Eisenberg, R. *J. Am. Chem. Soc.* **1987**, *109*, 2963.

(3) Venanzi, L. *Coord. Chem. Rev.* **1982**, *43*, 251.

(4) (a) Drouin, M.; Harrod, J. F. *Inorg. Chem.* **1983**, *22*, 999. (b) Jones, W. D.; Maguire, J. A. *J. Am. Chem. Soc.* **1985**, *107*, 4544.

(5) (a) Barefield, E. K.; Parshall, G. W.; Tebbe, F. N. *J. Am. Chem. Soc.* **1970**, *92*, 5234. (b) Foust, D. F.; Rogers, R. D.; Rausch, M. D.; Atwood, J. L. *J. Am. Chem. Soc.* **1982**, *104*, 5646.

(6) Fisher, B. J.; Eisenberg, R. *Organometallics* **1983**, *2*, 764.

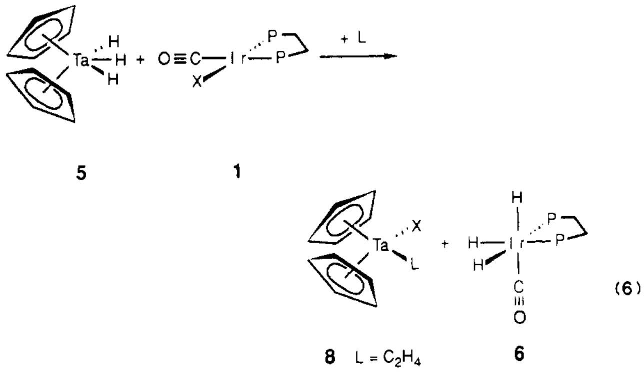


**2** **1** **6-$d_3$** (5)

at δ −9.48 ppm. It has been shown previously that the coupling in the two outer lines of this hydride resonance, due to $J_{H-H}$, occurs only in the trihydride complex, **6**,[6] or a symmetry-related dihydride, $IrH_2(CN)(CO)(dppe)$, in which both hydrides are trans to the dppe P donors.[1b] When some deuterium is incorporated into **6**, the second-order hydride resonance at −9.48 ppm becomes a simple doublet of doublets. The hydride region of the $^1H$ NMR spectrum for the $IrH_3(CO)(dppe)$ product of these reactions is shown in Figure 1. As before, no other iridium or tantalum products were observed.

In order to confirm the production of "$Cp_2TaX$" (**7**), IrX(CO)(dppe) and $Cp_2TaH_3$ were allowed to react, followed by addition of other ligands to the product mixture. The reaction of added L with **7** was slow, but led to the formation of $Cp_2TaXL$ (X = Br, L = $C_2H_4$ (**8a**), $C_3H_7C{\equiv}CC_3H_7$ (**9a**), CO (**10a**); X = I, L = $C_3H_7C{\equiv}CC_3H_7$ (**9b**)). Approximately 0.15 equiv of **8a** was formed within 30 min under 1 atm of $C_2H_4$, based upon NMR integration of the resonances from **8a** vs those from the $IrH_3(CO)(dppe)$ product. With L = $C_3H_7C{\equiv}CC_3H_7$, formation of ~0.50 equiv of **9a** or **9b** was observed after 2 h. The use of CO as added ligand led to recovery of 0.85 equiv of "$Cp_2TaBr$" as **10a** after 5 h.

When extra ligands, $C_2H_4$ or $C_3H_7C{\equiv}CC_3H_7$, were added *before* allowing **1** and **5** to react, clean and rapid formation of $IrH_3(CO)(dppe)$ and $Cp_2TaXL$ (X = Br, L = $C_2H_4$, $C_3H_7C{\equiv}CC_3H_7$; X = I, L = $C_2H_4$ (**8b**),[7] $C_3H_7C{\equiv}CC_3H_7$) was observed (eq 6). The amount of $Cp_2TaXL$ produced in these reactions was greater than 0.85 equiv per mole of **5** consumed and of **6** formed. The formation of $Cp_2TaHL$ was not observed in any of these reactions. With CO as the added ligand, formation of $Cp_2TaBr(CO)$ and a mixture of $IrH_3(CO)(dppe)$ and $IrH(CO)_2(dppe)$ was observed. Independent reaction of $IrH_3(CO)(dppe)$ with the adduct $IrBr(CO)_2(dppe)$ also gave rise to formation of $IrH(CO)_2(dppe)$ as well as other products, so that the formation of $IrH(CO)_2(dppe)$ in the reaction between $Cp_2TaH_3$ and **1** under CO may be due to secondary reaction chemistry and not to a process involving dihydride transfer.



