crystal was mounted on the goniometer head with its long dimension nearly parallel to the phi axis of the diffractometer. A total of 8327 independent reflections having $2\theta_{\mathrm{MoK}\bar{\alpha}} < 55°$ (the equivalent of 1.0 limiting Cu K$\bar{\alpha}$ spheres) were measured in two concentric shells of increasing 2θ, each of which contained approximately 4150 reflections. A scanning rate of 6°/min was used for all others. Each of these 1.1° wide scans were divided into 19 equal (time) intervals, and those 13 contiguous intervals which had the highest single accumulated count at their midpoint were used to calculate the net intensity from scanning. Background counts, each lasting for one-fourth the total time used for the net scan (13/19 of the total scan time), were measured at ω settings 1.1° above and below the calculated K$\bar{\alpha}$ doublet value for each reflection. Since ψ scans for several intense reflections confirmed the anticipated absence of variable absorption for this sample, the intensities were reduced without absorption corrections to relative squared amplitudes, $|F_o|^2$, by means of appropriate Lorentz and polarization corrections.

The structure was solved by using the "heavy-atom" technique. Unit-weighted full-matrix least-squares refinement which utilized anisotropic thermal parameters for all 39 crystallographically independent nonhydrogen atoms converged to R_1 (unweighted, based on F)[48] = 0.046 and R_2 (weighted, based on F)[48] = 0.057 for 3482 independent reflections having $2\theta_{\mathrm{MoK}\bar{\alpha}} < 43°$ and $I > 3\sigma(I)$. A difference Fourier synthesis at this point permitted the location of all 59 hydrogen atoms in the asymmetric unit. All additional least-squares cycles for 1 refined hydrogen atoms with isotropic thermal parameters and nonhydrogen atoms with anisotropic thermal parameters. Unit-weighted cycles gave $R_1 = 0.023$ and $R_2 = 0.025$ with 3482 reflections. Similar unit-weighted refinement cycles with the more complete ($2\theta_{\mathrm{MoK}\bar{\alpha}} < 55°$) data set gave $R_1 = 0.028$ and $R_2 = 0.029$ for 6133 reflections. The final cycles of empirically weighted[49] full-matrix least-squares refinement with 98 independent atoms gave $R_1 = 0.028$ and $R_2 = 0.034$ for 6133 independent reflections having $2\theta_{\mathrm{MoK}\bar{\alpha}} < 55°$ and $I > 3\sigma(I)$. Since a careful comparison of final F_o and F_c values[22] indicated the absence of extinction effects, extinction corrections were not made.

All structure factor calculations employed recent tabulations of atomic form factors[46b] and anomalous dispersion corrections[46c] to the scattering factors of the Rh and P atoms. All calculations were performed on a Data General Eclipse S-200 computer with 65K of 16-bit words, a floating point processor for 32- and 64-bit arithmetic and versions of the Nicolet E-XTL interactive crystallographic software package as modified at Crystalytics Co.

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Registry No. 1, 79499-71-1; $\{HRh[P(O\text{-}i\text{-}C_3H_7)_3]_2\}_2$, 70727-44-5; ($\eta^3$-cyclohexenyl)$Rh[P(O\text{-}i\text{-}C_3H_7)_3]_2$, 79499-72-2; $(C_6H_6)Rh[P(O\text{-}i\text{-}C_3H_7)_3]_2{}^+BF_4{}^-$, 79499-74-4; $(C_6(CH_3)_6)Rh[P(O\text{-}i\text{-}C_3H_7)_3]_2{}^+BF_4{}^-$, 79499-76-6; $[ClRh(C_2H_4)_2]_2$, 12081-16-2; 1,3-C_6H_8, 592-57-4; C_6H_6, 71-43-2.

Supplementary Material Available: Crystal structure analysis report, anisotropic thermal parameters (Table III), bond lengths and angles involving hydrogen atoms (Table VI), and a listing of structure factors for $(\eta^3\text{-}CH_2C_6(CH_3)_5)Rh[P\text{-}(O\text{-}i\text{-}C_3H_7)_3]_2$ (38 pages). Ordering information is given on any current masthead page.

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[48] The R values are defined as $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_2 = \{\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2\}^{1/2}$, where w is the weight given each reflection. The function minimized is $\sum w(|F_o| - K|F_c|)^2$, where K is the scale factor.

[49] Empirical weights were calculated from the equation $\sigma = \sum_0^2 a_n|F_o|^n = 0.769 + (3.00 \times 10^{-3})F_o + (1.09 \times 10^{-5})|F_o|^2$, the a_n being coefficients derived from the least-squares fitting of the curve $||F_o| - |F_c|| = \sum_0^2 a_n|F_o|^n$, where F_c values were calculated from the fully refined model using unit weighting and an $I > 3\sigma(I)$ rejection criterion.

Hydrido Formyl, Methoxycarbonyl, Hydroxymethyl, and Methyl Complexes of Iridium: Syntheses and Reactivities[†]

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Several hydrido formyl complexes of iridium(III) have been isolated and their chemical properties examined. Two synthetic methods have been employed. The oxidative addition of a C–H bond of formaldehyde to reactive Ir(I) compounds has been used for the preparation of $[IrH(CHO)(P(CH_3)_3)_4][PF_6]$ (3), $IrClH(CHO)(P(CH_3)_3)_3$ (4), and $Ir(CH_3)H(CHO)(P(CH_3)_3)_3$ (5). The reduction of (methoxycarbonyl)iridium(III) compounds $[IrH(CO_2CH_3)(P(CH_3)_3)_4][PF_6]$ (1) and $IrClH(CO_2CH_3)(P(CH_3)_3)_3$ (2), prepared respectively by addition of methanol to $[Ir(CO)(P(CH_3)_3)_4]^+$ and oxidative addition of methyl formate by $IrCl(C_8H_{14})(P(CH_3)_3)_3$, has also been used for the preparation of the formyl compounds 3 and 4. Reduction of the formyl group of 3 to hydroxymethyl and to methyl groups has been demonstrated; thus, the reduction of carbon monoxide to a methyl group has been achieved and the intermediate complexes, containing formyl and hydroxymethyl groups, have been characterized. This conversion takes place even in the presence of a hydrido ligand. Facile reductive elimination, which might be expected for compounds containing a hydrido ligand cis to a carbon-bound organic fragment, is not observed.

Introduction

Intense interest in the transition-metal-mediated reactions of carbon monoxide with hydrogen to form utilizable organic products[1] has prompted many investigations of compounds which serve as models for postulated intermediates in carbon-monoxide hydrogenation.[2] These in-

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[†] Contribution No. 2937.

[1] Eisenberg, R.; Hendriksen, D. E. *Adv. Catal.* **1979**, *28*, 79–172.

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vestigations have resulted in syntheses of mononuclear transition-metal compounds[3] with bound formyl groups,[2d,4-25] hydroxymethyl groups,[16,19,20,22,24,26] and carbon monoxide or formyl derived methyl groups.[16,20,23,25-28] Many of these compounds have been sufficiently stable to be isolated, yet they have also been found to undergo a number of remarkable reactions.

