

monomer) will soon be investigated in collaboration with Josef Michl and we predict a dimer with four equivalent and orthogonal bridging lithiums:



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### Synthesis, Insertion, and Reductive Elimination Reactions of a Hydridoalkoxyiridium Complex

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Low-valent, mononuclear late-transition-metal alkoxides, once very rare, are becoming increasingly well-known.<sup>1</sup> Recent studies have demonstrated that such complexes exhibit interesting insertion chemistry, although mechanistic information is still quite sparse.<sup>2</sup> We wish to report here the isolation and some reactions of a mononuclear late-transition-metal alkoxy hydride.<sup>3</sup> Preliminary mechanistic studies of apparent insertion and reductive elimination reactions demonstrate some surprising contrasts with analogous reactions of the corresponding alkyl hydrides.<sup>4</sup>

Our results are summarized in Scheme I. Addition of  $\text{Cp}^*\text{Ir}(\text{PPh}_3)\text{Cl}_2$  (**1**,  $\text{Cp}^* = \text{C}_5\text{Me}_5$ )<sup>5</sup> to a solution of sodium ethoxide in dry ethanol forms an orange slurry which leads to the formation of a new, soluble complex as detected by <sup>1</sup>H NMR. After removal of the solvent in vacuo and extraction into pentane, yellow microcrystals of  $\text{Cp}^*\text{IrPPh}_3(\text{OEt})\text{H}$  (**2**) are obtained from a concentrated pentane solution at  $-40^\circ\text{C}$  in 79% yield. Compound **2** exhibits a characteristic Ir-H absorption at  $2035\text{ cm}^{-1}$  in the infrared as well as a resonance at  $\delta -13.20$  in the <sup>1</sup>H NMR spectrum. The diastereotopic methylene protons in the ethoxy ligand exhibit a complex pattern at  $\delta 3.79$  in the <sup>1</sup>H NMR. The complex was further characterized by <sup>13</sup>C NMR and elemental analysis.<sup>6</sup>

Hydrido(ethoxy) complex **2** undergoes reaction with a wide range of substrates under mild conditions. Irradiation of **2** in cyclooctane leads to cyclometalation product **3**, the same material obtained upon photolysis of  $\text{Cp}^*\text{PPh}_3\text{IrH}_2$  in cyclooctane.<sup>4a,b</sup>

(1) For some leading references, see: (a) Mehrotra, R. C. *Adv. Inorg. Chem. Radiochem.* **1983**, *26*, 269. (b) Michelin, R. A.; Napoli, M.; Ros, R. *J. Organomet. Chem.* **1979**, *175*, 239. (c) Bryndza, H. E.; Calabrese, J. C.; Wreford, S. S. *Organometallics* **1984**, *3*, 1603. (d) Rees, W. M.; Atwood, J. D. *Ibid.*, **1984**, *3*, 402; (e) Rees, W. M.; Churchill, M. R.; Fetting, J. C.; Atwood, J. D., unpublished results. (f) Abel, E. W.; Farrow, G.; Towie, I. D. H. *J. Chem. Soc., Dalton Trans.* **1979**, 71. (g) Komiya, S.; Tane-ichi, S.; Yamamoto, A.; Yamamoto, T. *Bull. Chem. Jpn.* **1980**, *53*, 673. (h) Michelin, R. A.; Napoli, M.; Ros, R. *J. Organomet. Chem.* **1979**, *175*, 239. (i) Yoshida, T.; Okano, T.; Otsuka, S. *J. Chem. Soc., Dalton Trans.* **1976**, 993. (j) Bennett, M. A.; Yoshida, T. *J. Am. Chem. Soc.* **1978**, *100*, 1750.

(2) See, however, ref 1d,e and: Bryndza, H. E. *Organometallics* **1985**, *4*, 406.

