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 \(\text{Ir(HCHO)}(\text{P(CH₃)₃})_2\) \(\text{[PF₆]}\) (3), \(\text{IrClH(CH₃)}(\text{P(CH₃)₃})_3\) (4), and \(\text{Ir(CH₃)H(CH₃)}(\text{P(CH₃)₃})_3\) (5). The reduction of (methoxycarbonyl)iridium(III) compounds \(\text{Ir(CHO)}(\text{P(CH₃)₃})_3\) \(\text{[PF₆]}\) (1) and \(\text{IrCl(CHO)}(\text{P(CH₃)₃})_3\) (2), prepared respectively by addition of methanol to \(\text{Ir(CHO)(P(CH₃)₃)}\) \(\text{[PF₆]}\) and oxidative addition of methyl formate by \(\text{IrCl(CH₃)}(\text{P(CH₃)₃})_3\), 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 usable organic products has prompted many investigations of compounds which serve as models for postulated intermediates in carbon-monoxide hydrogenation. These in-
vestigations have resulted in syntheses of mononuclear transition-metal compounds with bound formyl groups,16,24,25 hydroxymethyl groups,26,27,28,29 and carbon monoxide or formyl derived methyl groups.30,31,32,33,34,35 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 other alkyl-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,36 only for the cyclopentadienylrhenium system studied by several research groups.26-28 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, hydridohydroxymethyl, and hydridomethyliridium compounds. A preliminary account of some of these results has been published.37

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.38-39 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. Carboxylic iridium complexes (vide infra) as well as by literature methods.32 Trimethylphosphine has been our preferred ligand because of its simple 1H 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(C5H5)2] results in the formation of the ionic complex [Ir(P(CH3)3)3]Cl.36,37 This complex is too insoluble in unreactive solvents, to react with formaldehyde; however, the PF6 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(CH3)3)3]PF6 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(CH3)3)3]Cl36 and [Ir(Pb(CH3)3)3][BF4]37 the compound [Ir(P(CH3)3)3]PF6 probably consists of discrete four-coordinated cationic Ir(I)

34 Tulip, T. H.; unpublished work.
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-(C8H14)2] and NaNPF6 in THF (see Experimental Section).

The insoluble compound [Ir(P(CH3)3)3][Cl] reacts readily with alkali or Grignard reagents to yield, at least initially, the corresponding Ir(I) alkyl compound.25,26 In this manner we have prepared the methyl compound Ir(CH3)3(P(CH3)3)2. This Ir(I) compound is off-white in color, dissolves readily in nonpolar solvents, and is quite reactive toward formaldehyde and other substrates.27

The addition of 3 equiv of trimethylphosphine to [IrCl(C8H14)2] results in the formation of the tris(phosphine) compound IrCl(P(CH3)3)3(C8H14). 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, [Ir(HCO2C8H14)P(CH3)3]2[Pd] (1) and Ir(HCO2C8H14)Cl(P(CH3)3)2 (2).28 The addition of methanol to the Ir(I) complex [Ir(CO)P(CH3)3]2[Pd] results in the formation of the cationic complex [Ir(HCO2C8H14)P(CH3)3] which has been isolated as the PF6 salt (eq 1). A closely related reaction is the formation of hydrido alkoxycarbonyl compounds of Ir(III) from [Ir(CO)(dimep)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(CH3)3)3Cl(C8H14) gives compound 2 IrH(CO2C8H14)Cl(P(CH3)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., HBF4) to give the cis hydrido carbonyl cation, [IrH(CO)(P(C8H14)2)3][BF4]. This sequence of reactions is summarized in eq 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 triphosphine carbonyl complex IrCl(CO)(P(CH3)3)2 have been unsuccessful, and only mixtures of the bis- and tetraakis(trimethylphosphine)iridium carbonyl compounds 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) complex25 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 H2O entity. Such a species has ample precedent in the numerous examples of π-bound aldehydes and ketones45 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 hydroformylosmium(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 d8 and d10 transition-metal centers are known.46-48

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(CH)2(P(C8H14)2)][PF6] (compound 3), the neutral chloro complex IrH(CO)(P(CH3)3)2 (compound 4), and the methyl complex Ir(C8H14)(H)(CHO)P(CH3)3 (compound 5).
other route, the reduction of a hydrido methoxycarbonyl complex to the corresponding formyl hydrido complex 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.5,6