Studies conducted in this laboratory have focused on the synthesis, characterization, interconversion, and reactivities of (trimethylphosphine)iridium complexes containing formyl and formyl- or carbonyl-derived functional groups. Using the reactions that have been observed, it is now possible to transform an iridium-bound carbon monoxide ligand into an iridium-bound methyl group by the action of borohydride reducing reagents, proceeding through a sequence of isolable intermediates. The transformation of a metal-bound carbon monoxide ligand into a methyl group has previously been observed, in well-characterized mononuclear transition-metal complexes,[3] only for the cyclopentadienylrhenium system studied by several research groups[16,20,23,28] and for the cyclopentadienylmolybdenum and -tungsten compounds examined by Treichel and Shubkin.[27] In this paper full synthetic details and characterization data are presented for several hydrido(methoxycarbonyl), hydridoformyl, hydrido(hydroxymethyl), and hydridomethyliridium compounds. A preliminary account of some of these results has been published.[25]

One important aspect of these iridium complexes, which contain a cis arrangement of a hydrido ligand and a carbon-bound organic fragment, is that they are quite stable; reductive elimination with concomitant C–H bond formation is not observed under ambient conditions. The reluctance of the hydrido formyl and hydrido methoxycarbonyl compounds to undergo reductive elimination is probably a result of unfavorable thermodynamics, since the reverse reaction—the oxidative addition of the C–H bond of formaldehyde or methyl formate—occurs readily at room temperature (vide infra). Reasons for the stability of the hydrido alkyl compounds are more complex. It is possible that many hydrido alkyl compounds of iridium are thermodynamically stable with respect to reductive elimination of the alkane. A number of examples are now known in which an iridium(I) complex spontaneously oxidatively adds an unactivated C–H bond to form a stable hydrido alkyl or aryl complex.[29-31] However, while these hydrido iridium complexes tend to be stable with respect to intramolecular reactions, they react readily with a number of reagents. These reactions will be discussed below.

Results and Discussion

Iridium(I) Starting Materials. For starting materials for many of the reactions discussed in this paper, we have used several extremely reactive, carbonyl-free trimethylphosphine iridium(I) complexes. Carbonyl-containing Ir(I) and Ir(III) complexes have been obtained as reaction products of formyl complexes (vide infra) as well as by literature methods.[32] Trimethylphosphine has been our preferred ligand because of its simple ^{1}H NMR spectrum, its small steric requirements, and its relative reluctance to undergo irreversible metalation reactions.[31,33,34]

The addition of 4 equiv of trimethylphosphine to $[IrCl(C_8H_{14})_2]_2$ results in the formation of the ionic complex $[Ir(P(CH_3)_3)_4][Cl]$.[33,35] This complex is too insoluble, in unreactive solvents, to react with formaldehyde; however, the PF_6 salt has appreciable solubility in tetrahydrofuran (THF) and reacts rapidly with formaldehyde to form the hydrido formyl complex (vide infra). The Ir(I) complex $[Ir(P(CH_3)_3)_4][PF_6]$ can be obtained as red columnar crystals by vapor diffusion of hexane into a THF solution. While the solid-state structure is not known, by analogy with the compounds $[Rh(P(CH_3)_3)_4][Cl]$[36] and $[Ir(PPh_2CH_3)_4][BF_4]$,[37] the compound $[Ir(P(CH_3)_3)_4][PF_6]$ probably consists of discrete four-coordinated cationic Ir(I)

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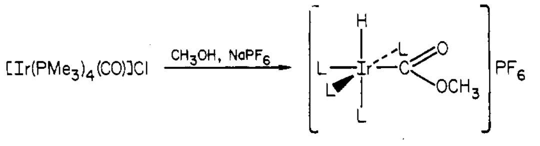
centers which may be appreciably distorted toward a tetrahedral geometry. For some purposes it is convenient to prepare this compound in situ by adding the appropriate amount of trimethylphosphine to a suspension of $[IrCl(C_8H_{14})_2]_2$ and $NaPF_6$ in THF (see Experimental Section).

The insoluble compound $[Ir(P(CH_3)_3)_4][Cl]$ reacts readily with primary alkyllithium or Grignard reagents to yield, at least initially, the corresponding Ir(I) alkyl compound.[25,29] In this manner we have prepared the methyl compound $Ir(CH_3)(P(CH_3)_3)_4$. This Ir(I) compound is off-white in color, dissolves readily in nonpolar solvents, and is quite reactive toward formaldehyde and other substrates.[38]

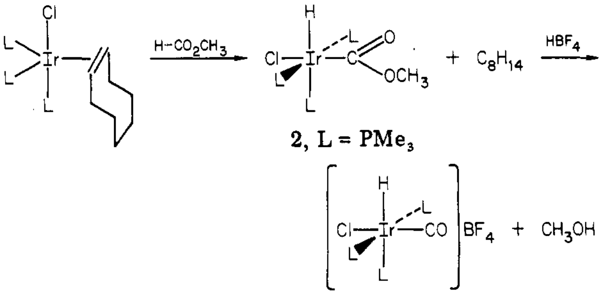
The addition of only 3 equiv of trimethylphosphine to $[IrCl(C_8H_{14})_2]_2$ results in the formation of the tris(phosphine) compound $IrCl(P(CH_3)_3)_3(C_8H_{14})$.[35] This material is soluble in aromatic solvents and in THF and is also quite reactive; the labile cyclooctene ligand permits rapid reactions with added reagents.

Hydrido Methoxycarbonyl Compounds. Two stable iridium(III) complexes containing cis hydrido and methoxycarbonyl ligands have been prepared, $[IrH(CO_2CH_3)(P(CH_3)_3)_4][PF_6]$ (1) and $IrH(CO_2CH_3)Cl(P(CH_3)_3)_3$ (2).[39] The addition of methanol to the Ir(I) complex $[Ir(CO)(P(CH_3)_3)_4]Cl$[32] results in the formation of the cationic complex $[IrH(CO_2CH_3)(P(CH_3)_3)_4]^+$ which has been isolated as the PF_6 salt (eq 1). A closely related reaction is the formation of hydrido alkoxycarbonyl compounds of Ir(III) from $[Ir(CO)(dmpe)_2][Cl]$ and alcohols.[40,41] Many other complexes containing alkoxycarbonyl groups have been synthesized from metal carbonyl complexes and alcohols or alkoxide reagents.[42] The oxidative addition of the formyl C–H bond of methyl formate to $Ir(P(CH_3)_3)_3Cl(C_8H_{14})$ gives compound 2 $IrH(CO_2CH_3)Cl(P(CH_3)_3)_3$ in high yield. This reaction has been observed only for this particular Ir(I) complex; other Ir(I) compounds studied in these experiments either have not been reactive toward methyl formate or have not given stable products. Compound 2 is stable in solution and in the solid state but reacts readily with acid (e.g., HBF_4) to give the cis hydrido carbonyl cation, $[IrClH(CO)(P(CH_3)_3)_3][BF_4]$. This sequence of reactions is summarized in eq 2.



