J. Am. Chem. Soc. 1987, 109, 6886-6887

Synthesis of a Heterobimetallic Dihydride by the Addition of a Rhenium Dihydride to a Platinum(0) Complex

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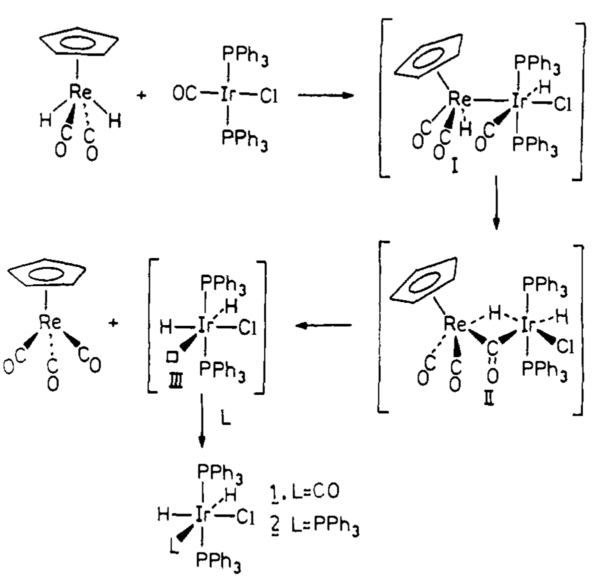
Received June 10, 1987

We have been searching for routes to heterobimetallic dihydrides since we anticipate that such compounds might be unusual reducing agents.[1-4] Here we report the synthesis of a heterobimetallic dihydride by oxidative addition of a metal dihydride to a second metal center. The thermodynamic driving force for the process is the formation of a new metal–metal bond.

$CpRe(CO)_2H_2$ (Cp = η-C_5H_5) reacts slowly ($t_{1/2}$ = 4 days) with *trans*-$Ir(CO)(Cl)(PPh_3)_2$ in C_6D_6 at 25 °C to produce $CpRe(CO)_3$[5] (77%) and nearly equal amounts of $H_2Ir(CO)(Cl)(PPh_3)_2$ (**1**, 39%)[6] and *mer*-$H_2Ir(Cl)(PPh_3)_3$ (**2**, 39%)[7] as determined by ^1H NMR. Neither the anticipated addition product $Cp(CO)_2(H)Re-Ir(H)(CO)(PPh_3)_2Cl$ (I) nor any other intermediate was observed. When the reaction was run under 1 atm of CO, the only iridium product formed was **1** (85%). When the reaction was carried out in the presence of excess PPh_3 (0.17 M), the only iridium product was **2** (78%), and the major rhenium product was $CpRe(CO)_3$ (80%); less than 1% of $CpRe(CO)_2PPh_3$[8] was observed. These results provide evidence for the initial formation of the 16-electron iridium intermediate III.



We propose that addition of $CpRe(CO)_2H_2$ to iridium occurs to produce the heterobimetallic dihydride intermediate I which immediately decomposes by transfering a second hydrogen from Re to Ir while back transfering a carbonyl from Ir to Re via the (μ-H, μ-CO) species II. This process readily explains the generation of the coordinatively unsaturated Ir intermediate III and of coordinatively saturated $CpRe(CO)_3$. The reaction of $CpRe(CO)_2H_2$ is thus quite different from the reaction of (η^4-C_5H_6)$Re(PPh_3)_2H_3$ with IrBr(CO)(dppe) in which transfer of two hydrides leads to a coordinatively unsaturated Re intermediate.[9] Jones and Eisenberg have proposed that their reaction occurs via a 20-electron (μ-H_2) intermediate or transition state; however, their experimental observations are also consistent with sequential hydride transfers involving only 18-electron intermediates.

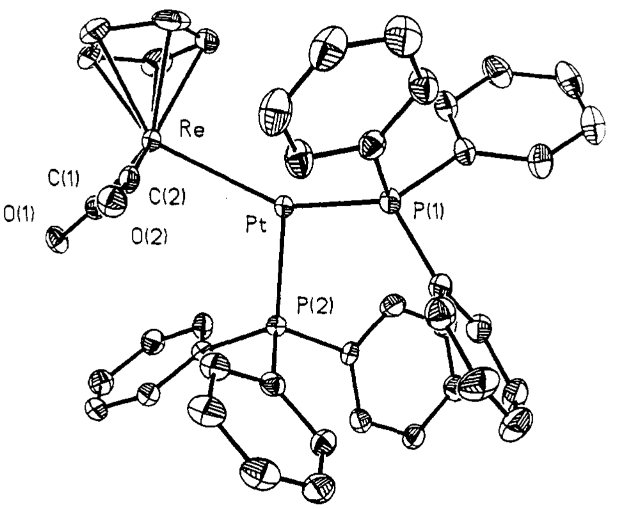
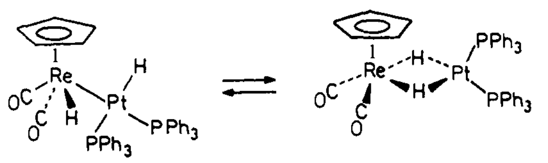


