Iridium Complexes of Orthometalated Triaryl Phosphites: Synthesis, Structure, Reactivity, and Use as Imine Hydrogenation Catalysts

Robin B. Bedford,[†] Sergio Castillòn,[‡] Penny A. Chaloner,*[,†] Carmen Claver,*[,‡] Elena Fernandez,[‡] Peter B. Hitchcock,[†] and Aurora Ruiz[‡]

School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ, U.K., and Departament de Quimica, Universitat Rovira i Virgili, Pl. Imperial Tárraco 1, 43005 Tarragona, Spain

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Di-orthometalated iridium complexes of triaryl phosphites have been prepared and characterized. The synthesis of the triphenyl phosphite derivative [IrH(cod){P(OC$_6$H$_4$)$_2$(OC$_6$H$_5$)}], **3**, requires a circuitous route by treatment of [IrCl(cod){P(OPh)$_3$}] with methyllithium and then methanol. However, with the hindered phosphites P(OAr)$_3$ (Ar = C$_6$H$_4$-2-^{t}Bu or C$_6$H$_3$-2,4-^{t}Bu$_2$) the di-orthometalated species **5a**,**b** are readily obtained by reaction of the phosphite with [{Ir(μ-OMe)(cod)}$_2$] or [Ir(cod)(py)$_2$][PF$_6$]. The mechanisms of these reactions have been investigated and are different. Both **5a** and **5b** are catalysts for imine hydrogenation. The complexes [IrH$_5${P(OAr)$_3$}$_2$] have been isolated from hydrogenation reactions and synthesized independently.

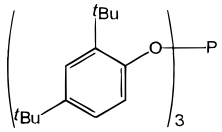
Introduction

We have recently been investigating the use of iridium complex catalysts for the homogeneous hydrogenation of imines.[1,2] We became interested in the synthesis of iridium complexes with orthometalated triaryl phosphites, and some of these results have recently been presented as a communication.[3]

Group 9 complexes with bulky triaryl phosphite ligands have proved successful catalysts for reduction of unsaturated organic compounds. For example, rhodium complexes catalyze the hydroformylation of otherwise unreactive species such as methylenecyclohexane, limonene, and cyclohexene[4] as well as cyclooctene[5] and various terminal[6] and hindered[7] alkenes, while selective catalyst systems have been developed with chiral diphosphites for the regio- and stereoselective hydroformylation of styrene.[8] [RuCl{P(OC$_6$H$_3$-2-Me)(OC$_6$H$_4$-2-Me)$_2$}(PPh$_3$)$_2$] has been found to be an active catalyst for alkene and alkyne hydrogenation,[9] with activity equivalent to [RuHCl(PPh$_3$)$_3$] and higher than that of [RhCl(PPh$_3$)$_3$]. Activity was also noted using [RuCl{P(OC$_6$H$_4$)(OC$_6$H$_5$)$_2$}{P(OPh$_3$)}$_3$], [Co{P(OC$_6$H$_4$)(OC$_6$H$_5$)$_2$}{P(OPh)$_3$}$_3$], or [PdCl{P(OC$_6$H$_4$)(OC$_6$H$_5$)$_2$}{P(OPh)$_3$}]. Orthometalation in these systems appears to be essential, as no hydrogenation was obtained with the non-metalated analogues [RuHCl{P(OPh)$_3$}$_4$], [CoH{P(OPh)$_3$}$_4$], or [PdCl$_2${P(OPh)$_3$}$_2$].

The catalytic hydrogenation of imines has attracted considerable interest in recent years, especially when the imines are prochiral.[10] Processes have been developed using titanium,[11] rhodium,[12] ruthenium,[13] and iridium[14] complexes as catalysts.

Here we describe the synthesis of iridium complexes with the bulky triaryl phosphite ligands tris(2,4-di-*tert*-butylphenyl) phosphite, Irgafos-168,[15] **1**, and tris(2-*tert*-butylphenyl) phosphite, **2**, and contrast these with the related derivatives of P(OPh)$_3$. The mechanisms of formation of the complexes will be discussed, as will their use as catalysts for the hydrogenation of *N*-benzylidene aniline.



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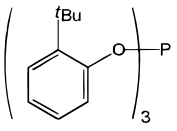

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[†] University of Sussex. E-mail: Penny.Chaloner@sussex.ac.uk.
[‡] Universitat Rovira i Virgili. E-mail: claver@quimica.urv.es.

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(1) Bedford, R. B.; Chaloner, P. A.; Claver, C.; Fernandez, E.; Hitchcock, P. B.; Ruiz, A. In *Catalysis of Organic Reactions (Chemical Industries Series 62)*; Scaros, M. G., Prunier, M. L., Eds.; Marcel Dekker: New York, 1994; pp 181−8.
(2) Bedford, R. B.; Chaloner, P. A.; Dewa, S. Z.; López, G.; Hitchcock, P. B.; Momblona, F.; Serrano, J. L. *J. Organomet. Chem.*, in press.
(3) Bedford, R. B.; Chaloner, P. A.; Hitchcock, P. B. *J. Chem. Soc., Chem. Commun.* **1995**, 2049.
(4) van Leeuwen, P. W. N. M.; Roobeek, C. F. *J. Organomet. Chem.* **1983**, *258*, 343.
(5) van Rooy, A.; Orij, E. N.; Kamer, P. C. J.; van den Aardweg, F.; van Leeuwen, P. W. N. M. *J. Chem. Soc., Chem. Commun.* **1991**, 1096.
(6) Cuny, G. D.; Buchwald, S. L. *J. Am. Chem. Soc.* **1993**, *115*, 2066.
(7) Polo, A.; Claver, C.; Castillón, S.; Ruiz, A.; Bayon, J. C.; Real, J.; Mealli, C.; Massi, D. *Organometallics* **1992**, *11*, 3525.
(8) Buisman, G. J. H.; Kamer, P. C. J.; van Leeuwen, P. W. N. M. *Tetrahedron Asym.* **1993**, *4*, 1625.
(9) Lewis, L. N. *J. Am. Chem. Soc.* **1986**, *108*, 743.
(10) Zhou, Z.; James, B. R.; Alper, A. *Organometallics* **1995**, *14*, 4209.
(11) Willoughby, C. A.; Buchwald, S. L. *J. Am. Chem. Soc.* **1992**, *114*, 7562.
(12) Levi, A.; Modena, G.; Scorrano, G. *J. Chem. Soc., Chem. Commun.* **1975**, 6.
(13) Kraslik, P.; Alper, H. *Tetrahedron: Asym.* **1992**, *3*, 1283.
(14) Osborn, J. A.; Chan, Y. N. *J. Am. Chem. Soc.* **1990**, *112*, 9400. Ng, Y.; Chan, C.; Meyer, D.; Osborn, J. A. *J. Chem. Soc., Chem. Commun.* **1990**, 869. Spindler, J.; Pugi, A.; Blaser, M. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 558.
(15) We thank Dr. Hans Zweifel of Ciba-Geigy for a generous gift of this material.

