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Photochemistry of Dihydrido(hydrotris(3,5-dimethylpyrazolyl)borato)(*Z*-cyclooctene)iridium. Synthetic Intermediates and Mechanism of the Photochemical Formation of Hydridophenyl(hydrotris(3,5-dimethylpyrazolyl)borato)(trimethyl phosphite)iridium

Arlen Ferrari,[†] Eleonora Polo,[†] Heinz Rüegger,[‡] Silvana Sostero,*,[†] and Luigi M. Venanzi[‡]

Dipartimento di Chimica, Centro di Studio su Fotoreattività e Catalisi, CNR, Università di Ferrara,
via Borsari 46, I-44100 Ferrara, Italy, and Laboratorium für Anorganische Chemie, ETHZ,
Universitätstrasse 6, CH-8092 Zürich, Switzerland

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The photolysis of a benzene solution of [$Tp^{Me2}IrH_2$(COE)], **1** (Tp^{Me2} = hydrotris(3,5-dimethylpyrazolyl)borate, COE = *Z*-cyclooctene), in the presence of $P(OMe)_3$, gives the stable novel complex [$Tp^{Me2}IrH(C_6H_5)(P(OMe)_3)$], **3a**. The photochemical syntheses of [$Tp^{Me2}IrH_2(P(OMe)_3)$], from **1** and $P(OMe)_3$ in diethyl ether, and [Tp^{Me2}-$IrH_2(CH_2{=}CHCOO^tBu)$], from **1** in *tert*-butyl acrylate, are also reported. The above reactions and several experiments using C_6D_6 and $P(OCD_3)_3$ show that, in all cases, the primary photoproduct is the 16-electron, five-coordinate iridium(III) intermediate {$Tp^{Me2}IrH_2$}, **6a**, produced by loss of COE from **1**. The above experiments also allow the postulation of a mechanistic pathway for the formation of **3a** which involves the oxidative addition of an aromatic C−H bond by **6a**. Furthemore, the photochemical reaction of **1** in the presence of $P(OCD_3)_3$ shows that, under the reaction conditions used, oxidative addition of C−H bonds of $P(OMe)_3$ and of coordinated Tp^{Me2}-ligands, presumably, to the intermediates **6a** and {$Tp^{Me2}IrH(C_6H_5)$}, also occurs. Thus, coordinatively unsaturated iridium(III) species readily activate C−H bonds.

Introduction

The chemistry of transition metal hydrides is one of the most actively pursued areas of modern inorganic chemistry, as shown by the number of special reviews[1] and monographs[2] which highlight the major scientific and technological interest of these compounds.

It is quite clear why transition metal hydrides with different types of ligands have attracted so much attention over the past decade: compounds of this type have been successfully used in organometallic synthesis,[3] catalysis,[4] and photochemistry.[5] Furthermore, they undergo a broad spectrum of reactions such as the thermal and photochemical generation of electronically and coordinatively unsaturated metal complexes,[5a,6] the formation of binuclear species,[6d,7] metallation,[6b,8] selective C−H bond activation of aromatic and saturated hydrocarbons,[9] and alkene hydrogenation.[10] This wide range of reactions has usually been mediated by hydrides of the transition metals with co-ligands such as Cp, Cp*, and PR_3 (Cp = C_5H_5; Cp* = C_5Me_5; R = Ph, Me, etc.) their main function being the stabilization of the metal center in the oxidation state and coordination number best suited for each of the above-mentioned reactions.

The metal hydride complexes stabilized only by nitrogen donors known to date are relatively few and are almost limited to coordination compounds of the tris(pyrazolylborate) anions, $Tp^{3R,4R,5R}$.[11−13] These uninegative terdentate ligands are particularly interesting because of their great structural versatility

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[†] Università di Ferrara.

[‡] ETHZ.

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and ability to form stable complexes with metal centers having open shell electron configurations.[11] In addition, these ligands allow the isolation of "nonclassical" polyhydride complexes, e.g., [Tp^{Me2}RhH$_2$(H$_2$)][14] and [Tp^{Me2}RuH(H$_2$)$_2$] (Tp^{Me2} = hydrotris(3,5-dimethylpyrazolyl)borate).[15] They also form very stable alkene complexes with six-coordinate d^6-metal centers, e.g., [Tp^{Me2}IrH$_2$(COE)] (COE = *Z*-cyclooctene) (**1**).[12]

Complexes of type **1** could be very useful from a photochemical point of view as they might generate *in situ* electronically and coordinatively unsaturated intermediates, e.g., {Tp^{Me2}-Ir(COE)} (**2**) by photochemical elimination of H$_2$. This fragment, as found for the related species {TpIr(COE)} (Tp = hydrotris(pyrazolyl)borate),[16] is expected to undergo oxidative-addition reactions with organic substrates, thus providing yet another entry into the field of C−H activation. Furthermore, the photolysis of **1,** in the presence of an alkene, not only could provide an important new route for the preparation of alkenyl hydride complexes, but also throw further light on the photoactivation of alkenes, a particularly interesting reaction because of the different results reported in the literature regarding the intra- or intermolecularity of this process.[5a,17]

This paper describes (a) the photolysis of [Tp^{Me2}IrH$_2$(COE)] (**1**) in C$_6$H$_6$ in the presence of P(OMe)$_3$, which gives the novel compound [Tp^{Me2}IrH(C$_6$H$_5$)(P(OMe)$_3$)] (**3a**) and (b) a series of related experiments using C$_6$D$_6$ and P(OCD$_3$)$_3$ which yield the corresponding deuterated compounds. The reactions of **1** with (a) P(OMe)$_3$ in diethyl ether, with formation of [Tp^{Me2}IrH$_2$-(P(OMe)$_3$)] (**4a**) and (b) in neat *tert*-butyl acrylate, which produces [Tp^{Me2}IrH$_2$(CH$_2$═CHCOO^{t}Bu)] (**5**) are also reported. Analysis of the NMR spectral data of photoproduct **3a** and of its deuterated derivatives provides a consistent model of the mechanistic pathway of the photoreactions of **1** leading to **4a**, i.e., (1) the initial formation of {Tp^{Me2}IrH$_2$} (**6a**) (2) its oxidative addition of a C−H bond of C$_6$H$_6$ yielding seven-coordinate iridium(V)−hydride complexes (3) the latter's decomposition into five-coordinate hydridophenyliridium(III) photointermediate and (4) formation of the final product **3a**. Finally, photochemical experiments using P(OCD$_3$)$_3$ showed that reversible oxidative-addition of C−D bonds of the phosphite is also taking place.

