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Hydrogen Transfer from $CpRe(CO)_2H_2$ to *trans*-$Ir(CO)(Cl)(PPh_3)_2$ via a Heterobimetallic Re–Ir Intermediate

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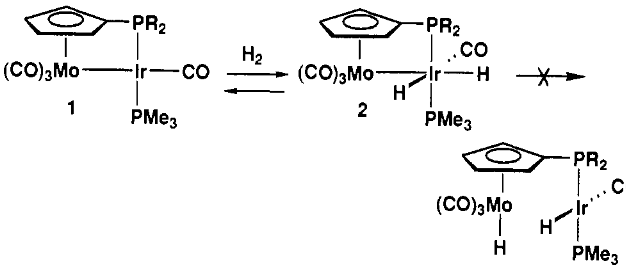
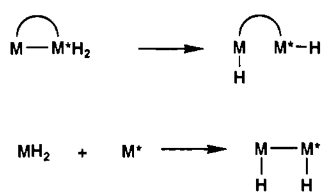
The reaction of $CpRe(CO)_2H_2$ (**3**) with *trans*-$Ir(CO)(Cl)(PPh_3)_2$ (**4**) led to the formation of $CpRe(CO)_3$ (**14**) and of equimolar amounts of $H_2Ir(PPh_3)_2(CO)(Cl)$ (**15**) and *mer*-$H_2Ir(PPh_3)_3(Cl)$ (**16**). When the reaction was carried out in the presence of added PPh_3, only **14** and **16** were formed. When the reaction was carried out under a CO atmosphere, only **14** and **15** were formed. Reaction of **3** with $(PPh_3)_3(CO)IrH$ led to the formation of **14** and *fac*- and *mer*-$IrH_3(PPh_3)_3$ (**20**). These reactions are proposed to proceed by oxidative addition of a rhenium–hydrogen bond to an iridium center. The resulting heterobimetallic dihydride intermediate then rapidly decomposes by simultaneous transfer of H from Re to Ir and transfer of CO from Ir to Re.

Introduction

For several years, we have been searching for new routes to heterobimetallic dihydrides, since we anticipated that such compounds might be unusual reducing agents.[1-3] In an earlier approach, we synthesized heterobimetallic species such as the molybdenum–iridium compound **1** in which the two metals were linked by a metal–metal bond and by a heterodifunctional ligand.[1] We hoped to oxidatively add H_2 to the coordinatively unsaturated iridium center to produce an iridium dihydride (**2**), which then might reductively eliminate molybdenum hydride to produce a compound with terminal hydride ligands on each of two different metals. Oxidative addition of H_2 to **1** proceeded smoothly at room temperature and atmospheric pressure. However, we failed to observe reductive elimination of molybdenum hydride.

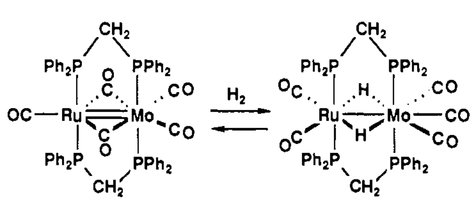


This failure to observe reductive elimination from **2** may well be due to a fundamental thermodynamic problem involving the net loss of a metal–metal bond in elimination of a metal hydride from any $M'–MH_2$ system.



By focusing on the importance of the metal–metal bond, we noted that the addition of a metal dihydride to a coordinatively unsaturated metal center should be thermodynamically favorable, since the process involves a net gain of a metal–metal bond. To initially explore this possibility, we began with the studies reported here of the reaction of the third-row metal dihydride $CpRe(CO)_2H_2$ (**3**) with Vaska's compound *trans*-$Ir(CO)(Cl)(PPh_3)_2$ (**4**).[4]