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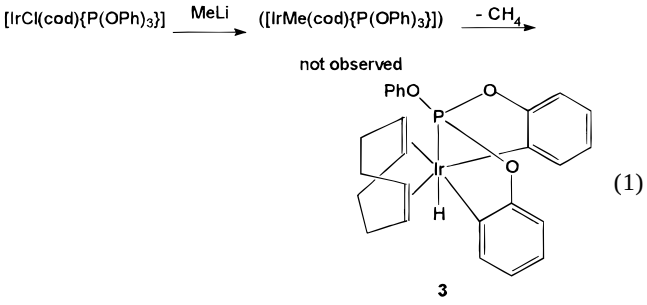
Table 1. Selected NMR Spectroscopic Data for Orthometalated Complexes

complex	$\delta(^{31}P)$ (ppm)	$\delta(^{1}H)$[hydride] (ppm)	$^{2}J_{PH}$ (Hz)
3	155.7	−7.65	195
5a	151.1	−7.18	190
5b	150.9	−7.18	187

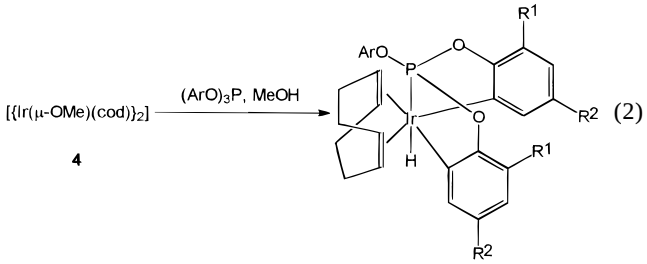
Results and Discussion

Synthesis of Di-orthometalated Iridium Triaryl Phosphite Complexes. The synthesis of [IrH{P(OC$_6$H$_4$)$_2$(OC$_6$H$_5$)}(cod)], **3** (cod = 1,5-cyclooctadiene), was effected by reaction of [IrCl(cod){P(OPh)$_3$}] with methyllithium and then methanol[3] (eq 1). A related



3 (1)

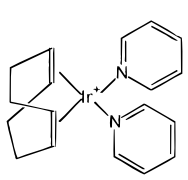
process was used by Parshall to prepare [Rh{(OC$_6$H$_4$)(OPh)$_2$}{P(OPh)$_3$}$_2$] from [RhCl{P(OPh)$_3$}$_3$] and PhMgCl.[16] The preparation of analogous di-orthometalated complexes of **1** or **2** is considerably easier. Reaction of [{Ir(μ-OMe)(cod)}$_2$], **4**, with **1** in methanol leads to the formation of [IrH{P(OC$_6$H$_2$-2,4-^{t}Bu$_2$)$_2$(OC$_6$H$_3$-2,4-^{t}Bu$_2$)}(cod)], **5a**, in 56% yield (eq 2). This formulation is



5a Ar = C$_6$H$_3$-2,4-^{t}Bu$_2$, R^1, R^2 = ^{t}Bu
5b Ar = C$_6$H$_4$-2-^{t}Bu, R^1 = ^{t}Bu, R^2 = H (2)

supported by the spectroscopic data, in particular the ^{1}H NMR spectrum which shows a high-field doublet at δ −7.18 ppm with a coupling of 190 Hz to the *trans* phosphorus, assigned to the metal hydride. It also indicates the presence of only one *ortho* ring proton, implying orthometalation of the other two rings. The ^{31}P{^{1}H} NMR spectrum shows a singlet at δ 151.1 ppm. Similarly, the reaction of **4** with **2** in methanol yields [IrH{P(OC$_6$H$_3$-2-^{t}Bu)$_2$(OC$_6$H$_4$-2-^{t}Bu)}(cod)], **5b**, in 92% yield, the spectroscopic properties of which are almost identical with those of **5a** (Table 1).

5a can also be produced from **1** and [Ir(cod)(py)$_2$][PF$_6$], **6** (py = pyridine), in 87% yield. **5b** was similarly prepared in 55% yield. However, **1** did not react with the analogous [Rh(cod)(py)$_2$][PF$_6$]. Reaction of triphenyl phosphite with **6** does not produce the comparable di-orthometalated complex **3** but rather the previously reported [Ir{P(OC$_6$H$_4$)(OC$_6$H$_5$)$_2$}(cod){P(OPh)$_3$}],[17] **7**.



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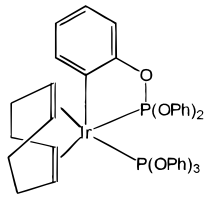

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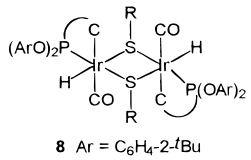
It appears, therefore, that the ease of di-orthometalation of **1** and **2** is a consequence of the steric bulk of the phosphites. This may be due to the fact that complexes containing two bulky phosphite ligands are unlikely to be thermodynamically stable, as previously demonstrated by the reaction of **6** with bulky triarylphosphines.[18] Also, di-orthometalation may be favored over mono-orthometalation as a means of minimizing intramolecular interaction between the ^{t}Bu groups in the phosphite ligand. However, the previously reported formation of **8** from [{Ir(μ-SR)(CO)$_2$}$_2$] (R = (CH$_2$)$_3$NMe$_2$) and **2**[19] indicates that this is not invariably the case.



8 Ar = C$_6$H$_4$-2-^{t}Bu

The similarity of the NMR spectroscopic data obtained for **5a**,**b** with those of the triphenyl phosphite analogue [IrH{P(OC$_6$H$_4$)$_2$(OC$_6$H$_5$)}(cod)], **3**, and the similarity of the ^{31}P{^{1}H} NMR shifts of the free phosphites[20] indicate that the substitution of the aromatic ring has little effect on the electronic properties of the phosphorus atom and that the chemical shift is determined by complex geometry rather than electronic factors.

Structures of 5a,b. The single-crystal X-ray structures of **5a**,**b** have been determined. Figure 1 shows the ORTEP drawing of **5a**, while Figure 2 shows an alternative view and Figure 3 shows the structure of **5b**. Selected bond lengths and angles for **5a**,**b** are given in Tables 2 and 3, respectively. The structures are in agreement with the spectroscopic data; in particular it is clear that in both cases the phosphite ligand has been doubly orthometalated, with the two metal bound rings occupying *cis* coordination sites. While the hydride was not located in either example, the gross structures are similar to that of **3**,[3] in which the hydride was located *trans* to the phosphorus. A comparison of certain structural data for **5a**,**b** with those of **3** is given in Table

(16) Barefield, E. K.; Parshall, G. W. *Inorg. Chem.* **1972**, *11*, 964. Coolen, H. K. A. C.; Nolte, R. J. M.; van Leeuwen, P. W. N. M. *J. Organomet. Chem.* **1995**, *496*, 159.

(17) Haines, L. M.; Singleton, E. *J. Organomet. Chem.* **1970**, *25*, C83.

(18) Abbassioun, M. S.; Chaloner, P. A.; Hitchcock, P. B. *Acta Crystallogr., Sect. C* **1989**, *C45*, 331. Abbassioun, M. S.; Chaloner, P. A.; Hitchcock, P. B. *Acta Crystallogr., Sect. C* **1990**, *C46*, 902. Bedford, R. B.; Chaloner, P. A.; Hitchcock, P. B. *Acta Crystallogr., Sect. C* **1993**, *C49*, 1461. Bedford, R. B.; Chaloner, P. A.; Hitchcock, P. B. *Acta Crystallogr., Sect. C* **1994**, *C50*, 356.

(19) Fernández, E.; Ruiz, A.; Castillón, S.; Claver, C.; Piniella, J. F.; Alvarez-Larena, A.; Germain, G. *J. Chem. Soc., Dalton Trans.* **1995**, 2137.

(20) ^{31}P{^{1}H} NMR (CDCl$_3$; δ): **1**, 131.4 ppm; **2**, 131.0 ppm; P(OPh)$_3$, 127.8 ppm.