Results and Discussion

Formation of [Tp^{Me2}IrH(C$_6$H$_5$)(P(OMe)$_3$)] (3a). Photolysis ($\lambda \geq 335$ nm) of **1**, in C$_6$H$_6$ in the presence of P(OMe)$_3$, produced **3a** and free cyclooctene (COE). The presence of the latter in the distillate at the end of the photolysis was confirmed by ^{1}H NMR spectroscopy. Complex **3a** was characterized by elemental analysis, FTIR, and ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy. The ^{1}H NMR spectrum of this complex showed the presence of six individual methyl groups and three different H-4 resonances in the expected spectral regions, consistent with the presence of three inequivalent pyrazolyl rings. Furthermore, constraints on internuclear distances, obtained by two-dimensional NOE spectroscopy, not only confirmed that the three pyrazolyl rings were coordinated to the metal but also allowed the individual stereochemical assignment of all methyl resonances.

The spectral studies also showed that H, C$_6$H$_5$, and P(OMe)$_3$ were the other ligands present in **3a**. Thus, its IR spectrum exhibited a band at $\nu = 2173$ cm^{-1} which was assigned to the Ir-H stretching vibration. Furthermore, the single resonance observed in the ^{31}P{H} NMR spectrum split into a doublet under off-resonance decoupling conditions, unambiguously showing that only one hydride ligand was present. Therefore, the NMR and IR data provided unequivocal evidence for the C−H activation of benzene and for the formulation of the product as [Tp^{Me2}IrH(C$_6$H$_5$)(P(OMe)$_3$)] (**3a**).

It was also found that, at room temperature, the phenyl group in **3a** did not freely rotate around the iridium−carbon bond as the ^{13}C and ^{1}H NMR spectra of this compound showed the presence of six inequivalent carbons and five inequivalent protons. Hindered rotation in similar systems, i.e., in [Tp^{Me2}-RhH(C$_6$H$_5$)(CO)], has been previously reported.[18] However, the activation energy for this type of process appears to be higher in the iridium than in the rhodium compound, probably because of the presence of the phosphite ligand which is bulkier than the carbon monoxide present in the rhodium analog. Furthermore, in contrast to the above rhodium complex,[18] NMR measurements showed that in **3a** there was no exchange between the H−, and C$_6$H$_5$− fragments bonded to iridium and the C$_6$D$_6$ used as a solvent for the NMR measurement, indicating that the C−H activation process in the iridium complex is irreversible under the reaction conditions employed. This was confirmed by subjecting [Tp^{Me2}IrH(C$_6$H$_5$)(P(OMe)$_3$)], **3a**, to photolysis, as above, in C$_6$D$_6$ in the presence of P(OCD$_3$)$_3$. No deuterium incorporation into **3a** was observed.

In order to establish the role of photochemical induction in the formation of **3a**, the following control experiment was carried out: the ^{1}H and ^{31}P NMR spectra of a benzene solution of **1** were recorded, at room temperature, before and after the addition of P(OMe)$_3$: no changes were observed; i.e., there was neither substitution of COE by P(OMe)$_3$ nor C−H activation of benzene under these thermal conditions.

Accordingly, the overall course of the photoreaction of **1** in benzene can be written as shown in eq 1.

$$\underset{\mathbf{1}}{[\mathrm{Tp^{Me2}IrH_2(COE)}]} \xrightarrow[\mathrm{P(OMe)_3}]{h\nu/\mathrm{C_6H_6}} \underset{\mathbf{3a}}{[\mathrm{Tp^{Me2}IrH(C_6H_5)(P(OMe)_3)}]} + \mathrm{COE} + \mathrm{H_2} \quad (1)$$

This reaction raised the question whether the primary photochemical event was the dissociation of the olefin, with formation of {Tp^{Me2}IrH$_2$} (**6a**) or of H$_2$ with formation of {Tp^{Me2}Ir(COE)} (**2**), as intermediates[19] of both types are known to be photochemically active.[5,7,17] This question was answered by carrying out the photochemical reaction in a solvent less likely to undergo an oxidative addition reaction with a photoproduct such as **6a** or **2**.

Formation of [Tp^{Me2}IrH$_2$(P(OMe)$_3$)] (4a). When complex **1** was photolyzed in diethyl ether, in the presence of P(OMe)$_3$, [Tp^{Me2}IrH$_2$(P(OMe)$_3$)] (**4a**) was formed, as shown by its

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elemental analysis and the IR, ^{1}H, ^{13}C, and ^{31}P NMR spectra. Thus, the ^{1}H NMR spectrum revealed two sets of resonances, in the ratio 2:1, assignable to two types of inequivalent pyrazolyl rings, a doublet for the phosphite methyl groups and another doublet for the hydride resonance at $\delta = -20.2$. Furthermore, the single resonance observed at $\delta = 99.5$ in the conventional ^{31}P NMR spectrum split into a triplet under off-resonance conditions, indicating the presence of two hydride ligands in this compound. The ^{13}C NMR data were also consistent with the above formulation.

The presence of 1 equiv of COE in the distillate after photolysis, showed that the photodissociation of COE was quantitative and indicated that the formation of **4a** proceeded as shown in eq 2a,b.

$$\underset{\mathbf{1}}{[\mathrm{Tp^{Me2}IrH_2(COE)}]} \xrightarrow{h\nu/\mathrm{Et_2O}} \underset{\mathbf{6a}}{\{\mathrm{Tp^{Me2}IrH_2}\}} + \mathrm{COE} \quad (2a)$$

$$\underset{\mathbf{6a}}{\{\mathrm{Tp^{Me2}IrH_2}\}} \xrightarrow{\mathrm{P(OMe)_3}} \underset{\mathbf{4a}}{[\mathrm{Tp^{Me2}IrH_2(P(OMe)_3)}]} \quad (2b)$$

Formation of [Tp^{Me2}IrH$_2$(P(OCD$_3$)$_3$] (4b). No significant deuterium incorporation into the Tp^{Me2} and H ligands was observed when [Tp^{Me2}IrH$_2$(P(OCD$_3$)$_3$)] (**4b**) was produced by photolysis of **1** in diethyl ether in the presence of P(OCD$_3$)$_3$. This rules out the possibility of deuterium/hydrogen scrambling between this iridium(III) dihydride complex and either a coordinated or a free phosphite.

