Reactions of Co-ordinated Ligands. Part X.[1] Reactions of Trifluoroacetonitrile with π-Allylic Complexes of Iridium(I) and with Dicarbonyl(cyclopentadienyl)methyliron: the Molecular and Crystal Structure of Carbonyl(η-cyclopentadienyl)-1-[(1-iminotrifluoroethyl)imino]trifluoroethyl-N^{ω}-iron †

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Reactions of trifluoroacetonitrile with $[Ir(\pi\text{-}2\text{-}MeC_3H_4)(CO)(L)_2]$ ($L = PPh_3$ or $AsPh_3$) yield six-membered chelate ring complexes $[IrNHC(CF_3)=C(CMe=CH_2)C(CF_3)=NH(CO)(L)]$ ($L = PPh_3$ or $AsPh_3$). A similar reaction of CF_3CN with $[Ir(\pi\text{-}C_3H_5)(CO)(PPh_3)_2]$ yields $[IrNHC(CF_3)=C(CH=CH_2)C(CF_3)=NH(CO)(PPh_3)]$ together with $[IrNH=C(CF_3)N=C(CF_3)NH(CO)(PPh_3)_2]$. Reactions of $[Ir(\pi\text{-}1\text{-}MeC_3H_4)(CO)(PPh_3)_2]$, $[IrH(CO)_2(PPh_3)_2]$, or $[IrH(CO)(PPh_3)_3]$ with CF_3CN yield a five-membered chelate ring complex *trans*-$[IrNH=C(CF_3)N=C(CF_3)(CO)(PPh_3)_2]$. An *X*-ray crystallographic study of the complex obtained from the reaction of CF_3CN with $[FeMe(CO)_2(\eta\text{-}C_5H_5)]$ shows it to have the five-membered ring structure $[FeNH=C(CF_3)N=C(CF_3)(CO)(\eta\text{-}C_5H_5)]$, in which the Fe–N–C–N–C ring together with the H atom of the NH group and the C atoms of the two CF_3 groups are planar. Reaction of this latter complex with dimethylphenylphosphine yields $[FeNH=C(CF_3)N=C(CF_3)(PMe_2Ph)(\eta\text{-}C_5H_5)]$.

THERE has been considerable interest in the reactions of electronegatively substituted multiple bonds with low-valent transition-metal complexes, and the reactions of fluorinated olefins, hexafluorobut-2-yne, and hexafluoroacetone have been studied in detail.[2] Trifluoroacetonitrile has, however, received relatively little attention. Reaction of CF_3CN with $[Pt(trans\text{-stilbene})(PPh_3)_2]$ has been reported to yield a complex which was crystallographically characterised as (I), in which the electronegatively substituted nitrile group is bonded side-on to the platinum in what is essentially an oxidative–addition product.[3] An analogous reaction of CF_3CN with $[Pt(PPh_3)_4]$ yielded, however, a different complex, (II), derived from two molecules of CF_3CN, the structure of which has also been confirmed crystallographically.[4] Finally, an iron complex, formulated by King as (IIIa), has been isolated from the reaction of CF_3CN with $[FeMe(CO)_2(\eta\text{-}C_5H_5)]$.[5] Complex (IIIa) purportedly contains an end-on bonded CF_3CN ligand, which is not displaced by donor ligands such as PPh_3, substitution of the carbonyl group being preferred. The nature of the bonding of the CF_3CN ligand in (IIIa) has been the subject of an extensive discussion by King.[5] The known chemistry of CF_3CN is apparently little understood and, in particular, any preferences in its nature of bonding to transition-metal systems are at present unclear.

RESULTS

We have previously reported the reactions of the allylic iridium complexes $[Ir(\pi\text{-allyl})(CO)(PPh_3)_2]$ with C_2F_4 [6] and $CF_3{\cdot}C{\equiv}C{\cdot}CF_3$ [7] to yield both insertion and oxidative-addition products. Treatment of $[Ir(\pi\text{-}2\text{-}MeC_3H_4)(CO)(PPh_3)_2]$ with an excess of CF_3CN in a Carius tube yielded, after two days at room temperature, a bright orange crystalline complex (IVa). The structure of this complex has been confirmed by an *X*-ray crystallographic study.[8] In this unusual reaction, two CF_3CN groups become bonded to the same terminal carbon atom of the original π-2-methylallyl ligand, displacing it from the iridium, while themselves becoming co-ordinated to the metal *via* their nitrogen atoms, forming a six-membered chelate ring.

Similarly, reaction of CF_3CN with $[Ir(\pi\text{-}2\text{-}MeC_3H_4)(CO)(AsPh_3)_2]$ produced a complex in very low yield whose spectroscopic properties indicated it to be (IVb).

Two products were obtained from the reaction of CF_3CN with $[Ir(\pi\text{-}C_3H_5)(CO)(PPh_3)_2]$: an orange complex whose i.r., mass, and n.m.r. spectra (^1H and ^{19}F) were all consistent with its formulation as (IVc), and variable yields of a yellow crystalline complex. This latter complex exhibited two singlet resonances in the ^{19}F n.m.r. spectrum at 73·2 and 74·4 p.p.m. (rel. $CFCl_3$ = 0·0 p.p.m.), but the ^1H n.m.r. spectrum showed only phenyl resonances and a broad NH resonance at τ 0·08. No vinylic olefin resonances were observed. This complex is tentatively suggested to be of structure (V), containing a chelate ring closely related to that found in the platinum complex (II).[4] Supporting evidence for the structure of (V) derives from microanalytical data, and from its mass spectrum, in which ions corresponding to ($P - PPh_3$) and ($P - PPh_3 - CO$) are observed.

An orange complex was also obtained from the reaction of CF_3CN with $[Ir(\pi\text{-}1\text{-}MeC_3H_4)(CO)(PPh_3)_2]$. In contrast to complexes (IV), however, microanalysis and mass spectral data indicated this complex to be of empirical

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† No reprints available.