(1)

1, L = PMe$_3$



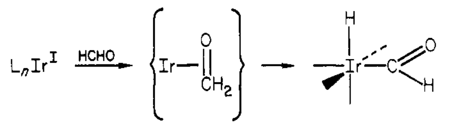
2, L = PMe$_3$

(2)

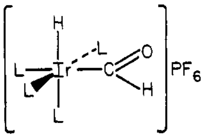
It has not been possible to prepare the neutral hydrido methoxycarbonyl complex 2 by the direct oxidative addition of methanol to the iridium-bound carbonyl. The reason for this is that attempts to prepare the required precursor for this reaction, the chloro trisphosphine carbonyl complex $IrCl(CO)(P(CH_3)_3)_3$ have been unsuccessful, and only mixtures of the bis- and tetrakis(trimethylphosphine)iridium carbonyl compounds[32] have been obtained.

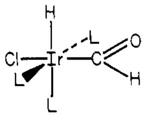
Oxidative addition of the C–H bond of formate esters by low-valent transition-metal complexes is not common. Compound 2 is the first stable hydrido methoxycarbonyl complex to be prepared by this method. Previous reports describe the addition of formate esters to Rh(I) compounds,[43] although the initial product, the hydrido alkoxycarbonyl complex, is unstable. Formic acid itself has been reported to react with an iridium compound to give the hydroxycarbonyl complex.[44]

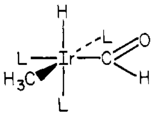
Hydrido Formyl Compounds. Three stable hydrido formyl complexes of Ir(III) have been prepared by two routes, the direct oxidative addition of the C–H bond of formaldehyde by an Ir(I) complex[25] and the reduction of a hydrido(methoxycarbonyl)iridium(III) complex. The mechanism most likely operating in the oxidative addition of formaldehyde, indicated in eq 3, involves the prior formation of a complex containing a π-bound H_2CO entity. Such a species has ample precedent in the numerous examples of π-bound aldehydes and ketones[45] and in the isolation and structural characterization of an osmium complex of formaldehyde.[19] Roper and co-workers have found that this osmium formaldehyde complex undergoes oxidative addition to form the hydridoformylosmium(II) complex, and that acetaldehyde reacts with Os(0) in an analogous fashion to form the hydrido acyl complex.[19,26] Other examples of additions of the C–H bond of aldehydes to d^8 and d^{10} transition-metal centers are known.[46–48]



(3)


3, L = PMe$_3$


4, L = PMe$_3$


5, L = PMe$_3$

With the iridium complexes studied here, π-bound aldehyde complexes have not been observed, and the only isolated products are the hydrido formyl compounds. This synthetic route has been utilized in the preparation of the cationic hydrido formyl complex $[IrH(CHO)(P(CH_3)_3)_4][PF_6]$ (compound 3), the neutral chloro complex $IrClH(CHO)(P(CH_3)_3)_3$ (compound 4), and the methyl complex $Ir(CH_3)H(CHO)(P(CH_3)_3)_3$ (compound 5). The

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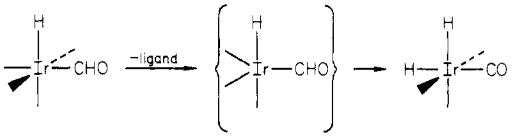
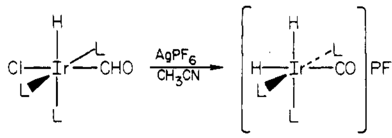
other route, the reduction of a hydrido methoxycarbonyl complex to the corresponding hydrido formyl compound using commercial borane–THF, has been demonstrated to provide compounds **3** and **4**. Likely mechanisms for this reduction reaction will be discussed below.

Although stable at room temperature, all the hydrido formyl complexes of Ir(III) herein reported decompose at elevated temperatures in solution or the solid state, with one product of the decomposition being hydrogen gas.[19,25] The resulting complex mixture of metal compounds contains the corresponding Ir(I) carbonyl compound in varying amounts. The carbonyl compounds resulting from H_2 loss from the cationic hydrido formyl complex **3**, $[Ir(CO)(P(CH_3)_3)_4]^+$, and from H_2 loss from the chloro hydrido formyl complex **4**, $IrCl(CO)(P(CH_3)_3)_2$ have both been previously reported.[32] Hydrogen loss from the methyl formyl complex **5** results in the formation of the methyl carbonyl complex $Ir(CH_3)(CO)(P(CH_3)_3)_3$. This latter compound is also available from the reaction of $Ir(CH_3)(P(CH_3)_3)_4$ with carbon monoxide and from the reaction of $[Ir(CO)(P(CH_3)_3)_4][Cl]$[32] with methyllithium. Loss of CH_4 from the methyl formyl complex **5**, a competing and sometimes dominating decomposition reaction, results in formation of the hydrido carbonyl complex $IrH(CO)(P(CH_3)_3)_3$ (see below).[49] A bimolecular decomposition mechanism has been established for the decomposition of hydridoacylosmium(II) complexes[50] and may be operative in the decomposition of the present complexes as well.

One likely mechanism for the unimolecular[50] decomposition of the hydrido formyl compounds is loss of a ligand with subsequent migration of a hydrogen atom from the formyl group to the metal (eq 4); reductive elimination of H_2 may occur in a succeeding step. Although fascinating reactions of several transition-metal hydrido complexes with carbon monoxide to give multinuclear formyl or other C–H bonded species have been demonstrated,[51] the reverse of this reaction, the "carbonyl insertion" into a metal–hydrogen bond, had not been observed in isolable mononuclear complexes until very recently.[52] This is in sharp contrast to the well-known "carbonyl insertion" into metal–alkyl bonds.[53] Two reactions of the hydrido formyl complexes illustrate this mechanism for the decomposition of the formyl group. Removal of the chloride ligand from complex **4** by $AgPF_6$ results in formation of the dihydrido cation $[IrH_2(CO)(P(CH_3)_3)_3]^+$ as the major product, presumably as a result of rapid hydrogen atom migration from the carbon of the formyl group to the metal (eq 5). Also, removal of the hydrido hydrogen atom of complex **3** *as a proton* (vide infra) results in formation of the hydrido carbonyl complex $IrH(CO)(P(CH_3)_3)_3$, also a result of hydrogen atom migration (eq 6).

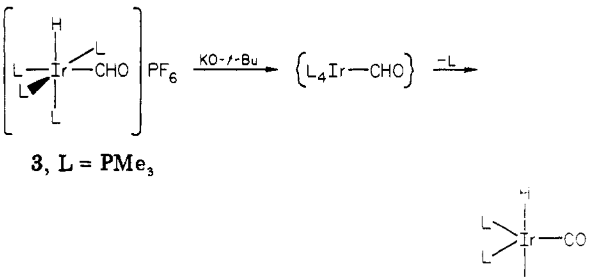


(4)



(5)

4, L = PMe₃



3, L = PMe₃

(6)

Hydrido Hydroxymethyl and Hydrido Methyl Complexes. The reaction of $NaBH_4$ with the cationic hydrido formyl complex **3** in wet THF[16] results in the formation of the cationic hydrido hydroxymethyl complex $[IrH(CH_2OH)(P(CH_3)_3)_4][PF_6]$ (**6**). This reaction does not work with the other Ir(III) hydrido formyl compounds; for instance, compound **4** reacts with wet $NaBH_4$ to form the *fac*-trihydrido compound $IrH_3(P(CH_3)_3)_3$.[54] Roper and colleagues have reported the isolation of hydroxymethyl complexes of osmium by protonation of the oxygen atom of osmium-bound formaldehyde.[19,26] Other researchers have isolated hydroxymethyl complexes of rhenium from reduction of rhenium-bound carbon monoxide.[16,20,22,24,55]