Furthermore, integration of the hydride signals in the ^{1}H NMR of a C$_6$D$_6$ solution of [Tp^{Me2}IrH$_2$(P(OMe)$_3$)] (**4a**) against those of the coordinated P(OMe)$_3$, showed that no thermal H/D scrambling had occurred.

Formation of [Tp^{Me2}IrH$_2$(CH$_2$=CHCOO^{t}Bu)] (5). The postulate that the dihydride intermediate {Tp^{Me2}IrH$_2$} (**6a**), a 16-electron, coordinatively unsaturated species, is the precursor for the dihydride complex [Tp^{Me2}IrH$_2$(P(OMe)$_3$)] (**4a**) raised the question whether ligands other than P(OMe)$_3$ could enter the free coordination site in **6a**. This was indeed the case as shown by the photolysis of [Tp^{Me2}IrH$_2$(COE)] (**1**) in *tert*-butyl acrylate solution: the ^{1}H NMR spectrum of the residue obtained after removal of the ester, showed the presence of ca. 85% of the theoretical amount of COE and of a new species which was formulated as [Tp^{Me2}IrH$_2$(CH$_2$=CHCOO^{t}Bu)] (**5**) on the basis of its ^{1}H NMR spectrum as, in addition to the usual resonances assignable to three inequivalent pyrazolyl rings, one observed signals characteristic of coordinated *tert*-butyl acrylate. Most significant was the presence of two doublets centered at $\delta = -14.95$ and -25.55 in the hydride region of the ^{1}H NMR spectrum, A homonuclear coupling with a ^2J(H,H) value of 7.3 Hz was confirmed by homodecoupling experiments: The coordination of this olefin renders the two hydride ligands diastereotopic and, therefore, inequivalent. Thus, the splitting of the hydride resonance in **5** into two doublets provided a reliable and sensitive indication of the π-coordination of acrylate without loss of dihydrogen.

It is noteworthy that during this photolytic process no products were found to indicate that activation of an olefinic C$-$H bond of *tert*-butyl acrylate had occurred. As the easy rearrangement of fragments {Tp^{3R,4R,5R}Ir^{I}(C$_2$H$_4$)} into the corresponding {Tp^{3R,4R,5R}Ir^{III}(H)(CH=CH$_2$)} moieties has been reported by different groups,[16,20] the failure to observe this type of transformation in the case of **1** provides additional evidence for the postulate that the intermediate {Tp^{Me2}Ir(COE)} (**2**) is not formed during the reactions described here.

Mechanistic Studies of the Photochemical Formation of [Tp^{Me2}IrH(C$_6$H$_5$)(P(OMe)$_3$)] (3a). Having shown that the 16-electron species {Tp^{Me2}IrH$_2$} (**6a**) was the most likely primary photoproduct in the photolysis of **1**, as the final isolated product proved to be [Tp^{Me2}IrH(C$_6$H$_5$)(P(OMe)$_3$)] (**3a**), one had to establish whether the oxidative addition of the C$-$H bond of C$_6$H$_6$ occurred at **6a** or at the iridium(I) intermediate {Tp^{Me2}Ir(P(OMe)$_3$)}, generated from [Tp^{Me2}IrH$_2$(P(OMe)$_3$)] (**4a**) by loss of H$_2$. This possibility had to be tested as the isolobal analog {Tp^{Me2}Rh(CO)} activates C$-$H bonds.[18]

When [Tp^{Me2}IrH$_2$(P(OMe)$_3$)] (**4a**) was subjected to photolysis (1 h) in benzene solution, under the conditions employed for **1**, [Tp^{Me2}IrH(C$_6$H$_5$)(P(OMe)$_3$)] (**3a**) was formed only in very low yield (ca. 2%). Prolonged periods of irradiation did not significantly increase the concentration of **3a**, indicating that the kinetics of the reactions involved in the formation of **3a** from **4a** are much slower than those observed for the conversion of **1**.

These results imply that the stable 18-electron complex [Tp^{Me}-IrH$_2$(P(OMe)$_3$)] (**4a**) is unlikely to be an intermediate in the reaction sequence summarized by eq 1. Interestingly, when the photolysis of **1** in benzene was carried out in the absence of phosphite, complete decomposition with precipitation of metallic iridium occurred.

In order to obtain further information about the mechanistic pathway for the reaction shown in eq 1, a series of photochemical experiments using C$_6$D$_6$ as a solvent and P(OCD$_3$)$_3$ as the added ligand, were carried out.

Photolysis of 1, in C$_6$D$_6$ in the Presence of P(OCH$_3$)$_3$. This reaction gave two products: [Tp^{Me2}IrH(C$_6$D$_5$)(P(OCH$_3$)$_3$)] (**3b**) and [Tp^{Me2}IrD(C$_6$D$_5$)(P(OCH$_3$)$_3$)] (**3c**). Thus, the ^{31}P NMR spectrum of the solution after irradiation showed two signals at $\delta = 83.0$ and 82.8, in a ratio ca. 1:2, respectively. The latter signal was split into a doublet under off-resonance conditions (see Figure 1a) showing presence of one hydride coupled to the corresponding phosphorus spin. Moreover, the magnitude of ^2J(P,H) indicated that these two donors occupied mutually *cis*-positions. Consistent with this assignment, the ^{1}H NMR spectrum of the above solution showed the expected doublet for an H-ligand at $\delta = -19.36$, as found in **3a**. However, no phenyl resonances were observed. Conversely, the ^{2}H NMR spectrum of this mixture exhibited a set of overlapping signals assignable to the C$_6$D$_5$ ligands in **3b** and **3c** and a doublet at $\delta = -19.2$ for the deuteride ligand in **3c**. Furthermore, as found for the corresponding perprotonated compound **3a**, the ^{1}H, ^{2}H, and ^{31}P NMR experiments indicated the absence of D/H exchange between [Tp^{Me2}IrH(C$_6$D$_5$)(P(OCH$_3$)$_3$)] (**3b**) and the solvent.