**5** **1** **8** L = $C_2H_4$ **6** (6)

**9** L = $C_3H_7C{\equiv}CC_3H_7$

To ascertain whether or not monohydride transfer occurs in this system, reactions between $Cp_2TaHL$ and IrBr(CO)(dppe) (**1a**) were investigated. A rapid reaction does occur between $Cp_2TaH(CO)$ and **1a** in benzene-$d_6$, giving rise to $IrH(CO)_2(dppe)$ and "$Cp_2TaBr$". However, when mixtures of **1a** with $Cp_2TaH(C_2H_4)$ or $Cp_2TaH(C_3H_7C{\equiv}CC_3H_7)$ were followed by $^1H$ NMR spectroscopy for 1 h, essentially no reaction was observed.

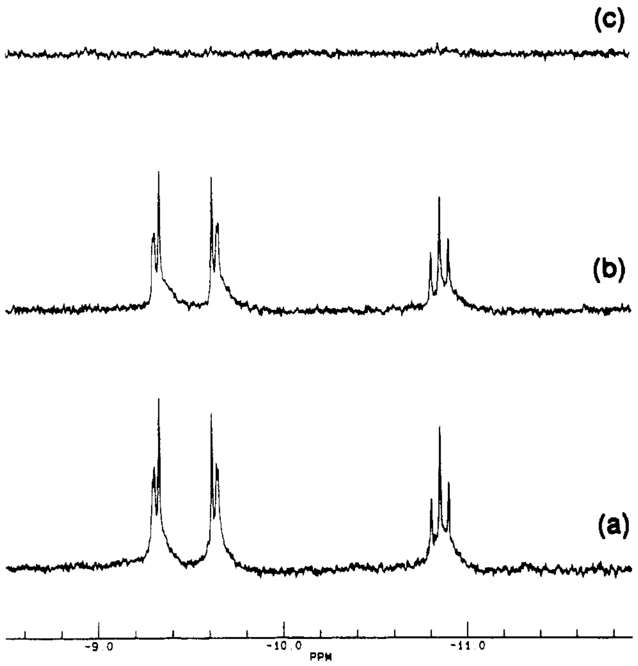


**Figure 1.** $^1H$ NMR spectra (400 MHz) showing the hydride region of the product $IrH_3(CO)(dppe)$ (**6**) in the reaction of (a) IrBr(CO)(dppe) (**1b**) with $Cp_2TaH_3$ (**5**) under $N_2$, (b) **1b** with **5**-$d_0$ under $D_2$, and (c) **1b** with **5**-$d_3$ under $H_2$.

Experiments aimed at determining if initial formation of free $IrH_2X(CO)(dppe)$ (**3**) followed by rapid hydride and halide transfer was occurring were also performed. Little or no reaction of **3a** was found to occur with $Cp_2TaH(CO)$, $Cp_2TaH(C_2H_4)$, or $Cp_2TaH(C_3H_7C{\equiv}CC_3H_7)$ when followed by $^1H$ NMR spectroscopy for 1 h.

## Discussion

Since loss of $H_2$ from $Cp_2TaH_3$ only occurs above 80 °C, the rapidity of the reaction between IrX(CO)(dppe) (**1**) and $Cp_2TaH_3$ (**5**) indicates that a bimolecular process is occurring. It appears that the coordinatively unsaturated complex **1** attacks **5**, abstracting all three hydride ligands and transferring the halide ligand to the tantalum center, forming $IrH_3(CO)(dppe)$, (**6**) and $Cp_2TaX$ (**7**).

The clean production of **6** is easily detected by $^1H$ NMR spectroscopy, and while **7** is not observed in benzene solution, its presence is confirmed by observation of $Cp_2TaXL$ in the trapping experiments. As a mononuclear species, **7** is coordinatively unsaturated and would undoubtly seek a donor, accounting for the formation of $Cp_2TaXL$. In the absence of added L, **7** may exist as a halide-bridged dimer, which would create saturated tantalum centers.[8] The formation of unobservable paramagnetic species such as $Cp_2TaX_2{}^{\bullet}$ or $Cp_2TaX_2{\cdot}Cp_2TaX$[9a] can be excluded on the basis of the sharpness of the $^1H$ NMR spectra. The disproportionation reaction of $Cp_2TaX$ giving rise to $[(Cp_2Ta)_2]$ and $Cp_2TaX_2{}^{\bullet}$ could be envisioned but can be ruled out because (a) a large amount of $Cp_2TaXL$ is formed, >80%, (b) $(Cp_2Ta)_2$ is not observed in the NMR,[9b] and (c) $Cp_2TaX_2{}^{\bullet}$ would not be expected to react with L to give $Cp_2TaXL$.