The resulting complex mixture of metal compounds contains the corresponding Ir(I) carbonyl complex in varying amounts. The carbonyl compounds resulting from H₂ loss from the cationic formyl complex 3, [IrH₂(CO)(P(CH₃)₃)₄]⁺, and from H₂ loss from the chloro formyl complex 4, IrCl(CO)(P(CH₃)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(CH₃)(CO)(P(CH₃)₃)₂. This latter compound is also available from the reaction of Ir(C₃H₄)₃P(CH₃)₃ with carbon monoxide and from the reaction of [IrH₂(CO)(P(CH₃)₃)₄][Cl]² with methyllithium. Loss of CH₄ from the methyl formyl complex 5, a competing and sometimes dominating decomposition reaction, results in the formation of the carbonyl hydrido complex IrH(CO)(P(CH₃)₃)₃ (see below).⁴⁹ A bimolecular decomposition mechanism has been established for the decomposition of hydridoacyleosmium(II) complexes⁵⁰ and may be operative in the decomposition of the present complexes as well.

One likely mechanism for the unimolecular decomposition of the hydrido formyl complexes is loss of a ligand with subsequent migration of a hydrogen atom from the formyl group to the metal (eq 4); reductive elimination of H₂ 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 isolated 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 AgPF₆ results in formation of the dihydrido cation [IrH₂(CO)(P(CH₃)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,

\[
\begin{align*}
4, \text{ L} &= \text{PMe₃,} \\
&\text{removal of the hydrido hydrogen atom of complex 3 as a proton (vide infra) results in formation of the hydrido carbonyl complex IrH(CO)(P(CH₃)₃)₃, also as a result of hydrogen atom migration (eq 6).}
\end{align*}
\]

\[
\begin{align*}
7a, b &\text{ and of the hydrido methyl formyl complex 5 is their apparent reluctance to undergo reductive elimination of methane, despite the well-established tendency of cis hydrido alkyl complexes to reductively eliminate the alkane.}^{56, 57}
\end{align*}
\]

Hydrido Hydroxymethyl and Hydrido Methyl Complexes. The reaction of NaBH₄ with the cationic hydrido formyl complex 3 in wet THF³⁶ results in the formation of the cationic hydrido hydroxymethyl complex [IrH₂(C₂H₅OH)(P(CH₃)₃)₄][PF₆] (6). This reaction does not work with the other Ir(III) hydrido formyl compounds; for instance, compound 4 reacts with wet NaBH₄ to form the fac-trihydrido compound IrH₃(CH₃)(P(CH₃)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.¹⁰, ¹⁶ Other researchers have isolated hydroxymethyl complexes of rhenium from reduction of rhenium-bound carbon monoxide.¹⁰, ²⁰, ²⁴, ³⁴

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(CH₃)(P(CH₃)₃)₄][PF₆] (7a) in 9–25% yield.²⁸ 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(CH₃)(P(CH₃)₃)₄][BF₄] (7b). The cationic hydridomethylidiridium(III) cation can be easily separately prepared by reacting Ir(CH₃)(P(CH₃)₃)₄ with either HBF₄ (to give 7a) or HBF₄ 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

\[
\begin{align*}
\end{align*}
\]


(56) &\text{Other stable cis hydrido methyl compounds have been reported: Chait, J.; Hayter, R. G. J. Chem. Soc. 1968, 6017–6027; Wood, C. D.; Schrock, R. R. J. Am. Chem. Soc. 1979, 101, 5421–5422. See also ref 25, 26, and 31.}
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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), it is less generally appreciated that second- or third-row transition-metal hydrido compounds also can show acidic behavior. 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).

\[
\text{HCO}_2\text{H} + \text{OsCl}_2\text{L}_2 \rightarrow \text{OsCO}_2\text{H} + \text{HCO}_2\text{H}^{+}
\]

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)]^+BF_4^- (7b) from Ir(CH_3)(P(CH_3)_3) (vide supra) and [IrH_2(CO)(P(CH_3)_3)]^+ from IrH(CO)(P(CH_3)_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 [IrH(CO)(P(CH_3)_3)]^- 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

\[
\text{IrH}_2\text{Ir}^+-\text{CO}(\text{P(CH}_3)_3)^{3+}
\]

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.

