Electrophilic Ligand Abstraction from Electron-rich Iridium(I) Complexes with Me_3SiOTf; Evidence for Direct Ligand Attack

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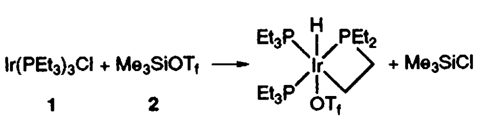
Me_3SiOTf (Tf = CF_3SO_2) is a useful reagent for electrophilic abstraction reactions involving electron-rich complexes $RIrL_n$ (R = H, Cl, Me, Ph; L = PMe_3, PEt_3); direct external attack of Me_3Si^+ on R is probably involved.

Generation of vacant coordination sites by ligand abstraction is commonplace in inorganic and organometallic chemistry. Normally, this abstraction is based on generation of insoluble salts, such as when Ag^+ or Tl^+ are used for halide abstraction. However, with electron-rich, low-valent complexes, this may be a problematic procedure because of competing electron transfer processes. Thus, in our attempt to abstract the chloride ligand from $Ir(PEt_3)_3Cl$ **1** with Ag^+, immediate formation of silver metal and uncharacterized iridium complexes took place. By contrast, reaction of **1** with trimethylsilyl triflate, Me_3SiOTf **2**[1] at room temperature in benzene results in immediate quantitative formation of the novel iridiacycle **3**† and Me_3SiCl‡ [eqn(1)].



(1)

1 **2** **3**

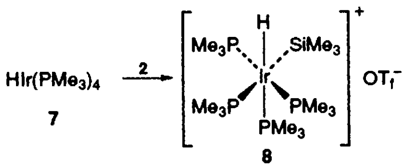
It is very likely that **3** is formed by ligand metallation in the unobserved intermediate $Ir(PEt_3)_3{}^+OTf^-$.

The reaction is not limited to halide abstraction. Facile dealkylation to form Me_4Si‡ and $Ir(PMe_3)_4{}^+OTf^-$ **4**§ is observed when the saturated $MeIr(PMe_3)_4$[2] is reacted with **2** under similar conditions [eqn. (2)]. The analogous dearylation involving the unsaturated complex $PhIr(PMe_3)_3$[3] is slow, taking hours at room temperature to reach completion and an added equivalent of PMe_3 is required for quantitative formation of **4** and $PhSiMe_3$.‡

$$RIr(PMe_3)_n \xrightarrow{\mathbf{2}} \underset{\mathbf{4}}{Ir(PMe_3)_4{}^+OTf^-} + RSiMe \qquad (2)$$

5; R = Me, *n* = 4
6; R = Ph, *n* = 3

Metal hydride complexes are also reactive. Reaction of the saturated $HIr(PMe_3)_4$[4] **7** with **2** leads to the remarkably sterically congested hydrido silyl complex **8**.¶ The reaction is relatively slow at room temperature, showing 30% conversion after 2 h and taking 24 h to reach completion [eqn(3)].

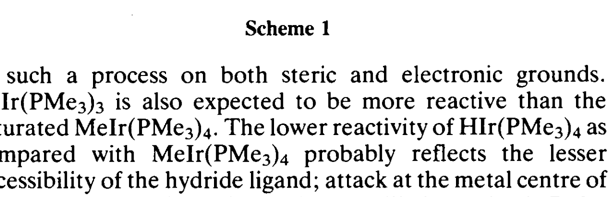


(3)

7 **8**

Mechanistically, these reactions may proceed *via* two main pathways: (*a*) electrophilic attack at the electron-rich metal centre followed by Si–X (X = Cl, Me, Ph) reductive elimination, (*b*) direct electrophilic attack of Me_3Si^+ on the ligand. It is likely that an η^2-SiR complex is formed, which then undergoes Si–H oxidative addition or dissociation of Me_3SiR (R = Ph, Me, Cl) (Scheme 1). η^2-Si-H complexes are well known.[5]

