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Adduct Formation and Single and Double Deprotonation of $Cp^*(PMe_3)Ir(H)_2$ with Main Group Metal Alkyls and Aryls: Synthesis and Structure of Three Novel Ir−Al and Ir−Mg Heterobimetallics

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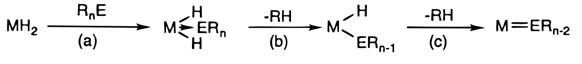
Although they are commonly referred to as “hydrides”, complexes with transition metal−hydrogen bonds display varying degrees of acidity. Treatment of hydrides with main group metal alkyls (R_nE) often results in deprotonation to give R−H and the corresponding metal anion complex M−E. In the case of a late transition metal dihydride (**1** in eq 1), such a transformation could



(1)

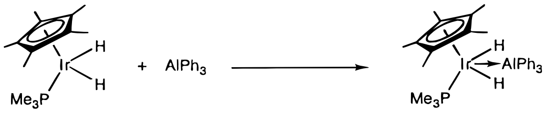
1 **2** **3** **4**

$$MH_2 \xrightarrow[(a)]{R_nE} M\overset{H}{\underset{H}{\Leftarrow}}ER_n \xrightarrow[(b)]{-RH} M\overset{H}{\underset{ER_{n-1}}{<}} \xrightarrow[(c)]{-RH} M{=}ER_{n-2} \qquad (1)$$

take place via the initial formation of a Lewis acid/base adduct (**2**), followed by loss of R−H to give the monoanion complex **3**. With a sufficiently strong base, loss of a second proton could also occur to give a dianion or multiply bonded complex (**4**).

The iridium dihydride $Cp^*(PMe_3)IrH_2$ ($Cp^* = \eta^5$-pentamethylcyclopentadienyl) is an example of a dihydride which potentially can undergo the transformations summarized in eq 1. We reported earlier that treatment of $Cp^*(PMe_3)IrH_2$ with alkyllithium reagents leads to a pyrophoric species whose spectroscopic properties and chemical reactivity are consistent with its assignment as the lithium iridate $Cp^*(PMe_3)Ir(H)(Li)$.[1,2] However, the high reactivity of this material has so far prevented detailed study of its formation or structure. Furthermore, little structural or mechanistic information is available on the small number of metalates that have been generated by deprotonation of other transition metal di- and polyhydrides.[3−6] As an approach to this problem, we have now investigated the reaction of $Cp^*(PMe_3)IrH_2$ with organomagnesium and aluminum compounds. The result of this study has been the isolation and structural characterization of three novel complexes that support each step of the sequence illustrated in eq 1, including the first observation of double deprotonation at the iridium center, and some preliminary information on the chemistry of these materials.

The reaction of $Cp^*(PMe_3)Ir(H)_2$ with Ph_3Al gives an example of step (a) in eq 1. In refluxing toluene this reaction leads to the 1:1 adduct, $Cp^*Ir(PMe_3)H_2AlPh_3$ (eq 2).[7] The ORTEP diagram of this material is shown in Figure 1.



(2)

Aluminum-metal hydride complexes are rare, but a known adduct related to $Cp^*Ir(PMe_3)H_2AlPh_3$ is $Cp_2WH_2AlMe_3$.[8−11]The IrH_2AlPh_3 portion of the iridium complex resembles the WH_2-$AlMe_3$ portion of the tungsten complex but with several important

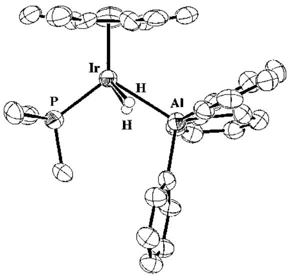
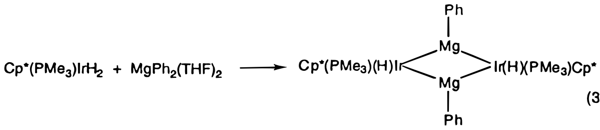


Figure 1. ORTEP diagram of $Cp^*(PMe_3)Ir(H)_2AlPh_3$. The hydride atoms were located in the difference Fourier map, placed in idealized positions, and included in the refinement but not refined.

differences. In the iridium adduct the dihedral angle formed by the intersection of the IrH_2 and H_2Al planes is 37°, but in the tungsten adduct the angle is near zero. Further, the IrH_2 angle opens by 20° upon coordination, while the WH_2 angle closes by 15°, allowing the Ir−Al distance of 2.684(2) Å to be substantially shorter than the W−Al distance of 3.110(3) Å. These changes imply that the bonding in these two adducts is rather different. In the tungsten case, the WH_2 unit appears to form bridge bonds to the Me_3Al fragment without much W−Al bonding. In contrast, the iridium adduct appears to have a Ir−Al bond that is bridged by hydrogen atoms. The origin of these structural differences is unknown.

