Iridium Hydrides with Di(tertiaryphosphine) Bridges and Chelates

by

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The complex $\text{Ir}^\text{III}(\text{CO})_2(\text{dpp})$ is found to promote the carbonylation of benzene to benzoaldyde upon photolysis under CO. This process C-O functionalization reaction appears to be thermodynamically limited. Long term photolyses show evidence of secondary products including benzoaldehyde, as well as of complex decomposition.
Introduction

The activation of substrate is an essential step in catalysis, and generally involves a weakening or breaking of bonds within the substrate. The effectiveness of transition metal complexes as catalysts is closely related to their ability to perform this process. Substrate activation is often accomplished by donation of electron density from filled metal d orbitals into vacant antibonding orbitals of the substrate, thus perturbing its electronic structure, and resulting in an oxidative addition reaction if a substrate bond is cleaved. Complexes of electron rich metals are particularly effective in activating substrates in this manner, and within this group, no set of complexes has been more vigorously studied over the past two decades than those of Rh(I) and Ir(I). Complexes of these metals possess a rich oxidative addition chemistry, and are active as catalysts for a variety of reactions including hydrogenations, hydroformylations, and carbonylations.1

While complexes of Ir(I) are often not as catalytically active as analogous Rh(I) systems, the electron richness of Ir(I) frequently yields more stable substrate adducts and oxidative addition products.2 In this context, Vaska's complex, Ir(CO)(PPh3)2+, is especially notable, undergoing reactions with numerous substrates including Hg, Ag, H(C=O), Br, I, Me, EtBr, NCS, and cysteine among others.3 In this reaction chemistry and that of closely related analogs, the phosphine ligands generally maintain their trans disposition and yield stable adducts having structures 1 or 2 depending on the substrate X and the mechanism of adduct formation.
In this paper, we describe our studies on iridium complexes containing di(tertiary phosphine) ligands. These ligand systems may either chelate a single metal center or bridge two Ir ions. The former leads to a six stereochemistry of phosphine donors different from that observed in most adducts of Vaska's complex and its analog, while the latter produces two metal centers in close proximity for the binding and activation of substrates.

The relative tendency of the di(tertiary phosphine) ligand system $\text{PhP(CH}_2_}_2\text{PPH}_2$ to bridge or chelate has been addressed by Sang in the synthesis of a manner only when $n=2$ and dimers when $n=1$ and 3 via eqn.(1).4 Compound 2, which was first reported by Vaska, forms because of the favorable driving force of five-membered chelate ring formation.5 Complexes 4 and 5, on the other hand, maintain what seems to be the electronically favorable disposition of trans P donors with the creation of face-to-face dimers of Ir(l) having ligand sets similar to that found in Vaska's complex.

$$\text{[IrCl(OMe)]} + \text{PhP(CH}_2_}_2\text{PPH}_2 + \text{CO} \rightarrow \text{IrCl}_{\text{CO}}$$

Our interest in dimeric compounds of this type was stimulated by the nature of two metal centers in close, fixed proximity for the activation of the substrates simultaneously, or for the activation of a single substrate using both metal centers and their attendant M's (two $\delta^2$ - $\delta^2$ act as effective

To improve the orientation of the two different metal ions in 3, we devised a series of molecules called molecular A-frames, 3. In previous papers, we have described the chemistry of some of these dpp complexes including 2 - 10 - 6

Complex 2 is modestly active as a catalyst for the water gas shift reaction, eqn.(1), but its catalyst lifetime is relatively short. Complex 10 forms

$$\text{CO} + \text{H}_2 \rightarrow \text{CO} + \text{H}_2$$

reversible adducts with CO and with $\text{H}_2$ but not with both simultaneously. Further studies on these and related A-frame systems are in progress.7

While the dpp ligand keeps the two bridged metal centers in close proximity, the dpp ligand allows the binuclear complexes to be more flexible with metal...metal distances ranging from 3.5 A to 4.5 A. The chemistry of 3 has recently been explored by Figgis and Town who find that 3 resistively adds $\text{H}_2$ to form a mixture of the dihydride $\text{[IrH}_2\text{(CO)}\text{Cl}_2\text{(dpp)}]$ and the
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The structural assignments of 11 and 12 are supported by crystallography evidence. Loss of Hg from 12 appears facile, and the increased steric bulk at one Ir center after the first oxidative addition appears to inhibit reactivity at the second metal center.

