A General Method of Promoting Oxidative Addition of C–H Bonds to Iridium(I) Using Azine Phosphines

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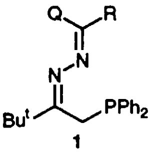
Treatment of [IrCl(CO)$_2$(*p*-toluidine)] with azine phosphines of type Z,E-$PPh_2CH_2C(Bu^t)$=N–N=C(Q)R, Q = H or Me, R = an organic group, activates aryl, heterocyclic, alkenyl or aliphatic C–H bonds to give cyclometallated iridium(III) hydrides.

We have described the crystalline hydrazone phosphine Z-$PPh_2CH_2C(Bu^t)$=NNH_2[1] which readily condenses with aldehydes or ketones, QC(=O)R, to give mixed azines Z,E-$PPh_2CH_2C(Bu^t)$=N–N=C(Q)R of type **1**, where Q is either H or Me, and R is a more sterically demanding group such as an aryl, heterocyclic, alkenyl or *tert*-butyl.[2] On coordination to a metal one would expect the phosphorus and one of the azine nitrogens to coordinate to the metal to give a six-membered chelate ring with the sterically demanding group (R) forced against the metal and, as discussed in the preceding communication, this can be used to generate a strong agostic interaction between R and Ru in some ruthenium complexes. In the present communication we demonstrate that one can similarly create a general method of C–H bond activation (fission) with iridium(I), applicable to aromatic, heterocyclic, alkenyl and saturated C–H bonds, giving a range of iridium(III) hydrides containing C–Ir–H, formed by oxidative addition.

A convenient source of iridium(I) is [IrCl(CO)$_2$(*p*-toluidine)][3] and this on heating with the azine (Z,E)-$PPh_2CH_2C(Bu^t)$=N–N=CHPh, **2a**[1,4] in benzene solution for 5 min at 75 °C, gives the cyclometallated iridium(III) hydride **3a** in 94% isolated yield.[†] Except for when stated otherwise, these conditions were used to react a range of azine phosphines with [IrCl(CO)$_2$(*p*-toluidine)], giving cyclometallated iridium(III) hydrides with excellent selectivity and in isolated yields of 96–68%, which are discussed below. The progress of all the reactions was followed by ^{31}P-{^1H} NMR spectroscopy which established that these cyclometallations were essentially quantitative and specific, apart from the cyclometallation of **12** (see below). The azine **2b** from 3,4,5-trimethoxybenzaldehyde reacts with [IrCl(CO)$_2$(*p*-toluidine)] under the standard conditions to give the cyclometallated hydride **3b** in 96% isolated yield; we have determined the crystal structure of **3b**.[5] We have similarly made the hydrides **3c** and **3d**, using the azines **2c** and **2d** prepared from 4-methoxybenzaldehyde and 4-nitrobenzaldehyde, respectively. Cyclometallation of the azines **2e**, **2f** or **2g** derived from 2-halobenzaldehydes resulted in C–H bond fission exclusively, to give the hydrides **3e**, **3f** or **3g** and not carbon–halogen bond fission. The azine **2h** from 2-hydroxybenzaldehyde underwent O–H fission quite rapidly, *e.g.* at 20 °C in CH_2Cl_2 solution with a reaction time of 20 min, giving **4** in 78% isolated yield. However, **4** isomerised in benzene solution over 1.5 h at *ca.* 75 °C to give the *C*-metallated isomer **3h**, for which ν(O–H) is 3225 cm^{-1}. Treatment of [IrCl(CO)$_2$(*p*-toluidine)] with **2h** in C_6H_6 for 3 h gave **3h** directly in 68% yield.

We have similarly effected C–H bond fission in a range of heterocyclic groups in mixed azines of type **1**. The azine **5a** derived from thiophene-2-carbaldehyde reacted with [IrCl(CO)$_2$(*p*-toluidine)] at 75 °C for 1 h to give the hydride **6a**, *i.e.* the heterocyclic ring is metallated in the 3-position; similarly the azine **5b** derived from *N*-methylpyrrole-2-carbaldeyde metallated in the 3-position to give **6b**. In contrast, the azine from pyrrole-2-carboaldeyde underwent *N*-metallation exclusively, to give **7**. The azine **8**, derived from indole 3-carbaldehyde, *C*-metallated exclusively in the 2-position to give **9**. We have also effected oxidative addition of alkenyl C–H bond. The azine **10a** from 3-methylpent-3-en-2-one gave **11a** in 72% isolated yield and the azine **10b** from *trans*-cinnamaldehyde gave **11b** in 92% yield. C–H bonds in saturated aliphatic groups can also be activated: the azine **12** when treated with [IrCl(CO)$_2$(*p*-toluidine)] for 1.5 h at 75 °C, gave