[1] Part IX, M. Green and S. H. Taylor, *J.C.S. Dalton*, 1975, 1142.

[2] F. G. A. Stone, *Pure Appl. Chem.*, 1972, **30**, 551.

[3] W. J. Bland, R. D. W. Kemmitt, and R. D. Moore, *J.C.S. Dalton*, 1973, 1292.

[4] W. J. Bland, R. D. W. Kemmitt, I. W. Nowell, and D. R. Russell, *Chem. Comm.*, 1968, 1065.

[5] R. B. King and K. H. Pannell, *J. Amer. Chem. Soc.*, 1968, **90**, 3984.

[6] M. Green and S. H. Taylor, *J.C.S. Dalton*, 1975, 1128.

[7] M. Green and S. H. Taylor, *J.C.S. Dalton*, 1975, 1142.

[8] M. Green, S. H. Taylor, J. J. Daly, and F. Sanz, *J.C.S. Chem. Comm.*, 1974, 361.

formula $[Ir(CF_3CN)_2H(CO)(PPh_3)_2]$, the fragment of butadiene having been eliminated from the original π-1-methylallyl ligand. The ^1H n.m.r. spectrum supported this conclusion, in that only phenyl resonances and a broad NH signal at τ 2·5 were observed. Two triplet resonances were observed in the ^{19}F n.m.r. spectrum at 62·8 and 67·7 p.p.m., due to two anisochronous CF_3 groups coupled to two isochronous phosphorus nuclei, this observation being confirmed by phosphorus-decoupling experiments. A structure consistent with the spectroscopic data is (VI), containing a protonated five-membered chelate ring derived from the head-to-tail dimerisation of two CF_3CN molecules. Complex (VI) was also obtained in improved yields from the reaction of CF_3CN with the hydrido-complexes $[IrH(CO)_2(PPh_3)_2]$ and $[IrH(CO)(PPh_3)_3]$.*

The tendency for CF_3CN to form chelate ring systems, both in its insertion-type reactions and also in those reactions leading to elimination of the allylic ligand, led us to suspect that the formulation (IIIa) of the complex obtained from $[FeMe(CO)_2(\eta\text{-}C_5H_5)]$ and CF_3CN by King and Pannell [5] might be incorrect. A reinvestigation of this reaction yielded a black crystalline complex, having identical spectroscopic properties to those of (IIIa). Irradiation of this complex in the presence of PMe_2Ph yielded a substitution product with displacement of CO. Attempts to prepare this black complex by analogous thermal reactions of $[FeR(CO)_2(\eta\text{-}C_5H_5)]$ ($R = C_2H_5$ or $PhCH_2$) with CF_3CN, or by u.v. irradiation of $[FeMe(CO)_2(\eta\text{-}C_5H_5)]$ in the presence of CF_3CN, yielded only starting materials and $[\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2]$. However, addition of the free-radical inhibitor galvinoxal to the thermal reaction of $[FeMe(CO)_2(\eta\text{-}C_5H_5)]$ with CF_3CN gave improved yields of the black complex.

The similarity between the ^{19}F chemical shifts for the CF_3 groups in King's complex (IIIa), and those in the iridium complex (VI), together with the substitution behaviour of King's complex towards tertiary phosphines, led us to suspect that the black iron complex might contain an identical five-membered chelate ring to that proposed for complex (VI) [*i.e.* (IIIb)]. Accordingly, an *X*-ray crystallographic study of the iron complex was undertaken.

The *X*-ray analysis (Tables 1—3) establishes that the molecule (IIIb) has the overall configuration shown in Figure 1. The central feature of the molecule [the Fe–N–C–N–C ring, together with the H atom on N(2) and the C atoms of the two CF_3 groups] is substantially planar (Table 3), and the iron atom forms approximately octahedral bonds if the C_5H_5 is considered to occupy three facial sites. Interest centres on the geometry of the $\overline{\text{Fe–N(2)–C(8)–N(1)–C(7)}}$ ring. The H atom is uniquely associated with N(2) and not with N(1); nor is it shared between N(1) and N(2). The planarity of the ring leads to extensive delocalisation: the bond angles at both the carbon atoms are close to 120°, and all bonds except Fe–N(2) are shorter than would have been expected for the

TABLE 1

Atomic positional parameters (*x*, *y*, and *z* are fractional crystal co-ordinates)

Atom	*x*	*y*	*z*	100 U/Å^2	Atom	*x*	*y*	*z*	100 U/Å^2
Fe	0·24195(12)	0·13115(7)	0·28998(10)	*	F(71)	0·2755(11)	0·9867(4)	0·5838(6)	*
C(1)	0·0887(18)	0·0236(10)	0·2187(16)	*	F(72)	0·1074(8)	0·0871(6)	0·5706(7)	*
C(2)	0·2336(24)	−0·0069(8)	0·2509(12)	*	F(73)	0·3138(6)	0·0928(3)	0·7279(4)	*
C(3)	0·3212(16)	0·0350(9)	0·1687(13)	*	C(81)	0·6361(9)	0·2762(6)	0·4939(8)	*
C(4)	0·2259(15)	0·0910(6)	0·0780(9)	*	F(81)	0·6183(7)	0·3439(5)	0·5729(7)	*
C(5)	0·0855(13)	0·0886(7)	0·1018(10)	*	F(82)	0·7515(6)	0·2302(4)	0·5687(6)	*
C(6)	0·1109(9)	0·2142(6)	0·3115(9)	*	F(83)	0·6816(6)	0·3115(4)	0·3882(5)	*
O(6)	0·0195(8)	0·2657(5)	0·3240(8)	*	H(1)	0·013(16)	0·032(9)	0·226(14)	10·98 †
C(7)	0·3214(7)	0·1257(5)	0·4890(6)	*	H(2)	0·309(13)	0·958(7)	0·312(10)	10·84 †
C(8)	0·4930(7)	0·2196(4)	0·4470(6)	*	H(3)	0·435(11)	0·025(6)	0·177(9)	10·41 †
N(1)	0·4427(6)	0·1763(4)	0·5513(5)	*	H(4)	0·271(10)	0·126(6)	−0·005(9)	8·50 †
N(2)	0·4197(7)	0·2097(4)	0·3181(5)	*	H(5)	−0·008(11)	0·121(6)	0·044(9)	9·02 †
C(71)	0·2562(12)	0·0741(6)	0·5922(9)	*	H(6)	0·452(8)	0·238(5)	0·252(7)	4·87 †