An arylmagnesium reagent removes one proton from the iridium center (step b in eq 1). $Cp^*(PMe_3)Ir(H)_2$ reacts with $Ph_2Mg(THF)_2$[12] at room temperature in toluene over the course of 1 day, as shown in eq 3. The starting material disappears and



(3)

$$Cp^*(PMe_3)IrH_2 + MgPh_2(THF)_2 \longrightarrow Cp^*(PMe_3)(H)Ir\overset{Mg-Ph}{\underset{Mg-Ph}{\langle\rangle}}Ir(H)(PMe_3)Cp^* \qquad (3)$$

hydride resonances associated with three new complexes appear in the ^1H NMR spectrum of this solution. The appearance of 1 equiv of benzene relative to the amount of starting material lost (^1H NMR) implies the formation of compounds having empirical formula $Cp^*(PMe_3)Ir(MgPh)(H)$. One of these products is not formed in the absence of THF, and so we believe this product is a THF adduct, probably $Cp^*(PMe_3)Ir(H)(PhMg)(THF)$. The two remaining complexes have very similar ^1H NMR spectra.

We have been able to crystallize one of these products and determine its structure by X-ray diffraction.[13] An ORTEP diagram is illustrated in Figure 2. This shows that the compound is a dimer in which the Cp^*IrPMe_3H fragments are bridged by two MgPh groups. The geometry at magnesium is trigonal planar, the angles sum to 360°, and the distances to iridium are slightly different, 2.669(2) Å and 2.748(2) Å. The orientation of the two

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(7) Synthesis of $Cp^*(PMe_3)Ir(H)_2(AlPh_3)$ was performed in an N_2 atmosphere glovebox. $Cp^*(PMe_3)Ir(H)_2$ (0.420 g, 1.03 mmol) and $AlPh_3$ (0.269 g, 1.04 mmol) were combined in a 25 mL scintillation vial. Toluene (10 mL) was added, and the resulting solution was briefly heated to reflux. Upon slow cooling to room temperature crystalline material precipitated. The mother liquor was removed via pipet, and the solid material dried in vacuo. Yield 0.506 g (74%). Mp 145 °C (dec). ^1H NMR (400 MHz, C_6D_6): δ 8.29 (d, J = 10.3 Hz, 6H, *o*-C*H*), 7.46 (t, J = 10.0 Hz, 6H, *m*-C*H*), 7.32 (t, J = 9.7 Hz, 3H, *p*-C*H*), 1.45 (d, J = 2.7 Hz, 15H, $C_5(CH_3)_5$), 0.88 (d, J = 14.4 Hz, 9H, $P(CH_3)_3$), −16.25 (d, J = 32 Hz, 2H, Ir*H*). $^{13}C\{^1H\}$(100 MHz, C_6D_6): δ 139.5, 127.0, 126.4, 95.6, 21.4 (d, J_{CP} = 40 Hz), 9.9. Quaternary resonance for phenyl carbon unobserved. $^{31}P\{^1H\}$ (162 MHz, C_6D_6): −48.03. LRMS: *m/z* 662 (M^+). IR (NaCl, Nujol mull): 2972 (m), 2902 (m), 2091 (s), 1281 (w), 1419 (m), 951 (m), 679 (w) cm^{-1}. Anal. Calcd for $C_{31}H_{41}AlIrP$: C, 56.09; H, 6.23. Found 55.77, 6.10.

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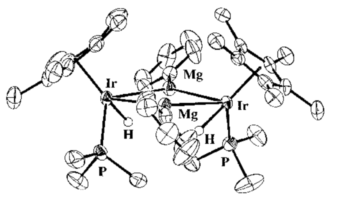


Figure 2. ORTEP diagram of $(Cp^*(PMe_3)Ir(H)MgPh)_2$. The metal-bound hydrogens were located in the difference Fourier map. They were placed in idealized positions and included in the refinement but not refined.