Only a small number of heterobimetallic compounds with hydride ligands on different metals have been reported. One of the more interesting compounds is Chaudret's ruthenium–molybdenum dihydride **5**, which reversibly loses hydrogen.[5] (The ^1H NMR spectrum of **5** led the authors to depict it as having two bridging hydrides. However, as drawn, **5** has a formal 20-electron count at each metal center. An 18-electron count can be achieved by drawing **5** with a single bridging hydride, a terminal hydride on ruthenium, and no additional metal–metal bond. Rapid exchange of bridge and terminal hydrides would give the observed spectra.) Compounds such as **6** and **7**, which contain hydrides bridging between tungsten and Pt or Rh, have been studied by Venanzi[6] and by Moore.[7] Other very interesting heterobimetallic hydrides include Venanzi's iridium–platinum complex **8**, which contains both bridging and terminal hydrides,[8] Venanzi's Rh–Ir complex **9**,[9] van Koten's palladium–platinum dihydride **10**,[10] Geoffroy's iron–iridium tetrahydride **11**,[11] Schubert's manga-



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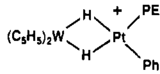

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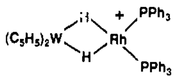

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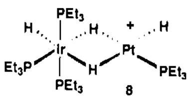

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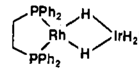

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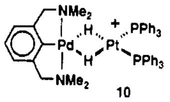

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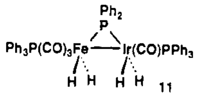

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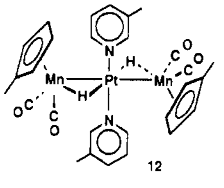

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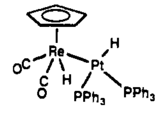

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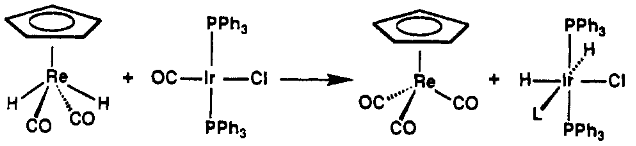
nese–platinum dihydrides **12**,[12] and our $RePtH_2$ **13**.[4]

Results

The reaction of $CpRe(CO)_2H_2$ (**3**)[13] with *trans*-Ir(CO)(Cl)$(PPh_3)_2$ (**4**)[14] was explored as a possible route to the heterobimetallic dihydride $Cp(CO)_2(H)Re–Ir(H)(CO)(PPh_3)_2Cl$ (I). When a solution of **3** (2 mg, 6.5 μmol) and **4** (4 mg, 5.1 μmol) in C_6D_6 (0.40 mL) was monitored by ^1H NMR spectroscopy using C_6Me_6 as internal standard, a slow reaction with a time for the half-reaction of 4 days was observed, which produced $CpRe(CO)_3$ (**14**)[15] (77%) and an equimolar mixture of $H_2Ir(PPh_3)_2(CO)(Cl)$ (**15**)[16] (39%) and *mer*-$H_2Ir(PPh_3)_3Cl$ (**16**)[17] (39%). **15** was identified by its hydride resonances at δ −6.68 (td, J_{PH} = 16.5 Hz, J_{HH} = 4.9 Hz) and −17.49 (td, J_{PH} = 13.2 Hz, J_{HH} = 4.9 Hz). **16** was identified by its hydride resonances at δ −10.67 (dtd, $J_{PH(trans)}$ = 130.3 Hz, $J_{PH(cis)}$ = 19.8 Hz, J_{HH} = 4.9 Hz) and −20.49 (qd, J_{PH} = 14.9 Hz, J_{HH} = 4.9 Hz). Neither the anticipated addition product $Cp(CO)_2(H)Re–Ir(H)(CO)(PPh_3)_2Cl$ (I) nor any other intermediate was observed.