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23} (× 10^2)
Fe	6·05(6)	4·65(5)	4·51(5)	−0·67(6)	−0·22(4)	−0·89(5)
C(1)	15·5(17)	13·3(13)	12·4(13)	−11·2(13)	6·1(10)	−7·6(10)
C(2)	26·6(23)	4·2(6)	6·3(7)	−2·6(10)	−0·7(11)	−1·6(4)
C(3)	13·9(10)	8·8(8)	9·7(8)	2·6(8)	0·0(8)	−5·1(6)
C(4)	9·8(8)	7·6(6)	5·8(5)	−0·6(6)	0·3(5)	−2·2(4)
C(5)	7·2(7)	9·9(7)	6·8(6)	−2·6(5)	−0·6(5)	−2·7(5)
C(6)	4·6(5)	8·1(6)	9·2(6)	−0·3(4)	−0·4(4)	−2·7(5)
O(6)	7·2(4)	12·8(6)	15·1(6)	2·7(4)	−1·1(4)	−5·0(4)
C(7)	4·7(4)	4·6(4)	5·7(4)	−0·6(4)	1·1(3)	0·1(3)
C(8)	4·1(4)	4·6(4)	4·2(4)	−0·2(3)	−0·8(3)	−0·1(3)
N(1)	5·4(3)	5·6(3)	3·6(3)	−1·5(3)	1·1(2)	0·1(2)
N(2)	5·6(3)	4·7(3)	3·5(3)	0·2(3)	0·9(3)	0·2(2)
C(71)	8·5(7)	8·5(6)	7·0(5)	−4·2(5)	2·5(5)	−1·1(4)
F(71)	34·2(11)	8·4(2)	12·3(4)	−7·8(5)	11·8(6)	−1·0(3)
F(72)	9·6(4)	28·2(9)	13·7(5)	−5·7(5)	4·7(4)	4·5(5)
F(73)	14·0(4)	11·7(3)	6·1(3)	−5·7(3)	3·3(3)	−0·4(2)
C(81)	5·9(5)	7·3(5)	5·4(4)	−1·2(4)	0·6(4)	1·0(4)
F(81)	14·8(5)	17·0(6)	20·1(6)	−10·8(5)	9·7(5)	−12·8(5)
F(82)	7·5(3)	16·5(5)	16·1(5)	−4·1(4)	−3·9(3)	7·8(4)
F(83)	9·1(3)	12·4(4)	8·5(3)	−4·3(3)	1·6(2)	2·7(3)

* Anisotropic thermal parameters in the form: $\exp - 2\pi^2[U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{12}a^*b^*hk + 2U_{13}a^*c^*hl + 2U_{23}b^*c^*kl]$. † U For H(1)–(6) inclusive fixed at 110% of the value for the atom to which each is bonded ($B = 8\pi^2U$).

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* Complex (VI) has been independently prepared elsewhere in an identical reaction.[9]

[9] R. D. W. Kemmitt, personal communication.

formal structure (IIIb). A Fe–C(sp^2) bond is expected to be *ca.* 2·04 Å [10] whereas Fe–C(7) is found to be 1·895(6) Å. Likewise the three C–N bonds are all different (because of their different chemical environments), and while the lengths of C(7)–N(1) and N(1)–C(8) lie close to the range expected in heterocyclic rings,[11] bond N(2)–C(8) is especially short at 1·272(7) Å. Atom C(8) is uniquely placed, however, in that it is surrounded by three highly electronegative groups which will tend to lower the energies of the antibonding orbitals for both the C–CF_3 and C–F bonds,[12] while N(2) is likely to have the energy of its lone-pair orbital raised as a result of its proximity to the electropositive metal atom. Electron delocalisation from N(2) towards C(8), with increase in bond order, is therefore probable. It is also noteworthy that the C–CF_3 bonds are shorter than single bonds (Table 2), that the C–F mean bond length is 1·307 Å compared with a mean for many fluorocarbons of 1·333(5) Å [13] (though the shortening of the bond length may be apparent rather than real because of the high thermal activity of the fluorine atoms; the bond lengths have not been corrected for libration effects), and that all the F–C–F angles are rather less than the ideal tetrahedral value (suggesting increased *p*-character in the C–F bonds and increased *s*-character in the C–CF_3 link). Several compounds have now been examined in which an abnormally short bond occurs in a metallocyclic system between an electronegative element attached to the metal and an adjacent carbon atom.[14]

TABLE 2

Interatomic distances (Å) and bond angles (°)