Reduction Reactions Using Borane. Borane in THF has been found to effect the reduction of methoxy carbonyl groups to formyl groups and formyl groups to methyl groups. Several proposals have been presented in the literature 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 incoyiently, a methylene ligand which is finally reduced by borane or borohydride to the methyl group.

The reduction of the methoxy carbonyl group to the formyl group, used to prepare formyl compounds 3 and 4, respectively, from the methoxy carbonyl 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 hydroxymethyl complex 7a.

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

\[
\text{HCO}_2\text{H} + \text{IrH}_2\text{Ir}^+-\text{CO}(\text{P(CH}_3)_3)^{3+} \rightarrow \text{IrH}_2\text{Ir}^+-\text{CO}(\text{P(CH}_3)_3)_3 + \text{HCO}_2\text{H}^{+}
\]


The first step is removal of the methoxy group by the Lewis acid BH$_3$ followed by reduction of the carbonyl function with eventual hydrogen atom transfer to the carbon. Other oxycarbonyl complexes are unlikely, since the carbonyl cation [IrClH(CO)(P(CH$_3$)$_3$)$_3$] has 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 [IrCl(P(CH$_3$)$_3$)$_4$] by alkylating at the carbonyl oxygen atom.

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; for instance, we have observed methyl group migration to an iridium-bound methylene group derived from a methoxymethyl ligand. 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 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. Borohydride (THF, 1 M, stabilized with small amounts of NaBF$_4$) and borohydride reagents, HBF$_4$, etherate, and AqBF$_4$, were also obtained from Aldrich and were used as supplied. $^{13}$C- and $^{1}$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, $^{13}$C NMR, high-field $^{1}$H NMR, and $^{31}$P NMR spectra were obtained using Perkin-Elmer 238B, Varian EM-390, Bruker HFX-400, 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.**

-- Tetraakis(trimethylphosphine)iridium(I) Hexafluorophosphate, [Ir(P(CH$_3$)$_3$)$_4$][PF$_6$].

-- Iridium(I) Hexafluorophosphate, [Ir(P(CH$_3$)$_3$)$_3$](PF$_6$)$_2$ (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$_3$)$_2$ (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%).

-- Compound was recrystallized from concentrated pentane solution. Anal. (Sample recrystallized from concentrated pentane solution) Calcd: C, 45.4; H, 7.68. Found: C, 30.18; H, 7.70.

**Hydridoiridium Compounds.**

-- Hydridomethylenecarbonyltetraakis(trimethylphosphine)iridium(III) Hexafluorophosphate (1). A methanol solution (10 mL) of lithium methoxide (0.02 g) and [IrCO(P(CH$_3$)$_3$)$_3$][Cl] (0.56 g) was stirred for 1 h, and the residue was 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 $-30^\circ$C and white crystals were obtained (224 mg, 85% yield). Analysis of the residue 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%).

-- Compound was recrystallized from concentrated pentane solution. Anal. (Sample recrystallized from concentrated pentane solution) Calcd: C, 45.4; H, 7.68. Found: C, 30.18; H, 7.70.

-- Hydrido(oxymethylenecarbonyl)chlorotris(trimethylphosphine)iridium(III) Hexafluorophosphate (II). Methyl formate (0.15 g) was added to a THF solution (30 mL) of IrCl(P(CH$_3$)$_3$)$_3$(C$_2$H$_4$)$_3$ (1.10 g, 2.58 mmol), 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 (85%) of compound 2: mp 138–140°C; IR 2060, 1620 (s) cm$^{-1}$; $^{1}$H NMR (CD$_2$CN) Ir$^-$H, $\delta$ = 130.0, d (J = 135 Hz) of quartets (J = 18 Hz); P(CH$_3$)$_2$ $\delta$ = 1.48, d (J = 8 Hz) of d (J = 6 Hz), 1.54, d (J = 7 Hz), 1.56, t (J = 6 Hz); OCH$_3$, $\delta$ = 3.28, s. Anal. Calcd: C, 32.37; H, 7.5. Found: C, 32.35; H, 7.57.