3 4 14 15 L = CO

16 L = PPh3

In an effort to intercept possible intermediates, we carried out the reaction in the presence of added CO or PPh_3. When the reaction of $CpRe(CO)_2H_2$ (**3**) with *trans*-$Ir(CO)(Cl)(PPh_3)_2$ (**4**) in C_6D_6 was carried out under 0.8 atm of CO at 46 °C and monitored by ^1H NMR spectroscopy over 3 days, only $H_2Ir(PPh_3)_2(CO)(Cl)$ (**15**) (79%) and $CpRe(CO)_3$ (**14**) (92%) were observed. No $H_2Ir(PPh_3)_3Cl$ (**16**) was seen. On a preparative scale, reaction of a slurry of **3** with **4** in C_6H_6 under 0.85 atm of CO over 13 days led to the isolation of $H_2Ir(PPh_3)_2(CO)(Cl)$ (**15**) in 74% yield and $CpRe(CO)_3$ (**14**) in 91% yield.

When the reaction of **3** with **4** in the presence of PPh_3 was monitored by ^1H NMR spectroscopy at 46 °C over 4 days, only $CpRe(CO)_3$ (**14**) (80%) and *mer*-$H_2Ir(PPh_3)_3Cl$ (**16**) (78%) were observed. No $H_2Ir(PPh_3)_2(CO)(Cl)$ (**15**) was seen. Furthermore, since less than 1% of $CpRe(CO)_2(PPh_3)$ (**17**)[18] was observed by ^1H NMR analysis, the coordinatively unsaturated intermediate $CpRe(CO)_2$ (II) cannot be involved in this reaction. In a preparative-scale reaction, *mer*-$H_2Ir(PPh_3)_3Cl$ (**16**) (80%) and $CpRe(CO)_3$ (**14**) (80%) were isolated.

The possibility that iridium dihydrides **15** and **16** are formed by reaction of Vaska's complex with H_2 gas derived from $CpRe(CO)_2H_2$ (**8**) can be discounted since Graham has demonstrated that $CpRe(CO)_2H_2$ (**3**) is stable to over 140 °C in solution.[13a]

In another effort to prepare a heterobimetallic dihydride, we studied the reaction of $CpRe(CO)_2H_2$ (**3**) with $(PPh_3)_3(CO)IrH$ (**19**).[19] Although **19** is a coordinatively saturated 18-electron complex, it readily undergoes oxidative addition reactions with silanes and H_2 via a coordinatively unsaturated 16-electron intermediate $(PPh_3)_2(CO)IrH$.[20,21] When the reaction of **3** (9 mg, 29.1 μmol) with **19** (29 mg, 26.4 μmol) in C_6D_6 (0.58 mL) was monitored by ^1H NMR spectroscopy, a slow reaction was observed, which was complete in 2 days. The ultimate products observed by NMR analysis were $CpRe(CO)_3$ (**14**), the sole cyclopentadienyl-containing species, and a 1.8:1 mixture of *fac*- and *mer*-$IrH_3(PPh_3)_3$ (**20**),[22,23] the only hydride-containing species. In the initial stages of the reaction, the only trihydride seen was *fac*-**20**. The formation of *mer*-**20** later in the reaction is presumably the result of equilibration of *fac*- and *mer*-**20**. The 1.8:1 ratio of *fac*-**20**:*mer*-**20** produced in the reaction of **3** with **19** is somewhat different from the 1.25:1 ratio of isolated yields from the reaction of Na_3IrCl_6 with $NaBH_4$.[22] Harrod has observed similar equilibration of *fac*- and *mer*-$(PPh_3)_2(CO)IrH_3$ by reversible elimination–addition of H_2.[21]

The reaction of **3** with the more electron-rich iridium complex *trans*-$(PEt_3)_2(CO)IrCl$ (**21**)[24] was studied in the hope that oxidative addition of rhenium dihydride might be accelerated so that a heterobimetallic dihydride might be observed. However, no reaction was observed by ^1H NMR spectroscopy in toluene-d_8 below −25 °C, and starting at −6 °C, the formation of a hopelessly complex mixture was seen with more than 10 different multiplets between δ −8 and −28 in the metal hydride region of the ^1H NMR spectrum. The major cyclopentadienyl resonance was that of $CpRe(CO)_3$.

