solved by running the experiment at lower temperature in mixed solvents;[12] the latter, by using ^6Li.[13] In contrast, the separated ions had detectable amounts of free HMPA only when >3 equiv of HMPA had been added and always showed well-resolved Li and P multiplets below −110 °C even with ^7Li.

In summary, the relative concentrations of $R^-Lih_n^+$ species during an HMPA titration provides reliable information on the CIP/SIP dichotomy which complements and supports assignments made on the basis of chemical shifts and other arguments. The formation of contact HMPA-coordinated lithium species during the early steps of an HMPA titration reliably identifies the ion pair structure as CIP in the absence of HMPA (i.e., in pure THF), since HMPA is unlikely to cause the conversion of a SIP to a CIP. We are now in an excellent position to study the effect of ion pair structure on reactivity.[2b]

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[12] We have found that we can routinely work with supercooled THF solutions at −116 to −125 °C with 0.16 M RLi and 0.04–1.6 M HMPA for Li and P NMR. The longer acquisition times of ^{13}C NMR can result in freezing of the solvent. In this situation and to work at still lower temperatures (to −135 °C), 60/40 THF/ether or THF/dimethyl ether mixtures can be used.

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Alkoxide π-Donation to Iridium(III)

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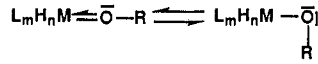
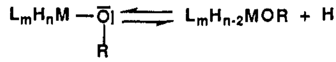
The overwhelming majority of transition-metal polyhydride compounds L_mMH_n ($L = PR_3$, η^5-C_5R_5)[1] are coordinatively saturated. As a result of the absence of empty metal d orbitals, such transition-metal polyhydrides are relatively unreactive toward nucleophiles, especially toward conventional unsaturated hydrocarbons.[2,3] Transition-metal polyhydrides do react readily with electrophiles,[4] and the case of H^+ as electrophile has led to H_2 complexes which can be useful precursors, via H_2 dissociation, to unsaturated metal complexes that catalyze hydrogenation under very mild conditions.[5-7] We explore here an alternative approach to reactive polyhydride compounds: the incorporation of π-donor coligands into a polyhydride environment in order to make unsaturated polyhydrides available either through nondissociative valence isomerization (eq 1) or via facilitation of H_2 loss (eq 2) with concomitant creation of unsaturation.



$$L_mH_nM{\leftleftharpoons}\bar{O}{-}R \rightleftharpoons L_mH_nM{-}\bar{O}(R) \qquad (1)$$



$$L_mH_nM{-}\bar{O}(R) \rightleftharpoons L_mH_{n-2}MOR + H_2 \qquad (2)$$

The recent work of Goldman and Halpern[8] supports this proposal, since they have shown $IrH_2(OR)(P^iPr_3)_2$ ($R = CH_2CF_3$) to be reactive for coupling of aldehydes and dehydrogenation of secondary alcohols to ketones. This molecule is much more reactive than IrH_3P_3 species. Those workers established that $IrH_2(OR)(P^iPr_3)_2$ is a monomer with equivalent phosphorus nuclei and apparently equivalent hydride ligands. We have determined the structure of the related $IrH_2(OR)(PCy_3)_2$, Figure 1.[9] Since the hydrides were not evident in the X-ray data, this discussion will be limited to the $Ir(OCH_2CF_3)(PCy_3)_2$ portion of the molecule. The IrP_2O substructure is planar to within 0.01 Å, and the O–C line makes an angle of only 9.9° with the IrP_2O plane. There is no evidence for agostic interactions with hydrogens of the alkoxy or the cyclohexyl groups. The Ir–O–C angle, 138.0 (11)°, is enlarged over the tetrahedral angle,[10] and the Ir–O bond length is 2.032 (10) Å. Without a reference value for an Ir–O *single* bond, the significance of this bond length is uncertain. However, we present the following evidence concerning the nature of the Ir–OR bond in $IrH_2(OR)(PCy_3)_2$:

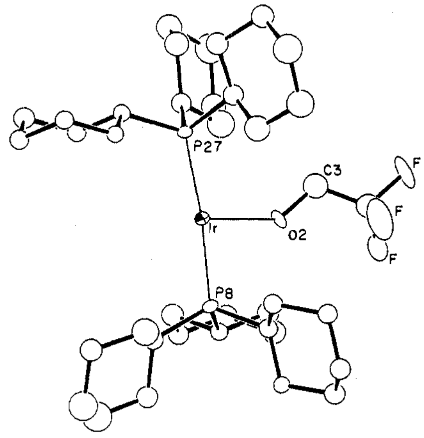


Figure 1. ORTEP drawing of the non-hydrogen atoms of $IrH_2(OCH_2CF_3)(PCy_3)_2$, showing selected atom labeling.

