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Preliminary communication

Reactions of nitrilium triflate salts with *trans*-$[IrCl(CO)(PPh_3)_2$

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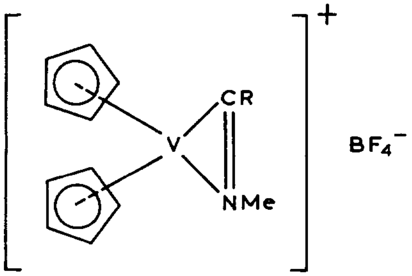
Abstract

Low yields of the ionic carbene complexes $[Ir(RC{=}NHMe)Cl(CO)(PPh_3)_2(O_3SCF_3)]O_3SCF_3$ ($R = Ph$ or $PhCH_2$) have been isolated from the reactions of *trans*-$[IrCl(CO)(PPh_3)_2]$ with the nitrilium triflate salts, $[RC{\equiv}NMe]O_3SCF_3$. The major products from these, and the similar reactions of the nitrilium salts where R = Me or Bu^t, are amorphous, yellow complexes $[Ir(RC{=}NMe)Cl(CO)(PPh_3)_2]O_3SCF_3$.

To our knowledge the only previous report of reactions between nitrilium salts and low valent transition metal complexes is that by Barefield and Carrier [1] on the reaction of vanadocene with $[RC{\equiv}NMe]BF_4$ ($R = Ph$ or Me) to give the maroon η^2-iminoacyl derivatives **1**.

We now report that reaction between the nitrilium triflate salts $[RC{\equiv}NMe]O_3SCF_3$ ($R = Ph$ or $PhCH_2$) [2] and *trans*-$[IrCl(CO)(PPh_3)_2]$ in dry chloroform over 48 h at room temperature give deep orange solutions from which white crystals of **2** (m.p.



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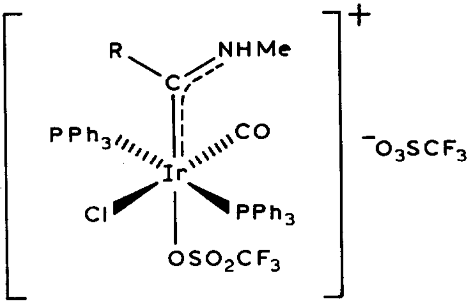
184–186 °C, 14%) and **3** (m.p. 222 °C with decomp., 9%) can be isolated by careful addition of diethyl ether. The major products of these reactions are the amorphous, pale yellow solids **4** (m.p. 116 °C with decomp., 58%) and **5** (m.p. 89–92 °C with decomp., 77%) respectively.

From elemental analysis (C, H, N and P), both **2** and **3** have the composition $[Ir(RC{=}NHMe)Cl(CO)(PPh_3)_2(O_3SCF_3)_2]$. The IR spectra are very similar and show ν(N–H) at 3200w and 3145m (for **2**) and 3200w, 3160m cm^{-1} (for **3**), with a strong, sharp ν(C≡O) band at 2080 cm^{-1} in the region expected for an iridium(III) complex [3] in which the carbonyl ligand is probably *trans* to Cl [4]. The spectra show no evidence of a ν(C≡N) vibration (cf. ν(C≡N) of nitrilium salts ca. 2325 cm^{-1} [2]), but have a strong, sharp ν(C=N) vibration at 1603 cm^{-1}, which is intermediate between the expected frequency for an η^1-iminoacyl ligand (ca. 1570 cm^{-1} [3]), and an η^2-iminoacyl ligand (cf. 1745 cm^{-1} in complex **1**), and is in the range of 1596–1607 cm^{-1} reported [5] for the ν(C=N) vibrations in the rhodium carbene complexes $[Rh(ArC{=}NHR)Cl_3(CO)(Ph_2PMe)]$. A *trans* arrangement for the triphenylphosphine ligands is assigned from the relative intensities (1570 > 1580 cm^{-1}) of the weak IR bands associated with these ligands [6,7]. The IR spectra also show strong triflate group absorptions at 1335, 1255–1270, 1220, 1200, 1120–1170, 1030, 980 and 630 cm^{-1}, and from the number and complexity of these absorptions it is evident that both an η^1-O_3SCF_3 ligand and $CF_3SO_3^-$ anion are present [8]. This is confirmed by the ^{19}F NMR spectrum ($CDCl_3$) which shows two singlets at 0.10 and 0.21 ppm (**2**), and 0.12, 0.16 ppm (**3**) to low field of trifluoroacetic acid reference. Addition of 0.3 cm^3 of $(CD_3)_2CO$ to the $CDCl_3$ solution of **3** caused immediate disappearance of the band at 0.16 ppm leaving only the singlet at 0.12 ppm for the triflate anion. In a separate experiment addition of methanol to solid **2** caused immediate and quantitative conversion to *trans*-$[IrCl(CO)(PPh_3)_2]$, confirming the lability of the η^1-O_3SCF_3 ligand in these complexes; a similar lability has been noted for the complex $[IrMeCl(O_3SF)(CO)(PPh_3)_2]$ in acetonitrile or nitromethane [9]. As the complexes were only sparingly soluble in $CDCl_3$ and polar, deuterated solvents could not be used the ^1H NMR spectra (220 MHz) were not of high quality, but were in general agreement with the assigned structures [**2** δ 3.50 (d, 3H, N-CH_3, $J \sim 5$ Hz) and 7.3–7.65 (broad m, ca. 33H, C_6H_5) ppm; **3** δ(H) 2.75 (d, 3H, N-CH_3, $J \sim 5$ Hz), 3.70 (s, 2H, CH_2) and 7.0–8.0 (broad m, ca. 33H, C_6H_5) ppm.