The reaction of commercial borane–THF with the cationic hydrido formyl complex **3** results in complete reduction of the formyl group to give the cis hydrido methyl complex $[IrH(CH_3)(P(CH_3)_3)_4][PF_6]$ (**7a**) in ~20–25% yield.[25] Several other products present in the reaction mixture have not been identified. The presence of **7a** among the reaction products is confirmed by comparison of the ^1H NMR spectrum of the crude product mixture with that of separately prepared $[IrH(CH_3)(P(CH_3)_3)_4][BF_4]$ (**7b**). The catonic hydridomethyliridium(III) cation can be easily separately prepared by reacting $Ir(CH_3)(P(CH_3)_3)_4$ with either HPF_6 (to give **7a**) or HBF_4 (to give **7b**) in pyridine or ether. The different products obtained from the different conditions used for reducing the formyl group of compound **3** are outlined in eq 7.[16] Perhaps the most remarkable feature of the hydrido methyl cations **7a,b** and of the hydrido methyl formyl complex **5** is their apparent reluctance to undergo reductive elimination of methane, despite the well-established tendency of cis hydrido alkyl complexes to reductively eliminate the alkane.[56,57]

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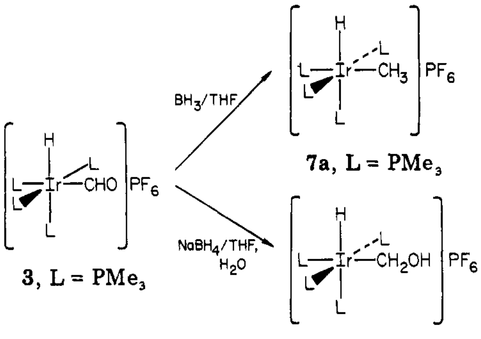
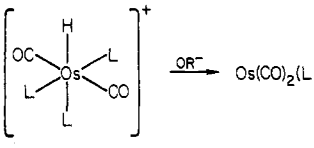


3, L = PMe₃ 7a, L = PMe₃ 6, L = PMe₃ (7)

Reactions of Hydrido Ir(III) Complexes with Strong Bases. While it has long been known that first-row transition-metal hydrido compounds can be quite acidic (e.g., eq 8a),[58] it is less generally appreciated that second- or third-row transition-metal hydrido compounds also can show acidic behavior.[59] An example of this is the reaction of an Os(II) hydrido compound with alkoxide to form an Os(0) compound and the alcohol (eq 8b).[60] The hydrido Ir(III) complexes studied in this laboratory also show acidic behavior in the sense that the "hydride" can often be removed from the metal with concomitant formal reduction of the metal center to Ir(I). This "deprotonation" reaction proceeds if the Ir(III) hydrido compound contains a good leaving anionic ligand or, preferably, an outer-sphere counteranion. A strong base is necessary for the reaction to be observed; potassium *tert*-butoxide has been found to be generally satisfactory and convenient. Pyridine is not nearly sufficiently basic, and in fact the conjugate acid of pyridine is a useful reagent for effecting the reverse reaction, the protonation of Ir(I) complexes to form Ir(III) hydrido complexes. Examples of this reaction are the formation of $[IrH(CH_3)(P(CH_3)_3)_4][BF_4]$ (**7b**) from $Ir(CH_3)(P(CH_3)_3)_4$ (vide supra) and $[IrH_2(CO)(P(CH_3)_3)_3]^+$ from $IrH(CO)(P(CH_3)_3)_3$.

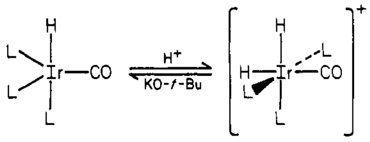
$$HCo(CO)_4 \rightleftharpoons H^+ + Co(CO)_4^- \qquad (8a)$$



(8b)

L = $P(C_6H_5)_3$

Of particular interest is the reaction of the hydrido formyl compounds **3** and **4** with potassium *tert*-butoxide to give $IrH(CO)(P(CH_3)_3)_3$. The probable mechanism is removal of the hydrido ligand as a proton by alkoxide (see eq 6), resulting in an Ir(I) formyl complex, followed by ligand dissociation and migration of the formyl hydrogen atom from the carbon of the formyl group to the metal atom. The major product of this reaction, $IrH(CO)(P(CH_3)_3)_3$ has not been previously reported. We have been able to prepare it by the reaction of $[Ir(CO)(P(CH_3)_3)_4][Cl]$[32] with borohydride reducing agents, e.g., $LiHBEt_3$, but the reaction of potassium *tert*-butoxide with complex **3** is more convenient. The compound can be protonated with either HBF_4 or HPF_6 in pyridine or ether to give $[IrH_2(CO)(P(CH_3)_3)_3]^+$ (see eq 9). This protonation reaction can be reversed with potassium *tert*-butoxide. The dihydrido carbonyl cation is also the dominant product when the neutral chloro hydrido formyl complex **4** reacts with $AgPF_6$, as discussed above.



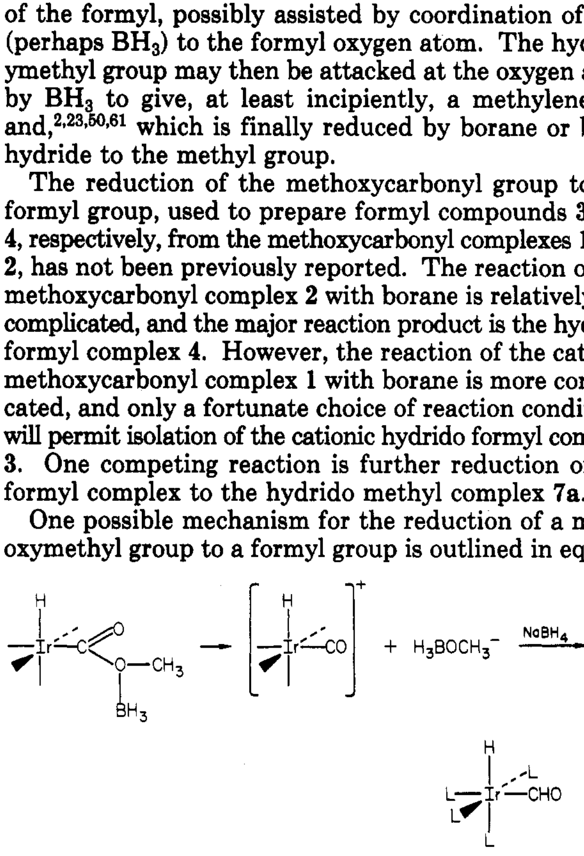
(9)