Figure 1. Selected bond lengths (Å) and angles (deg) for $Cp(CO)_2(H)Re-Pt(H)(PPh_3)_2$ (**3**): Re–Pt, 2.838 (1); Pt–P(1), 2.249 (1); Pt–P(2), 2.336 (1); Re–C(1), 1.881 (5); Re–C(2), 1.891 (5); nonbonded Pt–C(2), 2.940; C(1)–Re–Pt, 109.4 (2); C(2)–Re–Pt, 73.8 (2); C(1)–Re–C(2), 91.4 (2); Re–Pt–P(1), 146.9 (1); Re–Pt–P(2), 108.2 (1); P(2)–Pt–P(1), 102.2 (1).

These results suggested that a stable heterobimetallic dihydride might be isolable if CO were not available for back transfer to Re. $CpRe(CO)_2H_2$[10] and $(Ph_3P)_2Pt(CH_2{=}CH_2)$[11] in C_6D_6 reacted rapidly ($t_{1/2}$ < 2 min) at 25 °C to liberate ethylene and form the heterobimetallic dihydride, $Cp(CO)_2(H)Re-Pt(H)(PPh_3)_2$ (**3**) which was isolated in 71% yield by crystallization from CH_2Cl_2–hexane. The X-ray structure of **3** (Figure 1) revealed a 2.838 (1) Å Pt–Re bond. The sum of the angles about platinum is 357.2° indicating an essentially planar platinum unit. We believe that one hydride ligand occupies a site on Pt trans to P(2) and that P(1) and Re are displaced from their idealized square-planar positions toward the small hydride ligand. The presence of a hydride trans to P(2) is consistent with the fact that the Pt–P(2) bond (2.336 (1) Å) is longer than the Pt–P(1) bond (2.249 (1) Å). The rhenium center can be considered to possess a four-legged piano stool geometry with hydride occupying a site cis to Pt. The geometry of **3** is very similar to that seen in the X-ray structure of $Cp(CO)_3Mo-Pt(PPh_3)_2H$ (**4**) reported by Braunstein and Geoffroy.[12,13]



3 **IV**

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[1] Earlier we attempted to synthesize heterobimetallic dihydrides by addition of H_2 to compounds such as $[C_5H_4PPh_2](CO)_3Mo-Ir(CO)PMe_3$.[2] These compounds reacted with H_2 to produce iridium dihydrides but then failed to eliminate Mo–H to form the desired heterobimetallic dihydride. We now believe that this elimination is thermodynamically unfavorable due to loss of a metal–metal bond. Consequently, our present approach utilizes the reverse process—addition of a metal dihydride to a second metal.

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0002-7863/87/1509-6886$01.50/0

In the ^{1}H NMR of **3**,[14] the metal hydrides are equivalent even at −111 °C. The metal hydride resonance for **3** in CD_2Cl_2 at −28 °C appears at δ −7.62 as a doublet of doublets (J_{PH} = 120.9 Hz, $J_{P'H}$ = −11.1 Hz) with satellites due to coupling to ^{195}Pt. The 593 Hz J_{PtH} is consistent either with an average of a terminal PtH and a noncoupled ReH or with two bridging hydrides. At higher temperature (60.7 °C), rapid exchange of the phosphine environments gives rise to a 1:2:1 triplet for the metal hydride signals. An interesting coalescence behavior of the metal hydride signals is seen. The inner lines of the doublet of doublets are due to coupling to $\alpha\alpha$ and $\beta\beta$ ^{31}P spins and remain sharp at all temperatures; the outer lines are due to coupling to $\alpha\beta$ and $\beta\alpha$ ^{31}P spins, and these lines broaden, coalesce, and sharpen to the center line of the 1:2:1 triplet as the temperature is increased. Similar temperature dependent spectra of **4** were observed by Braunstein and Geoffroy.[12] Hydride exchange while maintaining the inequivalence of the phosphine ligands requires accessing a $(\mu\text{-H})_2$ structure similar to IV which has a pseudotetrahedral d^{10} Pt center in which the phosphines remain inequivalent due to their relationship to the Cp ligand on Re. The conversion of IV back to **3** can occur via two pathways. The major pathway returns the phosphines to their original environments. The minor pathway occurs via an alternative geometry and exchanges the phosphine environments.[15]