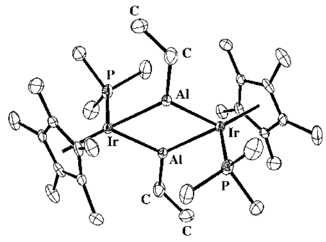
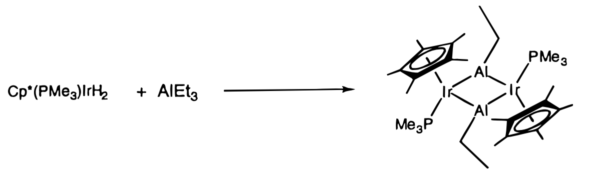


Figure 3. ORTEP diagram of $(Cp^*(PMe_3)IrAlEt)_2$.

Cp^*IrPMe_3H fragments in the dimer is staggered (looking down the Ir−Ir vector), and the Cp* groups have a cis orientation relative to each other; the idealized symmetry is C_2. In solution two dimers are present in a 1:10 ratio; these are presumably rotamers in which the Cp* groups are cis, as in Figure 2, and trans.

Reaction of $Cp^*(PMe_3)IrH_2$ with triethylaluminum, which has a weaker Al−C bond than that in Ph_3Al[14] and is also less sterically encumbered, results in double deprotonation at the iridium center (step (c) in eq 1). Two moles of ethane ultimately are eliminated over the course of 2 weeks at 20 °C; the immediate disappearance of $Cp^*(PMe_3)Ir(H)_2$ is followed by formation of several intermediates (^1H NMR) which are gradually converted (eq 4) to the centrosymmetric dimer $[Cp^*IrPMe_3AlEt]_2$.[15]



(4)

The ORTEP diagram in Figure 3 shows that this complex contains two Cp^*IrPMe_3 fragments bridged by two EtAl units. The structure is similar to that found in $(Cp^*Co(C_2H_4)AlEt)_2$.[18] The geometry around aluminum is trigonal planar, and the two individual Ir−Al distances are 2.456(1) Å and 2.459(1) Å.

Elimination of hydrocarbons to form magnesium heterobimetallic complexes has precedent for molybdenum and tungsten,[3] but to our knowledge no Ir−Mg compounds have been reported in the literature. The recently reported compound $Cp^*AlFe(CO)_4$ is the only known example of a mixed metal organometallic complex in which aluminum acts as a two-electron donor.[16] In the case of our aluminum complexes, two different types of Ir−Al bonds are observed, one a dative bond and the other a covalent Ir−Al bond. The geometry of both $(Cp^*(PMe_3)Ir(MgPh)(H))_2$ and $Cp^*(PMe_3)Ir(H)_2AlPh_3$ indicate that the Ir center in $Cp^*(PMe_3)Ir$ is Lewis basic. Very few three-coordinate aluminum-transition metal organometallic complexes have been prepared and structurally characterized;[17] $(Cp^*(C_2H_4)CoAlEt)_2$,[18] mentioned above, and $(CpNiAlCp^*)_2$[19] are 3d transition metal examples.

Preliminary studies of the chemistry of $(Cp^*(PMe_3)Ir(MgPh)(H))_2$ and $(Cp^*(PMe_3)IrAlEt)_2$ show that they are synthetically useful. The phenylmagnesium complex reacts with D_2O to form cleanly the mixed isotopomer $Cp^*(PMe_3)Ir(H)(D)$ (85%).[1] Reaction with trimethylsilyl triflate gives the known silyl hydride $Cp^*(PMe_3)Ir(H)(SiMe_3)$ in quantitative yield by ^1H NMR spectrometry.[1] The complex also reacts with CO_2 to form the metal carbonyl $Cp^*(PMe_3)IrCO$, also in quantitative yield (^1H NMR). The ethylaluminum dimer behaves similarly; D_2O gives dideuterated $Cp^*(PMe_3)Ir(D)_2$ (98% by ^1H NMR) without incorporation of deuterium into the Cp* or PMe_3 substituents, as evidenced by the ^2H NMR spectrum. In addition, the Ir−Al compound reacts with excess CO_2 to produce $Cp^*(PMe_3)IrCO$.