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[7] NMR data for $Cp_2TaI(C_2H_4)$ reported by Schrock, R. R.; Sharp, P. R. *J. Am. Chem. Soc.* **1978**, *100*, 2389.

[8] A reviewer has suggested the use of IrMe(CO)(dppe) in these reactions. We have considered this possibility, and are currently investigating the synthesis and chemistry of IrX(CO)(dppe) complexes where X is an organic group.

[9] (a) Antiolo, A.; Fajardo, M.; Otero, A.; Royo, P. *J. Organomet. Chem.* **1983**, *246*, 269. (b) Tebbe, F. N.; Parshall, G. W. *J. Am. Chem. Soc.* **1971**, *93*, 3793.

The reaction of **1** with **5** is very fast, and no intermediates are observed at low temperatures (−60 to −70 °C). The only tantalum products observed in any of the reactions are $Cp_2TaXL$. Products such as $Cp_2TaHL$ are never found, suggesting that free $[Cp_2TaH]$ is not an intermediate in the reaction.

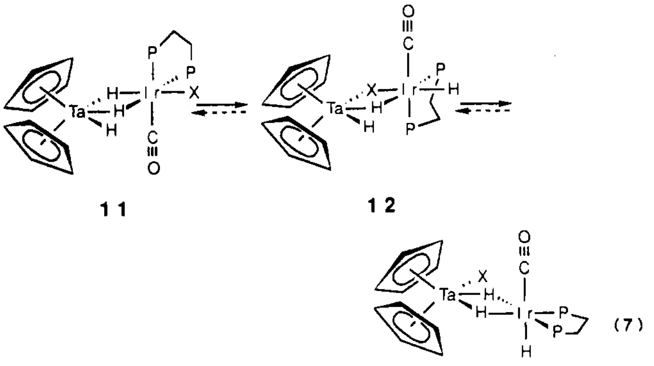
Similarly, the iridium product observed in most of these reactions is $IrH_3(CO)(dppe)$. An exception to this trend is the formation of some $IrH(CO)_2(dppe)$ in reactions performed under CO, but this product has been independently shown to arise from scrambling between iridium centers.

The kinetic dihydrogen addition product $IrH_2X(CO)(dppe)$ (**2**) is not a reaction product. This complex is never observed except when the reactions were performed under $H_2$ or $D_2$, where it is formed by reaction of **1** with free $H_2$ according to eq 5, and not by reaction with **5**. Further evidence in support of the fact that **2** is not a reaction product or intermediate is provided by the isotope labeling. The reversibility of $H_2$ or $D_2$ addition to **1** forming **2** would also have led to isotope scrambling in these experiments if **2** were one of the initial reaction products.

The thermodynamically favored $H_2$ addition product $IrH_2X(CO)(dppe)$ (**3**) is also never observed as a final reaction product or as an intermediate. One could envision the reaction of **1** and **5** proceeding through initial formation of **3** and $Cp_2TaHL$, **8c**, **9c**, or **10c**, followed by rapid subsequent reaction between these two species. However, such a possibility is unlikely on the basis of the results of independent reaction of **3** with **8c**, **9c**, and **10c**, in which it was found that these compounds reacted only slowly if at all.

It is also important to note that free $[IrH(CO)(dppe)]$ is not formed in any of the above reactions. If it were, the isotope-labeling experiments, which were performed under $H_2$ and $D_2$, would have led to significant H/D scrambling in the $IrH_3(CO)(dppe)$ product, formed by irreversible $D_2$ addition to $[IrH(CO)(dppe)]$ or $H_2$ addition to $[IrD(CO)(dppe)]$, which is inconsistent with the observed experimental results (Figure 1).