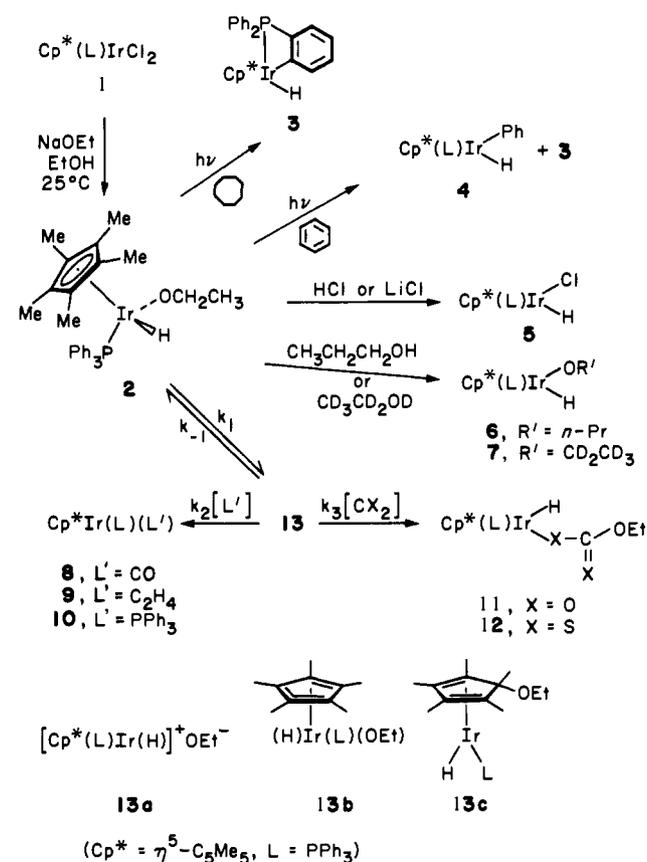
(3) For an example of a thorium hydridoalkoxy complex, see: (a) Katarahira, D. A.; Moloy, K. G.; Marks, T. J. *Organometallics* **1982**, *1*, 1723. For an analogous zirconium complex, see: (b) Bercau, J. E. *Acc. Chem. Res.* **1980**, *13*, 121. *cis*-( $\text{PMe}_2$ )<sub>2</sub>Os(H)(OH) has recently been isolated, along with spectroscopic evidence for the corresponding methoxy hydride: (c) Gotzlig, J.; Werner, R.; Werner, H. *J. Organomet. Chem.* **1985**, *285*, 99. For a hydroxy(hydrido)platinum complex, see: (d) Yoshida, T.; Matsuda, T.; Okano, T.; Kitani, T.; Otsuka, S. *J. Am. Chem. Soc.* **1979**, *101*, 2027.

(4) (a) Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 3929. (b) Bergman, R. G., *Science (Washington, D.C.)* **1984**, *223*, 902. (c) Wax, M. J.; Stryker, J. M.; Buchanan, J. M.; Kovac, C. A.; Bergman, R. G.; *J. Am. Chem. Soc.* **1984**, *106*, 1121. (d) Buchanan, J. M.; Stryker, J. M.; Bergman, R. G., submitted for publication.

(5) Kang, J. W.; Mosely, K.; Maitlis, P. M. *J. Am. Chem. Soc.* **1969**, *91*, 5970.

(6) See supplementary material. Complex **9** was synthesized independently by William D. McGhee of this group.

### Scheme I



Irradiation in benzene leads to a mixture of **3** and  $\text{Cp}^*(\text{L})\text{Ir}(\text{Ph})(\text{H})$  (**4**), products which are also observed on photolysis of  $\text{Cp}^*(\text{PPh}_3)\text{IrH}_2$ . Photochemical activation therefore appears to induce reductive elimination and extrusion of ethanol from the coordination sphere of the metal, in analogy to the thermal activation of  $\text{Cp}^*(\text{L})\text{Ir}(\text{R})(\text{H})$ .<sup>4b-d</sup> Few other reactions of **2**, however, find direct precedent in the chemistry of the (superficially) closely related hydridoalkyliridium complexes. For example, on heating in benzene, a complex mixture of products is formed, in which  $\text{Cp}^*(\text{L})\text{IrH}_2$  is the major (and at present only identified) product. More tractable chemistry is observed in the presence of ligands such as CO, ethylene, and phosphines. Under these conditions, ethanol and the corresponding iridium(I) adducts **8-10** are produced.<sup>6</sup> Although these appear to be direct reductive elimination reactions, mechanistic studies (see below) indicate they are more complicated.

Treatment of the hydridoalkoxy complex with alkyl halides does not lead to haloalkoxy complexes; rather, displacement of the alkoxy ligand is observed. Thus, treatment of **2** with 0.5-1.0 equiv of carbon tetrachloride or chloroform in benzene forms mixtures of the corresponding hydridoalkoxyiridium and dichloroalkoxyiridium complexes **5** and **1**, in ratios that depend upon the amount of halogenating agent used. Treatment of **2** with either HCl or lithium chloride also leads to **5** (97% and 74% yield, respectively). This reactivity is consistent with electrophilic attack on ethoxide (or incipient ethoxide; see below) ion by the substrate.