-- Hydridoformyltetrakis(trimethylphosphine)iridium(III) Hexafluorophosphate (III). Method a. [Ir(P(CH$_3$)$_3$)$_3$][PF$_6$] (0.34 g) in 100 mL of THF was treated with 0.23 g of paraformaldehyde, and the mixture was stirred 2 h. The off-white product was filtered and recrystallized from warm methanol: mp 230°C; mp > 250°C; IR 2922 (m), 1607 (s) cm$^{-1}$; $^{1}$H NMR (pyridine-d$_5$) Ir$^-$H, $\delta$ = 12.0, d (J = 123 Hz) of quartets (J = 18 Hz); Ir$^-$CHO, $\delta$ = 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$_3$)$_2$, $\delta$ = 5.12–1.4, m; $^{13}$C NMR (acetone-d$_6$) forml C, $\delta$ = 225.40, d (J(C-P$_{trans}$) = 10 Hz) of t (J(C-P$_{cis}$) = 10 Hz).
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Method b. A solution of IrCl(C6H5P2)3 (0.9 g) was suspended in 150 mL of THF and 0.35 g of NaPF6 was added, followed by a solution of 0.62 g of P(CH3)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 (86%) of compound 3.

Method c. A suspension of 0.5 g of compound 1 in 5 mL of THF was treated with a slight excess of LiHB(C,H5)2. The solution was stirred for 6 h, and the resulting white suspension was filtered, washed with pentane, and dried under vacuum; yield 0.48 g of white solid (83%): IR (KBr) 3070, 2970, 2915, 1370, 1300, 770 cm-1; 'H NMR (CDCl3, 6 = 7.26 ppm) t (J = 7.2 Hz) of d (J(H-hydride) = 17 Hz); P(CH3)3, 6 = 16.2, 6 (J = 76 Hz) of d (J = 10 Hz); P(CH3)2, 6 = 8.7, 6 (J = 7 Hz) of d (J = 5 Hz). Anal. Calcd: C, 42.42; H, 6.31. Found: C, 24.42; H, 6.30.

Acknowledgment. Discussions with T. Herskovitz, T. Tulip, and other members of this department, valuable suggestions by referees, and the competent technical as-

concentrated. Pentane was added and the resulting white precipitate was dried and redissolved in pyridine-d6. The 1H NMR spectrum of this solution had a multiplet at δ -0.05, characteristic of the hydromethyl cation (see below). From the integral of this NMR spectrum, the stoichiometry of this compound was found to comprise ca. 23% of the total phosphine–Ir species.

Hydrido(methyl)tetraakis(trimethylphosphine)iridium(III) Tetrafluoroborate (7b). An ether solution (5 mL) of Ir(CH3)(P(CH3)3)4 (0.8 g) was treated dropwise with a solution of HBF4·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 150-160 °C. Anal. Calcd for Ir(CH3)(P(CH3)3)4·HBF4: C, 65.03; H, 6.19. Found: C, 65.0; H, 6.20. The closely related compound [Ir(CH3)(P(CH3)3)4]2 has been obtained analytically pure by another preparative method and has an identical 1H NMR spectrum: 1H NMR (pyridine-d5) δ -13.2, J (d, 1H) = 138 Hz of quartet (J = 20 Hz); Ir-CH3, δ -0.05, quartet (J = 8 Hz) of d (J = 4 Hz) of d (J(H-hydride) = 1 Hz); P(CH3)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 C34Ir6H44P8: C, 69.32; H, 6.31. Found: C, 69.3; H, 6.30.

Hydridochlorocarbonyliris(trimethylphosphine)iridium(III) Tetrafluoroborate, [IrHCl(CO)(P(CH3)3)4][BF4]. Methyl formate (0.070 g) was added to a THF solution (20 mL) of Ir(CH3)(P(CH3)3)4·HBF4 (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 0.5 g of HBF4·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 (v, kr) cm-1; 1H NMR (pyridine-d5) δ -9.1, J (d, 1H) = 155 Hz of t (J = 17 Hz); P(CH3)3, 6 = 1.56, d (J = 9 Hz) of d (J = 1 Hz), 1.72, t (J(eff) = 4 Hz).