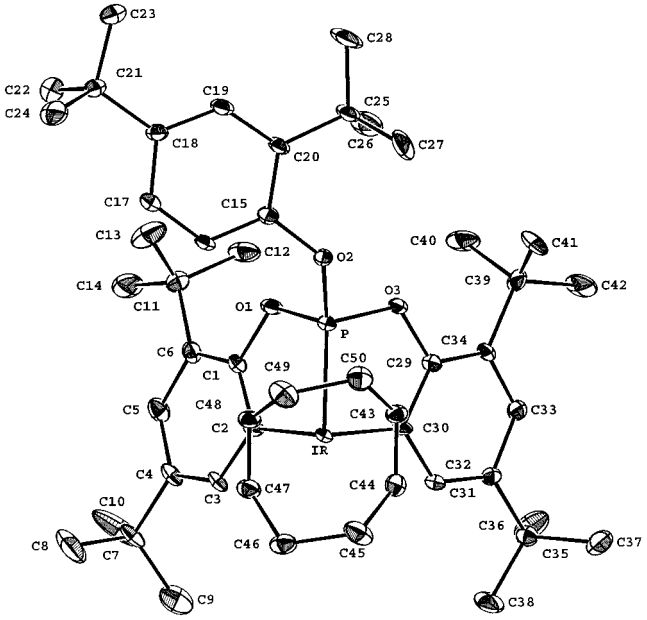


Figure 1. ORTEP representation of [IrH{P(OC_6H_2-2,4-^{t}Bu$_2$)$_2$(OC_6H_3-2,4-^{t}Bu$_2$)}(cod)], **5a**.

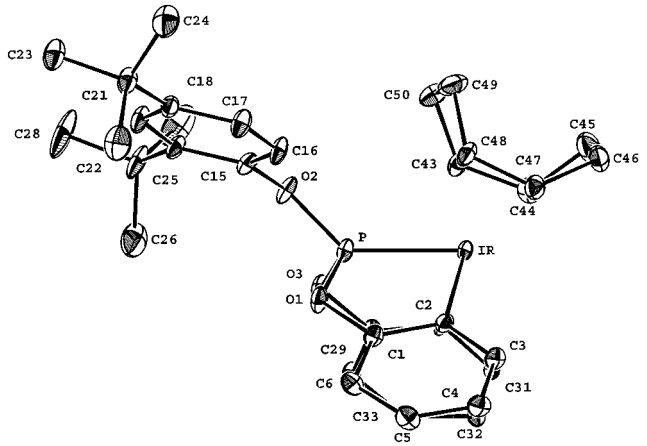


Figure 2. Alternative view of [IrH{P(OC_6H_2-2,4-^{t}Bu$_2$)$_2$(OC_6H_3-2,4-^{t}Bu$_2$)}(cod)], **5a**.

4. From these data it can be seen that the orthometalated moieties of all three compounds are essentially the same, with the only significant difference being between the three Ir−P−Oβ angles, which open up slightly as the steric bulk of the aryl rings increases. The mean M−Ir−C(*trans*) angles (172.1−176.4°) indicate little deviation from octahedral with respect to the metalated aryl or cod ligands. Significant distortion is noted, however, in the coordination of the phosphorus atoms, which are tilted toward the orthometalated rings. The mean P−Ir−C(metalated) angles of these systems are similar to that in the previously reported [IrCl{P(OC_6H_3-2-Me)$_2$(OC_6H_4-2-Me)}(γ-picoline)$_2$][21] (79.5°). Interestingly, the P−Ir−C(metalated) angle of the mono-orthometalated complex, [Ir{P(OC_6H_3-2-Me)(OC_6H_4-2-Me)$_2$}(cod){P(OCH_2)$_3$CMe}],[22] is 80°, which implies that orthometalation of a second ring does not greatly increase distortion, and would therefore be comparatively facile providing that the complex is coordinatively unsaturated and has an appropriate available oxidation state. The Ir−C bond lengths in **5a** (2.089(11) and 2.052(9) Å) and **5b** (2.067(8) and 2.064(8) Å) are similar to those established[21] for [IrCl{P(OC_6H_3-2-Me)$_2$(OC_6H_4-2-Me)}(γ-picoline)$_2$] (2.04−2.05 Å). However the Ir−P bonds in **5a** (2.258(3) Å) and **5b** (2.257(2) Å) are slightly longer than that (2.141(1) Å) in the *ortho*-tolyl derivative suggesting that this parameter is more sensitive to steric hindrance.

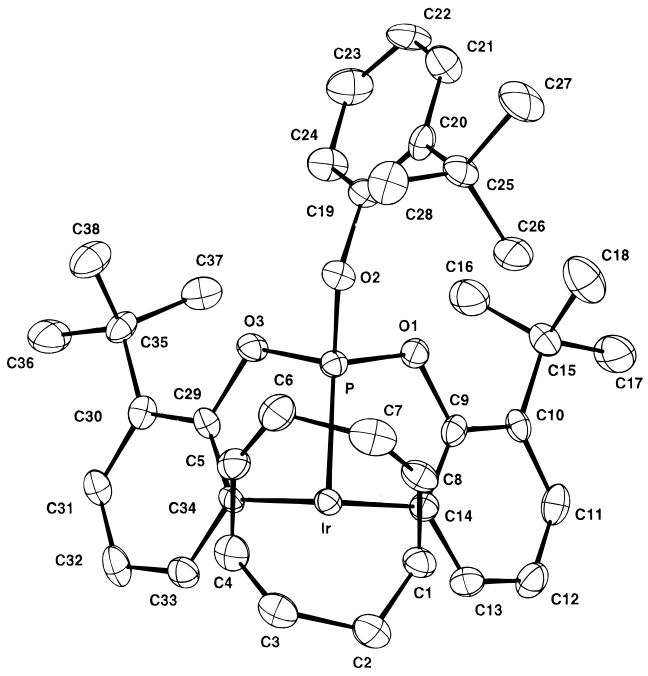


Figure 3. CAMERON representation of [IrH{P(OC_6H_3-2-^{t}Bu)$_2$(OC_6H_4-2-^{t}Bu)}(cod)], **5b**.

Table 2. Selected Bond Lengths (Å) and Angles (deg) with Estimated Standard Deviations in Parentheses for 5a

		Bonds	
Ir−M1[a]	2.154(12)	Ir−M2[a]	2.130(10)
Ir−P	2.258(3)	Ir−C2	2.089(11)
Ir−C30	2.052(9)	Ir−C43	2.274(10)
Ir−C44	2.264(12)	Ir−C47	2.242(11)
Ir−C48	2.250(10)	P−O1	1.587(8)
P−O2	1.588(6)	P−O3	1.596(7)
O1−C1	1.426(11)	O2−C15	1.395(12)
O3−C29	1.418(11)		
		Angles	
M1−Ir−M2	85.6(4)	M1−Ir−P	104.4(3)
M1−Ir−C2	176.4(4)	M1−Ir−C30	89.4(4)
M2−Ir−P	108.6(3)	M2−Ir−C2	93.5(4)
M2−Ir−C30	172.6(4)	P−Ir−C2	79.2(3)
P−Ir−C30	78.0(3)	C2−Ir−C30	91.1(4)
Ir−P−O1	108.2(3)	Ir−P−O2	134.1(4)
Ir−P−O3	107.7(3)	O1−P−O2	101.7(4)
O1−P−O3	106.0(4)	O2−P−O3	96.2(3)
P−O1−C1	115.6(7)	P−O2−C15	128.9(6)
P−O3−C29	114.4(6)		

[a] M1 and M2 are the midpoints of the C43−C44 and C47−C48 bonds.

Mechanistic Studies on the Formation of the Orthometalated Complexes. In an attempt to understand the mechanism of formation of **5a**, **1** was treated with **6** in $CDCl_3$/MeOH (4:1) on an NMR tube scale, and the reaction was monitored by ^{1}H and ^{31}P{^{1}H}

(21) Singleton E.; van der Stok, E. *J. Chem. Soc., Dalton Trans.* **1978**, 926.