Further indication of the reactivity of the alkoxy group is provided by exchange studies with other alcohols. For example, dissolution of **2** in 1-propanol, or treatment with 1 equiv of sodium *n*-propoxide in tetrahydrofuran, leads to the hydrido(*n*-propoxy)iridium complex **6** in 73% yield (NMR).<sup>7</sup> Surprisingly, alkoxy exchange occurs without hydride loss, even in protic sol-

(7) Attempts to isolate pure samples of this material have been frustrated so far by cocrystallization with nonstoichiometric amounts of solvent. Its identification has been made on the basis of spectroscopic (<sup>1</sup>H, <sup>13</sup>C, <sup>31</sup>P NMR; IR) data.

vents. Thus, treatment of **2** with perdeuterated ethanol forms only **7**, in which the alkoxy group has been exchanged but the hydrido ligand has not.

The insertion chemistry of this complex also differs from that of other, more common, group 8-10<sup>11</sup> alkyl- and hydridometal complexes. Dative ligands such as CO and ethylene do not promote insertion (see above), and **2** catalyzes decomposition of (trimethylsilyl)ketene. However, insertion does take place with more electrophilic reagents such as CO<sub>2</sub> and CS<sub>2</sub>, leading to the metallocarbonate Cp\*(L)(H)Ir-O-C(O)-OEt (**11**; 78% by NMR) and the corresponding xanthate **12** (58%, isolated).<sup>8</sup> Note that this transformation involves only the metal-oxygen bond; no insertion into the M-H bond is observed.<sup>9</sup> The CO<sub>2</sub> insertion product **11** is thermally unstable in solution and as a solid and therefore has been characterized only by <sup>1</sup>H NMR and IR spectroscopy. The metallaxanthate **12**, however, is stable indefinitely as a solid at room temperature under a nitrogen atmosphere and has been fully characterized.<sup>6</sup>

Preliminary studies of the mechanisms of the PPh<sub>3</sub>-induced (apparent) reductive elimination and CS<sub>2</sub> insertion reactions have been carried out. Unlike reductive elimination of Cp\*(PMe<sub>3</sub>)<sub>3</sub>Ir(R)(H)<sup>4d</sup>, the rate of disappearance of **2** is dependent upon the concentration of added trapping reagent (PPh<sub>3</sub>). Typical saturation kinetics are observed; when excess phosphine is used, at low absolute concentrations of added ligand, the pseudo-first-order rate constant *k*<sub>obsd</sub> increases with increasing [PPh<sub>3</sub>], but it levels off to a maximum *k*<sub>obsd</sub> of 5.7 × 10<sup>-4</sup> s<sup>-1</sup> at high concentrations. This requires the reversible formation of a reactive intermediate that can be trapped by phosphine; at high [PPh<sub>3</sub>] it is trapped essentially every time it is formed. The complete absence of cyclometallation product **3** or hydridophenyl complex **4**, even in benzene solvent, makes it very unlikely that this intermediate is the earlier-identified C-H activating species Cp\*Ir(PPh<sub>3</sub>). Similar kinetic studies carried out on the CS<sub>2</sub> insertion reveal no dependence of *k*<sub>obsd</sub> on the concentration of CS<sub>2</sub>. Thus once again an intermediate capable of being trapped by the added reagent is implicated, except in this case return of the intermediate to **2** is too slow to compete with the trapping step. Significantly, the value of *k*<sub>obsd</sub> for the CS<sub>2</sub> insertion is 7.2 × 10<sup>-4</sup> s<sup>-1</sup>, very similar to the limiting value of *k*<sub>obsd</sub> for the reaction induced by phosphine.