Distances			
Fe–C(1)	2·079(18)	C(6)–O(6)	1·146(11)
Fe–C(2)	2·066(9)	Fe–C(7)	1·895(6)
Fe–C(3)	2·084(14)	C(7)–N(1)	1·332(8)
Fe–C(4)	2·124(9)	N(1)–C(8)	1·375(8)
Fe–C(5)	2·108(9)	C(8)–N(2)	1·272(7)
C(1)–C(2)	1·39(3)	N(2)–Fe	1·932(5)
C(2)–C(3)	1·40(2)	C(7)–C(17)	1·495(11)
C(3)–C(4)	1·35(1)	C(71)–F(71)	1·304(10)
C(4)–C(5)	1·35(2)	C(71)–F(72)	1·309(12)
C(5)–C(1)	1·45(2)	C(71)–F(73)	1·326(8)
C(1)–H(1)	0·67(14)	C(8)–C(81)	1·499(9)
C(2)–H(2)	0·92(10)	C(81)–F(81)	1·297(10)
C(3)–H(3)	1·03(10)	C(81)–F(82)	1·294(9)
C(4)–H(4)	1·11(9)	C(81)–F(83)	1·314(9)
C(5)–H(5)	0·99(10)	N(2)–H(6)	0·88(8)
Fe–C(6)	1·745(9)		
Angles			
C(1)–C(2)–C(3)	109·5(12)	C(7)–C(71)–F(71)	112·0(8)
C(2)–C(3)–C(4)	107·8(13)	C(7)–C(71)–F(72)	112·1(6)
C(3)–C(4)–C(5)	109·7(10)	C(7)–C(71)–F(73)	116·8(7)
C(4)–C(5)–C(1)	109·2(10)	F(71)–C(71)–F(72)	106·3(8)
C(5)–C(1)–C(2)	103·8(15)	F(71)–C(71)–F(73)	104·1(6)
Fe–C(6)–O(6)	176·9(7)	F(72)–C(71)–F(73)	104·5(8)
C(6)–Fe–C(7)	89·5(3)	N(1)–C(8)–C(81)	116·6(5)
C(6)–Fe–N(2)	97·1(3)	N(2)–C(8)–C(81)	123·3(6)
C(7)–Fe–N(2)	78·7(2)	C(8)–C(81)–F(81)	112·5(7)
Fe–C(7)–N(1)	119·5(5)	C(8)–C(81)–F(82)	112·4(6)
C(7)–N(1)–C(8)	107·8(4)	C(8)–C(81)–F(83)	113·2(5)
N(1)–C(8)–N(2)	120·0(5)	F(81)–C(81)–F(82)	105·7(6)
C(8)–N(2)–Fe	113·9(4)	F(81)–C(81)–F(83)	106·0(7)
Fe–C(7)–C(71)	127·4(5)	F(82)–C(81)–F(83)	106·5(7)
N(1)–C(7)–C(71)	113·0(5)		

TABLE 3

Equation of least-squares plane with distances of relevant atoms from the plane in square brackets

Fe, C(7), N(1), C(8), N(2)

[Fe 0·016, C(7) −0·025, N(1) 0·023, C(8) 0·005, N(2) 0·009, C(71) −0·013, C(81) −0·043, H(6) 0·019]

$$-5{\cdot}5699x + 11{\cdot}4632y + 2{\cdot}3229z = 0{\cdot}8135$$

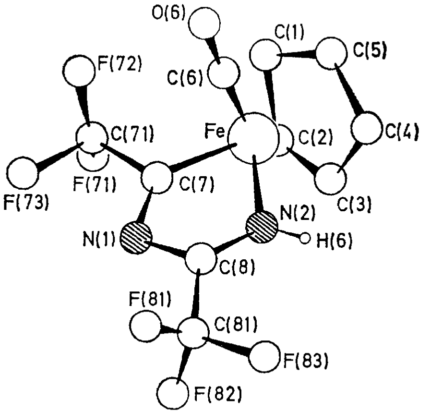

FIGURE 1 View of the molecule down *b* in the monoclinic cell, showing atom numbering

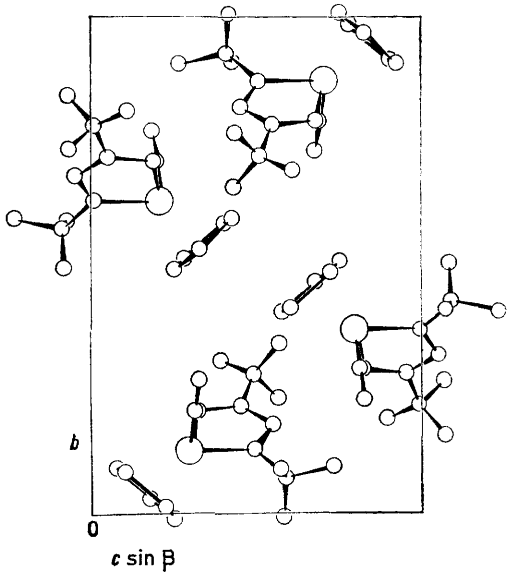

FIGURE 2 Arrangement of molecules in the unit cell viewed down *a* looking away from the origin

For the (η-C_5H_5)Fe(CO) moiety the mean dimensions are as found in other structures containing this grouping; but it may be noted (Table 2) that differences amongst the individual Fe–C_5 bond lengths appear to be significant, and that the longest of these, Fe–C(4) and Fe–C(5), lie *trans* to the very short bond Fe–C(7). There are no significantly short intermolecular contacts.

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[10] M. R. Churchill, 'Perspectives in Structural Chemistry,' 1970, **3**, 91.

[11] 'International Tables for *X*-Ray Crystallography,' Vol. III, Kynoch Press, Birmingham, 1940.

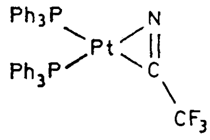
[12] J. F. Liebman, *J. Fluorine Chem.*, 1973, **3**, 27.

[13] 'Table of Interatomic Distances and Configuration in Molecules and Ions,' Supplement 1956–9, The Chemical Society, Special Publication No. 18, London, 1965.

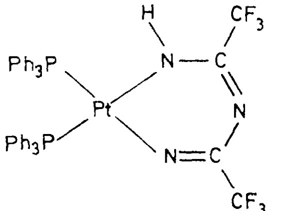
[14] A. Modinos and P. Woodward, *J.C.S. Dalton*, 1974, 2065.