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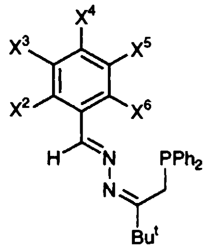
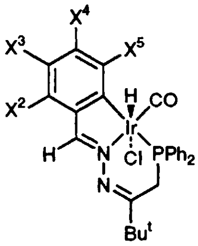
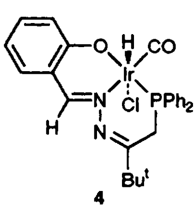


	X^2	X^3	X^4	X^5	X^6
2a	H	H	H	H	H
2b	H	OMe	OMe	OMe	H
2c	H	H	OMe	H	H
2d	H	H	NO_2	H	H
2e	Br	H	H	H	H
2f	Cl	H	H	H	H
2g	F	H	H	H	H
2h	OH	H	H	H	H



	X^2	X^3	X^4	X^5
3a	H	H	H	H
3b	H	OMe	OMe	OMe
3c	H	H	OMe	H
3d	H	H	NO_2	H
3e	Br	H	H	H
3f	Cl	H	H	H
3g	F	H	H	H
3h	OH	H	H	H



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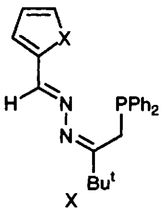
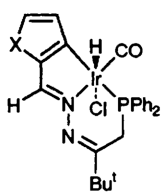
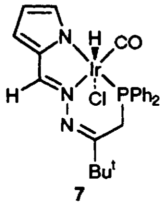


	X
5a	S
5b	NMe
5c	NH



	X
6a	S
6b	NMe



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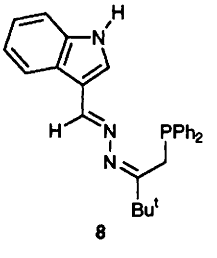

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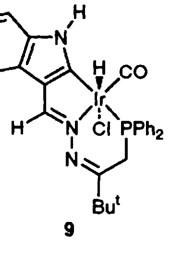

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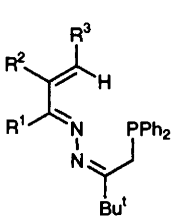
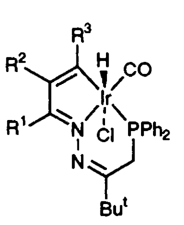
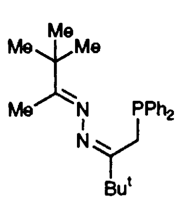


	R^1	R^2	R^3
10a	Me	Me	Me
10b	H	H	Ph



	R^1	R^2	R^3
11a	Me	Me	Me
11b	H	H	Ph



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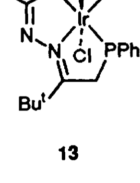

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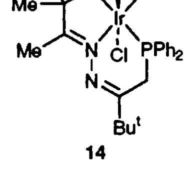

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the hydride **13** in 62% yield, another product was formed but was only characterised by its phosphorus NMR resonance $\delta(P) = 16.7$; this product was possibly **14** formed by oxidative addition of a *tert*-butyl C–H bond.

In this work we have shown that the hydrazone phosphine *Z*-$PPh_2CH_2C(Bu^t)=NNH_2$ is a reagent for converting aldehydes and ketones into azines which cycloiridate readily and with very high selectivity. This synthetic strategy should be applicable to other systems and we are extending the work to other R-groups, particularly to saturated alicyclic rings and to groups containing functionalities; to metals other than iridium; and to other types of azines. We are also studying the chemistry of the cyclometallated hydride species of iridium and of other metals. There is a lot of interest in C–H bond activation and cyclometallation[6–9] and, previously, we have discovered a method of cyclopalladating 'unactivated' *gem*-dimethyls using oximes.[10] This has been coupled with an oxidative cleavage of the metal–carbon bond and has been applied in organic syntheses with excellent results.[11,12] Suitable oxidising agents for breaking the metal–carbon bond include I_2 and particularly $Pb(OAc)_4$–HOAc,[11,12], which converts $C(=O)CMe_2$ into $C(=O)CMe(CH_2OAc)$ and, with a second treatment, into $C(=O)C(CH_2OAc)_2$. Our new cyclometallated compounds might be similarly useful in synthesis.

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Footnote

† New compounds were characterised by elemental analyses and by IR, ^{31}P-$\{^1H\}$ NMR (36.2 MHz), proton NMR (100 MHz) and mass spectrometry. The carbon metallated iridium hydrides each showed a doublet hydride resonance within the range δ −16.7 to −17.8, $^2J(P\text{–}Ir\text{–}H)$ = 9.8 −10.3 Hz. The *O*-metallated hydride **4** had δ_H −16.10 $^2J(P\text{–}Ir\text{–}H)$ = 15.4 Hz. The phosphorus chemical shifts of the various iridium(III) hydrides were within the range δ 9.9–14.6 (in CD_2Cl_2). In the infrared spectra ν(Ir–H) occurred within the range 2170–2195 cm^{-1} apart from **3h**, 2215 cm^{-1}; ν(C≡O) 2030–2055 cm^{-1} (KBr discs).

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