The postulate that the fragment {Tp^{Me2}IrH$_2$} (**6a**) is the primary photoproduct and the formation of the isotopomers **3b** and **3c** implies that **6a** undergoes a photoinduced reaction with C$_6$D$_6$. This is most likely to occur through an oxidative-addition reaction with formation of the seven-coordinate iridium(V) intermediate {Tp^{Me2}IrH$_2$D(C$_6$D$_5$)} (**7b**) (eq 3).

$$\underset{\mathbf{6a}}{\{\mathrm{Tp^{Me2}IrH_2}\}} \xrightarrow{\mathrm{C_6D_6}} \underset{\mathbf{7b}}{\{\mathrm{Tp^{Me2}IrH_2D(C_6D_5)}\}} \quad (3)$$

Several thermally stable seven-coordinate iridium(V) complexes, e.g., [IrH$_5$(P-*i*-Pr$_3$)$_2$],[21a] [IrH$_3$(η^5-C$_5$H$_5$)(P-*i*-Pr$_3$)],[21b] and [IrH$_{(4-n)}$(Si R$_3$)$_n$(C$_5$Me$_5$)] (n = 1 and 2),[21c,d] are known. The

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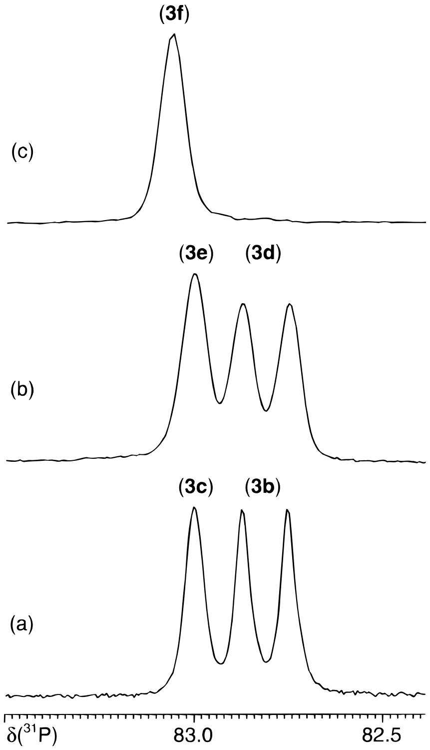

Figure 1. 202-MHz ^{31}P NMR spectra recorded under off-resonance conditions to show hydride multiplicities of (a) [$Tp^{Me2}IrH(C_6D_5)(P(OCH_3)_3)$] (**3b**) and [$Tp^{Me2}IrD(C_6D_5)(P(OCH_3)_3)$] (**3c**), (b) [$Tp^{Me2}IrH(C_6H_5)(P(OCD_3)_3)$] (**3d**) and [$Tp^{Me2}IrD(C_6H_5)(P(OCD_3)_3)$] (**3e**), and (c) [$Tp^{Me2}IrD(C_6D_5)(P(OCD_3)_3)$] (**3f**).

photochemical loss of H_2 from species of this type is also amply documented.[22] Thus, subsequent photochemically induced, reductive elimination of either HD or H_2 from a species such as **7b** is likely to occur and give the five-coordinate intermediates **8b** and **8c** (parts a and b of eq 4, respectively).

$$\underset{\mathbf{7b}}{\{Tp^{Me2}IrH_2D(C_6D_5)\}} \rightarrow \underset{\mathbf{8b}}{\{Tp^{Me2}IrH(C_6D_5)\}} + HD \qquad (4a)$$

$$\underset{\mathbf{7b}}{\{Tp^{Me2}IrH_2D(C_6D_5)\}} \rightarrow \underset{\mathbf{8c}}{\{Tp^{Me2}IrD(C_6D_5)\}} + H_2 \qquad (4b)$$

These could then react with $P(OMe)_3$ giving the final products **3b** and **3c**, respectively (eq 5).

$$\underset{\substack{X = H;\ \mathbf{8b} \\ X = D;\ \mathbf{8c}}}{\{Tp^{Me2}IrX(C_6D_5)\}} + P(OMe)_3 \rightarrow \underset{\substack{X = H;\ \mathbf{3b} \\ X = D;\ \mathbf{3c}}}{[Tp^{Me2}IrX(C_6D_5)(P(OMe)_3)]} \qquad (5)$$

The Photochemical Cycle. As mentioned earlier, all the data on the photoreaction of **1** lead to the postulation of a primary step consisting of the elimination of COE with formation of {$Tp^{Me2}IrH_2$} (**6a**). Interestingly, this iridium(III) intermediate was formed in preference to the iridium(I) transient {$Tp^{Me2}Ir(COE)$} (**2**) although this species could have been readily produced from **1** by release of H_2. A related intermediate, i.e., {TpIr(COE)}, (Tp = hydridotris(pyrazolyl)borate) is likely to have been thermally generated when [$Ir_2Cl_2(COE)_2$] was reacted with KTp as this reaction gave [TpIrH(η^3-cyclooctenyl)].[16] However, after the photolysis of **1**, there was no evidence for the formation of an η^3-allyl derivative in the reaction mixture.

The preferential elimination of COE from **1** is worthy of comment. The geometric structure of **1** in the solid state,[12] as determined by X-ray diffraction, shows that the C═C fragment of COE takes an unusual orientation relative to the other donor atoms; i.e., it roughly bisects the angle defined by the H−Ir−H moiety. Extended Hückel MO calculations, using the solid state structure of **1**, indicate that the origin of this structural feature is electronic; i.e., it arises from the interactions between three of the *d*-block orbitals of the {$TpIrH_2$} fragment and the π^*-C═C orbitals. As the LUMO-orbital in **1** appears to be metal−COE antibonding, a simple one-electron model predicts that a HOMO−LUMO excitation would result in a considerable weakening of the Ir−COE bond and, therefore, its easy dissociation.