Our proposed mechanism for decomposition of the putative heterobimetallic dihydride intermediate requires a hydride on the rhenium center and a carbonyl on the iridium center (see Discussion). This suggested that a bimetallic species might be isolated in the absence of one of these structural features. The reaction of *trans*-$Cp(CO)_2Re(H)(SiPh_3)$ (**22**)[25] with *trans*-Ir(CO)(Cl)$(PPh_3)_2$ (**4**) was briefly investigated in an effort to isolate a heterobimetallic compound. However, no reaction between these species was observed even upon heating at 74 °C for 1 day. The sterically huge $SiPh_3$ group on rhenium may have precluded formation of a heterobimetallic compound.

The reaction of **3** with the non-carbonyl-containing iridium complex $(PPh_3)_3IrCl$ (**23**)[26] was also briefly investigated. However, no reaction was seen over 2 months at room temperature. Once again steric hindrance may have prevented formation of a heterobimetallic compound.

Discussion

The reaction of $CpRe(CO)_2H_2$ with Vaska's compound can be understood in terms of the mechanism shown in Scheme I. We propose that addition of $CpRe(CO)_2H_2$ to iridium occurs to produce the originally desired heterobimetallic dihydride intermediate I, which immediately decomposes by transferring a second hydrogen from Re to Ir while back-transferring a carbonyl from Ir to Re via the (μ-H)(μ-CO) species III. This process explains the generation of coordinatively saturated $CpRe(CO)_3$ and of the coordinatively unsaturated Ir intermediate IV, which can be trapped by added PPh_3 or added CO. In the absence of added ligand, this unsaturated Ir(III) dihydride intermediate IV apparently abstracts either CO or PPh_3 from Vaska's complex.

Jones and Maguire have observed a similar transfer of two hydride ligands from Re to Ir in the reaction of $(\eta^4\text{-}C_5H_6)Re(PPh_3)_2H_3$ with (dppe)Ir(CO)(Br), which produces $(\eta^5\text{-}C_5H_5)Re(PPh_3)_2H_2$ and the thermodynamically favored isomer $H_2IrBr(CO)(dppe)$ (**18T**), which has the hydrides trans to phosphorus and bromide.[27] This observation excludes a mech-

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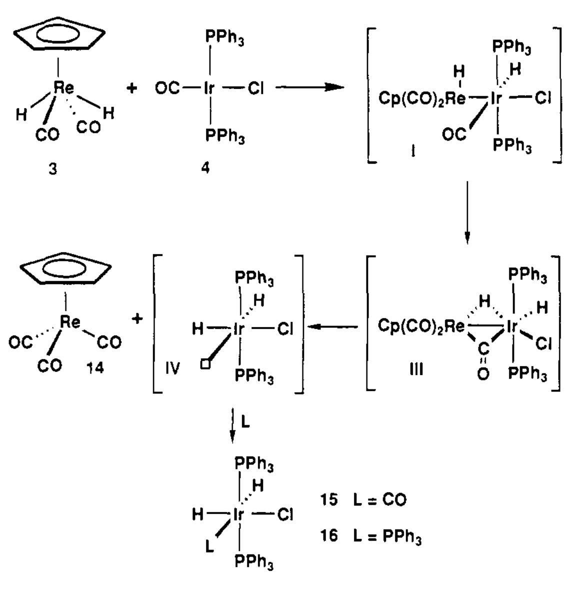
Scheme I



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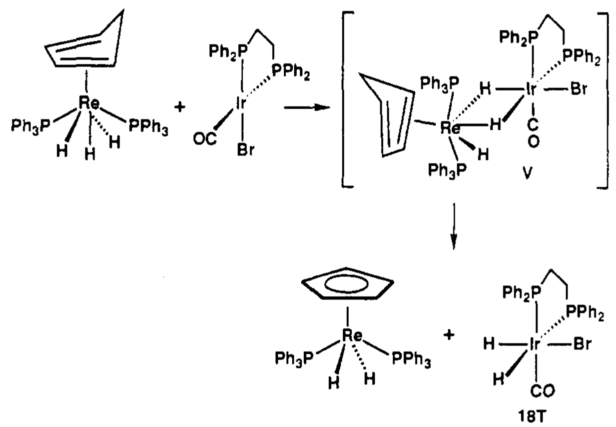
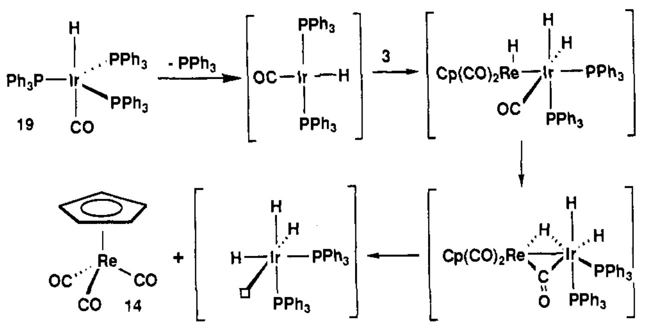