(22) Laing, M.; Nolte, M. J.; Singleton, E.; van der Stok, E. *J. Organomet. Chem.* **1978**, *146*, 77.

Table 3. Selected Bond Lengths (Å) and Angles (deg) with Estimated Standard Deviations in Parentheses for 5b

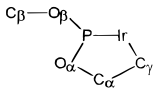
	Bonds		
Ir−P	2.257(2)	Ir−C1	2.245(9)
Ir−C4	2.293(9)	Ir−C5	2.262(9)
Ir−C8	2.293(9)	Ir−C14	2.064(8)
Ir−C34	2.067(8)	Ir−M1[a]	2.165(9)
Ir−M2[a]	2.171(9)		
	Angles		
P−Ir−C14	75.8(2)	P−Ir−C34	78.8(2)
C14−Ir−C34	92.4(3)	Ir−P−O1	108.1(2)
Ir−P−O2	132.3(2)	Ir−P−O3	107.2(2)
O1−P−O2	100.6(3)	O1−P−O3	104.2(3)
O2−P−O3	101.5(3)	M1−Ir−M2	83.7(2)
M1−Ir−P	108.2(2)	M1−Ir−C14	92.7(2)
M1−Ir−C34	172.1(2)	M2−Ir−P	106.8(2)
M2−Ir−C14	174.3(2)	M2−Ir−C34	90.8(2)

[a] M1 and M2 are the midpoints of the C1−C8 and C4−C5 bonds.

Table 4. Comparison of Structural Data (Bond Lengths in Å, Angles in deg) for 3, 5a, and 5b[a]

	complex		
	3	**5a**	**5b**
Ir−P	2.246(2)	2.258(3)	2.257(2)
mean Ir−Cγ	2.07	2.07	2.07
P−Oβ	1.580(5)	1.588(6)	1.590(6)
mean P−Oα	1.606	1.59	1.60
Oβ−Cβ	1.409(8)	1.395(12)	1.430(10)
mean Oα−Cα	1.43	1.42	1.42
mean Ir−P−Oα	108.1	108.0	107.7
Ir−P−Oβ	130.9(2)	134.1(4)	132.3(2)
mean P−Oα−Cα	113.7	115.0	115.3
P−Oβ−Cβ	127.1(4)	128.9(6)	126.6(5)
mean Ir−Cγ−Cα	119.2	119.7	121.0

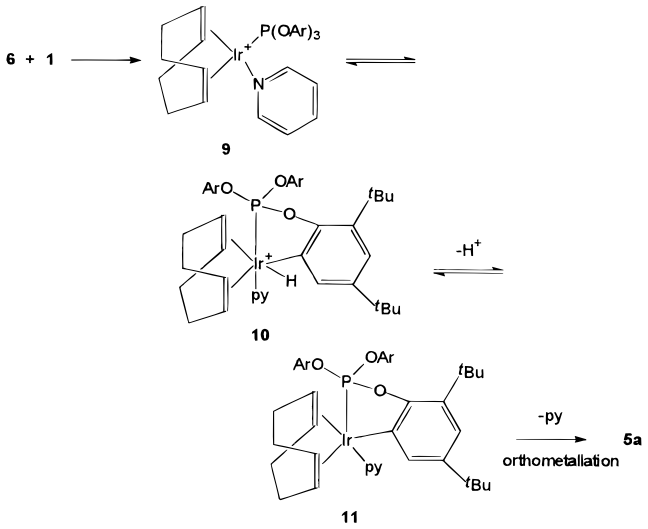
[a] Labeling scheme defining terms:



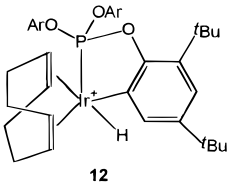
NMR spectroscopy. The $^{31}P\{^1H\}$ spectra recorded after either 20 min or 3 h show the presence of only one intermediate species, which gives rise to a singlet at δ 96.8 ppm. Even after 20 min formation of some **5a** was evident. The ^1H NMR spectrum of the intermediate recorded after 45 min shows a doublet at δ −17.23 ppm integrating to one proton with $^2J_{PH} = 10.7$ Hz, indicative of a *cis* arrangement of phosphite and hydride ligands. While the aromatic region of the spectrum appeared complex, it is clear that only 1 equiv of free pyridine was produced in the formation of the intermediate, implying that the other remains coordinated. The observation of signals ascribed to six *tert*-butyl environments is consistent with the orthometalation of a single ring. We therefore tentatively assign the intermediate as [IrH{P(OC$_6$H$_2$-2,4-^{t}Bu$_2$)(OC$_6$H$_3$-2,4-^{t}Bu$_2$)$_2$}(cod)(py)][PF$_6$], **10** (Scheme 1). Attempts to isolate this species in a pure form have failed. The reaction of **1** with **6** in dry dichloromethane also leads to the formation of some **5a**; indeed the conversion of **10** to **5a** appears to be faster under aprotic conditions.

Overall the reaction involves an oxidative addition followed by a deprotonation; thus we would expect it to be retarded by the presence of acidic solvents such as alcohols, as was found. Loss of H^+ from a cationic metal center on orthometalation of a triaryl phosphite has been previously observed in the reaction of [Ir(C$_5$Me$_5$)(acetone)$_3$][PF$_6$]$_2$ with triphenyl phosphite to give [Ir(C$_5$Me$_5$){P(OC$_6$H$_4$)(OC$_6$H$_5$)$_2$}{P(OPh)$_3$}][PF$_6$].[23] While the intermediates **9** and **11** are not formed in high enough concentration to be directly observed by NMR spectroscopy, neither is unprecedented.

Scheme 1. Mechanism of Reaction of Irgafos, 1, with [Ir(cod)(py)$_2$]$^+$



A hydridic species similar to **10** but lacking the pyridine ligand, [IrH{P(OC$_6$H$_2$-2,4-^{t}Bu$_2$)(OC$_6$H$_3$-2,4-^{t}Bu$_2$)$_2$}(cod)]$^+$, **12**, is generated by the reaction of H[BF$_4$](aq) with **5a**. Its composition was tentatively assigned on the basis of NMR spectroscopic data. In particular we note the appearance of a new hydride signal at δ −21.7 with $^2J_{PH} = 13.9$ Hz. The low value of the coupling constant implies that the hydride and phosphorus must be *cis*. The high downfield shift of the resonances assigned to two of the cod alkene protons (δ 6.07, 5.79 ppm) suggests that one of the double bonds is *trans* to an electronegative substituent. Although the geometry shown approximates to a square-based pyramid, the evidence we have for the exact stereochemistry of the complex is limited; the geometry is in any event likely to be quite distorted. Attempts to isolate **12** have been unsuccessful. Removal of the excess acid by washing the reaction mixture with aliquots of water led to the re-formation of **5a**.



The mechanism of Scheme 1 explains why **3** cannot be produced from **6** and triphenyl phosphite, the reaction giving **7** instead. It would be expected that an intermediate similar to **10** is formed but with triphenyl phosphite in place of pyridine. In this case the bis(phosphite) complex is not sterically destabilized and deprotonation leads to **7**. The reaction was too rapid to be studied by NMR spectroscopy, but Singleton and his

(23) Thompson, S. J.; White, C.; Maitlis, P. M. *J. Organomet. Chem.* **1977**, *136*, 87.

co-workers[24] have previously isolated the proposed intermediate in this reaction, $[IrH\{P(OC_6H_3\text{-}2\text{-}R)(OC_6H_4\text{-}2\text{-}R)_2\}(cod)\{P(OC_6H_5\text{-}2\text{-}R)_3\}]^+$ (R = H), by the reaction of **7** with $H[PF_6]$ and have also shown that the analogous compound with R = Me is readily reconverted to $[Ir\{P(OC_6H_3\text{-}2\text{-}R)(OC_6H_4\text{-}2\text{-}R)_2\}(cod)\{P(OC_6H_5\text{-}2\text{-}R)_3\}]$.