In summary, three new heterobimetallic Ir−Al and Ir−Mg compounds have been synthesized. These have interesting structural features, and their formation supports the deprotonation sequence postulated in eq 1. With different substitution, the aluminum reactions either stop at the initial adduct stage or proceed on to double deprotonation of the iridium dihydride. In the case of magnesium the reaction stops after the elimination of one hydride per iridium. While we have characterized the final complexes formed in these transformations, there are a number of other metastable species that are apparent by NMR monitoring which remain to be identified. In addition, the fact that two of the compounds we have isolated are dimers suggests that the corresponding monomers may be precursors to these species and can potentially be trapped by other additives. Experiments designed to explore this possibility are under way.

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Supporting Information Available: Data collection and refinement details and listings of atomic coordinates, thermal parameters, bond lengths and bond angles of all three crystallographically characterized complexes (32 pages). See any current masthead page for ordering and Internet access instructions.

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(13) Synthesis of $Cp^*(PMe_3)Ir(H)(MgPh)$ was accomplished as follows. $Cp^*(PMe_3)Ir(H)_2$ (1.13 g, 2.77 mmol) and $MgPh_2(THF)_2$ (0.927 g, 2.88 mmol) were combined in a 125 mL Schlenk tube in an N_2 glovebox. Toluene (60 mL) was added via cannula, and the resulting solution was stirred. After 15 min the solution became a slightly greenish-yellow in color. The reaction mixture was stirred for 30 h resulting in a bright yellow solution. The volatile materials were removed in vacuo yielding a bright yellow powder. The powder was washed with pentane (3 × 25 mL portions). The remaining solid was dried in vacuo. Yield 1.14 g (81%). Mp 125 °C (dec). ^1H NMR (400 MHz, C_6D_6) major isomer: δ 8.27 (d, $J = 6.2$ Hz, 2H, $o-CH$), 7.56 (t, $J = 7.2$ Hz, 2H, m-CH), 7.39 (t, $J = 7.2$ Hz, 1H, p-CH), 2.03 (d, $J = 1.3$ Hz, 15H, $C_5(CH_3)_5$), 1.36 (d, $J = 9.2$ Hz, 9H, $P(CH_3)_3$), −18.50 (d, $J = 28.0$ Hz, 1H, IrH). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): δ 141.5, 140.8, 126.8, 125.1, 92.1, 23.6 (d, $J_{CP} = 40$ Hz), 11.7. $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6): δ −59.76. IR (Nujol mull): 2013 (s), 1278 (s), 1230 (m), 1055 (m), 1038 (w), 991 (w), 933 (s), 847 (m), 714 (s), 677 (s), 634 (w), 606 (w) cm^{-1}. Anal. Calcd for $C_{19}H_{30}IrMgP$: C, 45.11; H, 5.98. Found C, 44.98; H, 5.89.

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(15) A Schlenk flask equipped with stir bar was charged with $Cp^*(PMe_3)Ir(H)_2$ (1.08 g, 2.66 mmol), 20 mL of toluene, and 0.40 mL of $AlEt_3$ (2.87 mmol) in an N_2 atmosphere glovebox. The reaction mixture was stirred for 2 weeks. Removal of volatile materials left a waxy yellow solid. Crystallization from a minimum volume of toluene at −80 °C yielded the desired $(Cp^*(PMe_3)IrAlEt)_2$. Final yield 85%, mp 131−135 °C (dec). ^1H NMR (400 MHz, C_6D_6): δ 2.045 (d, $J = 0.56$ Hz, 15H, $C_5(CH_3)_5$), 1.613 (t, $J = 8.0$ Hz, 3H, CH_2CH_3), 1.41 (d, $J = 8.8$ Hz, 9H, $P(CH_3)_3$), 1.29 (m, 1H, CHHCH$_3$), 0.75 (m, 1H CHHCH$_3$). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): δ 91.40, 79.58, 21.97 (d, $J_{CP} = 43$ Hz), 9.60, 8.00. $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6): δ −60.23. IR (Nujol mull): 1157 (m), 1085 (w), 1030 (w), 951 (s), 858 (m), 733 (m), 681 (m), 552 (s) cm^{-1}. Anal. Calcd for $C_{30}H_{58}Al_2Ir_2P_2$: C, 39.20; H, 6.36. Found: 39.64, 6.76.

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