Reactions involving Transition Metals. Part 16.[1,2] Rhodium, Iridium, Platinum, and Gold Complexes containing the Bis(trifluoromethyl)-amino-oxy-ligand

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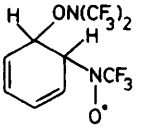
The stable complexes $[Ir\{ON(CF_3)_2\}_2Cl(CO)L_2]$ (L = PPh_3, $AsPh_3$, or $PMePh_2$) and $[Pt\{ON(CF_3)_2\}_2(PPh_3)_2]$ have been prepared by oxidative addition of the radical $(CF_3)_2NO^{\bullet}$ to *trans*-$[IrCl(CO)L_2]$ and either $[Pt(\eta^2\text{-}C_2H_4)(PPh_3)_2]$ or $[Pt(PPh_3)_4]$ respectively. The compounds *trans*-$[IrX(CO)(PPh_3)_2]$ (X = Br or I) react with the radical to give a mixture of $[Ir\{ON(CF_3)_2\}_2\{CO_2N(CF_3)_2\}(PPh_3)_2]$ and $[IrX_3(CO)(PPh_3)_2]$. The platinum(II) complexes $[Pt\{ON(CF_3)_2\}_2L_2]$ (L = PPh_3, $AsPh_3$, or $PMePh_2$) and the gold(I) complex $[Au\{ON(CF_3)_2\}(PPh_3)]$ have been synthesized by metathetical exchange of the chlorine atoms in *cis*-$[PtCl_2L_2]$ and $[AuCl(PPh_3)]$ using $[Hg\{ON(CF_3)_2\}_2]$. The weak nucleophile $Na[ON(CF_3)_2]$ has been shown to react with the complexes $[M(CO)(MeCN)(PPh_3)_2]ClO_4$ (M = Rh or Ir) to give the compounds *trans*-$[M\{ON(CF_3)_2\}(CO)(PPh_3)_2]$, while reaction with the complexes *trans*-$[PtX(CO)L_2]BF_4$ (X = Cl, L = PPh_3 or $AsPh_3$; X = Br, L = PPh_3) occurs at the carbonyl ligand giving $[PtX\{CO_2N(CF_3)_2\}L_2]$. The new iridium(I) complex *trans*-$[Ir\{ON(CF_3)_2\}(CO)(PPh_3)_2]$ forms an oxygen complex in solution, and reacts with halogens, CF_3CO_2H, $HgCl_2$, and $C_6H_5CH_2COCl$ to give the products $[IrX_3(CO)(PPh_3)_2]$ (X = Cl or I), $[IrH(O_2CCF_3)_2(CO)(PPh_3)_2]$, $[IrCl_2(HgCl)(CO)(PPh_3)_2]$, and $[IrCl_2(COCH_2C_6H_5)(CO)(PPh_3)_2]$ respectively, with loss of the $(CF_3)_2NO$ ligand; unstable oxidative-addition products $[Ir\{ON(CF_3)_2\}(R)I(CO)(PPh_3)_2]$ (R = CF_3, CH_3, or C_2H_5) have been characterized from the reactions with iodoalkanes.

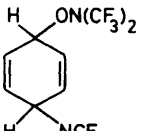
THE 'persistent'[3] radical, bis(trifluoromethyl)amino-oxyl, $(CF_3)_2NO$, has been likened to a halogen atom.[4] It has a similar oxidizing power to that of chlorine, and it reacts directly with several main-group elements to form derivatives which have similar properties to the well known halides.[5,6] It also displaces chlorine, bromine, iodine, and hydrogen from compounds of the main-group elements.[5,6] Consequently, many derivatives of the main-group elements containing the $(CF_3)_2NO$ ligand have been prepared, and their chemistry has been studied in some detail. In contrast, the chemistry of bis(trifluoromethyl)amino-oxyl derivatives of the transition elements is almost unknown. The only complexes reported prior to our investigations were the unstable binary compounds $[Ti\{ON(CF_3)_2\}_4]$[7] and $[Co\{ON(CF_3)_2\}_2]$[4] and the poorly characterised manganese derivative $[Mn\{ON(CF_3)_2\}(CO)_5]$.[8] In part this can be attributed to the fact that in our experience and that of other workers[4,7] the simple binary $(CF_3)_2NO$ derivatives of transition metals are extremely moisture sensitive and are often thermally unstable. For this reason it was decided to attempt the synthesis of transition-metal derivatives co-ordinatively saturated with phosphine and carbonyl ligands, which might stabilize the metal–$ON(CF_3)_2$ bond towards hydrolysis. We now report the preparation of a number of stable iridium(I), iridium(III), rhodium(I), platinum(II), and gold(I) complexes containing $(CF_3)_2NO$ ligands.

RESULTS AND DISCUSSION

Reactions of Bis(trifluoromethyl)amino-oxyl.—Reaction between $[MnH(CO)_5]$ and $(CF_3)_2NO$ was reported to give $[Mn\{ON(CF_3)_2\}(CO)_5]$,[8] but no experimental details or physical characteristics of this complex were given. In our experience reaction between an equimolar mixture of the hydride and $(CF_3)_2NO$ at −78 °C in a tube sealed under vacuum always gives a mixture of $[Mn\{ON(CF_3)_2\}(CO)_5]$ and $[Mn_2(CO)_{10}]$. Attempts to separate the mixture by various procedures invariably resulted in decomposition of the nitroxide complex to manganese carbonyl. This suggests that the expected hydrogen abstraction by $(CF_3)_2NO^{\bullet}$ does occur, but dimerization of the $[Mn(CO)_5]$ radical formed competes with the combination with $(CF_3)_2NO$. Attempts to confirm the formation of $[Mn(CO)_5]$ by repeating the reaction in benzene in the presence of a trace of CF_3NO as a spin-trapping agent gave only an e.s.r. spectrum consisting of six doublets ($a_N = a_{CF_3} = 11.07$ G,* $a_H = 2.87$ G, $g = 2.003\,98$) due to the radical, (1a) or (1b), derived by spin-trapping of the adduct radical formed on reaction of $(CF_3)_2NO^{\bullet}$ with benzene. No e.s.r. signals were detected when the reaction was repeated in carbon tetrachloride solvent.



(1a)

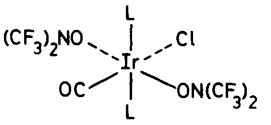


(1b)

The strong oxidizing properties of $(CF_3)_2NO$[4] and the fact that it reacts with many derivatives of the main-group elements to give oxidative-addition products[5,6] suggested that this type of reaction might occur very readily with low-valent transition-metal complexes. Passage of a slow stream of $(CF_3)_2NO$ through a solution of *trans*-$[IrCl(CO)(PPh_3)_2]$ at room temperature led to the

* Throughout this paper: 1 G = 10^{-4} T; 1 atm = 101 325 Pa.