L = PMe₃

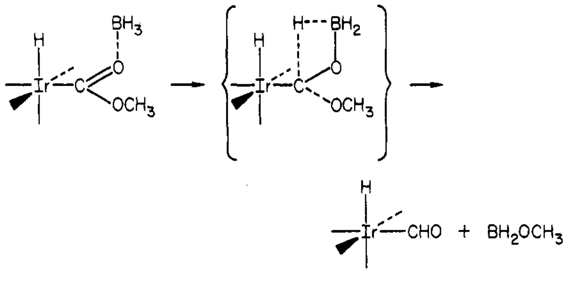
Reduction Reactions Using Borane. Borane in THF has been found to effect the reduction of methoxycarbonyl groups to formyl groups and formyl groups to methyl groups. Several proposals have been presented in the literature[2] as to likely mechanisms for reduction of metal-bound formyl groups with borane. To these proposals we can add little except to note that the mixture of BH_3 and $NaBH_4$ which exists in the commercial "borane–THF" solution used in this work may well be more effective as a reducing agent than either BH_3 or $NaBH_4$ alone. In particular, the formyl group may be reduced to the hydroxymethyl group by borohydride H attack at the carbon of the formyl, possibly assisted by coordination of acid (perhaps BH_3) to the formyl oxygen atom. The hydroxymethyl group may then be attacked at the oxygen atom by BH_3 to give, at least incipiently, a methylene ligand,[2,23,50,61] which is finally reduced by borane or borohydride to the methyl group.

The reduction of the methoxycarbonyl group to the formyl group, used to prepare formyl compounds **3** and **4**, respectively, from the methoxycarbonyl complexes **1** and **2**, has not been previously reported. The reaction of the methoxycarbonyl complex **2** with borane is relatively uncomplicated, and the major reaction product is the hydrido formyl complex **4**. However, the reaction of the cationic methoxycarbonyl complex **1** with borane is more complicated, and only a fortunate choice of reaction conditions will permit isolation of the cationic hydrido formyl complex **3**. One competing reaction is further reduction of the formyl complex to the hydrido methyl complex **7a**.

One possible mechanism for the reduction of a methoxymethyl group to a formyl group is outlined in eq 10a.



(10a)



(10b)

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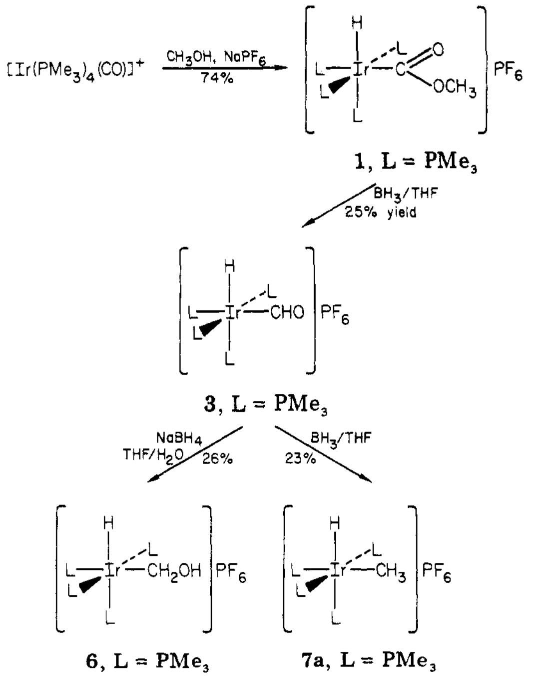
The first step is removal of the methoxy group by the Lewis acid BH_3 followed by reduction of the carbonyl cation by borohydride. We consider this mechanism to be unlikely, since the carbonyl cation $[IrClH(CO)(P(CH_3)_3)_3]^+$ (separately prepared by reaction of the methoxycarbonyl complex **2** with HBF_4; vide supra) reacts with $NaBH_4$ to give, not the formyl complex **4**, but rather the dihydrido carbonyl cation $[IrH_2(CO)(P(CH_3)_3)_3]^+$. A more plausible alternative mechanism is illustrated in eq 10b; here the BH_3 molecule attacks the "carbonyl" oxygen atom with eventual hydrogen atom transfer to the carbon. Other methoxycarbonyl compounds are known to react with $(C_2H_5)_3O^+$ by alkylating at the carbonyl oxygen atom.[42]

In the complexes examined in these experiments, one possibility is that the iridium-bound hydrido ligand may actively participate in the reduction of the carbon-containing groups. It may participate by migrating from the iridium atom to methylene- or carbene-resembling ligands, created by coordination of the Lewis acid BH_3 to the oxygen atom of a formyl or hydroxymethyl group. External hydride sources (e.g., $NaBH_4$) then could transfer a new hydrido ligand to the iridium center. That these latter reaction pathways are viable possibilities has been shown by studies of model compounds;[49] for instance, we have observed methyl group migration to an iridium-bound methylene group derived from a methoxymethyl ligand.[38] It is not yet known whether the present reactions themselves involve active participation of the hydrido ligand.

The set of reactions described above provides a pathway for the stepwise conversion of iridium-bound carbon monoxide to iridium-bound methyl or hydroxymethyl groups, as indicated in eq 11. Several steps proceed in unfortunately poor yield (see Experimental Section), and compounds **3** and **7** are more conveniently prepared by other routes, as discussed above. Continuing studies of the reduction reactions and other reactions involving these compounds may provide more mechanistic details.



(11)

Experimental Section

General. While the Ir(III) complexes described in this paper all appear to be air stable in the solid state and the Ir(I) complex $[Ir(P(CH_3)_3)_4][PF_6]$ also is air stable when in crystalline form, all reactions were carried out under a nitrogen atmosphere by using either Schlenk-type reaction vessels or a Vacuum Atmospheres drybox. Solvents were dried and degassed prior to use. Paraformaldehyde and methyl formate were obtained from Aldrich and were used without purification save for brief degassing. Borane–THF (1 M, stabilized with small amounts of $NaBH_4$), borohydride reagents, HBF_4 etherate, and $AgBF_4$ were also obtained from Aldrich and were used as supplied. ^{13}C- and ^{2}H-labeled paraformaldehyde were obtained from Merck Isotopes. Trimethylphosphine was obtained from Strem Chemical Co. and was handled exclusively in the drybox. **Caution**: *Trimethylphosphine is toxic and may ignite spontaneously upon exposure to air, and its extreme volatility increases the hazards associated with its use.* Infrared, ^1H NMR, high-field ^1H NMR, and ^{31}P-decoupled ^1H NMR spectra were obtained by using Perkin-Elmer 283B, Varian EM-390, Bruker HFX400, and Varian XL-100 spectrometers, respectively. All infrared (IR) data are from solid samples in Nujol and are reported in units of cm^{-1}. All reactions were carried out at room temperature.

Iridium(I) Starting Materials. Tetrakis(trimethylphosphine)iridium(I) Hexafluorophosphate, $[Ir(P(CH_3)_3)_4][PF_6]$. $IrCl(P(CH_3)_3)_3(C_8H_{14})$[35,38] (2.53 g, 4.47 mmol) and $NaPF_6$ (1.50 g, 8.9 mmol) were suspended in 200 mL of tetrahydrofuran (THF). A solution of $P(CH_3)_3$ (0.34 g, 4.47 mmol) in 5 mL of THF was added dropwise with stirring. The resulting cloudy red suspension was filtered after stirring for 15 h. The cooled solution deposited 0.30 g of red solid; hexane was then added to the solution by vapor diffusion, and 1.42 g of red crystals was obtained after 3 days, giving a total yield of 1.72 g (2.68 mmol, 60%), decomposition at 194 °C; mp >300 °C. Anal. Calcd: C, 22.47; H, 5.66. Found: C, 22.84; H, 5.62.