The efficiency of the photodissociation of COE suggests that the quantum yield for its loss may be as high as that found in many metal carbonyls.[5a] Therefore, as shown by the nature of the products of the photoreactions of **1** in *tert*-butyl acrylate, or in diethyl ether in the presence of $P(OMe)_3$, this methodology should be generally applicable for the preparation of compounds of type **3** although COE is strongly bound to iridium.[11]

The results described above and their interpretation imply that the reaction of the five-coordinate, 16-electron intermediate {$Tp^{Me2}IrH_2$} (**6a**) with an aromatic C−H bond must be favored relative to that with a good donor such as $P(OMe)_3$ as, in benzene, one obtains a species which contains a phenyl group bonded to iridium. This transient, for the reasons mentioned earlier, is likely to be the seven-coordinate iridium(V) intermediate {$Tp^{Me2}IrH_3(C_6H_5)$} (**7a**). As also this species is expected to be photochemically unstable, one can postulate a subsequent reductive elimination of H_2 yielding another 16-electron intermediate, i.e., {$Tp^{Me2}IrH(C_6H_5)$} (**8a**). This could be in an electronic/vibrational excited state rather than in the ground state. However, it is unlikely that a second photon is required since there should then be a sufficient buildup of this intermediate for its interaction with $P(OCD_3)_3$. This is not unreasonable considering the high electronic and coordinative unsaturation of the {$Tp^{Me2}IrH(C_6H_5)$} fragment. As it is the latter species which reacts with the phosphite to give the final product **3a**, the principal role of $P(OMe)_3$ is to act as a Lewis base and form a coordinatively saturated metal center, a necessary requirement for the photochemical stability of the final product. The above results do not exclude the possibility that the intermediate {$Tp^{Me2}IrH(Ph)$} oxidatively adds a molecule of benzene with formation of {$Tp^{Me2}IrH_2(Ph)_2$}. However, given the nature of the final product, this reaction must be photochemically reversible.

It is also worth recalling that the dihydrido complex [$Tp^{Me2}IrH_2(P(OMe)_3)$] (**4a**) is not involved as an intermediate in the reaction shown in eq 1 as there is neither significant deuterium incorporation into **4a** nor formation of [$Tp^{Me2}IrD(C_6D_5)(P(OMe)_3)$] (**3c**) during the thermal or the photochemical reaction of **4a** with C_6D_6. Summing up, the above results lead one to conclude that the photochemical pathway for the reaction shown in eq 1 is that oulined in Scheme l.

However, as previously noted by Gilbert et al.,[21c] coordinatively unsaturated intermediates may undergo oxidative addition even with ligands such as $P(OMe)_3$. This proved to be the case also in this study as during the photoreactions of [$Tp^{Me2}IrH_2(COE)$] (**1**) (a) with $P(OCD_3)_3$ in C_6H_6 and (b) with $P(OCD_3)_3$ in C_6D_6, one found that some incorporation of deuterium in the

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(21) (a) Garlaschelli, L.; Kahn, S. I.; Bau, R.; Longoni, G.; Koetzle, T. F. *J. Am. Chem. Soc.* **1983**, *107*, 7212 and references quoted therein. (b) Werner, H.; Wolf, J.; Höhn, A. *J. Organomet. Chem.* **1985**, *287*, 395. In this compound, the η^5-C_5H_5− 6-electron donor is considered as being equivalent to a terdentate ligand. (c) Gilbert, T. M.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 3508.

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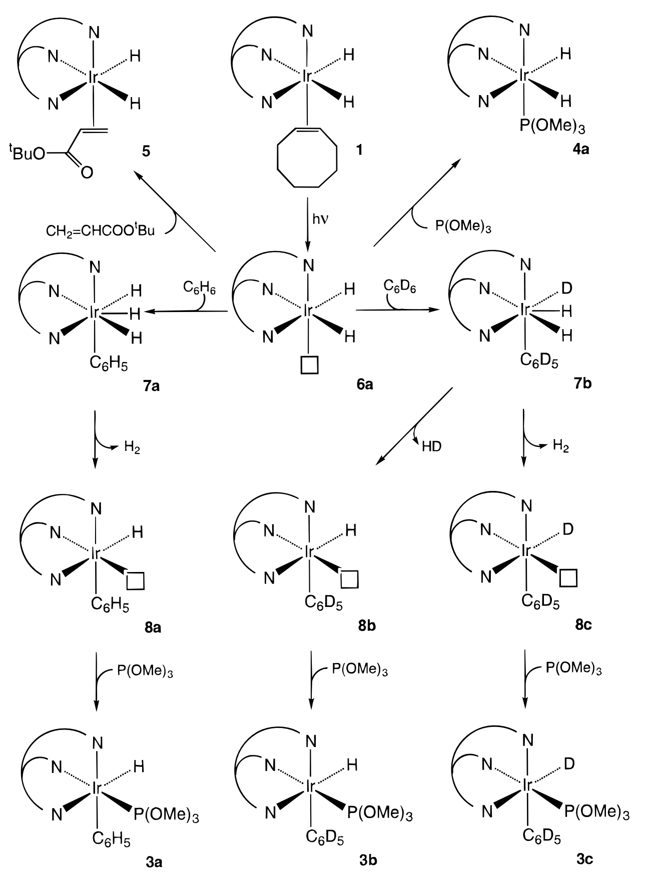
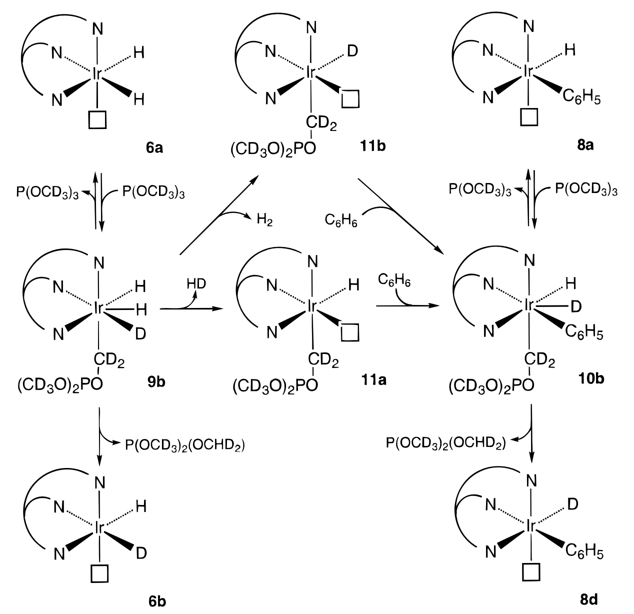
Scheme 1



Scheme 2



methyl groups of the phosphite and in those of the pyrazolylborate ligand had occurred. It is proposed that these deuterated compounds were produced by the photochemical processes outlined below.