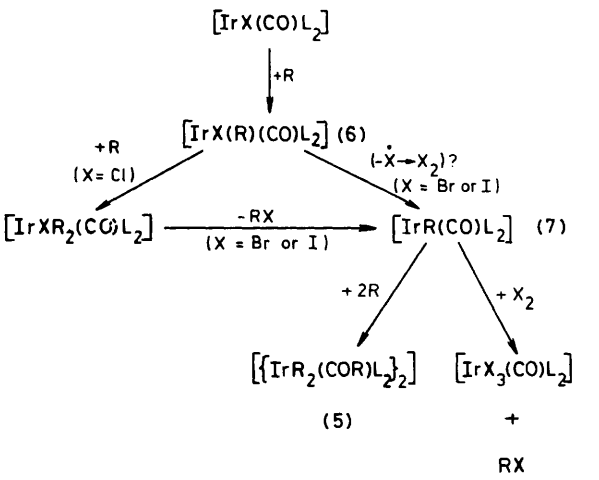
rapid formation of the adduct (2). The isolated product from experiments carried out in different solvents always



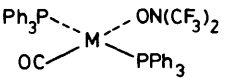
(2) L = PPh_3
(3) L = $AsPh_3$
(4) L = $PMePh_2$

contained solvent of crystallization which could not be removed even on gentle heating under vacuum. Similar reactions between $(CF_3)_2NO$ and *trans*-$[IrCl(CO)L_2]$ (L = $AsPh_3$ or $PMePh_2$) gave the adducts (3) and (4) respectively. These compounds are stable for several days in air, and for several months under nitrogen. Their i.r. spectra show a strong band in the metal–carbonyl region of 2 050—2 060 cm^{-1} typical of an iridium(III) complex,[9] and bands at 1 280—1 291, 1 248—1 260, 1 190—1 195, 1 020, and 950 cm^{-1} characteristic[4,5] of the $(CF_3)_2NO$ group. In the ^1H n.m.r. spectrum of (4) the resonance for the methyl group of the phosphine ligand appears as an apparent 1 : 2 : 1 triplet due to strong virtual coupling of the two ^{31}P nuclei. Although cases of virtual coupling between *cis* ligands are known[10-12] these are rare, and the triplet pattern is usually characteristic of *trans* phosphorus ligands.[13] Support for a *trans* arrangement comes from the i.r. spectra of complexes (2) and (4) which show that the aromatic ring skeletal vibration at 1 572 cm^{-1} is more intense than that at 1 586 cm^{-1}. This is frequently interpreted as an indication of *trans*-arylphosphine ligands.[14,15] Since the complexes (2)—(4) have only a single band in their ^{19}F n.m.r. spectra, the $(CF_3)_2NO$ ligands are presumed to be in identical environments and the most likely stereochemical arrangement of the ligands is that shown.

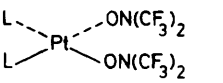
The bromo- and iodo-iridium complexes *trans*-$[IrX(CO)(PPh_3)_2]$ (X = Br or I) behave differently on reaction with $(CF_3)_2NO$ and give a mixture of the novel complex $[Ir\{ON(CF_3)_2\}_2\{CO_2N(CF_3)_2\}(PPh_3)_2]$ (5) and the known trihalogen derivatives $[IrX_3(CO)(PPh_3)_2]$. Compound (5) is probably dimeric with $(CF_3)_2NOCO$ bridges. The ν(C=O) band in the i.r. spectrum of this complex is shifted to lower frequency by more than 100 cm^{-1} relative to the corresponding band in the spectra of the platinum complexes (13)—(15) (see below). It seems probable that these oxidative-addition reactions occur in a stepwise manner with formation of an iridium(II) intermediate (6) (see Scheme 1). When X = Cl this reacts with another molecule of $(CF_3)_2NO$ to give the observed adducts. When X = Br or I, loss of a halogen atom may occur to give the iridium(I) complexes $[Ir\{ON(CF_3)_2\}(CO)L_2]$ (7). Alternatively, formation of (7) may arise by reductive elimination of the unstable compounds $(CF_3)_2NOX$ from the adducts $[IrX\{ON(CF_3)_2\}_2(CO)L_2]$. It has been suggested[14,16] that $(CF_3)_2NOCl$ may be formed during the reaction of $(CF_3)_2NO$ with hydrogen chloride, but it has never been detected and, if formed, it must decompose rapidly to $(CF_3)_2NO$ [and hence $(CF_3)_2NOH$] and molecular chlorine. Support for the sequence of reactions shown in Scheme 1 comes from the observation that complex (7; L = PPh_3), synthesised independently by a different route



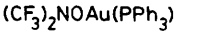
SCHEME 1 R = $(CF_3)_2NO$



(7) M = Ir
(12) M = Rh



(8) L = PPh_3
(9) L = $AsPh_3$
(10) L = $PMePh_2$



(11)

(see below), reacts with halogens to give the complexes $[IrX_3(CO)(PPh_3)_2]$ (X = Cl or I), and with $(CF_3)_2NO$ to afford compound (5).

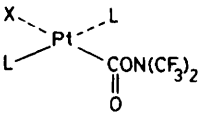
Benzene solutions of both $[Pt(PPh_3)_4]$ and $[Pt(\eta^2\text{-}C_2H_4)(PPh_3)_2]$ react readily with $(CF_3)_2NO$ at room temperature to give compound (8). In the i.r. spectrum of this compound the band at 1 586 cm^{-1} is more intense than that at 1 572 cm^{-1} indicating *cis*-phosphine ligands; since the same compound may also be prepared from *cis*-$[PtCl_2(PPh_3)_2]$ by a metathetical halogen-exchange reaction with $[Hg\{ON(CF_3)_2\}_2]$ (see below) this assignment seems reasonable. Attempts to prepare a palladium analogue by reaction of $(CF_3)_2NO$ with $[Pd\{(CN)_2C_2(CN)_2\}(PPh_3)_2]$, $[Pd(PPh_3)_3]$, or $[Pd(dba)_2]$ (dba = dibenzylideneacetone) gave only palladium metal. There was no reaction between $(CF_3)_2NO$ and $[W(CO)_6]$, $[AuCl(PPh_3)]$, $[PtCl_2(phen)]$ (phen = 1,10-phenanthroline), $[Ni(CO)_2(PPh_3)_2]$, or $[\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2]$. The rhodium(I) complex $[\{RhCl(PPh_3)_2\}_2]$ reacted with a saturated solution of $(CF_3)_2NO$ in carbon tetrachloride