The studies described in this paper use the work of Sanger and Figueras as a starting point. Because the bromo and iodinopolyethane of Fusha's complex were known to be more reactive than the parent chloro-ether system [IrCl(CO)(PPh3)], we commenced studies on the bromo and iodo analogs of 9. The context in which our studies were undertaken was the development of Hg reduction catalysts for CO2, a goal that still remains to be reached. Based on Horner's work, it was known that electron-rich Ir(1) centers are capable of reacting with CO2. We envisioned that the presence of bulky ligands on a second metal center would facilitate the desired reduction of bound CO2.

The investigations which we outline here include studies of bimetallic dopp complexes and the hydrides which they form. The cleavage of these donors into mononuclear species, and the formation and reaction chemistry of previously unknown mononuclear complexes containing only one dopp ligand, one of these dopp systems upon treatment activates areas 2-4 bonds and promotes the formation of benzotriazole and benzyl alcohol from benzene and synthesis gas. This reaction represents an important example of C-H bond functionalization.

The Synthesis and Characterization of New Iridium Hydrides Containing Biarylyl Phosphine Ligands

The iridium(I) halide [Ir(CO)2Br]2 as its p-butoxide salt serves as the convenient starting material for the preparation of the mononuclear complexes of iridium reported here.

**Dopp Complexes.** The room temperature reaction of (μ-butoxide)Ir(CO)2Br with dopp in toluene under H2 leads to the evolution of CO and the essentially quantitative production of the p-butoxide complex [Ir(butoxide)CO]2(dopp)]. 12. The diatomic structure of 12 is assigned based on HPLC analysis, a singlet at δ 10.43 in the 31P NMR spectrum of the complex, and by analogy with the chloro complex 11 reported by Sanger. The CO ligands in 12 are shown in cis orientation because of two ppm at 100 and 171 ppm. The dopp analog of 12 is prepared by metathesis using a 100-fold excess of C11 and a stoichiometry of chloro complex 12 to become and based on the single ppm at 100 ppm. It assigned a structure with CO ligands in the trans orientation as found in 12.

The oxidative addition of Hg to 11 and 12 yields bimetallic hydride complexes. Under 1 atm H2 in DCl, 11 and 12 form the tetrahydride complexes 13 and 14. The formation of 11 is 100% at 90°C is essentially complete within 1 hr compared with 24 hr for the formation of 13 and only incomplete conversion of the chloro complex 11 to its tetrahydride 13 under the
Addtional support for our interpretation of the $\text{Ir}^\text{III}$ nmr spectral data is obtained by analogy to the known molecular hydride complexes $\text{IrH}2\text{(CO)(PPPh)}3$ which possess geometry $A$. The $\text{Ir}^\text{III}$ spectra of these complexes is essentially the same as we observe for $A - I$.

A very different hydride pattern is obtained, however, when a reaction solution of $\text{Ir}^\text{III} \text{H}_2\text{Ir}^\text{III} + \text{dpp} \text{Ir}^\text{III} \text{H}_2\text{Ir}^\text{III} + \text{dpp}$ is treated with $\text{Hg}$. Prior to treatment with $\text{Hg}$, a complex may be isolated which exhibits $v_{\text{CO}}$ at 2000 and 1955 cm$^{-1}$ and a singlet in the $\text{Hg}$ nmr spectrum at $- 26.6$. The $\text{Hg}$ nmr spectrum obtained upon the addition of $\text{Hg}$ is shown in Fig. 2. The main features of the hydride pattern are two groups of resonances separated by $- 6$ ppm, one of which is a broad doublet of doublets and the other a more complicated multiplet. The spectrum is consistent with a molecularly different $P$ metal and the magnitude of the larger doublet-of-doublet splitting ($2\times128$ Hz) suggests that one of the hydrides is trans to a phosphine donor. "Micro" structure $A$ is consistent with the $\text{Hg}$ nmr results. The second hydride is located trans to iodide based on its chemical shift.

