Fluoroalkylimido-complexes of Group VIII Metals

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Summary 2*H*-Hexafluoropropyl azide reacts with a number of low-valent metal complexes to form a series of mononuclear fluoroalkylimido-derivatives: some of these complexes undergo ligand-addition reactions.

A NITRENE† complex of ruthenium has recently been postulated as an unstable intermediate in the conversion of $[(H_3N)_5RuN_3]^{2+}$ into $[(H_3N)_5RuN_2Ru(NH_3)_5]^{4+}$ by acid,[1] while organic azides and $(Ph_3P)_2Ir(CO)Cl$ afford the dinitrogen complex $(Ph_3P)_2Ir(N_2)Cl$ rather than "nitrenes".[2] Isolation of a stable perfluoromethylimidoiridium complex by N–N bond cleavage of hexafluoroazomethane[3] suggests that fluoroalkylimido-complexes might have enhanced stability, thereby permitting more detailed study of the chemistry of this type of complex.

Reaction between 2*H*-hexafluoropropyl azide[4] and $(Ph_3P)_2Ir(CO)Cl$ in benzene at room temperature affords $(Ph_3P)_2Ir(CO)(Cl)(NR_F)$ ($R_F = CF_3{\cdot}CHF{\cdot}CF_2$) (I), the i.r. spectrum of which shows ν_{CO} at 2069 cm^{-1} indicating the presence on iridium of a strongly electron-withdrawing ligand.[5] The ^{19}F n.m.r. spectrum [δ 74·3 (3F), 139·5 (2F), and 152·4 (1F) p.p.m. (relative to CCl_3F)] is consistent with the presence of a $CF_3{\cdot}CHF{\cdot}CF_2$ group.[4] The compound $(Ph_3P)_2Ir(N_2)Cl$[2] reacts with $CF_3{\cdot}CHF{\cdot}CF_2{\cdot}N_3$ to give the four-co-ordinate complex $(Ph_3P)_2Ir(NR_F)Cl$ (II) with concomitant loss of molecular nitrogen. Similarly, $(Ph_3P)_3RhCl$[6] with $CF_3{\cdot}CHF{\cdot}CF_2{\cdot}N_3$ affords $(Ph_3P)_2Rh(NR_F)Cl$ (III) [ν_{Rh-Cl} 289 cm^{-1}].

2*H*-Hexafluoropropyl azide also reacts with metals of the iron triad in zero-oxidation state (d^8). The compounds $(Ph_3P)_2M(CO)_3$ (M = Ru or Os) yield complexes $(Ph_3P)_2M(CO)_2(NR_F)$, the i.r. spectra of which show two ν_{CO} bands at 1979 and 2046 cm^{-1} (IV; M=Ru) and 1968 and 2042 cm^{-1} (V; M=Os), respectively, indicating a *cis*-arrangement of the carbonyl groups.

The d^{10} compounds $(Ph_2PMe)_4M$ (M = Pd or Pt) react with $CF_3{\cdot}CHF{\cdot}CF_2{\cdot}N_3$ in benzene to give the deep-red microcrystalline trico-ordinate complexes $(Ph_2PMe)_2MNR_F$ (VI; M=Pd, VII; M=Pt). The ^1H n.m.r. spectra show the CH_3 signal as a doublet (J_{PH} 12 Hz).

With the exception of (VI), the above complexes are air stable at room temperature. They are all insoluble in most non-polar solvents, and all have ^{19}F n.m.r. signals at about δ 75 (3F), 140 (2F), and 152 (1F) p.p.m. (relative to CCl_3F).

If the imido-ligand may be regarded formally as being in the singlet state, then a *p*-orbital on the nitrogen would be vacant, and so able to accept electron density from a filled metal *d*-orbital; back-bonding would be enhanced by the strongly electron-withdrawing fluoroalkyl group. It may be essential for the metal to have σ-donor ligands, *e.g.* phosphines, present so as to enhance its ability to engage in synergic bonding with the fluoroalkylimido-ligand. Interestingly, $Ru_3(CO)_{12}$, which contains only strongly π-acceptor ligands, reacts with $CF_3{\cdot}CHF{\cdot}CF_2{\cdot}N_3$ to give a cluster compound $Ru_3(CO)_9(NR_F)_2$ (VIII), analogous to the product from $Fe_2(CO)_9$ and $CH_3{\cdot}N_3$.[7]

The co-ordinatively unsaturated complexes (II) and (III) undergo ligand-addition reactions. For example, (III) reacts with hexafluoroacetone and acetyl chloride to give $(Ph_3P)_2Rh(NR_F)[(CF_3)_2CO]Cl$ (IX) and $(Ph_3P)_2Rh(NR_F)(COCH_3)Cl_2$ (X), respectively. The ^{19}F n.m.r. spectrum of complex (IX) shows bands at δ 75·9 (3F), 78·1 (6F), 140·1 (2F), and 153·0 (1F) p.p.m., as expected for the presence of co-ordinated $CF_3{\cdot}CHF{\cdot}CF_2{\cdot}N$ and $(CF_3)_2CO$[8] groups. The ^1H and ^{19}F n.m.r. spectra of (X) are consistent with the formulation, as is the presence of ν_{CO} (max) at 1615 cm^{-1}. Complex (II) reacts with mercuric chloride to form $(Ph_3P)_2Ir(NR_F)(HgCl)Cl_2$, and on carbonylation affords (I) without displacement of the R_FN ligand. In contrast, (III) reacts with CO to give $(Ph_3P)_2Rh(NR_F)(CO)Cl$ (XI) (ν_{CO} 2088 cm^{-1}) and $(Ph_3P)_2Rh(CO)Cl$. Satisfactory analytical and molecular weight data have been obtained on all of the above complexes.

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† A referee has pointed out that according to IUPAC rules such compounds should more correctly be referred to as imido-complexes. Accordingly, the new compounds described herein are referred to as fluoroalkylimido-derivatives.

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