to give an orange-yellow solid [m.p. 210 °C (decomp.)], which showed i.r. bands at 275 and 260 cm^{-1} indicative of bridging chlorine ligands, in addition to bands for $(CF_3)_2NO$ ligands. A singlet in the ^{19}F n.m.r. spectrum at −920 p.p.m., a molecular weight of 1 904, and microanalysis results (C, H, N, and F) suggested that it is a dimer of stoicheiometry $C_{77}H_{60}Cl_8F_{12}N_2O_2P_4Rh_2$ (M = 1 886), having two $(CF_3)_2NO$ ligands in identical environments, with structure $[(Ph_3P)_2(Cl_3C)\{(CF_3)_2NO\}Rh(\mu\text{-}Cl)_2Rh\{ON(CF_3)_2\}(CCl_3)(PPh_3)_2]$ or $[(Ph_3P)_2Cl\{(CF_3)_2NO\}Rh(\mu\text{-}Cl)_2Rh\{ON(CF_3)_2\}Cl(PPh_3)_2]\cdot CCl_4$. The stoicheiometry of the product was dependent on the concentration of $(CF_3)_2NO$ used, and anything less than a saturated solution gave intractable mixtures. No reaction occurred when $[\{RhCl(PPh_3)_2\}_2]$ and $(CF_3)_2NO$ were mixed in benzene, nitrobenzene, chlorobenzene, or benzotrichloride.

Reactions of Bis[bis(trifluoromethyl)amino-oxy]mercury(II).—Metathetical halogen-exchange reactions with $[Hg\{ON(CF_3)_2\}_2]$ have been used with considerable success for the synthesis of bis(trifluoromethyl)amino-oxy-derivatives of the main-group elements,[5,16–19] but they have not been applied previously to transition-metal halides. It has now been found that the mercurial in dry trichlorofluoromethane reacts slowly with the compounds *cis*-$[PtCl_2L_2]$ (L = PPh_3, $AsPh_3$, or $PMePh_2$) and $[AuCl(PPh_3)]$ at room temperature to give the complexes (8)—(11). Samples of (9) and (11) could not be obtained free of the recrystallization solvent, cyclohexane, and compound (10) could only be obtained as an oil, which was not analytically pure, but was characterized by i.r. and n.m.r. spectroscopy only. The ^1H n.m.r. spectrum of this last compound showed no virtual coupling between the ^{31}P nuclei of the phosphine ligands implying retention of the *cis* configuration during this reaction, and, by inference, during the reactions of the other platinum complexes, Compound (8) has also been obtained in 16% yield. together with mercury metal, from the reaction between the mercurial and $[Pt(PPh_3)_4]$. The similar reactions of *trans*-$[IrCl(CO)(PPh_3)_2]$, $[PdCl_2(PPh_3)_2]$, and $[NiBr_2(PPh_3)_2]$ gave complex product mixtures and no pure products could be isolated. One of the major complications in the use of the mercurial is the difficulty in separating the product from the mercury(II) halide and unchanged mercurial. This frequently results in only moderate to poor yields of isolated pure products. For example, an attempt to prepare a pure sample of $[Mn\{ON(CF_3)_2\}(CO)_5]$ by reaction of the mercurial with $[MnCl(CO)_5]$ failed because the product could not be separated from the mercury derivatives without causing extensive decomposition.

Reactions of the Sodium Salt of Bis(trifluoromethyl)hydroxylamine.—The sodium salt of bis(trifluoromethyl)-hydroxylamine, $(CF_3)_2NO^-Na^+$, is only a weak nucleophile, which has been found to undergo substitution reactions with acid chlorides,[20] pentafluoropyridine,[20] chlorotrimethylsilane,[20] and cyclophosphonitrile chlorides.[21] It did not displace chloride ion from *trans*-$[IrCl(CO)(PPh_3)_2]$ or $[RhCl(PPh_3)_3]$ and it did not cleave the chlorine bridge of $[Pt_2Cl_2(PPh_3)_4][BF_4]_2$ even after several hours at the reflux temperature of acetone. However, good yields of the iridium(I) complex (7; L = PPh_3) and the rhodium(I) analogue (12) were obtained by reaction of the compounds $[M(CO)(MeCN)(PPh_3)_2]ClO_4$ (M = Ir or Rh) with an excess of the sodium salt at room temperature. The i.r. spectra of these compounds show a strong metal–carbonyl absorption in the region 1 955—1 965 cm^{-1} typical of iridium(I) and rhodium(I) complexes.[22] Evidence for the *trans* arrangement of the phosphine ligands rests on the observation that the i.r. band at 1 572 cm^{-1} is of greater intensity than that at 1 586 cm^{-1}. Attempts to confirm this by preparation of $[Ir(CO)(MeCN)(PMePh_2)_2]ClO_4$, required as a precursor to $[Ir\{ON(CF_3)_2\}(CO)(PMePh_2)_2]$, met with as little success as those of previous workers.[22,23] Only decomposition products were obtained from reactions of the sodium salt with $[Ir(CO)(MeCN)(AsPh_3)_2]ClO_4$, $[Mn(CO)_5(MeCN)]PF_6$, and $[Pd(dmf)_4][ClO_4]_2$ (dmf = dimethylformamide), while $[Rh(MeCN)(PPh_3)_2]PF_6$ and $[Fe(CO)_2(Me_2CO)(\eta\text{-}C_5H_5)]ClO_4$ failed to react at room temperature.

Nucleophilic attack at the carbonyl ligand occurs with the complexes *trans*-$[PtX(CO)L_2]BF_4$ (X = Cl, L = PPh_3 or $AsPh_3$; X = Br, L = PPh_3) to give the complexes (13)—(15). These are characterized by a ν(C=O)

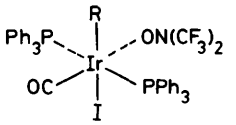


(13) X = Cl, L = PPh_3
(14) X = Cl, L = $AsPh_3$
(15) X = Br, L = PPh_3

band in the i.r. region at 1 707—1 709 cm^{-1}, and strong bands at 1 288, 1 172, 1 152, 1 047, and 985 cm^{-1} for the bis(trifluoromethyl)amino-oxycarbonyl ligand. The ^{19}F chemical shift of the CF_3 group in the region of −24.1 to −24.8 p.p.m. was very different from that of the $(CF_3)_2NO$ ligand (−9.5 to −11.7 p.p.m.). From the relative intensities of the i.r. bands due to the phosphine ligands (1 572 > 1 586 cm^{-1}) it would appear that the *trans* arrangement of the ligands is retained in these complexes. The compounds *trans*-$[PtCl(CO)(SbPh_3)_2]BF_4$ and *trans*-$[PtI(CO)(PPh_3)_2]BF_4$ failed to react with $Na[ON(CF_3)_2]$ under similar conditions. These compounds are known to exist in solution mainly as the halogen-bridged dimers, $[Pt_2X_2L_2][BF_4]_2$ with loss of CO,[24] but even when this reaction was repeated under an atmosphere of CO to force the equilibrium towards the monomeric species the result was the same. The iridium complex $[Ir(CO)_3(PPh_3)_2]BPh_4$ also failed to react at room temperature, while extensive decomposition occurred with $[Fe(CO)_3(\eta\text{-}C_5H_5)]PF_6$. A product having metal–carbonyl bands in the i.r. region at 1 999 and 1 970 cm^{-1} and a strong band at 1 744 cm^{-1} was formed during the reaction of the sodium salt with pentacarbonyliron. This may be the

