The Synthesis and Single-crystal X-Ray Structure of the First Example of a Tridentate, Di-orthometallated Triphenyl Phosphite Complex

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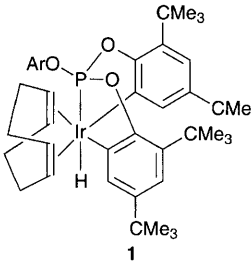
Reaction of $[Ir(cod)(py)_2][PF_6]$ with triphenyl phosphite leads to the previously reported complex $[Ir(cod)\{P(OC_6H_4)(OPh)_2\}\{P(OPh)_3\}]$, but reaction of $[Ir(cod)\{P(OPh)_3\}Cl]$ with methyllithium and subsequent treatment with methanol yields the tridentate di-orthometallated complex $[IrH(cod)\{P(OC_6H_4)_2(OPh)\}]$.

Recently there has been considerable interest[1] in the use of triaryl phosphite complexes of group 9 metals as catalysts in hydroformylation reactions. We wished to extend their use to the hydrogenation of imines,[2] and have prepared a number of novel orthometallated triaryl phosphite iridium precatalysts.[3] There have been several studies of orthometallated phosphite complexes,[4] especially by Singleton and coworkers.[5] We have found that the reaction of tris(2,4-di-*tert*-butylphenyl) phosphite with $[Ir(cod)(py)_2][PF_6]$ produces the di-orthometallated complex $[IrH(cod)\{P(OC_6H_2Bu^t{}_2\text{-}2,6)_2(OC_6H_3Bu^t{}_2\text{-}2,4)\}]$ **1**.[3] The analogous reaction with triphenyl phosphite in methanol did not lead to $[IrH(cod)\{P(OC_6H_4)_2(OPh)\}]$ **2** but rather gave the previously reported[6] compound $[Ir(cod)\{P(OC_6H_4)(OPh)_2\}\{P(OPh)_3\}]$ **3**, presumably due to the lower steric profile of the phosphite. The structure of **3** was confirmed by a poor-quality single-crystal X-ray structure determination,[3] which showed that one of the triphenyl phosphite ligands was mono-orthometallated; the structure was similar to that of the known tri-*o*-tolyl phosphite complex $[Ir(cod)\{P(OC_6H_3Me\text{-}2)(OC_6H_4Me\text{-}2)_2\}\{P(OCH_2)_3CMe\}]$.[7]

To prevent the formation of the bis-phosphite complex we needed to produce a starting material with only one coordinated phosphite. The bridge fission reaction of $[\{Ir(cod)Cl\}_2]$ with triphenyl phosphite in dichloromethane–light petroleum (3 : 1) gave $[Ir(cod)\{P(OPh)_3\}Cl]$ **4**[†] as an orange crystalline solid in 87% yield. Its $^{31}P\{^1H\}$ NMR spectrum consists of a singlet at δ 87.8.

In an attempt to prepare **2**, **4** was heated in methanol at reflux for 6 hours to facilitate orthometallation by hydride transfer from the alcohol to the metal centre. This gave a mixture, the major component of which was identified by $^{31}P\{^1H\}$ NMR spectroscopy as **3**. Reaction of **4** with pyridine in methanol again gave **3** as the only phosphorus-containing species. To encourage removal of the chloride ion, **4** was treated with a methanol solution of ammonium hexafluorophosphate. Whilst this did induce metallation, the predominant phosphorus-containing species was again **3**. It seems that **3** is formed very readily, and, one formed, is relatively inert. This is demonstrated by a lack of reactivity with hydrogen in dichloromethane solution, even after 24 hours.