We firmly believe that route (*b*) is operative. The observed trend of relative rates of the reaction with **2**, $Ir(PEt_3)_3Cl$ > $MeIr(PMe_3)_4$ > $PhIr(PMe_3)_3$ > $HIr(PMe_3)_4$ is not the expected one for electrophilic attack on the metal. Thus, $PhIr(PMe_3)_3$ is expected to be more reactive than $Ir(PEt_3)_3Cl$ in such a process on both steric and electronic grounds. $PhIr(PMe_3)_3$ is also expected to be more reactive than the saturated $MeIr(PMe_3)_4$. The lower reactivity of $HIr(PMe_3)_4$ as compared with $MeIr(PMe_3)_4$ probably reflects the lesser accessibility of the hydride ligand; attack at the metal centre of the saturated $HIr(PMe_3)_4$ is highly unlikely. Indeed, PMe_3 dissociation from this complex is very difficult.[4]



Scheme 1

In addition, the Ir^{III} complexes that would be formed by attack at the metal, $(PMe_3)_4Ir(R)(SiMe_3)^+$ are expected to be stable towards Si–R reductive elimination at 25 °C. For example, heating at 100 °C is required in order to cause reductive elimination from *mer*-$(PMe_3)_3Ir(H)(SiR_3)(Me)$ (R = Et, Ph, EtO).[6] Also, $(PMe_3)_4IrMe(H)^+$ is thermally stable.[2]

The reagent Me_3SiOT_f is very useful in organic chemistry[7] and has been utilized with metal complexes as well,[8] although to a much lesser extent. This work clearly demonstrates that it is of particular advantage for electrophilic ligand abstraction from electron-rich metal systems, where competing electron transfer processes may otherwise prevail. Since, as we show here, the bulky Me_3Si^+ most likely attacks the ligand directly, coordinative unsaturation at the metal centre is not required.

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Footnotes

† *Spectral data* for **3**: ^1H NMR (C_6D_6): δ −29.57 (dt, $J_{H\text{-}P_1}$ 11.5, $J_{H\text{-}P_2}$ 14.5, $J_{H\text{-}P_3}$ 14.5 Hz, 1 H, Ir–H); 0.8–0.9 (m, 24 H, PCH_2CH_3); 1.5, 1.9 (multiplets, 16 H, PCH_2CH_3); 3.96 (m, 1 H), 3.57 (m, 1 H); 2.57 (m, 1 H); 1.23 (m, 1 H); C-Hs of the ring. $^{31}P\{^1H\}$ NMR (C_6D_6): δ −5.70 (t, *J* 11.0 Hz, 1 P, PEt_3 *trans* to CH_2); −6.09 (dd, $J_{P\text{-}P\,(trans)}$ 335.6, $J_{P\text{-}P\,(cis)}$ 10.8 Hz, 1 P, PEt_3 *trans* to P); −77.05 (dd, $J_{P\text{-}P\,(trans)}$ 335.6, $J_{P\text{-}P\,(cis)}$ 11.3 Hz, 1 P, ring P).

‡ These silyl compounds were detected by ^1H NMR and GC-MS.

§ ^{31}P and ^1H NMR of **4** are essentially the same as reported for $Ir(PMe_3)_4{}^+PF_6{}^-$.[2]

¶ *Spectral data* for **8**: ^1H NMR (C_6D_6): δ −14.4 (ddt, $J_{H\text{-}P\,(trans)}$ 109.6, $J_{H\text{-}P\,(cis)}$ 13.8, $J_{H\text{-}P\,(cis)}$ 20.7 Hz, 1 H, Ir–H); 0.32 (d, *J* 2.1 Hz, 9 H, $SiMe_3$); 1.32 (d, *J* 7.4 Hz, 9 H, PMe_3); 1.33 (vt, *J* 3.2 Hz, 18 H, 2PMe_3 *trans*); 1.55 (d, *J* 7.3 Hz, 9 H, PMe_3). $^{31}P\{^1H\}$ NMR (C_6D_6): δ −67.9 (dt, J_d 22.6, J_t 25.4 Hz, 1 P); −63.6 (dt, J_d 22.7, J_t 20.9 Hz, 1 P); −56.5 (dd, J_1 25.3, J_2 20.6 Hz, 2 P).

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