The similarity of these limiting rate constants provide strong evidence that the two reactions, despite their apparent overall dissimilarity, proceed through the same intermediate, indicated as **13** in Scheme I. Three possible structures for this intermediate (**13a-c**) are illustrated at the bottom of the scheme. Additional data provided insight into the nature of **13**. Kinetic studies on the maximum rate (where *k*<sub>obsd</sub> = *k*<sub>1</sub>) of reaction of PPh<sub>3</sub> with **2**, in which the metal-bound hydrogen has been replaced with deuterium, reveal that the process occurs with [*k*<sub>H</sub>/*k*<sub>D</sub>] = 1. This lack of an isotope effect confirms the absence of a direct reductive elimination to either free or coordinated ethanol and argues against mechanisms that involve M-H bond cleavage in the rate-determining step (e.g., reversible transfer of hydrogen to the Cp\* ring). Kinetics carried out in dimethylformamide again show no dependence on [PPh<sub>3</sub>] at high concentrations of entering ligand and give *k*<sub>1</sub> = 3.6 × 10<sup>-4</sup> s<sup>-1</sup>, very close to the rate constant measured in toluene. This argues strongly against ion pair intermediate **13a**, which should be formed at a much higher rate in the more polar solvent.<sup>10</sup> We conclude that the intermediate is an uncharged,

coordinatively unsaturated species, perhaps formed by either "slippage" of the Cp\* ring (**13b**) or direct transfer of the alkoxy group to this ring (**13c**). Experiments are now under way aimed at distinguishing these possibilities.

In summary, hydridoalkoxyiridium hydrides can be prepared but are quite reactive; their chemistry is substantially different from that of early or higher valent metal alkoxides. Further reactions of these materials, as well as additional information on the mechanism of the reactions summarized here, will be reported in a full paper.

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**Supplementary Material Available:** Spectral and analytical data for **2**, **6-8**, and **10-12** (3 pages). Ordering information is given on any current masthead page.

(11) In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of the wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18 (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

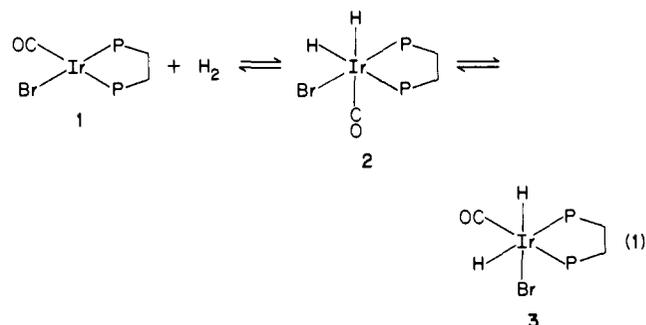
## Diastereoselection and the Influence of Chiraphos on Metal-Centered Chirality in Cis Oxidative Addition of Hydrogen and Triphenylsilane

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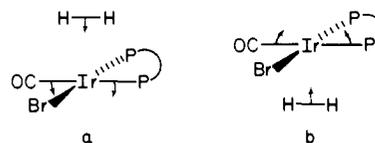
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In the stereoselective, kinetically controlled oxidative addition of H<sub>2</sub> to IrBr(CO)(dppe) (**1**) (dppe = bis(diphenylphosphino)ethane),<sup>1</sup> both the kinetic isomer **2** and the thermodynamic isomer **3** form as racemates resulting from H<sub>2</sub> approach to the metal



center from above and below the Ir(I) square-planar complex. This is illustrated for **2** as a and b with H<sub>2</sub> aligned parallel to the



(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.

(8) A referee has pointed out that metal alkyls often insert CS<sub>2</sub> to give M-CS<sub>2</sub>R rather than M-S-C(S)R complexes and asked how we ruled this out in the case of **12**. This type of insertion seems particularly unlikely in our case, since it would lead to the formation of an S-O bond in M-C(S)S-OR. However, experimental evidence is supplied by the lack of phosphorus-carbon coupling to the sulfur-bound carbon in the <sup>13</sup>C NMR spectrum; a typical value for this coupling constant in iridium complexes that do have a P-M-C linkage is 13 Hz.

(9) For example of CO<sub>2</sub> and CS<sub>2</sub> insertion into a metal-hydrogen bond, see: (a) Butler, A. S.; Fenster, A. E. *J. Organomet. Chem.* **1974**, *66*, 162. (b) Volpin, M. E.; Kolomnikov, I. S. *Organomet. React.* **1975**, *5*, 313.

(10) As discussed in ref 1d, a cationic iridium/anionic methoxide ion pair has been postulated as an intermediate in the carbonylation of the 16-electron complex MeOIr(CO)(PPh<sub>3</sub>)<sub>2</sub>; however, a similar platinum alkoxide CO insertion is thought not to proceed via ionic intermediates.<sup>2</sup>