Hence, the available spectroscopic evidence indicates that **2** and **3** are carbene complexes, although the relative contributions of the two canonical forms, Ir=CR–NHMe ↔ Ir–CR=NHMe, and a definite assignment of the positions of the other ligands must await an X-ray structure determination.

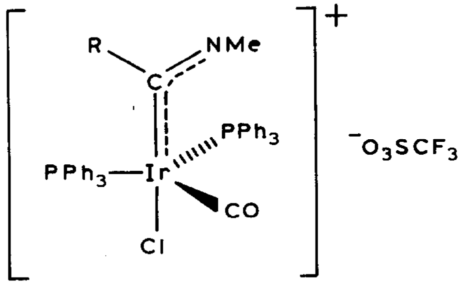
Some indication of the strength of the Ir–carbene bond comes from mass spectrometry. Electron impact mass spectrometry was ineffective for samples of **2** and **3**, but an excellent spectrum of **2** was obtained by the fast atom bombardment (FAB) technique [10] using 3-nitrobenzyl alcohol as the matrix. This spectrum exhibits an intense cluster at m/z 1048, which may be interpreted as the ion $[IrCl(O_3SCF_3)(PhC{=}NHMe)(CO)(PPh_3)_2]^+$ (A) loss of the triflate ligand from **A** gives rise to a fragment ion at m/z 899. However, the isotope pattern is not characteristic and an interpretation involving the loss of both the ligand and the ligand plus hydrogen may offer an explanation. A similar isotopic pattern is observed at m/z 871 which would arise owing to the loss of CO from both the



(2,R = Ph;
3,R = PhCH$_2$)

above species. The loss of PPh$_3$ from A leads to a fragment ion peak seen at m/z 786 from which elimination of triflate plus hydrogen gives rise to the peak observed at m/z 636, subsequent loss of CO produces the fragment ion at m/z 608. A peak observed at m/z 572 may be interpreted as the elimination of (Cl + H) from m/z 608. There appears to be no evidence for the loss of PhC=NHMe, suggesting that the carbene structure may make the major contribution to the bond to Ir in this complex.

The amorphous, yellow complexes **4** and **5** proved difficult to purify. They cannot be chromatographed and on attempted crystallisation form thick oils which froth and solidify on removal of solvent under high vacuum. Elemental analysis indicates a stoichiometry [Ir(RC=NMe)Cl(CO)(PPh$_3$)$_2$(O$_3$SCF$_3$)]. The IR spectra (CHCl$_3$) show no N–H absorption, and two bands (one strong and sharp at 2080 cm^{-1} and the other broad at 2060 cm^{-1}) in the iridium(III) metal carbonyl region. Both spectra show characteristic strong bands at 1220, 1240–1290, 1155, 1090, 1028 and 632 cm^{-1} for CF$_3$SO$_3^-$ anion, but no bands in the region 1330–1380 cm^{-1} indicative of an η^1-O$_3$SCF$_3$ ligand. The spectra also have a broad absorption in the



(4,R = Ph;
5,R = PhCH$_2$)

ν(C=N) region, 1550–1680 cm^{-1}, but this is too complex to be due to a simple C=N stretching vibration. The ^1H NMR spectra ($CDCl_3$, 220 MHz) show the following bands: **4** δ 3.13 (s, 3H, N-CH_3)), 7.2–8.00 (m, ca. 35H, C_6H_5); **5** δ 2.55 (s, 3H, N-CH_3), 3.40 (s, 2H, CH_2), 7.2–8.10 (m, ca. 35H, C_6H_5) ppm. The ^{19}F spectra have only a single band at 0.05 (**4**) and 0.06 (**5**) ppm downfield of TFA confirming that only anionic triflate groups are present. Attempts to obtain FAB mass spectra in 3-nitrobenzyl alcohol gave no assignable fragment ions. The very limited evidence available suggests that the compounds may have the iminoacyl structures shown below, but they do not behave as simple monomers and may be polymeric.

Analogous yellow complexes **6** (R = Me, m.p. 113°C with decomp., 65%) and **7** (R = CMe_3, m.p. 82°C with decomp., 100%) have also been obtained from the reactions of *trans*-$[IrCl(CO)(PPh_3)_2]$ with $[MeC{\equiv}NMe]O_3SCF_3$ and $[Me_3CC{\equiv}NMe]O_3SCF_3$ respectively under similar conditions. There was no evidence in these reactions for formation of white complexes analogous to **2** and **3**, and it is possible that **2** and **3** are by-products arising from reaction of the yellow complexes (or a precursor) with adventitious triflic acid present in the nitrilium salts used. This possibility is being investigated.

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