compound Na[Fe{$CO_2N(CF_3)_2$}(CO)], but it could not be separated from unchanged iron carbonyl, and is possibly in equilibrium with the carbonyl as found with carbamoyl derivatives of $[Fe(CO)_5]$.[25,26] Thus the bis(trifluoromethyl)hydroxylamine anion under the conditions investigated can be considered to have a nucleophilic strength between that of an alcohol and an aliphatic amine, and only reacts with metal carbonyl cations having highly electrophilic carbonyl ligands.

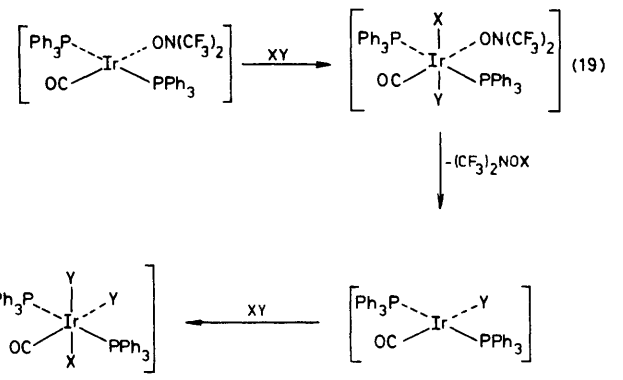
Reactions of [Bis(trifluoromethyl)amino-oxy]carbonylbis(triphenylphosphine)iridium(I).—Like the halogen analogues $[IrX(CO)(PPh_3)_2]$ (X = Cl, Br, or I), complex (7) readily undergoes oxidative addition reactions, but the $(CF_3)_2NO$ ligand appears to be much more labile than the corresponding halogen ligands in the iridium(III) adducts. This is illustrated by the reaction of (7) with CF_3I, MeI, and EtI which afford the expected adducts (16)—(18). These complexes could not be isolated



(16) R = CF_3
(17) R = CH_3
(18) R = C_2H_5

analytically pure as they decompose quite rapidly in solution at room temperature with loss of the $(CF_3)_2NO$ and carbonyl ligands as shown by i.r. spectroscopy. Gas-liquid chromatography (g.l.c.) and i.r. spectroscopic examination of the volatile products obtained on decomposition of complex (18) showed the presence of $(CF_3)_2NOCH_2CH_3$, $(CF_3)_2NO$, and carbon monoxide. It appears that these compounds decompose by competing reductive elimination of both $(CF_3)_2NOR$ and $(CF_3)_2NOI$ [and hence $(CF_3)_2NO$ and I_2, see above] leading to complete decomposition. Characterization of the adducts (16)—(18) is based on the i.r. spectra which show a strong metal–carbonyl band in the region of 2 040—2 072 cm^{-1} typical of iridium(III) complexes, in addition to the usual bands for the $(CF_3)_2NO$ ligand. The ^{19}F n.m.r. spectra show singlets in the region of −9.4 to −10.1 p.p.m. consistent with a $(CF_3)_2NO$ ligand attached directly to the iridium atom. The rate of addition of iodoethane to (7) at room temperature was much slower than that of iodomethane, while 2-iodopropane failed to react over 7 h. This suggests that the $(CF_3)_2NO$ ligand introduces considerable steric constraints in the oxidative addition reaction, and this, in part, may explain the lability of the adducts. Chlorine and iodine react with (7) in benzene at room temperature to give $[IrCl_3(CO)(PPh_3)_2]$ and $[IrI_3(CO)(PPh_3)_2]$ respectively, rather than the expected adducts. In a similar manner the reactions of (7) with CF_3CO_2H, $HgCl_2$, and $PhCH_2COCl$ gave $[IrH(O_2CCF_3)_2(CO)(PPh_3)_2]$, $[IrCl_2(HgCl)(CO)(PPh_3)_2]$, and $[IrCl_2(COCH_2Ph)(CO)(PPh_3)_2]$ with loss of the $(CF_3)_2NO$ ligand.

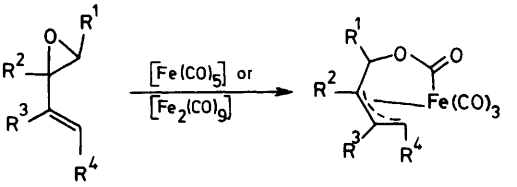
These reactions, like those of the alkyl iodides, can be understood in terms of an oxidative addition reaction to give an adduct (19) followed by reductive elimination (see Scheme 2). Reaction between (7) and $(CF_3)_2NO$ in



(19)

SCHEME 2 X = Cl, Y = Cl; X = I, Y = I; X = H, Y = CF_3CO_2; X = HgCl, Y = Cl; or X = $PhCH_2CO$, Y = Cl

benzene at room temperature gave a 41% yield of the bis(trifluoromethyl)amino-oxycarbonyl derivative (5) previously isolated from the reaction of *trans*-$[IrX(CO)(PPh_3)_2]$ (X = Br or I) with an excess of $(CF_3)_2NO$. It is likely that (5) is formed by rearrangement of the expected oxidative-addition product $[Ir\{ON(CF_3)_2\}_3(CO)(PPh_3)_2]$, and, if so, may be caused by the increased steric demand of the $(CF_3)_2NO$ ligand since $[IrCl\{ON(CF_3)_2\}_2(CO)(PPh_3)_2]$ does not rearrange under similar conditions. However, the possibility that rearrangement of an iridium(II) intermediate may be involved in this reaction cannot be excluded. Rearrangements involving carbon monoxide insertion into a transition metal–oxygen bond are not common, but there are several examples [27] of the formation of tricarbonyliron–lactone complexes on reaction of vinyloxirans with $[Fe(CO)_5]$ or $[Fe_2(CO)_9]$ (Scheme 3) which may take place by a similar insertion.