Oxidative Addition Reactions Involving $P(OCD_3)_3$. Photolysis of 1, in C_6H_6 in the Presence of $P(OCD_3)_3$. This experiment gave some unexpected results as one observed the formation of two isotopomers, namely $[Tp^{Me2}IrH(C_6H_5)(P(OCD_3)_3)]$ (**3d**) and $[Tp^{Me2}IrD(C_6H_5)(P(OCD_3)_3)]$ (**3e**). The components of this mixture were, once again, characterized by ^1H, ^2H, ^{13}C, and ^{31}P NMR spectroscopy. The presence of both an iridium hydride and of the corresponding deuteride was evident from the ^{31}P NMR spectrum of the above solution, recorded under off-resonance conditions (see Figure 1b). These conclusions were fully supported by the ^1H and ^2H NMR spectra which showed the presence, in both compounds, of high-field resonances at δ = ca. −19.3 assignable to Ir−H and Ir−D entities, respectively.

The presence of the deuteride ligand in **3e** indicated that also the labeled phosphite, the only source of deuterium in this set of experiments, had been involved in a photochemical reaction and that, in all likelihood, a C−D bond of the phosphite had undergone an oxidative addition reaction with intermediates **6a** and/or **8a** as shown in parts a and b of eq 6, respectively.

$$\underset{\textbf{6a}}{\{Tp^{Me2}IrH_2\}} + P(OCD_3)_3 \rightarrow \underset{\textbf{9b}}{\{Tp^{Me2}IrH_2D(CD_2OP(OCD_3)_2)\}} \quad (6a)$$

$$\underset{\textbf{8a}}{\{Tp^{Me2}IrH(C_6H_5)\}} + P(OCD_3)_3 \rightarrow \underset{\textbf{10b}}{\{Tp^{Me2}IrHD(C_6H_5)(CD_2OP(OCD_3)_2)\}} \quad (6b)$$

Both of these postulated seven-coordinated iridium(V) intermediates could reductively eliminate $P(OCD_3)_2(OCHD_2)$, in a fast subsequent step, forming $\{Tp^{Me2}IrHD\}$ (**6b**) and $\{Tp^{Me2}IrD(C_6H_5)\}$ (**8d**) respectively (eq 7a,b).

$$\underset{\textbf{9b}}{\{Tp^{Me2}IrH_2D(CD_2OP(OCD_3)_2)\}} \rightarrow \underset{\textbf{6b}}{\{Tp^{Me2}IrHD\}} + P(OCD_3)_2(OCHD_2) \quad (7a)$$

$$\underset{\textbf{10b}}{\{Tp^{Me2}IrHD(C_6H_5)(CD_2OP(OCD_3)_2)\}} \rightarrow \underset{\textbf{8d}}{\{Tp^{Me2}IrD(C_6H_5)\}} + P(OCD_3)_2(OCHD_2) \quad (7b)$$

Intermediates **6b** and **8d** would then enter the normal photochemical reaction sequence, i.e., **6b** by undergoing reactions analogous to those described for **6a** in eqs 3, 4b and 5b while, in the case of **8d**, only the reaction corresponding to that shown in eq 5b would have to follow. The product ratios observed for the reaction with $P(OCD_3)_3$ can be best explained by postulating that C−D oxidative addition takes place both at **6a** and **8a**. The above results are quite interesting because they reveal that **3d**, and probably **3e**, may be formed as kinetic rather than thermodynamic products from the reaction sequences 6, 7 and 5. The proposed reactions involving $P(OCD_3)_3$ are summarized in Scheme 2.

While one can presume that the main pathways for the formation of the deuteride $[Tp^{Me2}IrD(C_6H_5)(P(OCD_3)_3)]$ (**3e**) are those described above, one cannot exclude a route involving a five-coordinate intermediate such as $\{Tp^{Me2}IrD(CD_2OP(CD_3)_2)\}$ (**11b**) produced by loss of H_2 from **9b**, as the oxidative addition reaction of the former species with C_6H_6 would also produce the seven-coordinate transient **10b**.

Additional information about the involvement of the phosphite in an oxidative addition reaction was obtained from the experiment described below.

Photolysis of 1, in C_6D_6 Containing $P(OCD_3)_3$. This experiment produced almost exclusively $[Tp^{Me2}IrD(C_6D_5)(P(OCD_3)_3)]$ (**3f**). ^{31}P (see Figure 1c), as well as ^1H, and ^2H and ^{13}C NMR spectroscopic studies allowed a full structural assignment for this complex. Only a negligible amount of the corresponding hydrido-complex $[Tp^{Me2}IrH(C_6D_5)(P(OCD_3)_3)]$ (**3g**) was present at the end of the reaction.

The observed ratios of the products **3d** and **3e** on one hand and **3f** and **3g** on the other, obtained from the latter two photolytic experiments, are best rationalized by assuming that the oxidative addition and reductive elimination reactions of the phosphite (see eqs 6 and 7) are either faster than the oxidative addition and reductive elimination of C_6H_6 (see eqs 3 and 4) or, more likely, that the reaction of **6a** and **8a** with the phosphite are reversible under the reaction conditions used, while that of **6a** with C_6H_6 is not.

Lastly, mention was made earlier that during the photoreactions of $[Tp^{Me2}IrH_2(COE)]$ (**1**) with (a) $P(OCD_3)_3$ in C_6D_6, and (b) $P(OCH_3)_3$ in C_6D_6, deuterium incorporation into the methyl groups of the pyrazolylborate ligand was observed and, in the latter case, also into the phosphite.