The reaction between **1** and **6** in CD_3OD led to the formation of **5a** with 95% of the hydride sites deuterated. This is indicated by a triplet in the $^{31}P\{^1H\}$ NMR spectrum at δ 152.2 ppm ($^2J_{PD}$ = 28.4 Hz) and a doublet in the ^2H NMR spectrum at δ −6.99 ppm ($^2J_{PD}$ = 29.8 Hz). Integration of the aryl region of the ^1H NMR spectrum shows that most of the *ortho* positions are also deuterated, indicating that metalated and non-metalated rings undergo exchange in a similar way to that reported for $[RuCl\{P(OC_6H_4)(OC_6H_5)_2\}\{P(OPh)_3\}_3]$.[25] This pattern of deuteration is rationalized by the exchange of the protons liberated in the reversible interconversion of **10** and **11** with deuterons. De-orthometalation of deuterated **10** leads to the formation of **9** with a deuterium atom in one *ortho* position. Assuming that the interconversions of **9**−**11** are rapid and reversible, this allows the complete deuteration of the hydride and all the *ortho*-sites. The second orthometalation, to give **5a**, must be comparatively slower.

Reaction of **2** with $[\{Ir(\mu\text{-}OCD_3)(cod)\}_2]$ in CD_3OD led to the formation of **5b** with no deuterium incorporation in either the hydride or the *ortho* aryl sites. This is consistent with two possible mechanisms. β-Hydride transfer from the methoxy group may occur after coordination of the phosphite to produce a deuteriophosphite complex **14** (Scheme 2) which orthometalates with the loss of HD. Alternatively, orthometalation occurs to provide a complex with *cis* hydride and OCD_3 groups which then reductively eliminates $HOCD_3$. A second orthometalation would then produce **5b**. As no cationic hydride complexes are produced in either of these mechanisms, exchange and reversible de-orthometalation is not possible and so no deuterium is incorporated. Precipitates formed in the early stages (<3 h) of the reactions were analyzed by ^{31}P NMR spectroscopy. This indicated the presence of a species, **16b**, analogous to **7**. Broad AB doublets were noted at δ 85 and 126, and these were not further broadened when the decoupler was switched off, indicating that they were not hydride coupled. This should be compared with the ^{31}P NMR spectroscopic data for **7** (δ 83.1, 126.2 ppm, $^2J_{PP}$ = 77 Hz) and the analogue $[Ir(cod)\{P(OC_6H_4\text{-}2\text{-}Me)_2(OC_6H_3\text{-}2\text{-}Me)\}\{P(OC_6H_4\text{-}2\text{-}Me)_3\}]$ (δ 86.6, 125.2 ppm, $^2J_{PP}$ = 79 Hz).[21,23] We postulate that this was formed by reversible coordination of free phosphite to **15**. The signals in the NMR spectrum are broad, suggesting a dynamic exchange which is fast on the NMR time scale at room temperature. Similar results were obtained with **5a**.

Catalytic Hydrogenation and Reaction of Orthometalated Complexes with H_2. The use of iridium triaryl phosphite complexes as precatalysts in the homogeneous catalytic hydrogenation of *N*-benzylideneaniline was studied; the results are summarized

Scheme 2. Mechanism of Reaction of $P(OC_6H_4\text{-}2\text{-}^tBu)_3$, 2, with $[\{Ir(\mu\text{-}OMe)(cod)\}_2]$

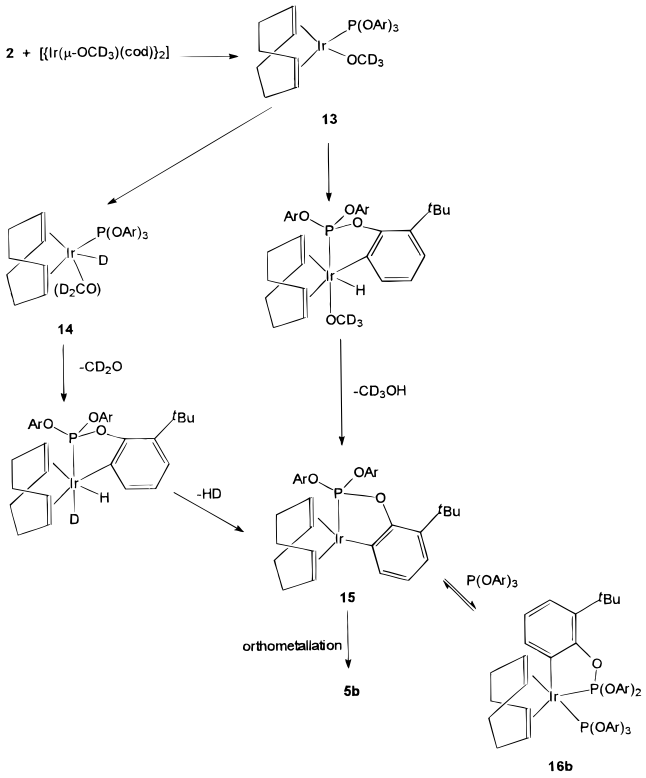


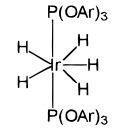
Table 5. Hydrogenation of *N*-Benzylideneaniline

	conversion (%) after			
precatal system[a]	1 h	2 h	3 h	5 h
5a	48	95	99	
5b	99.2	99.4	99.6	
6 + **2**[b]			98	
5a + **1**[c]	20	71	86.5	
7	1.8	2.4		5.4

[a] Conditions: 30 atm of H_2; 40 °C; 50:1 substrate:precatalyst, methanol. [b] Precatalyst formed *in situ*. [c] Ir:P = 1:2.

in Table 5. The rates of hydrogenation with **5a**,**b** are both good, with the reactions complete within 3 h. The better rate for **5b** may be attributed to its lower steric bulk The species formed *in situ* from **6** and **2**, presumably **5b**, was also an excellent catalyst. Interestingly, the rate of reaction catalyzed by **5a** is reduced by the presence of 1 equiv of free phosphite, suggesting that a monophosphite species may be more reactive than species containing two bulky ligands.

During the hydrogenation of the imine in the presence of **5b** a white powder was precipitated which was shown to be $[IrH_5\{P(OC_6H_4\text{-}2\text{-}^tBu)_3\}_2]$, **17b**. **17b** could also be



17a Ar = $C_6H_3\text{-}2,4\text{-}^tBu_2$

17b Ar = $C_6H_4\text{-}2\text{-}^tBu$

obtained by reaction of **5b** with hydrogen at 1 atm. The $^{31}P\{^1H\}$ NMR spectrum consists of a singlet at δ 83.9 ppm. When the ^{31}P NMR spectrum was recorded without decoupling the spectrum showed splitting of the phosphite signal into a sextet with $^2J_{PH}$ = 16.5 Hz,

(24) Chalmers, A. A.; de Waal, D. J. A.; Oosthuizen, H. E.; Singleton, E.; van der Stok, E. *S. Afr. J. Chem.* **1983**, *36*, 37.
(25) Lewis, L. N. *Inorg. Chem.* **1985**, *24*, 4433.

indicating that the compound contains five equivalent hydrides *cis* to the phosphites. The ^{1}H NMR spectrum shows a high-field triplet at δ −9.47 ppm ($^2J_{PH}$ = 16.5 Hz), indicative of *cis* coupling to two equivalent phosphites. No peaks corresponding to the cyclooctadiene ligand were observed. The analogous phosphine derivatives [$IrH_5(PR_3)_2$] (R = Ph, cyclohexyl, or ^{i}Pr) have been prepared previously.[26] A neutron diffraction study of one of them (R = ^{i}Pr)[27] showed that the hydrides adopt five equivalent equatorial sites in a pentagonal bipyramid. **17b** is itself a reasonable hydrogenation catalyst with activity comparable to those formed *in situ* from **2** and **6** or **4**.