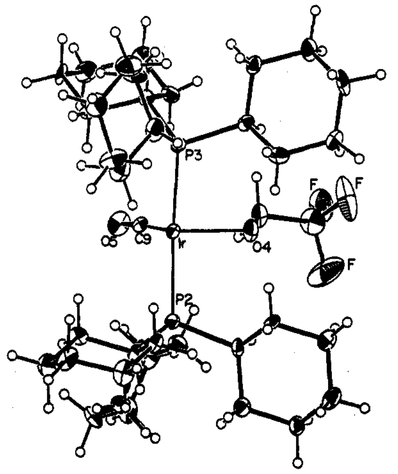


Figure 2. ORTEP drawing of $IrH_2(OCH_2CF_3)(CO)(PCy_3)_2$, showing selected atom labeling. Hydride hydrogens were not located.

1. The structure of $IrH_2(OR)CO(PCy_3)_2$ (Figure 2)[11] provides an opportunity to compare an Ir–OR bond length which is unequivocally a single bond, and in a ligand environment most relevant to that in $IrH_2(OR)(PCy_3)_2$. The Ir–O distance of 2.169 (7) Å and the Ir–O–C angle of 118.4 (7)° are sufficiently longer and smaller, respectively, than in $IrH_2(OR)(PCy_3)_2$ to support the conclusion that there is O→Ir π-donation in $IrH_2(OR)(PCy_3)_2$.[12]

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[9] Crystal data (−170 °C): $a = 21.884$ (6) Å, $b = 33.299$ (9) Å, $c = 10.816$ (3) Å with $Z = 8$ in space group *Pbca*. With 2315 reflections with $F > 3\sigma(F)$, $R(F) = 0.0441$ and $R_w(F) = 0.0433$.

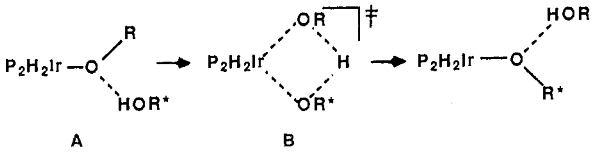
[10] For aryloxides (as distinct from alkoxides), M–O–C angles *may* not be indicative of O→M π-donation. See: Coffindaffer, T. W.; Steffy, B. D.; Rothwell, I. P.; Folting, K.; Huffman, J. C.; Streib, W. E. *J. Am. Chem. Soc.* **1989**, *111*, 4742. Coffindaffer, T. W.; Rothwell, I. P.; Huffman, J. C. *Inorg. Chem.* **1983**, *22*, 2906.

[11] Crystallographic data (−154 °C): $a = 17.919$ (6) Å, $b = 10.909$ (3) Å, $c = 22.304$ (7) Å, $\beta = 114.56$ (2)°, $Z = 4$ in space group $P2_1/c$. With 4187 reflections with $F > 3\sigma(F)$, $R(F) = 0.0516$ and $R_w(F) = 0.0471$.

To gauge the effect of increased coordination number on bond length, note that the Ir–P distance increases only 0.04 Å upon addition of CO.[13,14]

2. The reactivity of $IrH_2(OR)(PCy_3)_2$ is high, consistent with it being unsaturated either in the ground state or in a thermally accessible excited state (eq 1). Thus, it adds CO under mild conditions (within time of mixing at <1 atm, 25 °C) to give *cis,trans*-$IrH_2(OR)CO(PCy_3)_2$.[15]