DISCUSSION

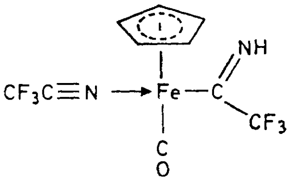
The protonation of π-allylic ligands to yield cationic olefin complexes is a well-documented reaction.[15] Similar electrophilic attack on π-allylic ligands by a neutral electrophilic reagent, hexafluorobut-2-yne, has been proposed to account for the products obtained on reaction of π-allylic iridium complexes with this substrate.[7] By analogy, electrophilic attack by CF_3CN on the allylic ligand of $[Ir(\pi\text{-}2\text{-}RC_3H_4)(CO)(PPh_3)_2]$ (R = H or CH_3) might be expected to be the initial step of the observed reaction, yielding an intermediate zwitterionic olefin complex (Scheme 1). Subsequent hydrogen migration to regenerate a π-allylic moiety, followed by a second electrophilic attack by CF_3CN, and a further hydrogen shift, yield the observed products of structure (IV).



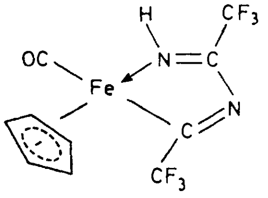
(I)



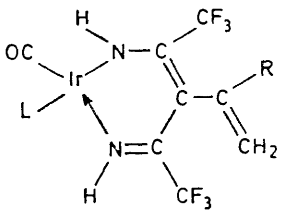
(II)



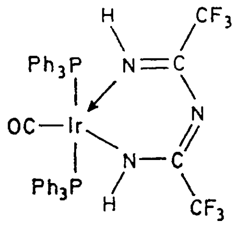
(IIIa)



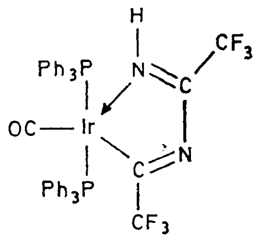
(IIIb)



(IV) a; R = Me; L = PPh$_3$
b; R = Me; L = AsPh$_3$
c; R = H; L = PPh$_3$



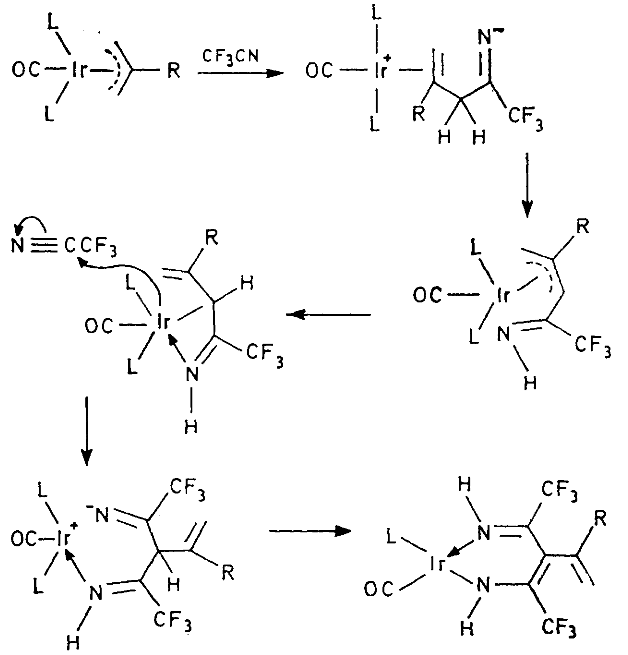
(V)



(VI)

Formation of (V), in addition to (IVc), in the reaction of $[Ir(\pi\text{-}C_3H_5)(CO)(PPh_3)_2]$ with CF_3CN, is more difficult to explain. Kemmitt *et al.*[4] have attributed the source of the additional nitrogen atom in the chelate ring of the platinum complex (II) to the *in situ* hydrolytic degradation of CF_3CN by traces of water present in the reaction mixture. A similar assumption may account for the formation of (V), although it is difficult to understand why the same complex (V) was not isolated from the other π-allylic iridium systems studied.

Formation of complex (VI), from the reaction of $[Ir(\pi\text{-}1\text{-}MeC_3H_4)(CO)(PPh)_2]$ with CF_3CN, presumably proceeds *via* an intermediate iridium-hydride complex (Scheme 2), generated by elimination of butadiene from the π-1-methylallyl ligand. The reverse of this process, addition of iridium hydrides to 1,3-dienes, is well documented.[16] Head-to-tail dimerisation of CF_3CN, followed by a hydrogen shift from iridium to nitrogen, yields the five-membered iridacyclic ring of (VI). This head-to-tail dimerisation is highly reminiscent of the reactions of hexafluoroacetone with low-valent transition-metal systems.[2] The intermediacy of an iridium-hydride species in this reaction is further supported by the observation that complex (VI) can also be obtained, in improved yields, by the reaction of $[IrH(CO)_2(PPh_3)_2]$ or $[IrH(CO)(PPh_3)_3]$ with CF_3CN.



SCHEME 1

The mechanism of formation of $[(\eta\text{-}C_5H_5)(CO)\text{-}FeNHC(CF_3)NC(CF_3)]$ from $[FeMe(CO)_2(\eta\text{-}C_5H_5)]$ and CF_3CN may also involve the intermediacy of an iron-hydride species, although its formation in this reaction