A solution of **5a** in $CDCl_3$ was treated with hydrogen in an NMR tube and the reaction followed by NMR spectroscopy. The ^{1}H NMR spectrum recorded after 70 min showed a second hydridic species giving rise to a triplet at δ −9.63 ppm ($^2J_{PH}$ = 16.5 Hz). After 20 h this was the sole hydride-containing species. Phosphorus decoupling of this triplet led to collapse to a singlet. The ^{31}P{^{1}H} NMR spectrum at this time showed only a singlet at δ 88.2 ppm. While the signal became more complex when the ^{31}P NMR spectrum was run without proton decoupling, the sextet could not be fully resolved in this case. These data are indicative of the formation of the analogue of **17b**, [IrH_5{$P(OC_6H_3$-2,6-^{t}Bu$_2)_3$}$_2$], **17a**. Continued hydrogenation of the reaction mixture for a further 24 h led to a complex mixture of polyhydridic species. We were not able to isolate pure **17a**, but further evidence for its formation was obtained from the positive FAB mass spectrum of a sample of **5a** which had been hydrogenated for 22 h in dichloromethane. This showed four main peaks at m/z = 2514, 1670, 1485, and 943. The species with m/z = 943 corresponds to unreacted **5a** while that with m/z = 1485 was assigned to a species of approximate formulation [IrH_x{**1** − H_y}$_2$]. This is in approximate agreement with the formula of **17a** (molecular mass = 1491); orthometalation would probably occur in the beam, with loss of hydrogen, which would account for the lower observed mass. The highest mass peak seems to arise from a single trimeric species of approximate formula [{IrH_x(**1** − H_y)}$_3$]. The peak at 1670 corresponds to dimers of formula [{IrH_x(**1** − H_y)}$_2$], the iridium isotope pattern being suggestive of the presence of more than one species. Whether the dimeric species observed represent discreet molecules in the reaction mixture or fragments from the trimer has not been established.

We have not been able to establish what other species are produced in the disproportionation that gives **17**. It seems unlikely that iridium metal is formed, since none was visible, and when the formation of **17a** was monitored by NMR spectroscopy, no significant broadening of the signals was observed.

Not only does the triphenyl phosphite complex **7** exhibit a low activity in the catalytic hydrogenation of *N*-benzylideneaniline, it also shows no reaction with hydrogen at atmospheric pressure. This is probably due to the fact that is a coordinatively saturated species which can only form a catalytically active 16 electron species if one of the cod double bonds decoordinates. **5a**,**b** can be activated by the reductive elimination of the hydride and an aryl group to give a 16e Ir(I) complex.

Conclusions

We conclude that the degree and ease of orthometalation of a triaryl phosphite at a 16e cod−Ir(I) center is a function of the steric profile of the ligand. The mechanism of formation of the di-orthometalated complexes depends on whether the starting iridium complex is neutral or cationic, with deprotonation of a cationic hydride being a fundamental step in the latter process. De-orthometalation to provide a vacant coordination site at the metal center appears to be an important factor in the activation of these species for catalysis. The scope of this process and its applications to catalysis will be investigated further.

Experimental Section

General Procedures and Materials. All manipulations of air-sensitive materials were performed under an atmosphere of dry nitrogen or argon. Solvents were distilled prior to use from the appropriate drying agent, ethers from sodium−potassium alloy, alcohols from their magnesium alkoxide, and dichloromethane from calcium hydride. C, H, and N analysis were performed by Medac Ltd. or on a Carlo-Erba microanalyzer. NMR spectra were recorded on the following spectrometers: a Bruker AC250Y, a Bruker AMX500, or a Varian Gemina 300 MHz. FAB mass spectra were obtained using a Kratos 80RF spectrometer coupled to a Kratos DS55M data system. Gas chromatography was performed on a Hewlett-Packard 5890 II chromatograph with an Ultra-3 (diphenylsilicone 5%, dimethylsilicone 95%) 25 m × 0.2 mm column. The compounds [{$IrCl(cod)$}$_2$],[28] [$Ir(cod)(py)_2$][PF_6],[29] [{$Ir(\mu$-OMe)(cod)}$_2$],[30] and $P(OC_6H_4$-2-^{t}Bu$)_3$[4] were prepared according to literature procedures.

Synthesis of 5a,b. Method a. A suspension of [{$Ir(\mu$-OMe)(cod)}$_2$] (0.1 g, 0.15 mmol) and **1** (0.2 g, 0.3 mmol) in methanol (20 mL) was stirred for 15 h. Recrystallization from dichloromethane/methanol gave **5a** (0.159 g, 56%). **5b** (57 mg, 92%) was similarly obtained from [{$Ir(\mu$-OMe)(cod)}$_2$] (26.5 mg, 0.04 mmol) and **2** (76.4 mg, 0.16 mmol).

Method b. A suspension of [$Ir(cod)(py)_2$][PF_6] (259 mg, 0.489 mmol) and **1** (320 mg, 0.495 mmol) in methanol (30 mL) was allowed to stir overnight at room temperature. The mixture was concentrated to about half its volume *in vacuo* and the supernatant removed from the white precipitate *via cannula*. **5a** (0.4 g, 87%) was obtained by recrystallization from dichloromethane/ethanol as colorless rods. An analogous procedure gave **5b** in 55% yield.

Data for 5a. Anal. Calcd for $C_{50}H_{74}IrO_3P$: C, 63.5; H, 7.9. Found: C, 63.4; H, 7.95. ^{1}H NMR ($CDCl_3$, 250 MHz): δ −7.18 (d, 1H, Ir*H*, $^2J_{PH}$ = 190 Hz), 1.28 (s, 36H, CH_3), 1.34 (s, 9H, CH_3), 1.60 (s, 9H, CH_3), 2.19 (m, 2H, cod CH_2), 2.27 (m, 2H, cod CH_2), 2.51 (m, 2H cod CH_2), 2.94 (m, 2H, cod CH_2), 3.87 (m, 2H, cod C*H*), 4.24 (m, 2H, cod C*H*), 7.15 (d of d, 1H, *m′-H* of unmetalated ring, J_{HH} = 8.6 Hz, J_{HH} = 2.5 Hz), 7.49 (d of d, 1H, *m-H* of unmetalated ring, J_{HH} = 2.4 Hz, J_{PH} = 1.2 Hz), 7.66 (d of d, 1H, *o-H* of unmetalated ring, J_{HH} = 8.6 Hz, J_{HH} = 1.4 Hz) and 7.72 (d, 2H, *m-H* of metalated ring, J_{HH} = 2.2 Hz) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ 29.9 (s, C(CH_3)$_3$, metalated ring), 30.2 (s, C(CH_3)$_3$ unmetalated ring), 31.5 (s, C(CH_3)$_3$ unmetalated ring), 31.6 (d, cod *C*H$_2$, J_{PC} = 4.0 Hz), 31.9 (s, C(CH_3)$_3$, metalated ring), 33.0 (s, cod *C*H$_2$), 34.2 (s,

(26) Grushin, V. V.; Vymenits A. B.; Vol'pin, M. E. *J. Organomet. Chem.* **1990**, *382*, 185.
(27) Garlaschelli, L.; Khan, S. I.; Bau, R.; Longoni, G.; Koetzle, T. F. *J. Am. Chem. Soc.* **1985**, *107*, 7212.
(28) Winkhaus, G.; Singer, H. *Chem. Ber.* **1966**, *99*, 3610.
(29) Crabtree, R. H.; Morehouse, S. M. *Inorg. Synth.* **1986**, *24*, 173.
(30) Pannetier, G.; Fougeroux, Bonnaire, R.; Platzer, N. *J. Less Common Met.* **1971**, *24*, 83.