The compound $[Ir(Me)(PPh_3)_3]$ has been shown to be thermally unstable with respect to orthometallation *via* reductive elimination of methane.[8] Thus we attempted to methylate **4**. Addition of methyllithium to an ether solution of **4** at −78 °C gave an immediate colour change from orange to red. Addition of methanol to the reaction mixture at room temperature produced, within an hour, a yellow solution. Removal of the solvent and recrystallisation of the residue (CH_2Cl_2–Et_2O) yielded **2** as air-stable colourless crystals in 47% yield. The $^{31}P\{^1H\}$ NMR spectrum of **2** consists of a singlet at δ 155.7 which is similar to that in **1** (δ 152.3), suggesting that the *tert*-butyl substituents have little effect on the electron density at posphorus. The ^1H NMR spectrum shows a doublet at δ −7.65 assigned to the metal hydride ($^2J_{PH}$ = 194.5 Hz). The large coupling constant indicates that the phosphorus and hydrogen atoms are *trans*, and is similar to that in **1** ($^2J_{PH}$ = 188.5 Hz). Single-crystal X-ray structure determination[‡] confirms this *trans*-arrangement, and clearly shows that the triphenyl phosphite ligand is doubly orthometallated (Fig. 1). The iridium(III) adopts a distorted octahedral geometry with the double bonds of the cyclooctadiene *trans* to the orthometallated aryl groups. The hydride ligand is tilted towards the metallated aryl groups [mean H(1)–Ir–C = 82(3)°], and away from the cod ligand [mean H(1)–Ir–M = 95.5°]. The largest distortion from ideal geometry is in the coordination of the phosphorus; the Ir–P vector is tilted towards the orthometallated rings, presumably due to ring strain. However, the fact that the mean P–Ir–C(aryl) angle is similar to that in $[Ir(cod)\{P(OC_6H_3Me\text{-}2)(OC_6H_4Me\text{-}2)_2\}\{P(OCH_2)_3CMe\}]$[7] suggests that the orthometallation of the second ring does not significantly increase distortion in the



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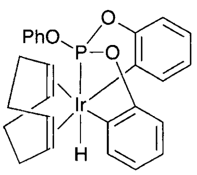

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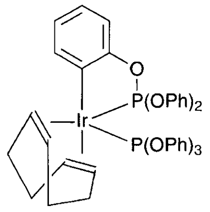

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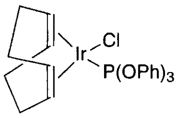

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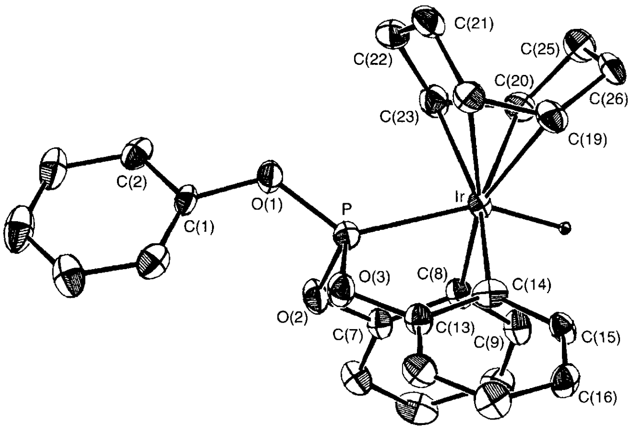

Fig. 1 ORTEP (50% thermal vibration ellipsoids with hydride H atom as an arbitrary sized sphere) view of the structure of $[IrH(cod)\{P(OC_6H_4)_2(OPh)\}]$ **2**. Selected distances (Å) Ir–P 2.246(2), Ir–C(8) 2.064(7), Ir–C(4) 2.070(7), Ir–M(1) 2.158(7), Ir–M(2) 2.168(7), Ir–H 1.45(8). Significant angles (°) M(1)–Ir–M(2) 84.0(3), M(1)–Ir–P 105.4(2), M(1)–Ir–C(14) 90.6(3), H–Ir–P 152(3), C(8)–Ir–C(14) 93.2(3), P–Ir–C(8) 79.6(2), P–Ir–C(14) 78.9(2). M(1) and M(2) are the mid-points of the C(19)–C(20) and the C(23)–C(24) bonds.

system, and should be easy, provided that the relevant vacant coordination site is available.

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Footnotes

† New compounds gave satisfactory spectroscopic and microanalytical data.

‡ *Crystal data* for **2**: $C_{26}H_{26}IrO_3P$, M = 609.7, monoclinic, space group $P2_1/n$ (non-standard no. 14), a = 12.918(6), b = 8.803(2), c = 21.082(7) Å, β = 90.37(3)°, Z = 4, Enraf-Nonius CAD4 diffractometer, λ = 0.71069 Å, T = 173 K, R = 0.032, R_w = 0.037, for 3132 significant reflections, 284 variables. Hydride freely refined isotropically, all other hydrogens fixed at calculated positions. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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