Methyltetrakis(trimethylphosphine)iridium(I), $Ir(CH_3)(P(CH_3)_3)_4$. A suspension of $[Ir(P(CH_3)_3)_4][Cl]$[33,35] (0.85 g, 1.60 mmol) in 10 mL of THF was added dropwise to a solution of methyllithium (2 mL of 1.6 M ether solution) in 10 mL of THF. The resulting yellow-brown solution was evaporated to dryness under vacuum and the residue extracted with pentane. Evaporation of the pentane solution yielded 0.69 g (1.35 mmol, 84%) of yellow solid, sufficiently pure for most purposes. ^1H NMR (C_6D_6) Ir–CH_3, quintet (J = 7 Hz) at δ 0.45; $P(CH_3)_3$, s, δ 1.50; decomposition at 50 °C; mp 165–194 °C. Anal. (Sample recrystallized from concentrated pentane solution) Calcd: C, 30.52; H, 7.68. Found: C, 30.18; H, 7.70.

Hydridoiridium Compounds. Hydrido(methoxycarbonyl)tetrakis(trimethylphosphine)iridium(III) Hexafluorophosphate (1). A methanol solution (10 mL) of lithium methoxide (0.02 g) and $[Ir(CO)(P(CH_3)_3)_4][Cl]$[32] (0.56 g) was stirred for 1 h, and then evaporated to dryness. The residue was suspended in 20 mL of THF, and $NaPF_6$ (0.18 g) was added. After filtration the solution was cooled to −30 °C and white crystals (0.52 g, 74%) of **1** were obtained: decomposition at 185 °C, mp 298–300 °C; IR of **1** 2100, 2060 (m), 1622 (s) cm^{-1}; ^1H NMR (CD_3CN) Ir–H, δ −13.0, d (J = 135 Hz) of quartets (J = 18 Hz); $P(CH_3)_3$, δ 1.48, d (J = 8 Hz) of d (J = 1 Hz), 1.54, d (J = 7 Hz), 1.58, t (J(eff) = 3.6 Hz); –OCH_3, δ 3.28, s. Anal. Calcd: C, 23.97; H, 5.75. Found: C, 23.83; H, 5.74.

Hydrido(methoxycarbonyl)chlorotris(trimethylphosphine)iridium(III) (2). Methyl formate (0.15 g) was added to a THF solution (30 mL) of $IrCl(P(CH_3)_3)_3(C_8H_{14})$[35,38] (1.10 g), and the solution was stirred 2.5 h. The solvent was evaporated under vacuum, and the off-white residue was recrystallized from hexane, yielding 0.83 g (83%) of compound **2**: mp 138–140 °C; IR 2060, 1620 (s) cm^{-1}; ^1H NMR (C_6D_6) Ir–H, δ −10.35, d (J = 154 Hz) of t (J = 20 Hz); $P(CH_3)_3$, δ 1.40, d (J = 8 Hz), 1.60, t (J(eff) = 4 Hz); –OCH_3, δ 3.40, s. Anal. Calcd: C, 25.61; H, 6.06. Found: C, 25.28; H, 5.97.

Hydridoformyltetrakis(trimethylphosphine)iridium(III) Hexafluorophosphate (3). Method a. $[Ir(P(CH_3)_3)_4][PF_6]$ (0.34 g) in 100 mL of THF was treated with 0.023 g of paraformaldehyde, and the mixture was stirred 2 h. The off-white product was filtered and recrystallized from warm methanol: yield 0.30 g (84%); mp >250 °C; IR 2622 (m), 2072 (s), 1600 (s) cm^{-1}; ^1H NMR (pyridine-d_5) Ir–H, δ −12.0, d (J = 123 Hz) of quartets (J = 18 Hz); Ir–CHO, δ 14.0, d (J = 49 Hz) of t (J = 6.5 Hz) of d (J = 4.0 Hz) of d (J = 2.5 Hz); $P(CH_3)_3$, δ 1.2–1.4, m; ^{31}P-decoupled ^1H NMR $P(CH_3)_3$, δ 1.20, s, δ 1.23, d (J(H-hydride) = 1 Hz), 1.26, s; Ir–CHO, d (J(H–hydride) = 2.5 Hz); ^{13}C NMR (acetone-d) formyl C, δ 225.40, d ($J(C–P_{trans\ to\ H})$ = 10 Hz) of t ($J(C–P_{cis})$ =

5.4 Hz) of d (J(C–P_{trans}) = 83 Hz), J(C–H_{formyl}) = 150 Hz; ^{31}P NMR (pyridine-d_5) t (J = 21 Hz) at δ −52.0 (external H_3PO_4), quartet (J = 21 Hz) at δ −55.8, quartet (J = 19 Hz) at δ −69.0; PF_6, δ −143.2, J(P–F) = 710 Hz. Anal. Calcd: C, 23.25; H, 5.70. Found: C, 23.35; H, 5.66.

Method b. $[IrCl(C_8H_{14})_2]_2$ (0.90 g) was suspended in 150 mL of THF and 0.35 g of $NaPF_6$ was added, followed by a solution of 0.62 g of $P(CH_3)_3$ in 5 mL of THF. The red suspension was stirred 10 min and 0.070 g of paraformaldehyde was added. After an additional 1 h of stirring, the off-white suspension was filtered, and the solids were extracted into acetone. Evaporation of the acetone extract yielded 1.11 g (82%) of compound **3**.

Method c. A suspension of 0.9 g of compound **1** in 3 mL of THF was treated with 4 mL of borane–THF solution and stirred 3 h, at which time another 3 mL of borane–THF solution was added. After an additional 20 h of stirring, the suspension was filtered, yielding 0.22 g (25%) of **3** (IR analysis).

Chlorohydridoformyltris(trimethylphosphine)iridium(III) (4). Method a. A solution of $IrCl(P(CH_3)_3)_3(C_8H_{14})$ (0.28 g) in 5 mL of THF was treated with 0.015 g of paraformaldehyde. After 0.5 h of stirring, the solution was evaporated to dryness and the residue washed with hexane, leaving 0.20 g (83%) of compound **4**, mp 130 °C dec. Recrystallization from THF/hexane yielded an analytically pure sample: IR 2585 (m), 1990 (s), 1600 (s) cm^{-1}; ^{1}H NMR (C_6D_6) Ir–H, δ −9.2, d (J = 140 Hz) of t (J = 20 Hz); $P(CH_3)_3$), δ 1.33, d (J = 8 Hz) of d (J(H–hydride) = 1 Hz), 1.50, t (J(eff) = 3.6 Hz); Ir–CHO, δ 15.0, t (J = 8 Hz) of d (J(H–hydride) = 3 Hz). Anal. Calcd: C, 24.72; H, 6.02. Found: C, 25.00; H, 6.02.

Method b. A solution of 0.20 g of compound **2** in 5 mL of THF was treated with 1 mL of borane–THF solution. The solution was filtered and evaporated after stirring for 2 h. IR and ^{1}H NMR analysis of the residue showed the presence of compound **4** in 70% yield (estimated). Recrystallization provided 0.045 g (24%) of pure compound **4**.