SCHEME 3

Complex (7) in dichloromethane solution at room temperature under 1 atm of dioxygen gives an equilibrium mixture containing *ca.* 5% of the complex $[Ir\{ON(CF_3)_2\}(CO)(O_2)(PPh_3)_2]$ as evidenced by the appearance of a metal–carbonyl band at 2 040 cm^{-1} in the i.r. spectrum. On removing the oxygen atmosphere this band disappeared and (7) was recovered quantitatively. This contrasts with the behaviour of *trans*-$[IrCl(CO)(PPh_3)_2]$ which forms a stable dioxygen adduct from which dioxygen can only be removed by refluxing in benzene.[28]

EXPERIMENTAL

Spectroscopic Analyses.—Infrared spectra were recorded on a Perkin-Elmer 621 spectrophotometer as mulls in Nujol and hexachlorobutadiene, and n.m.r. spectra were recorded on a Perkin-Elmer R10 or an Hitachi–Perkin-Elmer R20A spectrometer operating at 60 MHz (^{1}H) and 56.46 MHz (^{19}F; trifluoroacetic acid external reference; chemical shifts to *low* field of the reference are designated *negative*). The following abbreviations are used: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. E.s.r. spectra were recorded using a Varian E9 spectrometer. Molecular weights were determined by the vapour-pressure (isopiestic) method using a Perkin-Elmer 115 molecular-weight apparatus.

Starting Materials.—Bis(trifluoromethyl)hydroxylamine,[29] bis[bis(trifluoromethyl)amino-oxy]mercury(II),[30] and bis(trifluoromethyl)amino-oxyl [29] were prepared by methods described in the literature. The sodium salt of bis(trifluoromethyl)hydroxylamine was prepared by dropwise addition of the hydroxylamine into a suspension of sodium hydride in dry diethyl ether.[31] The compounds $[MnH(CO)_5]$,[32] *trans*-$[IrCl(CO)(PPh_3)_2]$,[33] *trans*-$[IrCl(CO)(AsPh_3)_2]$,[34] *trans*-$[IrCl(CO)(PMePh_2)_2]$,[33] *trans*-$[IrBr(CO)(PPh_3)_2]$,[35] *trans*-$[IrI(CO)(PPh_3)_2]$,[35] $[Pt(\eta\text{-}C_2H_4)(PPh_3)_2]$,[36] *cis*-$[PtCl_2(AsPh_3)_2]$,[37] *cis*-$[PtCl_2(PPh_3)_2]$,[37] *cis*-$[PtCl_2(PMePh_2)_2]$,[38] $[Pt(PPh_3)_4]$,[39] $[AuCl(PPh_3)]$,[40] $[PtCl(CO)(AsPh_3)_2]BF_4$,[41] $[PtBr(CO)(PPh_3)_2]BF_4$,[42] $[PtCl(CO)(SbPh_3)_2]BF_4$,[41] and $[PtI(CO)(PPh_3)_2]BF_4$ [41] were synthesized according to previously reported procedures.

All solvents were purified and dried by established procedures and were deoxygenated before use. Except where stated all reactions were carried out under an atmosphere of dry nitrogen.

Reactions of Bis(trifluoromethyl)amino-oxyl.—(*a*) *With* $[MnH(CO)_5]$. A mixture of the manganese hydride (1.9 g, 9.7 mmol) and bis(trifluoromethyl)amino-oxyl (1.68 g, 10.0 mmol), cooled to −196 °C in a tube sealed under vacuum, was allowed to warm to −78 °C in a ' Cardice '–ethanol bath, and was kept at this temperature until the characteristic purple colour of the amino-oxyl had disappeared (10 min). Bis(trifluoromethyl)hydroxylamine (1.2 g, 7.1 mmol) and hydride (0.25 g, 1.2 mmol) were removed under vacuum to give a yellow solid residue of decacarbonyldimanganese [ν(CO) 2 050, 2 005, and 1 980 cm^{-1}] mixed with another product [ν(CO) 2 030 and 1 995 cm^{-1}; ν(C–F) 1 280—1 180, 1 040, and 955 cm^{-1}] believed to be $[Mn\{ON(CF_3)_2\}(CO)_5]$. Attempts to separate this mixture by recrystallization and chromatography were unsuccessful.

(*b*) *With trans*-$[IrCl(CO)(PPh_3)_2]$. Bis(trifluoromethyl)-amino-oxyl (2.7 g, 16.1 mmol) was bubbled slowly through a solution of the iridium complex (0.5 g, 0.6 mmol) in carbon tetrachloride (50 cm^3) for 15 min. The excess of amino-oxyl was removed and the volume of the solution was reduced to 10 cm^3 under reduced pressure before addition of hexane (30 cm^3) to give a white precipitate of *bis[bis(trifluoromethyl)-amino-oxy]carbonylchlorobis(triphenylphosphine)iridium*(III)–*carbon tetrachloride* (1/1), (2) (0.4 g, 0.3 mmol, 50%), m.p. 170 °C (decomp.), which was recrystallized from carbon tetrachloride–methanol (1 : 1) [N.m.r. ($CDCl_3$): ^{1}H, δ 8.2 (m, C_6H_5); ^{19}F, −9.5 p.p.m. (s, CF_3). I.r.: ν(CO) 2 052 cm^{-1}] (Found: C, 39.5; H, 2.4; Cl, 12.8; F, 17.5. $C_{41}H_{30}ClF_{12}IrN_2O_3P_2{\cdot}CCl_4$ requires C, 39.8; H, 2.4; Cl, 14.0; F, 17.9%).

When this reaction was repeated in benzene as solvent, the product, m.p. 161 °C (decomp.), isolated in 53% yield contained benzene (0.75 mol) of crystallization (Found: C, 46.7; H, 2.7; F, 19.1. $C_{41}H_{30}ClF_{12}IrN_2O_3P_2{\cdot}0.75C_6H_6$ requires C, 46.5; H, 3.0; F, 19.4%).

(*c*) *With trans*-$[IrCl(CO)(AsPh_3)_2]$. Under similar conditions reaction between the amino-oxyl and the iridium complex (0.6 g, 0.7 mmol) in benzene gave *bis[bis(trifluoromethyl)amino-oxy]carbonylchlorobis(triphenylarsine)iridium*(III), (3) (0.37 g, 3.00 mmol, 44%), as a white solid, m.p. 152—155 °C (decomp.), which was recrystallized from benzene–methanol (1 : 2) [N.m.r. ($CDCl_3$): ^{1}H, δ 8.3 (m, C_6H_5); ^{19}F, −9.7 p.p.m. (s, CF_3). I.r.: ν(CO) 2 058 cm^{-1}] (Found: C, 40.7; H, 2.5; F, 17.9; N, 2.1. $C_{41}H_{30}As_2ClF_{12}IrN_2O_3$ requires C, 40.9; H, 2.5; F, 18.9; N, 2.3%).