Scheme III



anism involving dissociation of H_2 from Re followed by oxidative addition of the liberated H_2 gas to (dppe)Ir(CO)Br, since this would have led to the formation of kinetic isomer **18K**, in which the hydrides are trans to CO and phosphorus.[28] This kinetic isomer **18K** slowly isomerized to the more thermodynamically stable isomer **18T**. To explain these results, Jones and Maguire suggested that simultaneous transfer of two hydrides occurs via the 20-electron intermediate or transition state V (Scheme II).[27] However, their experimental observations are also consistent with sequential hydride transfers involving only 18-electron intermediates. Our mechanism involving sequential transfer of hydrides does not involve any intermediate that exceeds an 18-electron count at either metal. These two mechanisms are kinetically indistinguishable, and no experiments have been designed to distinguish between the two proposals.

The reaction of $(PPh_3)_3(CO)IrH$ (**19**) with $CpRe(CO)_2H_2$ (**3**) apparently occurs by a mechanism similar to that proposed for the reaction of **3** with Vaska's compound **4**. In most oxidative additions to **19**, a PPh_3 ligand is lost from Ir.[20,21] However, the reaction of **19** with $CpRe(CO)_2H_2$ (**3**) involves a very unusual loss of a tightly bound CO from Ir. The mechanism shown in Scheme III readily explains the unusual transfer of CO from Ir to Re. We propose that the reaction of **19** is initiated by loss of PPh_3, as has been seen in other reactions of **19**.[20,21] Oxidative addition of Re–H to the coordinatively unsaturated intermediate $(PPh_3)_2(CO)IrH$ then produces a heterobimetallic trihydride. Rearrangement of this intermediate by simultaneous transfer of CO from Ir to Re and transfer of H from Re to Ir then produces $CpRe(CO)_3$ and coordinatively unsaturated $(PPh_3)_2IrH_3$, which is trapped by PPh_3.

The hypothesis that a stable heterobimetallic dihydride might be isolable from the addition of $CpRe(CO)_2H_2$ to a second metal if no carbonyl were present on the second metal center was eventually shown to be valid. In a subsequent paper, we will present full details of our studies of the formation of the heterobimetallic dihyride $Cp(CO)_2(H)Re–Pt(H)(PPh_3)_2$ (**13**) from the reaction of $CpRe(CO)_2H_2$ (**3**) with $(PPh_3)_2Pt(CH_2=CH_2)$.[4]

Experimental Section

General Methods. ^1H NMR spectra were obtained on Bruker WP200, WP270, and AM500 spectrometers. ^{13}C and ^{31}P NMR spectra were obtained on a AM500 spectrometer operating at 126 and 202 MHz. ^{13}C samples contained 0.07 M $Cr(acac)_3$ as a shiftless relaxation agent. Infrared spectra were obtained on a Mattson FTIR spectrometer or a Beckman IR 4230 spectrometer.