3. Addition of stoichiometric water to $IrH_2(OR)(PCy_3)_2$ also gives an adduct. On the basis of the minimal change in the hydride chemical shift (0.55 ppm), we conclude that this adduct involves only hydrogen bonding of water to the alkoxide oxygen.[16,17] Consistent with weak bonding of this type, exposure of $IrH_2(OR)(PCy_3)_2 \cdot H_2O$ to vacuum (1 h) during and after removal of solvent furnishes $IrH_2(OR)(PCy_3)_2$ again. It is noteworthy that there is no evidence for conversion to $IrH_2(OH)(PCy_3)_2$. Proton NMR monitoring of a titration of $IrH_2(OR)(PCy_3)_2$ with the *alcohol* ROH shows rapid exchange (i.e., a single coalesced OCH_2 signal) at 25 °C.[15] Although this process may be initiated by formation of a hydrogen bond to uncoordinated alcohol (A), we suggest that formation of an Ir–O bond to the incoming alcohol (B) is the next step. This is why $IrH_2(OR)CO(P^iPr_3)_2$ does not exchange rapidly with free ROH.[8] Intermediate or transition-state B requires conversion of the original π-donor alkoxide in A to a simple σ-donor mode of bonding, which simultaneously makes that oxygen a better proton acceptor.



4. Goldman and Halpern demonstrated[8] the rapid conversion shown in eq 3. We suggest that this heterolytic splitting of the

$$IrH_2(OR)(P^iPr_3)_2 + 2H_2 \rightarrow IrH_5(P^iPr_3)_2 + ROH \quad (3)$$

first mole of H_2 consumed in this reaction proceeds via an H_2 adduct $Ir(H)_2(H_2)(OR)(P^iPr_3)_2$, in which the alkoxide oxygen is more electron rich (i.e., minimal π-donation to Ir) and thus well suited to accept H^+ from the Bronsted acidic η^2-H_2 ligand. This Ir–O hydrogenolysis also occurs within the time of mixing for $IrH_2(OR)(PCy_3)_2$, and we are studying this mechanistic proposal with further experiments.[18]

It is generally true that chloro compounds and hydride/chloro compounds are frequently isolable as unsaturated species, while unsaturated polyhydrides devoid of π-donor ligands are almost never isolable. For example, compare[1] the formulas $ReCl_4P_2$ with ReH_7P_2; $ReCl_3P_3$ with ReH_5P_3; $OsCl_4P_2$ with OsH_6P_2; $OsCl_3P_3$ with OsH_4P_3; $RuH_3Cl(PCy_3)_2$[20] with $RuH_6(PCy_3)_2$; $IrHCl_2P_2$,[19] $IrH_2Cl_2P_2$,[21] and IrH_2ClP_2[19] with IrH_5P_2. On the basis of our structural results with alkoxide as the coligand, we propose that this trend exists because any unsaturation is moderated by the presence of the (weak) π-donor chloride ligands.[22] More importantly however, this hypothesis seems to translate into a valuable method for enhancing the reactivity of transition-metal polyhydrides. While π-donation by alkoxides is well established toward early transition metals,[23] the same is not true for the late transition elements.[24] Indeed, it has been concluded[24] that "...there are no significant π interactions between...alkoxide...ligands and late-transition-metal centers...." While this may be true for four-coordinate Rh^I and Pd^{II} or Pt^{II}, the evidence we present here indicates significant alkoxide π-donation to Ir^{III}. We propose that the difference originates in the higher electrophilicity of the higher valent metal, as well as the presence of a more suitable acceptor orbital on a five-coordinate d^6 complex than on a four-coordinate d^8 species.

Acknowledgment. This work was supported by the National Science Foundation. We thank Johnson Mathey, Inc., for material support, Odile Eisenstein for valuable discussion, and Scott Horn for skilled technical assistance. We thank the referees for useful suggestions.

Supplementary Material Available: Listing of fractional coordinates and spectroscopic data for $IrH_2(OCH_2CF_3)(PCy_3)_2$ and $IrH_2(OCH_2CF_3)CO(PCy_3)_2$ (3 pages). Ordering information is given on any current masthead page.

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Evidence for a Weak Mn=O Bond and a Non-Porphyrin Radical in Manganese-Substituted Horseradish Peroxidase Compound I

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We have recently described the isolation and characterization of several oxomanganese(IV) porphyrin complexes.[1] Interest in these complexes derives from the activity of manganese porphyrins as oxidation catalysts[2] and as comparators for the biologically significant iron heme derivatives.[3] These synthetic manganese(IV) species exhibit the characteristic EPR spectra of an $S = {}^3/_2$ Mn(IV) spin system, and surprisingly, the resonance Raman (RR) and IR spectra revealed an unusually weak Mn=O stretching frequency in the range of 711–757 cm^{-1} depending on the trans-axial ligand.[1b,c] We have ascribed this feature to the unique high-spin d^3 electronic state of these complexes. Oxidized forms of manganese-substituted horseradish peroxidase[4,5] (MnHRP) and

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