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# Coordinatively unsaturated σ-aryl iridium(III) complexes containing iridium–mercury bonds

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## Abstract

Reaction between the iridium(III) complex $IrHCl_2(PPh_3)_3$ and Hg(*o*-tolyl)$_2$ yields the red, coordinatively unsaturated, mercury-containing, iridium(III) complex Ir(*o*-tolyl){Hg(*o*-tolyl)}Cl$(PPh_3)_2$ (**1**). $^{31}$P–$^{199}$Hg coupling in the $^{31}$P NMR spectrum of **1** confirms the presence of Ir–Hg bonding. Compound **1** undergoes reversible addition of CO to give the six-coordinate complex Ir(*o*-tolyl){Hg(*o*-tolyl)}Cl(CO)$(PPh_3)_2$ (**2**), which, in turn, undergoes reductive-elimination of Hg(*o*-tolyl)$_2$ to give IrCl(CO)$(PPh_3)_2$. Treatment of **1** with HCl or iodine preferentially cleaves the Hg–C bond to give the complexes Ir(*o*-tolyl)Cl(HgX)$(PPh_3)_2$.

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We have been investigating the reaction between transition metal hydrides and organomercury compounds as a route to σ-aryl complexes of transition metals. Recently we reported the syntheses of the σ-aryl ruthenium(II) and osmium(II) complexes MRCl(CO)$(PPh_3)_2$ (M = Ru, Os; R = phenyl, *p*-tolyl, *o*-tolyl) from MHCl(CO)$(PPh_3)_2$ and $HgR_2$ (eq. 1) [1].

$$MHCl(CO)(PPh_3)_3 + HgR_2 \rightarrow MRCl(CO)(PPh_3)_2 + Hg + PPh_3 + RH \quad (1)$$

(R = phenyl, *p*-tolyl, *o*-tolyl)

The reaction is thought to proceed either via oxidative addition of $HgR_2$ followed by reductive elimination of RH and thermal elimination of mercury, or via a hydrido-bridged species. Results reported here support the oxidative addition pathway. The scope of this reaction has been extended to include a route to coordinatively unsaturated σ-aryl complexes of iridium(III). Thus the reaction between $IrHCl_2(PPh_3)_3$ and $HgR_2$ (R = phenyl, *p*-tolyl) gave $IrRCl_2(PPh_3)_2$ in ca. 50% yield (eq. 2) [2].

$$IrHCl_2(PPh_3)_3 + HgR_2 \rightarrow IrRCl_2(PPh_3)_2 + Hg + PPh_3 + RH \quad (2)$$

Herein we report the anomalous reaction between $IrHCl_2(PPh_3)_3$ and Hg(*o*-tolyl)$_2$.

On heating $IrHCl_2(PPh_3)_3$ and Hg(*o*-tolyl)$_2$ in benzene at reflux for ca. 1 h a deep red solution developed and some elemental mercury was deposited. From this solution a red crystalline solid was isolated in 20% yield. Analytical and spectro-

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Table 1

$^1$H NMR data [a] for iridium compounds [b]