Hydrido(carbonyl)tris(trimethylphosphine)iridium(I) and Dihydridocarbonyliris(trimethylphosphine)iridium(III) Tetrafluoroborate, Ir(CO)(P(CH3)3)3 and Ir(CO)(P(CH3)3)2[C1]. Methyl formate (0.5 g) in 20 mL of THF was treated with a slight excess of KH(O-i-Pr)2. No reaction was apparent after several minutes, so a slight excess of LiHB(C,H5)2 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, which was assigned to the residual borane,2 but upon subsequent handling of this compound, this IR band was lost and only strong bands at 1010 and 1900 cm-1 were observed. 1H NMR (CD2Cl2) δ -12.5, 13.62, 1.83, 6 (J = 12 Hz); P(CH3)3, 6 = 1.6, br m. In THF-d5, 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(CH3)3)2, was then dissolved in 20 mL of ether and treated with 0.18 g of HBF4·etherate. A white solid precipitated immediately and was filtered, washed with ether, and dried, yielding 0.52 g (54%, based on [Ir(CO)(P(CH3)3)2][Cl]) of [IrH(CO)(P(CH3)3)2][BF4]: mp 132-136 °C; IR 2095 (s), 2040 (s), 1988 (s) cm-1; 1H NMR (CD3CN) δ -11.2 and -11.9, m; P(CH3)3, δ 1.70, d (J = 9 Hz) of d (J = 1 Hz), 1.76, t (J(eff) = 4 Hz); 1H NMR (high field, pyridine-d5) δ -11.2, d (J = 17 Hz) of t (J = 20 Hz) of d (J(H-hydride) = 4 Hz), -11.9, d (J = 11 Hz) of t (J = 20 Hz); P(CH3)3, 6 = 1.6, br m. Anal. Calcd: C, 32.36; H, 5.44. Found: C, 32.51; H, 5.51.

Method b. A compound (3) (0.38 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 slightly off-white residue. The IR and NMR spectra of this material were identical with those of IrH(CO)(P(CH3)3)2 (see above). This material has not been successfully recrystallized owing to its extreme solubility in inert solvents.
Stereocchemistry of Transition Metal Cyclooctatetraenyl Complexes. Molecular Structure of (\(\eta^7\)-Cyclooctatetraenyl)(\(\eta^1\)-allyl)-\(\eta^1\)-tert-butoxyzirconium

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Crystals of (\(\eta^7\)-cyclooctatetraenyl)(\(\eta^1\)-allyl)-\(\eta^1\)-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, \(\beta = 111.05\) (1)°, \(Z = 8\), and \(\rho_{calc} = 1.39\) g/cm\(^3\). 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 \(\eta^1\)-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 \(\eta^7\) 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 \(C_3\) symmetry in the Zr-COT bonding apparently relate to the orientation of the COT moiety with respect to the allyl and \(\eta^1\)-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)\(_2\)ZrTHF (1) (COT = 1,3,5,7-cyclooctatetraene and THF = tetrahydrofuran) and (COT)ZrCl\(_2\)THF\(^2\) showed that both compounds contained a nearly planar COT ligand bonded \(\eta^7\) 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.\(^3\) 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\(_5\)H\(_3\))(t-C\(_3\)H\(_4\)O)Zr (I)\(^4\) 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 Weisenberg 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 (\(\lambda(\text{Mo Kα}) = 0.71069\) Å) and are given in the summary. Intensity data (\(hkl, hkl, 2 \leq \theta \leq 25\)°) were measured and reduced as described previously.\(^5\) No absorption correction was applied because of the irregular crystal shape; however, corrections would have been small \(\mu = 7.2\) cm\(^{-1}\). Of the 5158 data collected, 4418 were unique and had I \(\geq 2\sigma(I)\). Only the corresponding \(|F_o|^2\)'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 \(\eta^1\)-butoxy group in molecule 2 which was related to the first by a rotation of \(\sim 60°\) about the O-\(\text{O}12\) 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 \(\eta^1\)-butoxy group of molecule 1 were obtained from a subsequent difference density map, and these atoms were refined isotopically. Methyl hydrogen atoms were not located for molecule 2. After several additional large-block least-squares cycles, convergence was reached with \(R = \Sigma||F_o|| - |F_c||/\Sigma||F_o|| = 0.025\) and \(R_w = (\Sigma w(\Delta||F_o||^2 - |F_c||^2))/\Sigma w|F_o||^2 = 0.048\). Positional parameters are given in Figure 1, the numbering scheme for both molecules being indicated. 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.\(^\text{3}\) On the average, librational corrections increase the C-C and Zr-C bond lengths by 0.018 and 0.025 Å, respectively. Unless specified 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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