Methylhydridoformyltris(trimethylphosphine)iridium(III) (5). Paraformaldehyde (0.030 g) was added to a solution of $Ir(CH_3)(P(CH_3)_3)_4$ (0.32 g) in 15 mL of THF. After 1 h of stirring, the mixture was filtered and the solution concentrated to ca. 1 mL. Pentane was added and the solution was cooled to −30 °C overnight to yield 0.21 g (72%) of white solid, mp 135 °C dec: IR 2490 (m), 1985 (s), 1589 (s) cm^{-1}; ^{1}H NMR (C_6D_6) Ir–H, δ −11.1, d (J = 137 Hz) of t (J = 21 Hz); Ir–CH_3, δ 0.71, m; $P(CH_3)_3$, δ 1.31, d (J = 8 Hz), 0.99, d (J = 7 Hz), 0.95, d (J = 8 Hz) of d (J(H–hydride) = 1 Hz); Ir–CHO, δ 15.2, d (J = 48 Hz) of br d (J = 3 Hz); ^{1}H NMR of $IrD(CDO)(CH_3)(P(CH_3)_3)_3$ (C_6D_6) Ir–CH_3, d (J = 10 Hz) of d (J = 7 Hz) of d (J = 5 Hz). Anal. Calcd: C, 28.38; H, 6.93. Found: C, 28.50; H, 6.88.

Hydrido(hydroxymethyl)tetrakis(trimethylphosphine)iridium(III) Hexafluorophosphate (6). Compound **3** (1.31 g) was suspended in a mixture of 20 mL of THF and 5 mL of H_2O, and 0.20 g of $NaBH_4$ was added. After 3 days of stirring, ether was added to the slurry and 0.95 g of white solid was obtained. IR analysis of this solid suggested that most of the starting formyl had been consumed, but very little of the hydroxymethyl compound **6** had been formed. Consequently the solid was suspended in a fresh mixture of 10 mL of THF and 6 mL of H_2O with 0.10 g of $NaBH_4$ and stirred overnight. Ether was added to this suspension, the precipitated solid was redissolved in 20 mL of THF, and 2 mL of H_2O and 0.30 g of $NaPF_6$ were added. After being stirred for 6 h, this mixture was dried under vacuum, and the residue was recrystallized from THF/pentane at −30 °C, yielding 0.34 g (26%) of white solid; decomposition at 148 °C, mp >250 °C: IR 3630, 3570 (m), 2040, 2020 (s) cm^{-1}. Anal. Calcd for **6**: C, 23.18; H, 5.99. Found: C, 23.15; H, 5.89. Samples prepared or handled differently had varying positions of these absorption bands, possibly ascribable to different crystalline modifications: ^{1}H NMR (pyridine-d_5) Ir–H, δ −13.2, d (J = 125 Hz) of t (J = 23 Hz) of d (J = 14 Hz); $P(CH_3)_3$, δ 1.22, d (J = 8 Hz) of d (J(H–hydride) = 1 Hz), 1.35, d (J = 8 Hz), 1.43, t (J(eff) = 3.6 Hz); Ir–C*H*$_2$–OH, δ 4.1, t (J = 9 Hz) of d (J = 6 Hz) of d (J = 1.5 Hz); –CH_2–O*H*, δ 4.3, br s.

Hydrido(methyl)tetrakis(trimethylphosphine)iridium(III) Hexafluorophosphate (7a). Compound **3** (0.14 g) was suspended in 10 mL of THF, and 4 mL of borane–THF (1 M) was added. The mixture was stirred overnight, filtered, and concentrated. Pentane was added and the resulting white precipitate was dried and redissolved in pyridine-d_5. The ^{1}H NMR spectrum of this solution had a multiplet at δ −0.05, characteristic of the hydridomethyl cation (see below). From the integral of this NMR spectrum, the methyl compound was found to comprise ca. 23% of the total phosphine–Ir species.

Hydrido(methyl)tetrakis(trimethylphosphine)iridium(III) Tetrafluoroborate (7b). An ether solution (5 mL) of $Ir(CH_3)(P(CH_3)_3)_4$ (0.8 g) was treated dropwise with a solution of HBF_4–etherate (0.24 g) in 5 mL of ether. The resulting white suspension was stirred 15 min and filtered, and the solid was washed with pentane and dried under vacuum; yield 0.75 g (80%); decomposition at 150 °C; mp 220–224 °C. Anal. Calcd for **7b**: C, 26.05; H, 6.73. Found: C, 26.51; H, 6.89. The closely related compound $[IrH(CH_3)(P(CH_3)_3)_4][I]$ has been obtained analytically pure by another preparative method[49] and has an identical ^{1}H NMR spectrum: ^{1}H NMR (pyridine-d_5) Ir–H, δ −13.2, d (J = 138 Hz) of quartets (J = 20 Hz); Ir–CH_3, δ −0.05, quartet (J = 8 Hz) of d (J = 4 Hz) of d (J(H–hydride) = 1 Hz); $P(CH_3)_3$, δ 1.31, d (J = 8 Hz) of d (J(H–hydride) = 1 Hz), 1.47, t (J(eff) = 3.3 Hz), 1.52, d (J = 8 Hz). Anal. Calcd for $C_{13}H_{40}I_1Ir_1P_4$: C, 24.42; H, 6.31. Found: C, 24.40; H, 6.30.

Hydridochlorocarbonyltris(trimethylphosphine)iridium(III) Tetrafluoroborate, $[IrHCl(CO)(P(CH_3)_3)_3][BF_4]$. Methyl formate (0.070 g) was added to a THF solution (20 mL) of $IrCl(P(CH_3)_3)_3(C_8H_{14})$ (0.57 g) and stirred 5 h. The solution was evaporated, and the residue was extracted with ether. The resulting solution (containing primarily compound **2**) was treated with 0.15 g of HBF_4 dimethyl etherate and stirred briefly. The white precipitate was collected, washed with ether, and dried, yielding 0.48 g of white solid (83%): IR 2055 (vs, br) cm^{-1}; ^{1}H NMR (pyridine-d_5) Ir–H, δ −9.1, d (J = 155 Hz) of t (J = 17 Hz); $P(CH_3)_3$, δ 1.56, d (J = 9 Hz) of d (J = 1 Hz), 1.72, t (J(eff) = 3.6 Hz).