(*d*) *With trans*-$[IrCl(CO)(PMePh_2)_2]$. Reaction between the amino-oxyl (1.2 g, 7.1 mmol) and the iridium complex (0.96 g, 1.5 mmol) in benzene gave *bis[bis(trifluoromethyl)-amino-oxy]carbonylchlorobis(methyldiphenylphosphine)-iridium*(III), (4) (0.71 g, 0.7 mmol, 49%), as a white solid, m.p. 140 °C (decomp.), recrystallized from benzene–methanol (1 : 3) {N.m.r. ($CDCl_3$): ^{1}H, δ 2.72 [apparent triplet, J(P–H) (apparent) = 5.9 Hz, CH_3] and 8.3 (m, C_6H_5); ^{19}F, −9.6 p.p.m. (s, CF_3). I.r.: ν(CO) 2 058 cm^{-1}} (Found: C, 37.4; H, 2.8; Cl, 4.0. $C_{31}H_{26}ClF_{12}IrN_2O_3P_2$ requires C, 37.4; H, 2.6; Cl, 3.6%).

(*e*) *With trans*-$[IrBr(CO)(PPh_3)_2]$. Passage of the amino-oxyl (1.3 g, 7.7 mmol) through a benzene solution of the iridium complex (0.6 g, 0.7 mmol), followed by removal of most of the solvent and addition of methanol, gave a yellow precipitate of $[IrBr_3(CO)(PPh_3)_2]$ (0.1 g, 0.1 mmol, 42%), identified by comparison of its i.r. spectrum with that of an authentic sample. Chromatography [Florisil, CH_2Cl_2–hexane (1 : 1) as eluant] of the filtrate gave *bis[bis(trifluoromethyl)amino-oxy][bis(trifluoromethyl)amino-oxycarbonyl]-bis(triphenylphosphine)iridium*(III), (5) (0.05 g, 0.04 mmol, 6%), isolated as an orange solid, m.p. 167—168 °C, which contained cyclohexane (1.2 mol) of crystallization after recrystallization from CH_2Cl_2–cyclohexane (1 : 2) {N.m.r. ($CDCl_3$): ^{1}H, δ 2.2 (s, 15, C_6H_{12}) and 8.1 (m, 30, C_6H_5); ^{19}F, −11.5 [s, 12, $(CF_3)_2NO$] and −22.0 p.p.m. [s, 6, $(CF_3)_2NOCO$]. I.r.: ν(C=O) 1 600 cm^{-1}} (Found: C, 44.9; H, 3.4; F, 24.5. $C_{43}H_{30}F_{18}IrN_3O_4P_2{\cdot}1.2C_6H_{12}$ requires C, 44.7; H, 3.3; F, 24.3%).

(*f*) *With trans*-$[IrI(CO)(PPh_3)_2]$. Reaction between the amino-oxyl (1.1 g, 6.5 mmol) and the iodo-complex (0.8 g, 0.9 mmol) in benzene gave, after chromatography, $[IrI_3(CO)(PPh_3)_2]$ (0.1 g, 0.09 mmol, 29%), m.p. 257—260 °C (decomp.) [lit.,[43] m.p. 263 °C (decomp.)], and (5) (0.12 g, 0.1 mmol, 10%).

(*g*) *With* $[Pt(\eta^2\text{-}C_2H_4)(PPh_3)_2]$. When the amino-oxyl (2.0 g, 11.9 mmol) was passed through a solution of the platinum complex (0.7 g, 0.9 mmol) in benzene it gave *cis-bis[bis(trifluoromethyl)amino-oxy]bis(triphenylphosphine)-platinum*(II), (8) (0.53 g, 0.5 mmol, 54%), as a white solid, m.p. 175—177 °C (decomp.), which was recrystallized from benzene–methanol (1 : 1). [N.m.r. ($CDCl_3$): ^{1}H, δ 8.1 (m, C_6H_5); ^{19}F, −11.7 p.p.m. (s, CF_3)] (Found: C, 46.1; H, 2.9; F, 20.1; N, 2.6. $C_{40}H_{30}F_{12}N_2O_2P_2Pt$ requires C, 45.5; H, 2.9; F, 21.6; N, 2.7%).

The same product was also obtained in 59% yield by passing the amino-oxyl (1.4 g, 8.3 mmol) for 3 min through a benzene solution of tetrakis(triphenylphosphine)platinum(0) (0.6 g, 0.5 mmol).

Reactions of Bis[bis(trifluoromethyl)amino-oxy]mercury(II).—(*a*) *With cis*-$[PtCl_2(AsPh_3)_2]$. The white mer-

curial (1.0 mmol) was prepared by shaking the amino-oxyl (1.0 g, 6 mmol) and triply distilled mercury (0.2 g, 1 mmol) for 24 h inside a Pyrex ampoule fitted with a polytetrafluoroethylene (ptfe) needle valve (Rotaflo) sealed under vacuum. The unreacted amino-oxyl was removed under reduced pressure, and the platinum complex (0.6 g, 0.7 mmol) was introduced into the tube while it was still under vacuum. Dry trichlorofluoromethane (10 cm^3) was then condensed into the tube, and the mixture was kept at room temperature for 18 h before removal of the solvent to give an orange solid. A slurry of this in dichloromethane was stirred in air for 1 h to decompose unreacted mercurial, the solution was filtered, and cyclohexane was added to the filtrate to give cis-*bis*[*bis*(*trifluoromethyl*)*amino-oxy*]*bis*(*triphenylarsine*)*platinum*(II)–*cyclohexane* (2/1), (9) (0.38 g, 0.33 mmol, 48%), as white crystals, m.p. 145—152 °C (decomp.) [N.m.r. ($CDCl_3$): ^1H δ 2.25 (s, 6, C_6H_{12}) and 8.2 (s, 30, C_6H_5); ^{19}F, −11.75 p.p.m. (s, CF_3)] (Found: C, 43.2; H, 3.1; F, 18.8. $C_{40}H_{30}As_2N_2O_2Pt{\cdot}0.5C_6H_{12}$ requires C, 43.5; H, 3.0; F, 19.2%).

(*b*) *With cis*-[$PtCl_2(PPh_3)_2$]. Under similar conditions the mercurial (*ca.* 1 mmol) and the phosphine complex (0.4 g, 0.5 mmol) in $CFCl_3$ gave (8) (0.2 g, 0.2 mmol, 37%).

(*c*) *With* [$Pt(PPh_3)_4$]. The same product was obtained in 16% yield on reaction of the mercurial (*ca.* 1 mmol) with the platinum(0) complex (0.6 g, 0.5 mmol) in $CFCl_3$ at room temperature after 2 d.