The deuteration of the phosphite is easily accounted for by assuming that $\{Tp^{Me2}IrD(C_6D_5)\}$ (**8c**) reacts with a C−H bond of $P(OMe)_3$ giving the corresponding seven-coordinate intermediate $\{Tp^{Me2}IrHD(C_6D_5)(CH_2OP(OMe)_2)\}$ (**10c**). The reductive elimination of phosphite from this species would then produce $CH_2DOP(OMe)_2$ and **8b**. The latter would then enter the normal photochemical reaction cycle.

The deuteration of the methyl groups of the nitrogen ligand could involve **6b** as well as **8c**. Thus, a CH_3 group of, e.g., of a product such as **3c**, could oxidatively add to $\{Tp^{Me2}IrD(C_6D_5)\}$ (**8c**). The resulting binuclear intermediate would then reductively eliminate the corresponding mononuclear complex containing the monodeuterated Tp- ligand, i.e., Tp^{Me2}-d_1, and give **3c**-d_1.

However, this reaction and the phosphite deuteration, although obviously only side-reactions, clearly indicate that all proposed 16-electron iridium(III) intermediates show a very strong tendency to oxidatively add C−H bonds. Thus, only the photochemical stability of the l8-electron six-coordinate compounds should be held responsible for the final formation of products of the type $[Tp^{Me2}IrX(C_6X_5)(P(OCX_3)_3)]$ (**3**) (X = H or D).

Finally, one may wonder whether oxidative addition of the olefinic C−H bonds of the acrylate does occur. This is quite likely but its demonstration would require the preparation of $CD_2{=}CD{-}COO^tBu$, $CH_2{=}CH{-}COOC(CD_3)_3$ and $[Tp^{Me2}IrD_2(COE)]$. This will be done within the framework of later studies devoted to other iridium olefin complexes.

Experimental Section

General Data. All preparations and photochemical experiments were carried out under an atmosphere of dry argon using standard Schlenk techniques. The solvents were dried by refluxing them over sodium/benzophenone and were distilled under argon prior to use. The starting material $[Tp^{Me2}IrH_2(COE)]$, **1**, was prepared as described elsewhere.[12] The deuterated phosphite $P(OCD_3)_3$ was synthesized as described below. Elemental analyses were performed by the Microanalytical Laboratory of the Department of Chemistry, University of Ferrara.

The photochemical reactions were performed with the output of a 500 W Oriel Hg lamp fitted with an IR blocking filter and a water filter to remove excess heat.

The NMR spectra were recorded in C_6D_6 solutions on a Bruker AC 200 instrument and, in part, on a Bruker AMX 500, operating for ^1H at 200.13 (500.13), ^2H at 30.7 (76.6), for ^{13}C at 50.2 (125.6) and for ^{31}P at 81.0 (202.4) MHz. The chemical shift scales are relative to internal TMS for ^1H, ^2H, and ^{13}C and to external H_3PO_4 for ^{31}P. The two-dimensional correlation experiments, i.e., $^{31}P,^1H$- ($\Delta = 20$ ms) and $^{13}C,^1H$-HMQC ($\Delta = 3.6$ ms),[23] ^1H-COSY,[24] and ^1H-NOESY ($t_{mix} = 800$ ms),[25] were carried out using standard sequences. The infrared spectra were recorded on a Bruker IFS 88 FT-IR spectrometer.

$P(OCD_3)_3$. A vigorously stirred solution of methanol-d_4 (8.88 g, 246 mmol) and anhydrous pyridine (19.56 g, 247 mmol) in diethyl ether (70 mL) was treated dropwise at −15 °C with a solution of phosphorous trichloride (11.33 g, 82 mmol) in diethyl ether (30 mL). Particular care should be taken to maintain the *internal* temperature of the solution below 0 °C. After the addition was complete (it required about 2 h), the resulting suspension was stirred a further 15 min and then filtered. The solid residue was washed with diethyl ether (3 × 50 mL), the collected organic fractions dried over anhydrous magnesium sulfate and filtered, and all the volatile components removed by evaporation at ambient pressure. The resulting oil was purified by distillation at 760 mmHg (bp = 112 °C) to give pure $P(OCD_3)_3$ (yield: 7.69 g, 70%).

Photochemical Preparation of $[Tp^{Me2}IrH(C_6H_5)(P(OMe)_3)]$, 3a. A solution of **1** (26 mg, 43.2 μmol) in benzene (3 mL) containing $P(OMe)_3$ (16 μL, 0.13 mmol) was degassed by three freeze−pump−thaw cycles on a high-vacuum line. The solution was transferred through a cannula to a quartz cuvette sealed with a septum cap. The solution was irradiated with $\lambda \geq 335$ nm at 15 °C. The progress of photoreaction was followed by monitoring the ^1H NMR and $^{31}P\{^1H\}$ NMR spectra of the solution. Irradiation was stopped after 70 min. The spectra showed a 98% conversion of **1** to **3a.** Removal of the solvent under vacuum and recrystallization of the residue from methanol (2 mL) at −10 °C gave pure **3a** in 52% isolated yield. Its ^1H NMR spectrum showed resonances of free COE in the distillate. Larger amounts of **3a** were obtained by repeating the above photoreaction 10 times. Anal. Found (calcd for $C_{24}H_{37}BIrN_6O_3P$): C, 41.68 (41.58); H, 5.39 (5.44); N, 12.15 (12.05). IR(KBr): 2522 cm^{-1}, ν(B−H); 2176 cm^{-1}, ν(Ir−H). ^{31}P NMR (ppm): 82.8 (d with off-resonance decoupling). ^{13}C NMR: 152.3, 151.9, 151.7 (3 × 1C, C-3); 147.1 (1C, Ph^{o}); 143.9, 143.3, 142.8 (3 × 1C, C-5); 140.0 (1C, Ph^{o}); 127.0 (1C, Ph^{m}); 125.6 (1C, Ph^{m}); 121.1 (1C, Ph^{p}); 107.5 (1C, C-4), 106.5 (1C, J(P,C) = 5.3 Hz, C-4′), 106.4 (1C, C-4″); 51.2 (3C, J = 4.6 Hz, $P(OMe)_3$; 15.6 (1C, C-3″); 15.2 (1C, C-3′); 15.0 (1C, C-3); 12.9 (2C, C-5, C-5″); 12.6 (1C, C-5′). ^1H NMR: 8.14 (1H, H^{o}); 7.12 (1H, H^{m}); 7.01 (1H, H^{p}); 6.93 (1H, H^{o}); 6.85 (1H, H^{m}); 5.84 (1H, H-4); 5.62 (1H, H-4″); 5.47 (1H, J(P,H) = 1.8 Hz, H-4′); 3.17 (9H, J(P,H) = 11.4 Hz, $P(OMe)_3$); 2.33 (3H, Me-3); 2.30 (3H, Me-3″); 2.22 (3H, Me-5″); 2.19 (3H, Me-5); 2.09 (3H, Me-5′); 1.75 (3H, Me-3′); −19.36 (1H, J(P,H) = 25.6 Hz, Ir−H). Primed atoms refer to those located *trans* to the $P(OMe)_3$ ligand. Double-primed atoms refer to those located *trans* to the C_6H_5 ligand.