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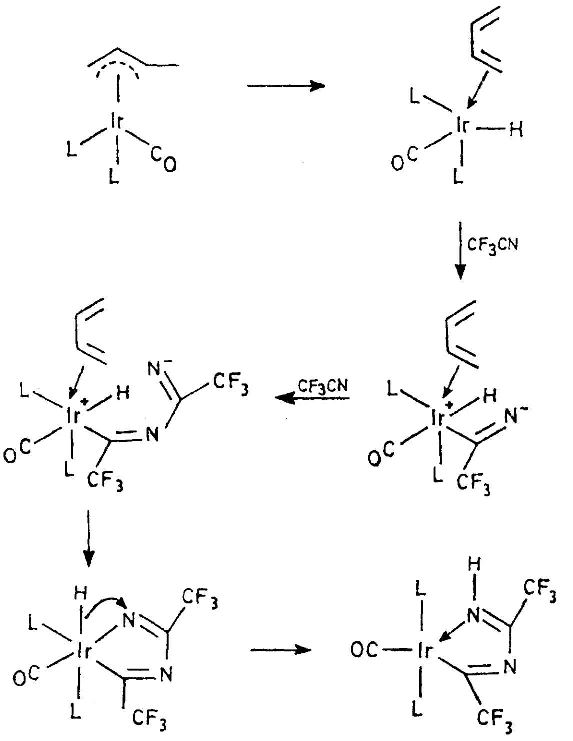
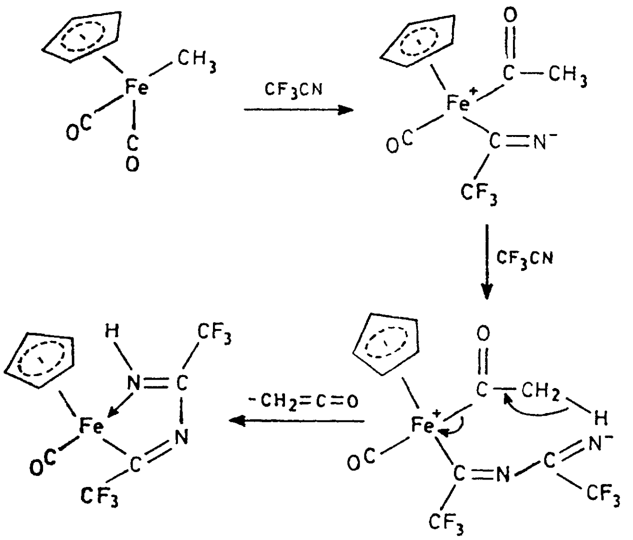
[15] M. L. H. Green and P. L. I. Nagy, *J. Chem. Soc.*, 1963, 189; G. Wilke, B. Bogdanovic, P. Hardt, P. Heimbach, W. Keim, M. Kröner, W. Oberkirch, K. Tanaka, G. Steinrücke, D. Walter, and H. Zimmerman, *Angew. Chem. Internat. Edn.*, 1966, **5**, 151.

[16] C. K. Brown, W. Mowat, G. Yagupsky, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1971, 850.

seems highly unlikely. A more plausible, though equally speculative, mechanism is outlined in Scheme **3**, the final step involving proton abstraction from either a methyl, or acetyl, grouping. Formation of [Fe(COMe)-$(CO)_2(\eta\text{-}C_5H_5)$] in the reaction system, observed by King and Pannell,[5] may lend weight to the latter proposal.



Scheme 2



Scheme 3

It is not clear, however, why the same iron complex is not isolated from reactions of CF_3CN with [FeR(CO)$_2$-$(\eta\text{-}C_5H_5)$] ($R = C_2H_5$ or $PhCH_2$), although this may relate to the migratory aptitudes of the different alkyl groups onto a co-ordinate CO molecule.

EXPERIMENTAL

All experiments were carried out in an atmosphere of dry oxygen-free nitrogen or in Carius tubes, when the reactants were sealed together at −196 °C *in vacuo*, unless otherwise stated.

^1H and ^{19}F N.m.r. spectra were recorded on a Varian Associates HA100 spectrometer at 100 and 94·1 MHz respectively. Chemical shifts are quoted as τ values and p.p.m. relative to $SiMe_4$ (τ 10·00) and $CFCl_3$ (0·00 p.p.m.) as internal standards. I.r. spectra were recorded on a Perkin-Elmer 257 instrument, and mass spectra on an MS9 spectrometer at an ionising voltage of 70 eV.

The complexes $[Ir(\pi\text{-all})(CO)L_2]$ [16] (π-all = 2-methylallyl, L = PPh_3 or $AsPh_3$; π-all = allyl or 1-methylallyl, L = PPh_3), $[IrH(CO)_2(PPh_3)_2]$,[17] $[IrH(CO)(PPh_3)_3]$,[18] and $[FeR(CO)_2(\eta\text{-}C_5H_5)]$ [19] were prepared by published methods. Trifluoroacetonitrile was purchased from Peninsular Chemresearch Inc., and was used without further purification.

Reactions of π-Allylic Iridium Complexes with Trifluoroacetonitrile.—A solution of carbonyl(π-2-methylallyl)bis(triphenylphosphine)iridium (0·500 g, 0·63 mmol) in benzene (30 ml) was treated with excess trifluoroacetonitrile (5 mmol) in a Carius tube at room temperature for two days. The solvent was removed *in vacuo* and the residue was chromatographed on alumina. Elution with benzene–hexane (1 : 1) developed a diffuse yellow band. Removal of the solvent and crystallisation of the residue from dichloromethane–hexane yielded complex (IVa), $[\overline{\mathrm{IrNHC(CF_3)=C(CMe=CH_2)C(CF_3)=N}}\mathrm{H(CO)(PPh_3)}]$, as bright orange *crystals* (0·070 g, 15%), m.p. 196—197 °C (Found: C, 44·5; H, 2·6; F, 15·0; N, 3·7; P, 4·4. $C_{27}H_{22}F_6IrN_2OP$ requires C, 44·5; H, 3·2; F, 15·7; N, 3·9; P, 4·5%), $\nu_{max.}$ (Nujol) 3385m, 3340m, 1961s, 1637w, 1546w, 1540w, 1478w, 1432m, 1395m, 1314m, 1299s, 1271s, 1205s, 1170s, 1165s, 1155s, 1116s, 919w, 750m, 730m, 702m, and 690s cm^{-1}. The ^1H n.m.r. spectrum showed resonances ($CDCl_3$) at τ −0·27 (br, s, 1H, N*H*), 2·12 (br, s, 1H, N*H*), 2·3—2·5 (m, 15H, Ph), 4·66 (s, 1H, CMe=C*H*$_2$), 5·07 (s, 1H, CMe=C*H*$_2$), and 8·12 (s, 3H, C*Me*=CH$_2$). The ^{19}F n.m.r. spectrum showed resonances (CH_2Cl_2) at 6·39 (s, 3F, CF_3) and 69·3 p.p.m. (s, 3F, CF_3). The mass spectrum showed peaks at *m/e* 728 (P^+) and 700 (P − CO).