Table 6. Crystal Data and Data Collection and Refinement Parameters for 5a,b

	5a	5b
formula	$C_{50}H_{74}IrO_3P$	$C_{38}H_{50}O_3PIr$
fw	946.3	778.0
cryst system	triclinic	monoclinic
space group	$P\bar{1}$ (No. 2)	$P2_1/n$ (non-standard No 14)
a (Å)	11.093(5)	11.446(3)
b (Å)	12.712(4)	14.958(7)
c (Å)	18.222(4)	20.610(4)
α (deg)	77.71(2)	90
β (deg)	75.13(3)	91.48(2)
γ (deg)	78.68(3)	90
V (Å^3)	2399(1)	3527(1)
Z	2	4
D_{calc}	1.31	1.47
$F(000)$	980	1576
radiation, λ (Å)	monochromated Mo Kα, 0.710 73	monochromated Mo Kα, 0.710 69
μ, abs coeff (cm^{-1})	28.4	38.5
crystal size (mm)	0.15 × 0.1 × 0.05	0.25 × 0.08 × 0.05
data reflcn ranges, θ min and max	h, 0 → 15; k, −17 → 17; l, −25 → 25; 2 → 30	h, 0 → 13; k, 0 → 17; l, −24 → 24; 2 → 25
tot. reflcns measd		6762
tot. unique reflcns measd	13 948	6443
R_{int}		0.045
significant reflcns, $\|F^2\| > 2\sigma(F^2)$	9057	3759
max change in std reflcns (%)	−6.5	−2.8
decay corr	yes	no
abs corr, T_{max}, T_{min}	1.00, 0.80 from ψ scans	1.12, 0.99 DIFABS
non-H atoms located	heavy atom methods, SHELXS-86	heavy atom methods, SHELXS-86
refinement by	full-matrix least squares, non-H atoms anisotropic, Enraf-Nonius MolEN programs	full-matrix least squares, non-H atoms anisotropic, Enraf-Nonius MolEN programs
H atoms	hydride H omitted, the rest fixed at calcd posns $U_{iso} = 1.3U_{eq}$ for parent atom	hydride H omitted, the rest fixed at calcd positions $U_{iso} = 1.3U_{eq}$ for parent atom
R[a]	0.082	0.040
R′	0.080	0.040
S	1.6	1.10
no. of variables	496	388
$(\Delta/\sigma)_{max}$	0.02	0.04
$(\Delta\rho)_{max,min}$ (e Å^{-3})	+4.00, −0.35 near Ir atom	+0.63, −0.23

[a] $\sigma(F^2) = \{\sigma^2(I) + (0.04I)^2\}^{1/2}/Lp$, $w = \sigma^{-2}(F)$, $\sum w(|F_o| - |F_c|)^2$ minimized.

$C(CH_3)_3$ metalated ring), 34.6 (s, $C(CH_3)_3$ free ring), 34.9 (s, $C(CH_3)_3$ metalated ring), 35.3 (s, $C(CH_3)_3$ free ring), 75.2 (s, cod *C*H), 85.2 (s, cod *C*H), 119−153 (aryl) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 152.26 ppm. MS (FAB): m/z 943 (100%) $[M - 3H]^+$.

Data for 5b. Anal. Calcd for $C_{38}H_{50}IrO_3P$: C, 58.7; H, 6.4. Found: C, 58.6; H, 6.4. ^1H NMR ($CDCl_3$, 300 MHz): δ −7.18 (1H, d, $^2J_{PH}$ = 187 Hz, Ir*H*), 1.24 (s, 9H, $C(CH_3)_3$ of unmetalated ring), 1.60 (s, 18H, $C(CH_3)_3$ of metalated rings), 2.21 (m, 2H, cod CH_2), 2.44 (m, 2H, cod CH_2), 2.92 (m, 4H, cod CH_2), 3.91 (m, 2H, cod C*H*), 4.22 (m, 2H, cod C*H*), 6.5−7.7 (m, 10H, aryl C*H*) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.46 MHz): δ 32.4, 31.9, 29.9, 29.7 (cod CH_2, $C(CH_3)_3$, CH_3), 75.6 (cod *C*H), 85.9 (cod *C*H), 119−144 (aryl) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.47 MHz): δ 150.9 ppm. MS (FAB): m/z 773 (24%, M − 5H).

Preparation of [IrCl(cod){P(OPh)$_3$}]. Triphenyl phosphite (0.16 mL, 0.61 mmol) was added to a solution of [{IrCl(cod)}$_2$] (0.205 g, 0.305 mmol) in light petroleum (bp 30−40 °C, 5 mL) and dichloromethane (15 mL) and the resultant mixture allowed to stand overnight at room temperature. The solution was concentrated *in vacuo* and the supernatant removed from the resultant orange precipitate *via cannula*. The product was used without further purification (0.30 g, 76%). Anal. Calcd for $C_{26}H_{27}ClIrO_3P$: C, 48.3; H, 4.2. Found: C, 48.9; H, 4.2. ^1H NMR ($CDCl_3$, 250 MHz): δ 1.7−2.0 (m, 8H, cod CH_2), 3.26 (m, 2H, cod C*H*), 5.38 (m, 2H, cod C*H*), 7.0−7.4 (m, 15H, aryl) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 28.7 (d, cod CH_2, J_{PC} = 3.0 Hz), 33.3 (d, cod CH_2, J_{PC} = 3.6 Hz), 54.5 (d, cod *C*H, J_{PC} = 1.9 Hz), 106.0 (d, cod *C*H, J_{PC} = 19.4 Hz), 152 −121 (aryl) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 87.8 ppm.

Preparation of [IrH{P(OC$_6$H$_4$)$_2$(OC$_6$H$_5$)}(cod)], 3. A solution of [IrCl(cod){P(OPh)$_3$}] (0.122 g, 0.189 mmol) in diethyl ether (10 mL) was cooled to −78 °C and a 1.6 M solution of methyllithium in diethyl ether (0.2 mL, 0.32 mmol) added. The color of the solution changed immediately from orange to red. The solution was allowed to warm to room temperature and the reaction then quenched with a few drops of methanol. The mixture was stirred for 1 h, after which time the color had changed to yellow-orange. The solution was filtered, and then the solvent was removed *in vacuo* from the filtrate to yield a pale yellow solid. Recrystallization from dichloromethane/methanol gave [IrH{P(OC$_6$H$_4$)$_2$(OC$_6$H$_5$)}(cod)] as colorless rods (0.06 g, 52%). Anal. Calcd for $C_{26}H_{26}IrO_3P$: C, 51.2; H, 4.3. Found: C, 51.0; H, 4.4. ^1H NMR ($CDCl_3$, 250 MHz): δ −7.65 (d, 1H, Ir*H*, $^2J_{PH}$ = 194.5 Hz), 2.27 (m, 2H, cod CH_2), 2.49 (m, 4H, cod CH_2), 2.89 (m, 2H, cod CH_2), 3.80 (m, cod C*H*), 4.19 (m, 2H, cod C*H*), 6.62 (m, 2H, aryl), 6.81 (m, 2H, aryl), 6.89 (m, 3H, aryl), 7.54 (m, 4H, aryl), 7.77 (m, 2H, aryl) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ 31.2 (cod CH_2), 32.7 (cod CH_2), 75.8 (cod *C*H), 83.7 (cod *C*H), 111−158 (aryl) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 155.7 ppm.