![Diagram](image)

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![Diagram](image)
The lack of integrity of 11 as a binuclear species was surprising since Pignat and Ungar had employed harsher conditions in their hydrosulphuration experiments with [Ir(CO)\(_2\)(dppm)]\(_2\) and had not observed any evidence of dimer cleavage. Moreover, reactions of similar complexes having dppm bridges under a variety of conditions have revealed no tendency of these dimers to break apart into mononuclear species. Our observation of dimer cleavage provides an important caveat to studies based on using di- and poly(tertiary phosphine) ligands to hold two or more metal atoms together in systems having structural integrity.

**dppm Complexes.** In order to provide additional support for the structural assignments of 11-12 as mononuclear species, the analogous complexes with dppm in place of dpp were synthesized and characterized. The ligand dppm shows a much greater tendency towards cleavage than dppm, and only rarely forms a bridge between two metals. The new mononuclear dppm(I) complexes [Ir(CO)\(_2\)(dppm)]\(_2\), \(\Delta\)II(=C=) and \(\Delta\)II(=O), were prepared by reacting

\[\text{Ir}^2\text{Br}_2\text{Br}[\text{Ir}(\text{CO})\text{dppm}]_2\text{Br} + \text{dppm} \rightarrow \text{Ir}^3\text{Br}^2\text{Br}\text{Ir}^3\text{CO}^2\text{dppm} + \text{Br}^2\text{Br}\text{dppm} + \text{Br}^2\text{Br}^2\text{dppm} \]

above the solution, and the formation of 13 which possesses "intramolecular structure B. Alternative binuclear formulations of 11 and 12 with bridging dppm ligands in cis positions of the coordination sphere are ruled out based on highly unfavorable steric interactions between neighboring diphosphine groups, and parallel reaction chemistry observed using dppm which is discussed below.

**Binuclear dppm-bridged Binuclear Hydrides.** When Oligo solutions of the binuclear hydride complex 11 is refluxed for extended times or heated in the presence of H\(_2\) for shorter times (2-5 hrs), a striking change occurs in the hydride region of the IR near spectrum. Specifically, the resonance characteristic of arrangement D is replaced by those consistent with arrangement C. The change from trans to cis P amine occurs with a cleavage of the binuclear hydride system to the mononuclear structure 13 as shown in eqn.(5).

\[\text{Ir}^2\text{Br}_2\text{Br}[\text{Ir}(\text{CO})\text{dppm}]_2\text{Br} + \text{dppm} \rightarrow \text{Ir}^3\text{Br}_2\text{Br}\text{Ir}^3\text{CO}^2\text{dppm} + \text{Br}^2\text{Br}^2\text{dppm} + \text{Br}^2\text{Br}^2\text{dppm} \]
species 15 and 16, respectively. These complexes are readily isolated as colorless crystals by the addition of DCM and removal of solvent. Complexes 15 and 16 are spectroscopically similar to complexes 13 and 14 (see Table I). The hydride region of the 1H NMR spectrum of 15 is shown in Figure 3. The "downfield" hydride resonance is a doublet of doublets \((J_{HH} = 166 \text{ Hz}; \Delta_{HH} = 16 \text{ Hz})\), and is separated from the "upfield" hydride multiplet by 9 ppm. Irradiation of the upfield multiplet results in loss of the smallest doublet splitting in the downfield hydride resonances, leaving a doublet of doublets pattern. The observation of hydride-hydride coupling for 15 and 16 represents the only difference in their 1H NMR spectra from those observed for the analogous dppm complexes, 13 and 14.