(*d*) *With cis*-[$PtCl_2(PMePh_2)_2$]. The mercurial (*ca.* 1 mmol) and the methyldiphenylphosphine complex (0.45 g, 0.7 mmol) in $CFCl_3$ after 18 h at room temperature gave *cis*-bis[bis(trifluoromethyl)amino-oxy]bis(methyldiphenylphosphine)platinum(II), (10), as an impure brown oil which could not be obtained analytically pure even after chromatography {N.m.r. ($CDCl_3$): ^1H, δ 2.8 [triplet of doublets, $J(P-H) = 12$, $J(Pt-H) = 32$ Hz, CH_3] and 8.2 (m, 20, C_6H_5); ^{19}F, −11.2 p.p.m. (s, CF_3)}.

(*e*) *With* [AuCl(PPh_3)]. After 8 d at room temperature a mixture of the mercurial (*ca.* 1 mmol) and the gold complex (0.6 g, 1.2 mmol) in $CFCl_3$ gave [*bis*(*trifluoromethyl*)*amino-oxy*](*triphenylphosphine*)*gold*(I)–*cyclohexane* (4/1), (11) (0.43 g, 0.69 mmol, 57%), as an off-white solid, m.p. 108 °C (decomp.), recrystallized from dichloromethane–cyclohexane–diethyl ether (1 : 1 : 1) [N.m.r. ($CDCl_3$): ^1H, δ 2.1 (s, 3, C_6H_{12}) and 8.1 (m, 15, C_6H_5); ^{19}F, −10.0 p.p.m. (s, CF_3)] [Found: C, 40.2; H, 2.9; F, 16.8; N, 2.0%; *M* (hexane) = 634. $C_{20}H_{15}AuF_6NOP{\cdot}0.25C_6H_{12}$ requires C, 39.8; H, 2.7; F, 17.6; N, 2.2%; *M* = 648].

Reactions of the Sodium Salt of Bis(*trifluoromethyl*)*hydroxylamine*.—(*a*) *With* [Ir(CO)(MeCN)(PPh_3)$_2$]ClO_4. A solution of the iridium complex (0.7 g, 0.79 mmol) in tetrahydrofuran (thf) (20 cm^3) was added to a solution of the sodium salt (0.4 g, 2.1 mmol) in the same solvent, and the mixture was stirred for 5 min before addition of ethanol (30 cm^3). The volume of the solution was reduced to 20 cm^3 under reduced pressure to give [*bis*(*trifluoromethyl*)*amino-oxy*]*carbonylbis*(*triphenylphosphine*)*iridium*(I)–*tetrahydrofuran* (1/1), (7) (0.5 g, 0.5 mmol, 63%), as a yellow solid, m.p. 190—200 °C (decomp.) [N.m.r. ($CDCl_3$): ^1H, δ 2.7 (m, 4, β-CH_2 of thf), 4.6 (m, 4, α-CH_2 of thf), and 8.3 (m, 30, C_6H_5); ^{19}F, −10.4 p.p.m. (s, CF_3). I.r.: ν(CO) 1 957 cm^{-1}] (Found: C, 52.5; H, 4.0; F, 9.8; N, 1.4. $C_{39}H_{30}F_6IrNO_2P_2{\cdot}C_4H_8O$ requires C, 52.4; H, 3.9; F, 11.6; N, 1.4%).

(*b*) *With* [Rh(CO)(MeCN)(PPh_3)$_2$]ClO_4. Addition of a solution of the rhodium complex (0.5 g, 0.63 mmol) in dichloromethane to an ethereal solution of the sodium salt (0.5 g, 2.6 mmol) gave, after 10 min at room temperature, [*bis*(*trifluoromethyl*)*amino-oxy*]*carbonylbis*(*triphenylphosphine*)*rhodium*(I)–*dichloromethane* (2/1), (12) (0.27 g, 0.32 mmol, 51%), which precipitated as a yellow solid, m.p. 160—180 °C (decomp.), on addition of ethanol [N.m.r. ($CDCl_3$): ^1H, δ 6.05 (s, 1, CH_2Cl_2) and 8.3 (m, 30, C_6H_5); ^{19}F, −9.9 p.p.m. (s, CF_3). I.r.: ν(CO) 1 960 cm^{-1}] (Found: C, 54.0; H, 3.3; F, 13.2; N, 1.6. $C_{39}H_{30}F_6NO_2P_2Rh{\cdot}0.5CH_2Cl_2$ requires C, 54.6; H, 3.6; F, 13.2; N, 1.6%).

(*c*) *With* [$PtCl(CO)(PPh_3)_2$]BF_4. Under similar conditions reaction between the sodium salt (0.8 g, 4.2 mmol) and the platinum complex (0.72 g, 0.83 mmol) gave [*bis*(*trifluoromethyl*)*amino-oxycarbonyl*]*chlorobis*(*triphenylphosphine*)*platinum*(II)–*dichloromethane* (4/1), (13) (0.38 g, 0.39 mmol, 47%), which was recrystallized from dichloromethane–hexane (1 : 1) as a yellow solid, m.p. 196 °C (decomp.) [N.m.r. ($CDCl_3$): ^1H, δ 6.1 (s, 0.5, CH_2Cl_2) and 8.3 (m, 30, C_6H_5); ^{19}F, −24.8 p.p.m. (s, CF_3). I.r.: ν(C=O) 1 707m—s cm^{-1}] (Found: C, 48.0; H, 3.2; F, 11.2; N, 1.4. $C_{39}H_{30}ClF_6NO_2P_2Pt{\cdot}0.25\ CH_2Cl_2$ requires C, 48.4; H, 3.2; F, 11.7; N, 1.4%).

(*d*) *With* [$PtCl(CO)(AsPh_3)_2$]BF_4. Using a similar procedure, reaction between the sodium salt (1.4 g, 7.3 mmol) and the triphenylarsine complex (1.0 g, 1.04 mmol) gave [*bis*(*trifluoromethyl*)*amino-oxycarbonyl*]*chlorobis*(*triphenylarsine*)*platinum*(II), (14) (0.37 g, 0.36 mmol, 34%), as yellow crystals, m.p. 142 °C (decomp.) [N.m.r. ($CDCl_3$): ^1H, δ 8.4 (m, C_6H_5): ^{19}F, −24.1 p.p.m. (s, CF_3). I.r.: ν(C=O) 1 708m—s cm^{-1}] (Found: C, 44.9; H, 3.1; F, 11.4; N, 1.3. $C_{39}H_{30}As_2ClF_6NO_2Pt$ requires C, 45.0; H, 2.9; F, 11.0; N, 1.3%).