Even though no intermediates are observed in these reactions, mechanistic insights can be inferred from the observation (or lack thereof) of various products. On the basis of the experimental evidence, it is believed that the attack of **1** on **5** leads to initial formation of a binuclear species, **11**, containing two bridging hydrides. It is clear that **11** does not simply break apart by scission of the two Ta–H bonds, since formation of $IrH_2X(CO)(dppe)$, **2** or **3**, and $[Cp_2TaH]$ or $Cp_2TaHL$ does not occur. The binuclear species **11** must therefore undergo rearrangement to form a species such as **12** and **13** (eq 7) before finally fragmenting to give $IrH_3(CO)(dppe)$ and $Cp_2TaX$. The rapidity of the reaction and lack of observation of intermediates makes it difficult to determine if the formation of **11** from **1** and **5** and the subsequent conversion of **11** to **12** and **13** are reversible. While these experiments suggest that the reaction proceeds through these binuclear species, these species are unobserved and unstable with respect to the final products. The formation of strong Ir–H and Ta–X bonds provides the underlying force that drives eq 4, especially if the unsaturated $Cp_2TaX$ can fill its coordination sphere by dimerizing or binding an added ligand.



**11** **12** **13**

(7)

Other possibilities for the first step of the reaction between **1** and **5** can be envisioned. Oxidative addition of a tantalum–hydride bond across the iridium center is one possibility. A mechanism such as this has recently been proposed by Casey in the reaction of $CpRe(CO)_2H_2$ with $IrCl(CO)(PPh_3)_2$.[10] Because of the steric crowding that would occur and the lack of reactivity of **1** with $Cp_2TaH(C_2H_4)$ (**8c**) and $Cp_2TaH(C_3H_7C{\equiv}CC_3H_7)$ (**9c**), it is believed that this oxidative addition mechanism is not operative in our system. The lack of reactivity of **1** with **8c** and **9c** also indicates that the first step does not involve transfer of a single $H^+$, $H^•$, or $H^-$ to the iridium center.

## Concluding Remarks

In this study, we have shown that $IrX(CO)(dppe)$ can abstract hydride ligands from $Cp_2TaH_3$ via polyhydride transfer. Subsequent hydride- and halide-transfer reactions occur in this system, leading to formation of $IrH_3(CO)(dppe)$ and "$Cp_2TaX$". Isotope-labeling and trapping experiments indicate that free species such as $IrH_2X(CO)(dppe)$, $[IrH(CO)(dppe)]$, and $[Cp_2TaH]$ are not produced. This implies that all three hydrides and the halide are transferred between the same tantalum and iridium centers by way of dihydride- and hydride–halide-bridged binuclear intermediates. While dihydride transfer has been observed, the subsequent transfer reactions have prevented observation of chemistry arising from a coordinatively unsaturated species such as $[Cp_2TaH]$. We are currently investigating reactions with other $L_nMH_x$ systems in hope of observing C–H activation or other chemistry derived from $L_nMH_{x-2}$ species formed by dihydride transfer.

## Experimental Section

All procedures were performed in a nitrogen-filled glovebox or under nitrogen or other appropriate gas on a Schlenk-type vacuum line. All solvents were reagent grade or better and were dried and degassed before use by accepted techniques.[11] Some reagents were used as received, including lithium aluminum hydride (Aldrich), hydrogen (Air Products, 99.9%), deuterium (Air Products, 99.99%), carbon monoxide (Air Products, CP 99.3%), and ethylene (Matheson, CP 99.5%). Boromoform (Aldrich, Gold Label 99+%), bromobenzene (Aldrich, Gold Label 99%), and iodobenzene (Aldrich) were dried and degassed prior to use.[11] 4-Octyne (Aldrich) was vacuum distilled from sodium prior to use.[11]

$^1H$ and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker WH-400 spectrometer at 400.13 and 161.98 MHz, respectively. Chemical shifts for $^1H$ NMR spectra are reported in ppm downfield from tetramethylsilane but were measured relative to residual $^1H$ resonances in the deuterated solvents $C_6D_5H$ ($\delta$ 7.150 ppm), $C_6D_5CD_2H$ ($\delta$ 2.100 ppm), and $CDHCl_2$ ($\delta$ 5.320 ppm). Chemical shifts for $^{31}P$ NMR spectra are reported in ppm downfield from external 85% $H_3PO_4$. A Bruker BV-T-1000 temperature control unit was used in the regulation of low temperature when needed and was calibrated against a standard methanol sample. Benzene-$d_6$ (MSD, 99.6% D) and toluene-$d_8$ (Aldrich, 99+% D) were vacuum distilled from sodium benzophenone ketyl, and dichloromethane-$d_2$ (Aldrich, 99.6% D) was vacuum distilled from phosphorus pentoxide. Infrared spectra were recorded on a Mattson Sirius 100 FT-IR instrument. Electron-impact mass spectral analyses were performed on a VG 7035 GC/MS instrument at 20 eV.