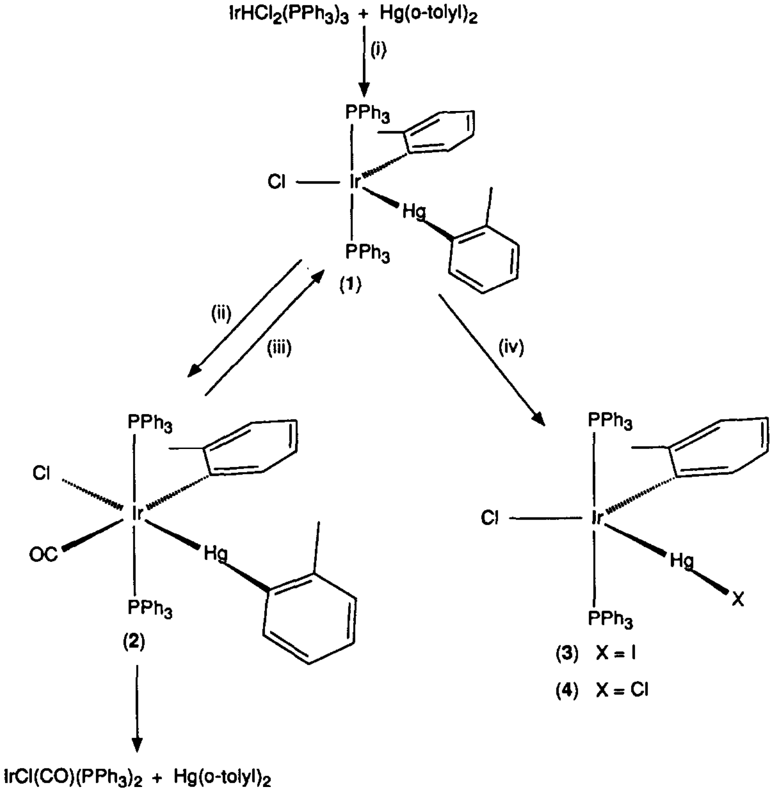
| Compound | $^1$H NMR data |
|---|---|
| **1** | 7.60 (12H, m, $PPh_3$), 7.48 (1H, m, $C_6\mathit{H}_4CH_3$), 7.30 (6H, m, $PPh_3$), 7.20 (12H, m, $PPh_3$), 7.01 (1H, m, $C_6\mathit{H}_4CH_3$), 6.92 (1H, m, $C_6\mathit{H}_4CH_3$), 6.41 (1H, m, $C_6\mathit{H}_4CH_3$), 6.06 [1H, d, $J$(H–H) 7.8, $C_6\mathit{H}_4CH_3$], 6.01 [1H, d, $J$(H–H) 7.5, $C_6\mathit{H}_4CH_3$], 5.80 (2H, m, $C_6\mathit{H}_4CH_3$), 2.07 (3H, s, $HgC_6H_4C\mathit{H}_3$), 1.45 (3H, s, $C_6H_4C\mathit{H}_3$) |
| **2** | 7.59 (12H, m, $PPh_3$), 7.49 (1H, m, $C_6\mathit{H}_4CH_3$), 7.22 (6H, m, $PPh_3$), 7.15 (12H, m, $PPh_3$), 7.06 (2H, m, $C_6\mathit{H}_4CH_3$), 6.98 [1H, vt, $J$(H–H) 7.2, $C_6\mathit{H}_4CH_3$], 6.80 [1H, d, $J$(H–H) 6.9, $C_6\mathit{H}_4CH_3$], 6.45 [1H, vt, $J$(H–H) 6.3, $C_6\mathit{H}_4CH_3$], 6.44 [1H, vt, $J$(H–H) 7.1, $C_6\mathit{H}_4CH_3$], 5.78 [1H, vt, $J$(H–H) 6.95, $C_6\mathit{H}_4CH_3$], 1.93 (3H, s, $C_6H_4C\mathit{H}_3$), 1.91 (3H, s, $C_6H_4C\mathit{H}_3$) |
| **3** | 7.54 (12H, m, $PPh_3$), 7.34 (6H, m, $PPh_3$), 7.25 (12H, m, $PPh_3$), 6.49 [1H, vt, $J$(H–H) 7.3, $C_6\mathit{H}_4CH_3$], 5.95 [1H, d, $J$(H–H) 6.7, $C_6\mathit{H}_4CH_3$], 5.84 [1H, vt, $J$(H–H) 7.4, $C_6\mathit{H}_4CH_3$], 5.38 [1H, d, $J$(H–H) 7.5, $C_6\mathit{H}_4CH_3$], 0.92 (3H, s, $C_6H_4C\mathit{H}_3$) |
| **4** | 7.54 (12H, m, $PPh_3$), 7.34 (6H, m, $PPh_3$), 7.25 (12H, m, $PPh_3$), 6.52 [1H, vt, $J$(H–H) 7.2, $C_6\mathit{H}_4CH_3$], 5.97 [1H, d, $J$(H–H) 7.2, $C_6\mathit{H}_4CH_3$], 5.83 [1H, vt, $J$(H–H) 7.5, $C_6\mathit{H}_4CH_3$], 5.40 [1H, d, $J$(H–H) 7.6, $C_6\mathit{H}_4CH_3$], 0.81 (3H, s, $C_6H_4C\mathit{H}_3$) |

[a] Recorded at 400 MHz in [$^2$H]-chloroform. Values given as chemical shift ($\delta$, relative to tetramethylsilane) [relative intensity, multiplicity, coupling ($J$ in Hz), assignment]; s = singlet, d = doublet, vt = virtual triplet, m = multiplet. [b] Satisfactory C, H, and Cl analyses were obtained for compounds **1**, **3** and **4**.