Hydrido(carbonyl)tris(trimethylphosphine)iridium(I) and Dihydridocarbonyltris(trimethylphosphine)iridium(III) Tetrafluoroborate, $IrH(CO)(P(CH_3)_3)_3$ and $[IrH_2(CO)(P(CH_3)_3)_3][BF_4]$. Method a. A suspension of $[Ir(CO)(P(CH_3)_3)_4][Cl]$ (1.0 g)[32] in 20 mL of THF was treated with a slight excess of $KHB(O\text{-}i\text{-}Pr)_3$. No reaction was apparent after several minutes, so a slight excess of $LiHB(C_2H_5)_3$ was added. The reaction proceeded immediately to give a clear yellow solution which was evaporated to dryness. The residue was extracted with pentane, and the pentane extract was sublimed under high vacuum, giving 0.52 g of a sticky, off-white solid. The IR spectrum of this solid had a broad band at 1600 cm^{-1}, suggestive of O-bound residual borane,[2] but upon subsequent handling of this compound, this IR band was lost and only strong bands at 2010 and 1900 cm^{-1} were observed. ^{1}H NMR (C_6D_6): Ir–H, δ −12.5, quartet (J = 12 Hz); $P(CH_3)_3$, δ 1.6, br m. In THF-d_8 the hydrido hydrogen signal is a quartet, J = 8 Hz. Signals appropriate for formyl hydrogen atoms were sought but never observed. This compound, $IrH(CO)(P(CH_3)_3)_3$, was then dissolved in 20 mL of ether and treated with 0.16 g of HBF_4–etherate. A white solid precipitated immediately and was filtered, washed with ether, and dried, yielding 0.52 g (54%, based on $[Ir(CO)(P(CH_3)_3)_4][Cl]$) of $[IrH_2(CO)(P(CH_3)_3)_3][BF_4]$: mp 132–136 °C; IR 2095 (s), 2040 (s), 1998 (s) cm^{-1}; ^{1}H NMR (CD_3CN) Ir–*H*, δ −11.2 and −11.9, m, br; $P(CH_3)_3$, δ 1.70, d (J = 9 Hz) of d (J = 1 Hz), 1.76, t (J(eff) = 4 Hz); ^{1}H NMR (high field, pyridine-d_5) Ir–H, δ −11.2, d (J = 17 Hz) of t (J = 20 Hz) of d (J(hydride–hydride) = 4 Hz), −11.9, d (J = 114 Hz) of t (J = 20 Hz) of d (J(hydride–hydride) = 4 Hz). Anal. Calcd: C, 22.36; H, 5.44. Found: C, 22.51; H, 5.51.

Method b. Compound **3** (0.33 g) was suspended in 5 mL of THF and 0.06 g of potassium *tert*-butoxide was added. The resulting off-yellow suspension was stirred 15 min and evaporated to dryness. The residue was extracted with hexane, and the hexane extract was evaporated, leaving 0.11 g (50% yield) of a sticky, off-white residue. The IR and NMR spectra of this material were identical with those of $IrH(CO)(P(CH_3)_3)_3$ (see above). This material has not been successfully recrystallized owing to its extreme solubility in inert solvents.

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Stereochemistry of Transition Metal Cyclooctatetraenyl Complexes. Molecular Structure of (η-Cyclooctatetraenyl)(η-allyl)-*tert*-butoxyzirconium

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Crystals of (η-cyclooctatetraenyl)(η-allyl)-*tert*-butoxyzirconium belong to the monoclinic space group $P2_1/n$ with a = 15.696 (6) Å, b = 16.117 (3) Å, c = 12.531 (6) Å, β = 111.05 (1)°, Z = 8, and d_{calcd} = 1.39 g/cm³. The structure was derived from 4418 counter-measured X-ray data and refined to a conventional R value of 0.039. Two crystallographically independent molecules were found, the second molecule displaying two distinct conformations of the *tert*-butoxy groups. Strong Zr–O bonding is indicated by the short Zr–O bond lengths, average 1.91 (1) Å, and the large Zr–O–C bond angles, average 169 (1)°. The Zr–allyl linkages are slightly asymmetric with a mean Zr–C(allyl) separation of 2.481 Å. The metal atoms are bonded to the COT ligands in an η^8 fashion, although highly significant deviations are found in the Zr–C(COT) bond lengths. These deviations are related to the patterns of nonplanarity revealed for the COT carbon atoms. In the first molecule the ring assumes a shallow tub confirmation while that of the second is slightly folded along a diagonal. The departures from C_{8v} symmetry in the Zr–COT bonding apparently relate to the orientation of the COT moiety with respect to the allyl and *tert*-butoxy groups, the longest Zr–C bond lengths being approximately trans to those ligands. The C–H bonds show an average tilt of 9.2 (9)° out of the COT carbon atom planes toward the metal atoms.

Introduction

Structural investigations of $(COT)_2Zr\cdot THF$[1] (COT = 1,3,5,7-cyclooctatetraene and THF = tetrahydrofuran) and $(COT)ZrCl_2\cdot THF$[2] showed that both compounds contained a nearly planar COT ligand bonded η^8 to the Zr atoms. In addition, the study of the dichloride revealed that the four Zr–C bonds approximately trans to the Zr–Cl linkages were elongated compared to the other four even though the Zr–Cl interactions appeared not to be particularly strong.[2] This evidence hints at a degree of compliance in the Zr–C(COT) bonds. To gain more information on this phenomenon, we have examined the structure of $(COT)(C_3H_5)(t\text{-}C_4H_9O)Zr$ (I)[3] and now wish to report the results.

Experimental Section

For the X-ray study, crystals of I, which were kindly supplied by Dr. R. Kallweit of this institute, were mounted in glass capillaries under argon. The space group was determined from Weissenberg photographs. Lattice constants were determined by a least-squares procedure from Bragg angles measured with a PDP-8/s automated Siemens diffractometer employing Zr-filtered Mo Kα radiation (λ(Mo K$\bar{\alpha}$) = 0.71069 Å) and are given in the summary. Intensity data (hkl, $\bar{h}kl$, $2 \le \theta \le 25°$) were measured and reduced as described previously.[2] No absorption correction was applied because of the irregular crystal shape; however, corrections would have been small (μ = 7.2 cm⁻¹). Of the 5158 data collected, 4418 were unique and had $I \ge 2\sigma(I)$. Only the corresponding $|F_o|$'s were assigned nonzero weights (w) and were used in subsequent calculations.

The structure was solved by the heavy-atom method and refined by least-squares techniques. Computing details have been cited previously.[2] After anisotropic refinement, a difference Fourier calculation indicated the presence of a second orientation (occupancy 0.7) of the *tert*-butoxy group in molecule 2 which was related to the first by a rotation of ~60° about the O–C(12) bond. The additional three carbon atoms were included isotropically in the refinement along with a constrained occupancy factor. Positional parameters for the hydrogen atoms of the COT and allyl ligands in both molecules as well as those of the *tert*-butoxy group of molecule 1 were obtained from a subsequent difference density map, and these atoms were refined isotropically. Methyl hydrogen atoms were not located for molecule 2. After several additional large-block least-squares cycles, convergence was reached with $R = \sum\Delta/\sum|F_o| = 0.039$, $\Delta = ||F_o| - |F_c||$, and $R_w = [\sum w\Delta^2/\sum w|F_o|^2]^{1/2} = 0.048$. Positional parameters are given in Table I, the numbering scheme for both molecules being indicated in Figure 1. The mean C–H distance is 0.97 (11) Å.

Thermal ellipsoids of each Zr–C(1)–C(8) fragment are well fit by a TLS rigid-body-motion model.[4] On the average, librational corrections increase the C–C and Zr–C bond lengths by 0.018 and 0.025 Å, respectively. Unless specified to the contrary, uncorrected values are given in the text.

Description of the Crystal Structure

Crystals of I are composed of discrete molecules, two of which make up the asymmetric unit. Both independent

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