The complexes $IrBr(CO)(dppe)$,[1a] $IrI(CO)(dppe)$,[1a] $IrH_2Br(CO)(dppe)$ (**3a**),[12] and $Cp_2TaH(C_2H_4)$[13] were prepared according to literature procedures.

**Preparation of $Cp_2TaH_3$ (5).** A modification of the original procedure reported by Green[14] was used for the synthesis of this complex. $TaCl_5$ (7.7 g, 21 mmol) was slowly added to an ice-cooled mixture of NaCp (7.9 g, 90 mmol) and $NaBH_4$ (2.5 g, 66 mmol) in 100 mL of THF. The resulting mixture was refluxed under $N_2$ for 4 h and then cooled to room temperature. After careful addition of 1.2 mL of $H_2O$ (66 mmol), the mixture was again refluxed for 5 min, followed by removal of the solvents in vacuo. The $Cp_2TaH_3$ product was collected from the residue by vacuum sublimation at 110 °C (0.1 Torr). Yield: 2.2 g, 33% isolated

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yield based upon $TaCl_5$. The $^1H$ NMR spectrum of **5**, prepared in this way, was identical with that originally reported by Green.[14] $^1H$ NMR ($C_6D_6$): $\delta$ 4.76 (s, 10 H, Cp), −1.62 (t, *J* = 10 Hz, 1 H, TaH), −3.02 ppm (d, *J* = 10 Hz, 2 H, TaH).

**Preparation of $Cp_2TaD_3$ (5-$d_3$).** The deuterated complex was prepared from **5**-$d_0$ by H/D exchange. A solution of $Cp_2TaH_3$ (0.38 g, 1.2 mmol), dissolved in $C_6D_6$ (15 mL), was placed under 3 atm of $D_2$ in a Fischer-Porter bottle and heated to 110 °C for 3 days. Concentration of the solution and addition of hexanes gave **5**-$d_3$ (isolated yield 0.25 g, 65% based upon $Cp_2TaH_3$). $^1H$ NMR spectroscopy indicated the product, **5**-$d_3$, was pure and was 97% exchanged in Ta–H resonances.

**Preparation of $Cp_2TaBr(C_2H_4)$ (8a).** $CHBr_3$ (1 equiv) was added to a stirred solution of $Cp_2TaH(C_2H_4)$ (**8c**) (10 mg, 0.03 mmol) in benzene (5 mL). After 15 min, the solution was filtered and then taken to dryness, leaving a yellow residue. This residue was taken up into $C_6D_6$ for $^1H$ NMR and mass spectroscopic analysis. $^1H$ NMR ($C_6D_6$): $\delta$ 4.736 (s, 10 H, Cp), 1.770 (t, *J* = 11 Hz, 2 H, $CH_2$), 1.447 ppm (t, *J* = 11 Hz, 2 H, $CH_2$).[15] Mass spectral data: no parent ion, but *m/e* 390 and 392 for $Cp_2Ta^{79}Br$ and $Cp_2Ta^{81}Br$, respectively.[16]

**Preparation of $Cp_2TaI(C_3H_7C{\equiv}CC_3H_7)$ (9b).** The procedure reported for the methylcyclopentadienyl analogue was followed.[17] A solution of $Cp_2TaH_3$ (0.16 g, 0.51 mmol), $C_6H_5I$ (61 μL, 1.1 equiv), and 4-octyne (170 μL, 2.2 equiv) in dioxane (5 mL) was refluxed for $^1/_2$ h under nitrogen. The solvent was stripped off, and the solid was extracted with hexanes. Concentrating and cooling the hexane extract gave **9b** as a yellow solid, which appeared pure by $^1H$ NMR spectroscopy (0.14 g, isolated yield 50%). Anal. Calcd for $C_{18}H_{24}ITa$: C, 39.44; H, 4.41; I, 23.15. Found: C, 37.03; H, 4.02; I, 19.22.[18] $^1H$ NMR ($C_6H_6$): $\delta$ 5.067 (s, 10 H, Cp), 3.140 (t, *J* = Hz, 2 H, α-$CH_2$), 2.433 (t, *J* = 7 Hz, 2 H, α-$CH_2$), 1.56 (complex multiplet, 4 H, both β-$CH_2$), 1.018 (t, *J* = 7 Hz, 3 H, $CH_3$), 0.924 ppm (t, *J* = 7 Hz, 3 H, $CH_3$). IR: $\nu_{C\equiv C}$ = 1772 cm$^{-1}$ (KBr).[19]