The addition of Hg to 15 and 16 is reversible, as is the addition of CO to form the five-coordinate dicarbonyl complexes 17 and 18 which are analogous to 13 and 14 (see Table I). Refluxing THF or benzene solutions of these adducts under CO

\[
\text{Ir(CO)}(\text{dppm}) + \text{CO} \rightarrow \text{Ir(CO)}(\text{dppm})_{2} \quad (8)
\]

leads to loss of the added molecule and regeneration of 15 or 16. The dicarbonyl complexes 17 and 18 exhibit two CO's at 1940 and 2040 cm\(^{-1}\), and at 1950 and 2040 cm\(^{-1}\), respectively, in close parallel with 15.

Preparation and Characterization of Ir(eq)(CO)(dppm). The hydrido complex

\[
\text{Ir(eq)(CO)(dppm)} \quad (9)
\]

is a particularly interesting compound which was prepared according to eqn. (9) by the reaction of NaH in ethanol with 18 in CCl\(_4\) under Hg. This complex was isolated as a tan, air-stable powder, and shown

\[
\text{Ir(eq)(CO)(dppm)} + \text{Hg} \rightarrow \text{Ir(eq)(CO)(dppm)} \quad (9)
\]

recrystallized, is colorless. The hydride region of the 1H NMR spectrum of 18 is shown in Figure 4 and based on the splitting pattern observed, a facial configuration for the hydridos can be assigned unambiguously. The equatorial hydridos, H\(_2\), is unique, and is cis to the 2 P donor atoms of dppm, giving rise to the triplet at \(\delta = -10.86 \text{ ppm} \quad (J_{HH} = 13 \text{ Hz})\). The apical hydridos, H\(_2\), are chemically equivalent, \((\delta = 9.27 \text{ ppm})\) and are split by a trans P (\(\delta_{	ext{P}} = 124 \text{ Hz}\)), a cis P (\(\delta_{	ext{P}} = 12.2 \text{ Hz}\)) and each other (4.5 Hz). A computer simulation of the hydride region confirms these assignments and is shown in Figure 4.

We found that complex 18 loses Hg both thermally and photochemically, with the rate of photogenerated loss much greater. This was demonstrated by photolyzing 18 in benzene-d\(_6\) solution under Hg and CO, and monitoring the 1H NMR spectral changes with time. In reactions under Hg and CO, only the hydride region of the spectrum was affected. After short photolysis times (20 s) or longer thermolysis times (2 h), the outermost doublets of the 9.27 ppm resonance were observed to lose their hydrido-hydride coupling as shown in Figure 4, and the integrated intensity of the hydride resonances decreased by
- 50 ppm relative to the dippe resonances of the complex. After 2.5 h of photolysis, only traces of the hydride resonances remained, indicating that deuteration incorporation was essentially complete, converting 22 to Ir[2p(CO)(dipp)]. 23. This conversion requires 8 h thermally. The IR spectrum of the isolated product (see Table) together with the 1H and 31P NMR data support the formulation of complex 23 as Ir[2p(CO)(dipp)]. When 23 dissolved in C6H6 is photolyzed under H2, it is converted back to the trihydride, 22.