(*e*) *With* [$PtBr(CO)(PPh_3)_2$]BF_4. [*Bis*(*trifluoromethyl*)*amino-oxycarbonyl*]*bromobis*(*triphenylphosphine*)*platinum*(II)–*dichloromethane* (1/1), (15) (0.91 g, 0.84 mmol, 66%), was obtained as a yellow solid, m.p. 180 °C (decomp.) [N.m.r. ($CDCl_3$): ^1H, δ 6.15 (s, 2, CH_2Cl_2) and 8.5 (m, 30, C_6H_5); ^{19}F, −24.5 p.p.m. (s, CF_3). I.r.: ν(C=O) 1 709s cm^{-1}] (Found: C, 45.3; H, 2.9; F, 10.5; N, 1.1. $C_{39}H_{30}BrF_6NO_2P_2Pt{\cdot}CH_2Cl_2$ requires C, 44.5; H, 3.0; F, 10.5; N, 1.3%) on reaction between the bromo-complex (1.17 g, 1.28 mmol) and the sodium salt (0.65 g, 3.4 mmol).

Reactions of [*Bis*(*trifluoromethyl*)*amino-oxy*]*carbonylbis*(*triphenylphosphine*)*iridium*(I).—(*a*) *With bis*(*trifluoromethyl*)*amino-oxyl*. The amino-oxyl (0.8 g, 4.8 mmol) was bubbled through a solution of the iridium complex (0.5 g, 0.55 mmol) in dry benzene (50 cm^3), and the mixture was then stirred at room temperature for 10 min. Removal of the solvent under reduced pressure gave an orange gum, which was crystallized from dichloromethane–cyclohexane (1 : 2) to give bis[bis(trifluoromethyl)amino-oxy][bis(trifluoromethyl)amino-oxycarbonyl]bis(triphenylphosphine)iridium(III)–cyclohexane (1/1.2) (0.3 g, 0.22 mmol, 41%).

(*b*) *With chlorine*. Passage of chlorine through a solution of the iridium complex (0.34 g, 0.37 mmol) in dichloromethane (15 cm^3) at room temperature for 2 min gave carbonyltrichlorobis(triphenylphosphine)iridium(III) (0.12 g, 0.14 mmol, 37%).

(*c*) *With iodine*. When a solution of the iridium complex (0.5 g, 0.55 mmol) in dichloromethane was stirred with iodine (0.2 g, 0.79 mmol) at room temperature for 10 min it gave carbonyltri-iodobis(triphenylphosphine)iridium(III) (0.21 g, 0.18 mmol, 34%), m.p. 258—260 °C (lit.,[44] m.p. 265 °C).

(*d*) *With trifluoroacetic acid*. Addition of the acid (0.2 g,

1.8 mmol) to the iridium complex (0.3 g, 0.33 mmol) in benzene followed by stirring at room temperature for 5 min gave carbonylhydridobis(trifluoroacetato)bis(triphenylphosphine)iridium(III)–trifluoroacetic acid (1/0.75) (0.23 g, 0.22 mmol, 67%) (Found: C, 47.8; H, 3.0; F, 14.6. Calc. for $C_{41}H_{31}F_6IrO_5P_2 \cdot 0.75CF_3CO_2H$: C, 48.3; H, 2.9; F, 14.8%).

(*e*) *With mercury*(II) *chloride*. Mercury(II) chloride (0.3 g, 1.1 mmol) was added to a solution of the iridium complex (0.4 g, 0.44 mmol) in thf and the mixture was stirred for 20 min at room temperature. Removal of most of the solvent and addition of hexane gave $[IrCl_2(HgCl)(CO)(PPh_3)_2]$ (0.17 g, 0.16 mmol, 36%) identified by comparison of its i.r. spectrum with that of an authentic sample.[45]

(*f*) *With phenylacetyl chloride*. Reaction between the iridium complex (0.2 g, 0.22 mmol) and phenylacetyl chloride (2 cm^3) over 2 h at room temperature followed by addition of diethyl ether gave $[IrCl_2(COCH_2Ph)(CO)(PPh_3)_2] \cdot 0.25CH_2Cl_2$ (0.15 g, 0.16 mmol, 73%) (Found: C, 57.5; H, 4.2; Cl, 9.7. Calc. for $C_{45}H_{37}Cl_2IrO_2P_2 \cdot 0.25CH_2Cl_2$: C, 56.9; H, 4.0; Cl, 9.3%) identified by comparison of its i.r. and ^{1}H n.m.r. spectra with those of an authentic sample.

(*g*) *With trifluoroiodomethane*. The iridium complex (0.3 g, 0.33 mmol) and trifluoroiodomethane (3 cm^3) were sealed *in vacuo* in a Pyrex tube (100 cm^3) and kept at room temperature for 1 h. Removal of the volatiles gave an unstable white solid believed to be [*bis(trifluoromethyl)amino-oxy*]*carbonyliodo*(*trifluoromethyl*)*bis*(*triphenylphosphine*)*iridium*(III), (16) (0.2 g, 0.18 mmol, 55%) {N.m.r. ($CDCl_3$): ^{1}H, δ 8.4 (m, C_6H_5); ^{19}F, −9.4 [s, 6, $(CF_3)_2NO$] and 31 p.p.m. (s, 3, CF_3). I.r.: ν(CO) 2 072 s cm^{-1}}.

(*h*) *With iodomethane*. Addition of diethyl ether to a mixture of the iridium complex (0.5 g, 0.55 mmol) and iodomethane (10 cm^3) which had been stirred at room temperature for 5 min gave [*bis*(*trifluoromethyl*)*amino-oxy*]*carbonyliodo*(*methyl*)*bis*(*triphenylphosphine*)*iridium*(III), (17) (0.51 g, 0.48 mmol, 89%), as an unstable white solid [N.m.r. ($CDCl_3$): ^{1}H, δ 2.3 (s, 3, CH_3) and 8.4 (m, 30, C_6H_5); ^{19}F, −9.6 p.p.m. (s, CF_3). I.r.: ν(CO) 2 052s cm^{-1}].

(*i*) *With iodoethane*. Under similar conditions iodoethane (10 cm^3) and the iridium complex (0.3 g, 0.33 mmol) gave [*bis*(*trifluoromethyl*)*amino-oxy*]*carbonyl*(*ethyl*)*iodobis*(*triphenylphosphine*)*iridium*(III), (18) (0.2 g, 0.19 mmol, 56%), as an unstable white solid [N.m.r. ($CDCl_3$): ^{1}H, δ 2.7 (t, 3, J = 7 Hz, CH_3), 3.95 (q, 2, CH_2), and 8.45 (m, 30, C_6H_5); ^{19}F, −10.1 p.p.m. (s, CF_3). I.r.: ν(CO) 2 040s cm^{-1}].

When a solution of this product (0.1 g, 0.09 mmol) in benzene was maintained at room temperature *in vacuo* for 2 h in a sealed tube, examination of the volatiles by g.l.c. (SE30 and APL columns) showed the presence of [bis(trifluoromethyl)amino-oxy]ethane (identified by comparison of its retention time and i.r. spectrum with that of an authentic sample), bis(trifluoromethyl)amino-oxyl, and carbon monoxide.

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