**Preparation of $Cp_2TaBr(C_3H_7C{\equiv}CC_3H_7)$ (9a).** With a procedure similar to that used in the synthesis of **9b**, $Cp_2TaH_3$ (0.16 g, 0.51 mmol) was allowed to react with $C_6H_5Br$ (60 μL, 1.1 equiv) and 4-octyne (240 μL, 1.63 mmol) in refluxing dioxane (10 mL) for a period of 4 days. A workup similar to that for **9b** gave **9a** as a pale yellow powder, yield of isolated product 40 mg (16%). This complex was pure on the basis of $^1H$ NMR spectroscopy. $^1H$ NMR ($C_6D_6$): $\delta$ 5.128 (s, 10 H, Cp), 3.292 (t, *J* = 7 Hz, 2 H, α-$CH_2$), 2.449 (t, *J* = 7 Hz, 2 H, α-$CH_2$), 1.665 (overlapping tq, 2 H, β-$CH_2$), 1.570 (overlapping tq, 2 H, β-$CH_2$), 1.025 (t, *J* = 7 Hz, 3 H, $CH_3$), 0.941 ppm (t, *J* = 7 Hz, 3 H, $CH_3$). IR: $\nu_{C\equiv C}$ = 1780 cm$^{-1}$ (KBr).[19]

**Preparation of $Cp_2TaH(C_3H_7C{\equiv}CC_3H_7)$ (9c).** This was prepared in a manner similar to the methylcyclopentadienyl analogue.[17] $Cp_2TaI(C_3H_7C{\equiv}CC_3H_7)$ (0.10 g, 0.24 mmol) and excess $LiAlH_4$ (0.10 g, 10 equiv) in ether (10 mL) were refluxed for 1 h. The ether was removed under vacuum, and the residue was extracted with toluene or hexanes. The extracts were filtered, concentrated, and cooled to give **9c** as an waxy cream-colored solid. $^1H$ NMR spectroscopy indicated the presence of only one tantalum product, **9c**, but revealed the presence of residual solvents that were not removed by exposure to vacuum. $^1H$ NMR ($C_6D_6$): $\delta$ 4.790 (s, 10 H, Cp), −0.556 (s, 1 H, TaH), 2.915 (t, *J* = 7 Hz, 2 H, α-$CH_2$), 2.786 (t, *J* = 7, Hz, 2 H, α-$CH_2$), 1.810 (overlapping tq, 2 H, β-$CH_2$), 1.741 (overlapping tq, 2 H, β-$CH_2$), 1.04 ppm (unresolved triplets, 6 H, both $CH_3$).[19]

The same complex is formed by heating solutions of $Cp_2TaH_3$ with 4-octyne. A toluene solution (25 mL) containing $Cp_2TaH_3$ (0.16 g, 0.5 mmol) and 4-octyne (1.1 g, 10 mmol) was refluxed for 16 h. An aliquot of this solution was removed, the solvent stripped, and $C_6D_6$ added. $^1H$ NMR spectroscopy revealed the solution to contain both **9c** and **5** in a 2:1 ratio. Prolonged heating increased this ratio (3:1 at 32 h), but also resulted in significant decomposition.

**Preparation of $Cp_2TaBr(CO)$ (10a).** $Cp_2TaH(CO)$ (0.17 g, 0.5 mmol) was dissolved in 10 mL of toluene. After $CHBr_3$ (48 μL, 1.1 equiv) was added, the solution was allowed to stir overnight. The resulting brown solution was filtered, concentrated, and cooled to give a brown solid, which was recrystallized from toluene/hexanes and dried in vacuo (isolated yield 0.10 g, 48%). Anal. Calcd for $C_{11}H_{10}BrOTa$: C, 31.53; H, 2.41; Br, 19.07. Found: C, 30.05; H, 2.67; Br, 21.81.[18] $^1H$ NMR ($C_6D_6$): $\delta$ 4.644 ppm (s). IR: $\nu_{CO}$ 1887 cm$^{-1}$ (KBr).[20] Mass spectral data: no parent ion, but *m/e* 390 and 392 for $Cp_2Ta^{79}Br$ and $Cp_2Ta^{81}Br$, respectively.[16]