Preparation of [Ir{P(OC$_6$H$_4$)(OC$_6$H$_5$)$_2$}(cod){P(OC$_6$H$_5$)$_3$}], 7. Triphenyl phosphite (0.5 mL, 1.9 mmol) was added to a stirred solution of [Ir(cod)(py)$_2$][PF$_6$] (0.401 g, 0.660 mmol) in methanol (25 mL). The mixture was stirred for 30 min and the supernatant removed from the resulting white precipitate with a syringe. The residue was washed with methanol (2 × 20 mL) and recrystallized from dichloromethane/diethyl ether yielding **7** as colorless blocks (0.14 g, 23%). ^1H NMR ($CDCl_3$, 250 MHz): δ 1.7−2.1 (m, br, 7H, cod CH_2), 2.4 (m, 2H, 1 cod C*H* and 1 cod CH_2), 3.01 (s, br, 1H, cod C*H*), 4.49 (s, br, 1H, cod C*H*); 4.71 (s, br, 1H, cod C*H*) and 6.7−7.4 (m, 29H, aryl). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 126.2 (d, J_{PP} = 77.4 Hz) and 83.1 (d, J_{PP} = 77.4 Hz) ppm. MS FAB: m/z 921 (100%,

MH^+), 807 (45%, M − cod − 5H), 715 (25%, M − cod − 4H − C_6H_6), 607 (45%, M − $P(OPh)_3$ − 2H), 501 (40%, M − $P(OPh)_3$ − cod).

Preparation of Deuterated 5a. A mixture of $[Ir(cod)(py)_2][PF_6]$ (0.061 g, 0.101 mmol) and **1** (0.066 g, 0.102 mmol) in CD_3OD (2.2 mL) and dichloromethane (1 mL) was stirred overnight and the solution then concentrated *in vacuo* to about 1 mL yielding a white precipitate. The supernatant liquid was removed with a cannula and the residue dried *in vacuo*. The product mixture was not purified further but was characterized by NMR spectroscopy. Yield: 0.078 g, 81%. ^{1}H NMR ($CDCl_3$, 250 MHz): δ 6.87 (d of d, 2H, *m′-H* metalated ring, $J_{HH} = 2.4$ Hz, $J_{HP} = 1.0$ Hz), 7.23 (d, 1H, *m′-H* unmetalated ring, $J_{HH} = 2.5$ Hz), 7.53 (d of d, 1H, *m-H* unmetalated ring, $J_{HH} = 2.5$ Hz, $J_{HP} = 1.1$ Hz) and 7.72 (d, 2H, *m-H* metalated ring, $J_{HH} = 1.8$ Hz) ppm. All other peaks the same as those of **5a**. ^{2}H NMR ($CDCl_3$, 38.38 MHz): δ −6.99 (d, Ir*D*, $J_{PD} = 29.8$ Hz), 7.36 (s, br, *o*-C*D*) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 152.0 (s, *P*IrH), 152.2 (t, *P*IrD, $J_{PD} = 28.8$ Hz) ppm.

Reaction of 5a with H[BF_4]. H[BF_4](aq) (48 wt %, 2 drops) was added to a solution of **5a** (7.0 mg, 7.4 μmol) in $CDCl_3$ (0.3 mL) in a 5 mm NMR tube which was shaken regularly and stirred horizontally to ensure maximum mixing of the two phase system. The reaction was followed by ^{1}H and $^{31}P\{^1H\}$ NMR spectroscopy. The data obtained after 20 h are given. On the basis of these data, the product was assigned as $[IrH\{P(OC_6H_2\text{-}^tBu_2\text{-}2,4)(OC_6H_3\text{-}^tBu_2\ 2,4)_2(cod)\}][BF_4]$, **12**. Attempts to isolate this product by washing out the excess of H[BF_4] with aliquots of degassed water led to conversion back to the starting material.

NMR Spectroscopic Data for 12. ^{1}H NMR ($CDCl_3$, 250 MHz): δ −21.7 (1H, d, $^2J_{PH} = 13.9$ Hz, Ir−*H*), 1.25, 1.28, 1.30, 1.31, 1.33, and 1.35, 6× (9H, s, C(CH_3)$_3$); 2.3−1.9 (4H, m, br, cod CH_2); 2.84 (4H, m, br, cod CH_2); 4.96 (1H, m, br, cod C*H*); 5.11 (1H, m, br, cod C*H*); 5.78 (1H, m, br, cod C*H*); 6.06 (1H, m, br, cod C*H*); 7.11 (1H, s, br, aryl); 7.15 (1H, d, $J_{HH} = 2.5$ Hz, aryl); 7.17 (1H, d, $J_{HH} = 2.3$ Hz, aryl); 7.20 (1H, d, $J_{HH} = 2.1$ Hz, aryl); 7.30 (1H, d, $J_{HH} = 8.7$ Hz, aryl); 7.34 (1H, d, $J_{HH} = 9.3$ Hz, aryl) and 7.44 (2H, s, br, aryl) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 98.7 ppm.

X-ray Diffraction Studies. Crystals of **5a** suitable for diffraction studies were grown from dichloromethane/ethanol, and those of **5b**, from methanol. Data were collected on an Enraf-Nonius CAD4 diffractometer at room temperature operating in the θ−2θ mode. A total of 25 reflections ($7 < \theta < 10°$) were used in each case to establish the cell parameters. Crystal data and data collection and refinement parameters are given in Table 6.

Catalytic Hydrogenation. Medium-pressure hydrogenation experiments (30 atm) were carried out in a Berghof autoclave, with electric heating and magnetic stirring. In a standard experiment a solution of *N*-benzylideneaniline (4 mmol) catalyst (0.08 mmol) in methanol/1,2-dichloroethane (1:1, 10 mL) was introduced into the evacuated autoclave and heated with stirring. Once the system had reached thermal equilibrium, hydrogen was introduced to reach the working pressure. Samples were taken at intervals for analysis. After each run the system was allowed to cool and the gas vented. The reaction mixture was then analyzed by GC and ^{1}H NMR spectroscopy.

Preparation of [$IrH_5\{P(OC_6H_4\text{-}2\text{-}^tBu)_3\}_2$], 17b. A solution of $[IrH(cod)\{P(OC_6H_3\text{-}2\text{-}^tBu)_2(OC_6H_4\text{-}2\text{-}^tBu)\}]$, **5b** (61.9 mg, 0.08 mmol), in dichloromethane (4 mL) was treated with hydrogen at 1 atm for 3 h. (The reaction was complete in 15 min at 5 bar of hydrogen pressure) The white precipitate produced was collected by filtration and washed with methanol to give **17b** (0.087 g, 95%). Anal. Calcd for $C_{60}H_{83}IrO_6P_2$: C, 62.4; H, 7.1. Found: C, 62.0; H, 7.3. ^{1}H NMR ($CDCl_3$, 300 MHz): δ −9.47 (5H, t, $^2J_{PH} = 16.5$ Hz, Ir−*H*), 1.37 (54H, s, C(CH_3)$_3$), 6.5−7.7 (24H, m, aryl) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.46 MHz): δ 30.4 (*C*H_3), 34.6 (*C*(CH$_3$)$_3$), 121.0, 123.45, 126.5, 127.0 (aryl) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.47 MHz): δ 83.9 ppm.

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Supporting Information Available: Tables of X-ray parameters, positional and thermal parameters, and bond distances and angles and an ORTEP diagram (25 pages). Ordering information is given on any current masthead page.

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