scopic data were consistent with the formulation Ir($o$-tolyl){Hg($o$-tolyl)}Cl$(PPh_3)_2 \cdot (CH_2Cl_2)_{0.33}$ (**1**). The $^1$H NMR spectrum (see Table 1) shows two sets of tolyl resonances, with two singlets at 2.07 and 1.45 ppm, which can be assigned to the –Hg($o$-tolyl) and the -($o$-tolyl) methyl groups respectively by comparison with the $^1$H NMR spectra of Hg$(o\text{-tolyl})_2$ (2.56 ppm) and Ru($o$-tolyl)Cl(CO)$(PPh_3)_2$ (1.47 and 1.14 ppm) [1]. The $^{13}C\{^1H\}$ NMR spectrum also shows two sets of tolyl resonances with the methyl carbon resonances at 28.21 and 24.12 ppm. The $^{31}P\{^1H\}$ spectrum exhibits a singlet at 15.70 ppm, and mercury satellites with a coupling constant, $J(^{31}P–^{199}Hg)$, of 204.5 Hz. Thus the spectroscopic data are consistent with a complex containing two equivalent phosphine ligands and with $o$-tolyl and Hg($o$-tolyl) groups bound to iridium. It is reasonable to assume that **1** adopts an approximately trigonal bipyramidal geometry with the phosphine ligands occupying the apical positions, as for Ru($o$-tolyl)Cl(CO)$(PPh_3)_2$ [1], for steric reasons. Unfortunately crystals of **1**, grown from dichloromethane–ethanol, were found to be unsuitable for single-crystal X-ray structure determination.

A simple reaction mechanism where oxidative addition of Hg$(o\text{-tolyl})_2$ is followed by reductive elimination of HCl may be proposed. The low yield of **1**, ca. 20%, would be explained by decomposition of **1** in the presence of HCl.. However, addition of a large excess of a non-coordinating base, such as 2,6-lutidine or triethylamine, to the reaction mixture failed to increase the yield, thus suggesting that the mechanism might be more complicated.

Compound **1** is soluble is common polar organic solvents and is stable to air and water in both the solid state and solution. It is reasonably thermally stable,



(i) $C_6H_6$, reflux, 1.5 hr., 20%. (ii) CO, 1 atm. (iii) Reduced pressure.
(iv) $I_2$ or HCl : **3** 78%, **4** 50%.

Scheme 1.

decomposing only slowly in boiling *o*-xylene (b.p. 145 °C) with deposition of elemental mercury.

A solution of compound **1** in dichloromethane readily added CO to give a colourless solution of Ir(*o*-tolyl){Hg(*o*-tolyl)}Cl(CO)$(PPh_3)_2$ (**2**) (see Scheme 1). Under reduced pressure the solution of **2** regenerated the red solution of **1**, indicating the labile nature of the carbonyl ligand. The characterization of **2** is based on spectroscopic data. The IR spectrum shows the carbonyl stretch at 2000 $cm^{-1}$. The $^1H$ NMR spectrum shows two sets of tolyl resonances with the methyl resonances at 1.93 and 1.91 ppm, and the $^{31}P\{^1H\}$ NMR spectrum exhibits a singlet at −4.93 ppm and mercury satellites with a coupling constant, $J(^{31}P–^{199}Hg)$, of 284.5 Hz. It is reasonable to assume that CO addition occurs *trans* to the *o*-tolyl group, since this has the largest *trans* influence. Compound **2** is unstable in particular with respect to reductive elimination of Hg(*o*-tolyl)$_2$ yielding IrCl(CO)$(PPh_3)_2$ as evidenced by $^1H$ NMR and IR spectroscopy. This further supports the formulations of **1** and **2**.

Treatment of compound **1** with one equivalent of iodine yielded the green, five-coordinate complex Ir(*o*-tolyl)Cl(HgI)$(PPh_3)_2$ (**3**) in 78% yield. Compound **3** was characterized by elemental analysis and IR, $^{1}H$ and $^{31}P\{^{1}H\}$ NMR spectroscopy. In particular the $^{1}H$ NMR spectrum shows only one set of tolyl resonances with the methyl resonance at 0.81 ppm, indicating that the tolyl group is bound to iridium not mercury, and the $^{31}P\{^{1}H\}$ NMR spectrum exhibits a singlet at 10.72 ppm and mercury satellites with a coupling constant, $J(^{31}P-^{199}Hg)$, of ca. 400 Hz. Careful addition of HCl to **1** yielded a green compound (**4**), the spectroscopic properties of which are very similar to those of **3**. The analytical data are consistent with the formulation $Ir(o\text{-tolyl})Cl(HgCl)(PPh_3)_2 \cdot (CH_2Cl_2)_{0.33}$. Thus the Hg–C bond is cleaved by $I_2$ and HCl in preference to the Ir–Hg and Ir–C bonds in **1**.

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