**Preparation of $Cp_2TaH(CO)$ (10c).** A solution of $Cp_2TaH_3$ (0.08 g, 0.25 mmol) in toluene (15 mL) was heated to 120 °C under 60 psi of CO for 18 h in a Fischer-Porter bottle. After cooling and venting, the solution was filtered under nitrogen and the solvent removed under vacuum, leaving $Cp_2TaH(CO)$ as a dark purple solid (0.55 g, isolated yield 65%). $^1H$ NMR ($C_6D_6$): $\delta$ 4.462 (s, 10 H, Cp), −6.777 ppm (s, 1 H, TaH).[22] IR ($C_6D_6$): $\nu_{CO}$ = 1890 cm$^{-1}$, $\nu_{Ta-H}$ = 1747 cm$^{-1}$.

**NMR Reaction of IrX(CO)(dppe) (1) with $Cp_2TaH_3$ (5).** The general procedure for the reaction of **1** and **5** will be described. Stock solutions of **1a** (3.3 mM in $C_6D_6$), **1b** (3.3 mM in $C_6D_6$), and **5** (10 mM in $C_6D_6$) were prepared and stored in a glovebox.

In the glovebox, some of the stock solution of **1** was placed in a vial. The vial was then taken out of the glovebox and purged with $H_2$, $D_2$, CO, or $C_2H_4$. A color change indicated reversible adduct formation, producing the known complexes IrLX(CO)(dppe) (X = Br, I; L = $H_2$, $D_2$, CO) or the new adducts $Ir(C_2H_4)X(CO)(dppe)$ (X = Br, I).[23,24] Again in the glovebox 0.05, 0.10, or 0.20 mL of the stock solution of **5** ($^1/_2$, 1, or 2 μmol, respectively) and enough extra $C_6D_6$ to bring the total volume up to 0.20 mL was added to an NMR tube, which was then sealed with a rubber septum. Outside of the glovebox the NMR tube was also flushed with $H_2$, $D_2$, CO, or $C_2H_4$, followed by addition of 0.30 mL of the gas-saturated solution of **1** (1 μmol) via syringe. The reactions were then monitored by $^1H$ NMR spectroscopy.

**Low-Temperature Reaction of 1a with 5.** For these experiments, **1a** and **5** (~2 mg each) were added as solids to an NMR tube fitted with a ground-glass joint. On a high-vacuum line, ~0.50 mL of $C_7D_8$ or $CD_2Cl_2$ was slowly vacuum distilled into the NMR tube at −196 °C prior to flame sealing the tube. The sample was subsequently thawed at −78 °C in an 2-propanol/dry ice bath and placed in the NMR probe, which was precooled to −60 or −70 °C.

**Reaction of $Cp_2TaHL$ (8c, 9c, of 10c) with 1a or 3.** In the glovebox, solutions of **1a** or **3a** (~2 mg each) in $C_6D_6$ were added to NMR tubes containing solutions of **8c**, **9c**, or **10c** in $C_6D_6$. The tubes were then sealed with rubber septa and the reactions followed by NMR spectroscopy.

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(15) Compare with $^1H$ NMR of $Cp_2TaI(C_2H_4)$ and $Cp_2TaH(C_2H_4)$ reported in refs 7 and 13 respectively. $Cp_2TaI(C_2H_4)$ $^1H$ NMR ($C_6D_6$): $\delta$ 4.80 (s, 10 H, Cp), 1.98 (t, *J* = 11.5 Hz, 2 H, $CH_2$), 1.26 ppm (t, *J* = 11.5 Hz, 2 H, $CH_2$). $Cp_2TaH(C_2H_4)$ $^1H$ NMR ($C_6D_6$): $\delta$ 4.37 (d, *J* = 0.6 Hz, 10 H, Cp), −3.50 (m, *J* = 2.6, 0.6 Hz, 1 H, TaH), 0.63 (td, *J* = 11, 2.6 Hz, 2 H, $CH_2$), 0.17 ppm (td, *J* = 11, 2.6 Hz, 2 H, $CH_2$).