A similar reaction using carbonyl(π-2-methylallyl)-bis(triphenylarsine)iridium (0·600 g, 0·68 mmol) and an excess of trifluoroacetonitrile yielded complex (IVb), $[\overline{\mathrm{IrNHC(CF_3)=C(CMe=CH_2)C(CF_3)=N}}\mathrm{H(CO)(Ph_3As)}]$, as an orange oil, which could not be crystallised; ν_{CO} (hexane) 1969s. The ^1H n.m.r. spectrum showed resonances ($CDCl_3$) at τ −0·44 (br, s, 1H, N*H*), 1·90 (br, s, 1H, N*H*), 2·2—2·9 (m, 15H, Ph), 4·66 (s, 1H, CMe=C*H*$_2$), 5·06 (s, 1H, CMe=C*H*$_2$), and 8·12 (s, 3H, C*Me*=CH$_2$). The ^{19}F n.m.r. spectrum showed resonances (CH_2Cl_2) at 63·3 p.p.m. (s, 3F, CF_3) and 64·1 (s, 3F, CF_3).

A similar reaction using (π-allyl)carbonylbis(triphenylphosphine)iridium (0·600 g, 0·77 mmol) and excess of trifluoroacetonitrile (3 mmol) yielded two bands on chromatographic analysis. Evaporation of the first orange band, followed by crystallisation of the residue from hexane, yielded complex (IVc), $[\overline{\mathrm{IrNHC(CF_3)=C(CH=CH_2)C(CF_3)=N}}\mathrm{H(CO)(PPh_3)}]$, as orange

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[17] G. Wilkinson and G. Yagupsky, *J. Chem. Soc.* (*A*), 1969, 725.

[18] *Inorg. Synth.*, 1971, Vol. XIII, 126.

[19] R. B. King, *Organometallic Synth.*, 1965, **1**, 151.

crystals (0·020 g, 4%), m.p. 145—147 °C (Found: C, 43·7; H, 2·8; N, 3·8. $C_{26}H_{20}F_6IrN_2OP$ requires C, 43·8; H, 2·8; N, 3·9%), $\nu_{max.}$ (Nujol) 3378m, 3335m, 1978s, 1971s, 1588w, 1570w, 1478m, 1438m, 1300s, 1267s, 1215s, 1190s, 1154s, 1137s, 1095m, 998w, 946w, 794w, 756w, 745m, 720m, 704sh, and 694s cm^{-1}. The ^1H n.m.r. spectrum showed resonances ($CDCl_3$) at τ 0·12 (br, s, 1H, N*H*), 2·2—2·7 (m, 15H, Ph), 4·18 (m, 2H, $CH=CH_2$), and 4·64 (m, 1H, $CH=CH_2$). The ^{19}F n.m.r. spectrum showed resonances (CH_2Cl_2) at 70·0 p.p.m. (s, 3F, CF_3) and 71·1 (s, 3F, CF_3). The mass spectrum showed peaks at *m/e* 714 (*P*), 688 ($P - C_2H_2$), 660 ($P - C_2H_2 - CO$). Evaporation of the second, yellow band, and crystallisation of the residue from hexane yielded complex (V), $[IrNH=C(CF_3)N=C(CF_3)NH(CO)(PPh_3)_2]$, as yellow *crystals* (0·025 g, 3%), m.p. 164—165 °C (Found: C, 51·6; H, 3·5; N, 4·3. $C_{41}H_{32}F_6IrN_3OP_2$ requires C, 51·8; H, 3·4; N, 4·4%), $\nu_{max.}$ (Nujol) 3330m, 3065w, 1997vs, 1587w, 1576w, 1569w, 1531w, 1502w, 1480w, 1439s, 1322m, 1310w, 1290s, 1212s, 1201s, 1178s, 1167s, 1153s, 1121m, 1098m, 1069w, 1029w, 997w, 934m, 760m, 754m, 747m, 742m, 720m, 698s, and 691s cm^{-1}. The ^1H n.m.r. spectrum showed resonances ($CDCl_3$) at τ 0·08 (br, s, 1H, N*H*) and 2·2—2·7 (m, 30H, Ph). The ^{19}F n.m.r. spectrum showed resonances (CH_2Cl_2) at 73·2 p.p.m. (s, 3F, CF_3) and 74·4 (s, 3F, CF_3). The mass spectrum showed peaks at *m/e* 689 ($P - PPh_3$) and 661 ($P - PPh_3 - CO$).

A similar reaction using carbonyl(π-1-methylallyl)bis(triphenylphosphine)iridium (0·500 g, 0·63 mmol) and an excess of trifluoroacetonitrile (3 mmol) yielded, after 9 days, (VI), *trans*-$[IrNH=C(CF_3)N=C(CF_3)(CO)(PPh_3)_2]$, obtained as orange *crystals* from dichloromethane–hexane (0·028 g, 5%), m.p. 241—243 °C (Found: C, 52·7; H, 3·6; N, 2·9. $C_{41}H_{31}F_6IrN_2OP_2$ requires C, 52·6; H, 3·3; N, 3·0%), $\nu_{max.}$ (Nujol) 3375w, 3052w, 1996vw, 1585w, 1571w, 1500w, 1480m, 1436s, 1302s, 1271s, 1225m, 1186m, 1170m, 1129s, 1104s, 1093s, 999s, 878w, 746m, 691s, and 653m cm^{-1}. The ^1H n.m.r. spectrum showed resonances ($CDCl_3$) at τ 2·51 (br, s, 1H, N*H*) and 2·6—3·2 (m, 30H, Ph). The ^{19}F n.m.r. spectrum showed resonances (CH_2Cl_2) at 62·8 p.p.m. [t, 3F, $CF_3(^4J_{F-F} = 14$ Hz)] and 67·7 [t, 3F, $CF_3(^5J_{F-P} = 8·5$ Hz)]. The mass spectrum showed peaks at *m/e* 936 (*P*), 674 ($P - PPh_3$), and 646 ($P - PPh_3 - CO$).