Reaction of $CpRe(CO)_2H_2$ (3) with *trans*-$Ir(CO)(Cl)(PPh_3)_2$ (4) under CO. **3** (270 mg, 0.873 mmol) and **4** (644 mg, 0.825 mmol) were stirred in C_6H_6 (15 mL) for 13 days at 40 °C under 0.85 atm of CO. Upon the initial introduction of CO, the yellow slurry turned white and a white solid slowly precipitated from a yellow solution. Hexane (50 mL) was added under N_2 to complete the precipitation. The precipitate was isolated by filtration, washed with hexane, and dried under vacuum to give **15**[16] (475 mg, 74%) as a pale yellow solid, which was shown to be pure by ^1H NMR spectroscopy. ^1H NMR (C_6D_6, 270 MHz, hydride region): δ -6.68 (td, J_{PH} = 16.5 Hz, J_{HH} = 4.9 Hz, 1 H), -17.49 (td, J_{PH} = 13.2 Hz, J_{HH} = 4.9 Hz, 1 H).

The hydrocarbon solution was evaporated under vacuum, and the residue was sublimed at 60 °C to yield $CpRe(CO)_3$ (**14**)[15] (267 mg, 91%) as a white solid. ^1H NMR (C_6D_6, 200 MHz): δ 4.32 (s, C_5H_5). IR (hexane): 2032 (m), 1940 (s) cm^{-1}.

Reaction of $CpRe(CO)_2H_2$ with *trans*-$Ir(CO)(Cl)(PPh_3)_2$ (4) and PPh_3. Complete dissolution occurred when a yellow slurry of **4** (585 mg, 0.750 mmol) in 20 mL of a benzene solution of **3** (225 mg, 0.727 mmol) and PPh_3 (220 mg, 0.839 mmol) was stirred for 30 h at 25 °C. Over the course of 7 days, a cream white precipitate formed. The precipitate was isolated by filtration and washed with hexane to give *mer*-$H_2Ir(PPh_3)_3Cl$ (**16**) (593 mg, 80%). ^1H NMR (C_6D_6, 270 MHz, hydride region): δ -10.67 (dtd, J_{HP} = 130.3 Hz, $J_{HP'}$ = 19.8 Hz, J_{HH} = 4.9 Hz, H trans to P), -20.49 (qd, J_{HP} = 14.9 Hz, J_{HH} = 4.9 Hz, H trans to Cl). The yellow filtrate was evaporated under vacuum, and the residue sublimed at 70 °C under high vacuum to give $CpRe(CO)_3$ (**14**) (195 mg, 80%).

Preparation of *fac*- and *mer*-$IrH_3(PPh_3)_3$ (20) from $CpRe(CO)_2H_2$ (3) and $(PPh_3)_3(CO)IrH{\cdot}C_6H_5CH_3$ ($19{\cdot}C_6H_5CH_3$). A solution of **3** (33 mg, 0.107 mmol) and **19**·$C_6H_5CH_3$ (112 mg, 0.102 mmol) in 20 mL of C_6H_6 was stirred for 5 days at 42 °C. The solvent was evaporated under vacuum, hexane (10 mL) was added, and the mixture was filtered. The resulting solid was washed with hexane (4 × 7 mL) and dried under vacuum to give a 1.8:1 mixture of *fac*- and *mer*-$IrH_3(PPh_3)_3$ (**20**) (77 mg, 77%). ^1H NMR (C_6D_6, 500 MHz): δ 6.8–7.7 (m, aromatic), -11.35 (dt, AA′A″XX′X″, $J_{PH(trans)}$ = 121 Hz, $J_{PH'(cis)}$ = -18 Hz, $J_{PP} \sim$ 6 Hz, *fac*-**20**), -10.21 (q, $J_{PH} = J_{P'H}$ = 16 Hz, H trans to H in *mer*-**20**), -12.01 (dt, $J_{PH(trans)}$ = 114.8 Hz, $J_{P'H(cis)}$ = 22 Hz, H trans to P in *mer*-**20**). ^{31}P NMR (CD_2Cl_2, 202 MHz): δ 5.8 (br d, peak separation 100 Hz, *fac*-**20**), 12.8 (br d, peak separation 102 Hz, P trans to H in *mer*-**20**), 16.1 (br s, P trans to P in *mer*-**20**). IR (CH_2Cl_2): 2090 (w) cm^{-1} (ν_{Ir-H}).

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