(16) No attempt was made to use fast-atom bombardment for ionization.

(17) Labinger, J. A.; Schwartz, J.; Townsend, J. M. *J. Am. Chem. Soc.* **1974**, *96*, 4009.

(18) Despite numerous attempts at purification of these complexes, better agreement between the calculated values and the found values for the elemental analyses could not obtained.

(19) Compare with $^1H$ NMR of $(\eta^5\text{-}C_5H_4Me)_2TaI(C_3H_7C{\equiv}CC_3H_7)$ shown in ref 17. $^1H$ NMR ($C_6D_6$): $\delta$ ~3.4 (t, *J* = ~7 Hz, α-C*H*$_2$), ~2.6 ppm (t, *J* = ~7 Hz, α-C*H*$_2$). IR: $\nu_{C\equiv C}$ = 1775 cm$^{-1}$ (*n*-$C_6H_{14}$). Also compare with the hydride analogue described in ref 17, $(\eta^5\text{-}C_5H_4Me)_2TaH(C_3H_7C{\equiv}CC_3H_7)$. $^1H$ NMR ($C_6D_6$): $\delta$ −0.2 (TaH), 2.9 (t, *J* = 7 Hz, α-C*H*$_2$), 2.8 ppm (t, *J* = 7 Hz, α-C*H*$_2$). IR: $\nu_{C\equiv C}$ = 1770 cm$^{-1}$.

(20) The chloro analogue, $Cp_2TaCl(CO)$, has been previously described; see ref 21. $^1H$ NMR ($C_6D_6$): $\delta$ 4.75 ppm (s). IR: $\nu_{CO}$ = 1885 cm$^{-1}$. Characterization of this complex was also reported in ref 9a.

(21) Klazinga, A. H.; Teuben, J. H. *J. Organomet. Chem.* **1979**, *165*, 31.

(22) In ref 9b, $Cp_2TaH(CO)$ is prepared by thermolysis of $Cp_2TaH_3$ at 80 °C in benzene under CO. $^1H$ NMR: $\delta$ −6.80 ppm (s, Ta–H). IR: $\nu_{CO}$ = 1885 cm$^{-1}$, $\nu_{Ir-H}$ = 1750 cm$^{-1}$. This complex was also described in refs 21 and 5b. From ref 21, $^1H$ NMR ($C_6D_6$): $\delta$ 4.50 (s, Cp), −6.75 ppm (s, TaH). From ref 5b, $^1H$ NMR ($C_6D_6$): $\delta$ 4.58 (d, *J* = 1 Hz, 10 Hz, Cp), −6.88 ppm (s, 1 H, TaH). IR (THF): $\nu_{CO}$ = 1890 cm$^{-1}$, $\nu_{Ta-H}$ = 1745 cm$^{-1}$.

(23) Complexes $IrH_2X(CO)(dppe)$, $IrD_2X(CO)(dppe)$, and $IrX(CO)_2(dppe)$ have been described previously: see ref 1b.

(24) Addition of ~700 Torr of $C_2H_4$ to 0.4 mL of 10 mM $C_6D_6$ solutions of IrX(CO)(dppe) (X = Br, I) causes rapid color change of the solutions from orange to yellow. For $IrBr(C_2H_4)(CO)(dppe)$, $^1H$ NMR ($C_6D_6$): $\delta$ 7.88 (broad s, 4 H, phenyl ortho H), 1.97 (broad s, 4 H, dppe –$CH_2$–), 5.093 ppm (s, excess $C_2H_4$).[25] $^{31}P\{^1H\}$ NMR ($C_6D_6$): $\delta$ 38.5 ppm (broad s). IR: $\nu_{CO}$ = 1974 cm$^{-1}$. For $IrI(C_2H_4)(CO)(dppe)$, $^1H$ NMR ($C_6D_6$): $\delta$ 7.70 (broad s, 4 H, phenyl ortho H), 1.92 (broad d, 4 H, dppe –$CH_2$–), 5.14 ppm (s, excess $C_2H_4$).[25] $^{31}P\{^1H\}$ NMR ($C_6D_6$): $\delta$ 39.4 ppm (broad s). IR: $\nu_{CO}$ = 1971 cm$^{-1}$. Removal of $C_2H_4$ leads to regeneration of IrX(CO)(dppe).

(25) In $C_6D_6$, uncoordinated $C_2H_4$ appears at $\delta$ 5.24 ppm.