Since access to bridging dihydride structure IV is required to explain the NMR equivalence of the metal hydrides of **3**, we considered the possibility that IV might be the solution structure of the $PtReH_2$ compound even though this seemed somewhat unlikely due to the large differences seen for J_{PH} and $J_{P'H}$. Saunders isotopic perturbation of equilibria technique[16] provides a definitive test to distinguish between symmetric $(\mu\text{-H})_2$ structure IV and nonsymmetric **3** by simply comparing the chemical shift of the $PtReH_2$ compound **3** with the PtReHD compound **3d**. If the material has terminal hydride ligands, then the equilibrium constant for HPtReD $\rightleftarrows$ DPtReH should not be unity because of differences in zero-point energy. The proton will spend more than 50% of the time on one of the metals, and the average chemical shift of **3d** will be substantially different from that of **3**. However, if the structure is $(\mu\text{-H})(\mu\text{-D})$ species IV, then a negligible difference in chemical shift would be expected. When a solution of **3** was shaken with D_2 at room temperature for 10 min, the ^{1}H NMR spectrum at 14 °C exhibited a multiplet at δ −7.62 due to **3** and a similar multiplet shifted 0.16 ppm upfield (δ −7.78) due to **3d**. When the temperature was lowered to −84 °C, the chemical shift difference increased to 0.24 ppm due to a change in the equilibrium constant. These results rule out the bridging dihydride IV as the only species in solution and are consistent with the solution structure of **3** being the same as the solid-state structure.

J_{PtH} increases from 593 Hz at 14 °C to 649 Hz at −84 °C for **3**. This variation suggests that two species are present in equilibrium. These two species have similar zero-point energies since **3d** behaves very similarly (J_{PtH} = 601 Hz at 14 °C, J_{PtH} = 654 Hz at −84 °C) and therefore cannot have different numbers of bridging and terminal hydrides. We believe this phenomenon may be due to a temperature dependent equilibrium between two rotamers of the terminal dihydride.

Acknowledgment. Support from the Department of Energy, Division of Basic Energy Sciences, is gratefully acknowledged.

Supplementary Material Available: Variable temperature ^{1}H NMR data of the hydride region of a mixture of **3** and **3d** and tables of positional and thermal parameters and interatomic distances and angles for **3** (9 pages); listing of observed and calculated structure factors (88 pages). Ordering information is given on any current masthead page.

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(13) The oxidative addition of $C_5H_5(CO)_3MoH$ to $(PPh_3)_2Pt(CH_2{=}CH_2)$ to produce **4** has been observed at du Pont. Janowicz, A. H.; Bryndza, H. E., private communication.

(14) $Cp(CO)_2(H)Re{-}Pt(H)(PPh_3)_2$ (**3**): ^{1}H NMR (270 MHz, CD_2Cl_2, 400 mm H_2, −28 °C) δ 7.3 (m, 30 H), 4.99, (s, 5 H), −7.62 (dd, J_{PH} = 120.9 $J_{P'H}$ = −11.1 Hz, 2 H, J_{PtH} = 593.4 Hz); ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, 400 mm H_2, 0.07 M $Cr(acac)_3$) δ 205.52 (CO), 129.96 (s, para), 139.25, (d, J_{CP} = 11.7 Hz, ortho or meta), 128.25, (d, J_{CP} = 11.7 Hz, ortho or meta), 80.98 (s, C_5H_5), ipso C not observed; ^{31}P NMR (202 MHz, CD_2Cl_2, 25 °C) δ 30.1 (t, J_{PH} = 49 Hz, J_{PtP} = 3308); ^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2, −70 °C) δ 29.9 (J_{PtP} = 3308 Hz), 30.3 (J_{PtP} = 3308 Hz); ^{195}Pt{^{1}H} (107 MHz, CD_2Cl_2, 400 mm H_2, 22 °C) δ −5823.4 relative to Na_2PtCl_6 in D_2O (t, J_{PtP} = 3224 Hz); IR (KBr) 2098 (m, MH), 1906 (s, CO), 1832 (s, CO) cm^{-1}.

(15) A symmetric $(\mu\text{-H})_2$ square planar Pt(II) intermediate cannot be responsible for the equivalence of the metal hydrides since it requires equal rates for hydride and phosphine exchange. However, phosphine exchange was observed to be much slower than hydride exchange.

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Electrocatalytic Hydrogenation of Organic Compounds on Carbon Electrodes Modified by Precious Metal Microparticles in Redox Active Polymer Films

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Received May 20, 1987

In contrast to catalytic hydrogenation which is a widely used procedure in organic synthesis, electrocatalytic hydrogenation has been largely neglected despite the advantages of very mild conditions (room temperature and atmospheric pressure) normally employed in electrosynthesis. However, in recent years an increasing number of papers on this subject have appeared with the development of hydrogen active powder cathodes, particularly those based on Raney-nickel[1-3] but also Devarda-copper[2] and palladium or platinum on carbon[3] catalysts. Some electrohydrogenations with metals deposited on carbon[4] or solid polymer electrolyte membranes[5] have also been reported. On the other hand, electrodes modified by conductive,[6] redox,[7] or even electroinactive[8] polymer films in which highly dispersed platinum or palladium microparticules have been deposited show a good catalytic activity toward reduction of protons to hydrogen. We find that hydrogen liberated by electrolysis in aqueous media on carbon electrodes modified by a redox polymeric film containing

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