Photochemical Preparation of $[Tp^{Me2}IrH_2(P(OMe)_3)]$, 4a. A solution of **1** (26 mg, 43.2 μmol) in diethyl ether (3 mL) containing $P(OMe)_3$ (16 μL, 0.13 mmol) was degassed and irradiated as described for the preparation of **3a**. Removal of the solvent under vacuum yielded a residue which was recrystallized from methanol and dried under vacuum (yield, 64%). The ^1H NMR spectrum of the distillate showed only the presence of free COE. Larger amounts of **4a** were obtained by repeating the above photochemical preparation 10 times. Anal. Found (calcd for $C_{18}H_{33}BIrN_6O_3P$): C, 35.12 (35.11); H, 5.40 (5.41); N, 13.65 (13.64). IR(KBr): 2510 cm^{-1}, ν(B−H); 2177, 2165 cm^{-1}, ν(Ir−H). ^{31}P NMR: 99.5 (t with off-resonance decoupling). ^{13}C NMR: 151.6 (2C, C-3); 150.1 (1C, J(P,C) = 5.3 Hz, C-3′); 143.3 (2C, C-5); 141.3 (1C, C-5′); 105.7 (2C, C-4); 104.9 (1C, J(P,C) = 5.2 Hz, C-4′); 50.6 (3C, J(P,C) = 2 Hz, $P(OMe)_3$); 17.3 (1C, Me-3′); 15.5 (2C, Me-3); 12.5 (2C, Me-5); 12.2 (1C, Me-5′). ^1H NMR: 5.72 (2H, H-4); 5.54 (J(P,H) = 1.9 Hz, 1H, H-4′); 3.23 (J(P,H) = 12.0 Hz, 9H, $P(OMe)_3$); 2.40 (9H, Me-3, Me-3′); 2.28 (6H, Me-5); 2.13 (3H, Me-5′); −20.19 (J(P,H) = 27.4 Hz, Ir-H). Primed atoms refer to those located *trans* to the $P(OMe)_3$ ligand.

The isotopomer $[Tp^{Me2}IrH_2(P(OCD_3)_3)]$, **4b**, was similarly synthesized by replacing $P(OMe)_3$ with $P(OCD_3)_3$.

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Photochemical Preparation of [Tp^{Me2}IrH$_2$(CH$_2$═CHCOO^{t}Bu)], 5. A solution of **1** (26 mg, 43.2 μmol) in *tert*-butyl acrylate (3 mL) was degassed and irradiated as described for the preparation of **3a**. Removal of the solvent under vacuum produced an oily residue which was recrystallized from methanol. ^{1}H NMR: 5.70, 5.51, 5.43 (3 × 1H, H-4); 4.79, 4.27, 3.34 (3 × 1H, olefinic); 2.4−2.0 (6 × 3H, Me-3, Me-5); 1.27 (9H, ^{t}Bu); −14.95, −25.55 (2 × 1H, J(H,H) = 7.3 Hz, Ir−H).

Deuteration Experiments. These were performed as described for the preparation of **3a**. The following reactions were carried out:

Photolysis of 1 and P(OCH$_3$)$_3$ in C$_6$D$_6$. ^{31}P NMR (ppm): 83.0 [Tp^{Me2}IrD(C$_6$D$_5$)(P(OCH$_3$)$_3$)], **3c** and 82.8 (d with off-resonance decoupling, [Tp^{Me2}IrH(C$_6$D$_5$)(P(OCH$_3$)$_3$)], **3b**. Apart from the changes due to presence of a deuterated phenyl group, the ^{13}C and ^{1}H NMR are as for **3a**. ^{2}H-NMR (C$_6$H$_6$, ppm): 8.16 (Ph^o); 7.5−6.8 (Ph); −19.2 (J(P,D) = 3 Hz, Ir−D).

Photolysis of 1 and P(OCD$_3$)$_3$ in C$_6$H$_6$. ^{31}P NMR (ppm): 83.0 [Tp^{Me2}IrD(C$_6$H$_5$)(P(OCD$_3$)$_3$)], **3e**, and 82.7 (d with off-resonance decoupling), [Tp^{Me2}IrH(C$_6$H$_5$)(P(OCD$_3$)$_3$)], **3d**. Apart from the changes due to presence of the deuterated phosphite, the ^{1}H and ^{13}C NMR are as those found for **3a**.

Photolysis of 1 and P(OCD$_3$)$_3$ in C$_6$D$_6$. ^{31}P NMR (ppm): 83.1 [Tp^{Me2}IrD(C$_6$D$_5$)(P(OCD$_3$)$_3$)], **3f**. The ^{1}H and ^{13}C NMR spectra are similar to those of **3a** if the deuterations are taken into account. ^{2}H NMR (C$_6$H$_6$): 8.2−6.8 (Ph); 3.1 (J(P,D) = 1.6 Hz, P(OMe)$_3$); 2.2−1.7 (Me); 19.2 (J(P,D) = 3 Hz, Ir−D).

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