Reactions of Hydridoiridium Complexes with Trifluoroacetonitrile.—A solution of dicarbonylhydridobis(triphenylphosphine)iridium (0·323 g, 0·42 mmol) in benzene (20 ml) was treated with excess trifluoroacetonitrile (13 mmol) in a Carius tube at 80 °C for 2 days. Evaporation of the solvent, followed by chromatography of the residue on alumina (benzene), yielded a single orange band. Removal of the solvent, and crystallisation of the residue from dichloromethane–hexane yielded complex (VI) as orange *crystals* (0·055 g, 14%) (Found: C, 52·3; H, 3·6; N, 3·3. $C_{41}H_{31}F_6IrN_2OP_2$ requires C, 52·6; H, 3·3; N, 3·0%).

A similar reaction of carbonylhydridotris(triphenylphosphine)iridium (0·50 g, 0·50 mmol) in benzene (20 ml) with an excess of trifluoroacetonitrile (13 mmol) yielded, after 28 days at room temperature, complex (VI) (0·033 g, 7%).

Preparation and X-Ray Crystal Structure of $[FeNHC(CF_3)NC(CF_3)(CO)(\eta\text{-}C_5H_5)]$.—The title complex was prepared according to the method of King and Pannell.[5] Crystals grow as black needles, from dichloromethane–hexane, with *a* as the needle axis. The dimensions of the one chosen for *X*-ray diffraction were 0·53 × 0·05 × 0·13 mm. Intensities were collected, according to methods described earlier,[14] on a Syntex $P2_1$ four-circle autodiffractometer, using Mo-K_α *X*-radiation for $2·9° < 2\theta < 50°$. Scan speeds varied from 0·0337° s^{-1} for the weakest reflections to 0·997° s^{-1} for the strongest. Reflections for which $I < 2·5(\sigma_I)$ were regarded as unobserved and were not included in the final refinement. Of the total of 2016 independent reflections, 1267 were observed.

Crystal Data.—$C_{10}H_6F_6FeN_2O$, $M = 340·0$, Monoclinic, $a = 8·975(7)$, $b = 14·696(13)$, $c = 9·785(4)$ Å, $\beta = 104·84(5)°$, $D_m = 1·825$ g cm^{-3}, $Z = 4$, $D_c = 1·810$ g cm^{-3}, $F(000) = 704$. Space group $P2_1/n$. Mo-K_α radiation (graphite monochromator), $\lambda = 0·71069$ Å; $\mu(\text{Mo-}K_\alpha) = 13·2$ cm^{-1}. The structure was solved by conventional heavy-atom methods and refined with anisotropic thermal parameters for all non-hydrogen atoms to *R* 0·049 (*R′* 0·048). The hydrogen atoms were all located from electron-density difference syntheses; their positional parameters were refined with thermal parameters invariant at $100U = 3·8$. Weights were applied according to the scheme: $1/w = (\sigma_F)^2$.

Final positional and thermal parameters are in Table 1, interatomic distances in Table 2, and a least-squares plane calculation in Table 3. No absorption correction was applied, and the atomic scattering factors were the analytic types of ref. 20 for Fe, C, F, N, and O, and those of ref. 21 for H. All computational work was carried out on the CDC 7600 computer of the University of London using the '*X*-Ray System' of programmes.[22] Observed and calculated structure factors are listed in Supplementary Publication No. SUP 21318 (8 pp).*

Preparation of $[FeNHC(CF_3)NC(CF_3)(PMe_2Ph)(\eta\text{-}C_5H_5)]$.—A solution of (IIIb) (0·600 g, 1·76 mmol) and dimethylphenylphosphine (2·50 g, 18 mmol) in hexane (250 ml) was irradiated for 10 days at room temperature. Removal of the solvent and chromatographic analysis on alumina with dichloromethane as eluant yielded the title complex as dark green *crystals* after crystallisation from hexane (0·170 g, 21%), m.p. 104—105 °C (Found: C, 45·3; H, 4·1; N, 6·0. $C_{17}H_{17}F_6FeN_2P$ requires: C, 45·4; H, 3·8; N, 6·2%), $\nu_{max.}$ (Nujol) 3205m, 1643w, 1510w, 1325m, 1259m, 1237s, 1180s, 1155s, 1140s, 1127s, 1100s, 985m, 943w, 929w, 905m, 823w, 750w, 711w, 680w, and 672w cm^{-1}. The ^1H n.m.r. spectrum showed resonances ($CDCl_3$) at τ 1·50 (br, s, 1H, N*H*), 2·5—2·6 (m, 5H, Ph), 5·60 (d, 5H, C_5H_5), 8·40 [d, 3H, P-*Me* ($^2J_{P-H} = 9·0$ Hz)], and 9·20 [d, 3H, P-*Me* ($^2J_{P-H} = 9·0$ Hz)]. The ^{19}F n.m.r. spectrum showed resonances ($CHCl_3$) at 63·90 p.p.m. (s, 3F, CF_3) and 68·35 (s, 3F, CF_3).

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* For details see Notice to Authors, No. 7, in *J.C.S. Dalton*, 1974, Index issue. (Items less than 10 pp. are sent as full-sized copies.)

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