Photolysis or thermal isomerization of 22 in benzene under CO leads to the rapid appearance of a new hydride resonance at 4 - 10.36 ppm (1) accompanied by new resonances in the methylene and phenyl regions of the spectrum. After 2.5 h of irradiation, all resonances of 22 are replaced by ones associated with the new triplet at -10.36 ppm. (The thermal reaction is complete in 8 h.) The methylene and phenyl regions of the 1H NMR spectrum of this material are nearly identical to those of the five-coordinate Ir(II) complex Ir(CO)(dipp), 24, which forms by CO addition to 22. A larger scale photolysis of 22 under CO allows isolation of this new material which we identify as Ir(CO)(dipp), 25, based on its and 1H spectral data. Both 23 and 25 exhibit only sharp triplets in their 31P(1H) NMR spectra indicating equivalence of the two dipp P donors in each complex at room temperature. Complex 25 may also be prepared from 23 and Hg by photolysis of the phenyl complex under H2 and CO, respectively, in consistent with the oxidative addition to 25, generating the reactive 4-coordinate species Ir(CO)(dipp), 26, which then adds CO or H2 as shown in eqn. (10). The formation of the trihydride 25 requires at least two passes through the oxidative addition/oxidative addition sequence as shown in eqn. (10) with production of one equivalent of H2. The photochemically promoted oxidative addition of H2 from metal hydrides is not well documented, and has been found in a number of cases to generate highly reactive species.10

The proposed four-coordinate Ir(II) intermediate, 25, is reactive to other substrates including benzene. When a benzene-d6 solution of 25 is photolyzed under H2 or vacuum, a change in the hydride spectrum similar to that seen under H2 as shown in Fig. 4 is observed after 20 min, with a corresponding loss in the integrated intensity of the hydride resonances relative to those of dipp. This result indicates that deuteration incorporation into 22 is taking place with the solvent serving as the deuteration source.

Although a phenyl hydride species 25 corresponding to the oxidative addition product of benzene to Ir(CO)(dipp) is not seen directly, the observed H/D exchange is most readily explained by its intermediacy.

Carbonylation of Benzene to Benzylidene. The proposed existence of 25 stimulated further experiments to determine if CO insertion and elimination of carbonylated product could be seen. This was indeed the case. In all photolyses of 22 in C6H6 under CO or CO/H2 mixture, a new resonance in the
chemistry to form reversible adducts with CO and H₂. The trityl(hydride complex \( \text{trityl(CO)}(\text{dmv}) \) in C$_2$H$_6$ under CO leads to the formation of benzaldehyde in possibly thermodynamically-limited amounts. An intriguing observation under continuing study is the subsequent conversion of benzaldehyde to benzyl alcohol. These observations represent an important example of C-H bond functionalization.

Acknowledgements. We wish to thank the National Science Foundation and the Office of Naval Research for partial support of this research and the Johnson Matthey Co., Inc. for a generous loan of iridium salts. We also wish to acknowledge valuable discussions with Professor William D. Jones, Professor Jack A. Kampwerth, Dr. Curtis Johnson, and Mr. Frank Fajer.
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<th>Compound</th>
<th>λ max (cm(^{-1}))</th>
<th>ν max (cm(^{-1}))</th>
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<td>2100, 2190</td>
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<tr>
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<td>1960, 1980</td>
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<td>22.8(d), 23.8(d)</td>
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In cm\(^{-1}\) (Hydride resonance only): -12.7 (t of d, Jp-H cis = 13 Hz, Jpp-H cis = 3 Hz) (CCl\(_{3}\))
Table I (continued)

a. IR Spectra were recorded on a Perkin-Elmer 467 Grating Infrared Spectrophotometer. All spectra were taken of KBr pellets except for 1, 2, 10 and 15 which were in benzene solution.

b. vsp.d not observed

c. All proton nmr spectra recorded on a Bruker WH-400 at 400.134 MHz. Positive chemical shifts are downfield from TMS.

d. Measured in 5 mm tubes on a Bruker WH-400 at 162 MHz. Positive chemical shifts are downfield from M2H2 (external).

e. Measured in 10 mm tubes on a Joel FT-1000 spectrometer at 41.25 MHz.

References


Figure Captions

Figure 1. Hydride Region of \[\text{13}\]
Figure 2. Hydride Region of \[\text{14}\]
Figure 3. Hydride Region of \[\text{15}\]
Figure 4. Hydride Region of \[\text{16}\]. a. Experimental spectrum. b. Simulated spectrum. c. Partial deuteration after thermalysis of \[\text{16}\] under \[\text{D}_2\] for 8 h.
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