Some Oxidative-addition Reactions of the Diradical, Perfluoro-*NN'*-dimethylethane-1,2-bis(amino-oxyl), $CF_3N(O)CF_2CF_2N(O)CF_3$, with Iridium(I) and Platinum(0) Complexes

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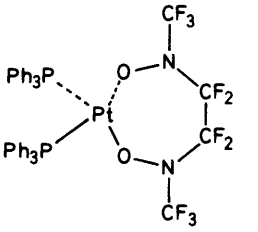
The stable diradical $CF_3N(O)CF_2CF_2N(O)CF_3$ reacts with *trans*-$[IrCl(CO)L_2]$ (L = PPh_3, $AsPh_3$, or $PMePh_2$), *trans*-$[Ir\{ON(CF_3)_2\}(CO)(PPh_3)_2]$, and $[Pt(PPh_3)_4]$ to form the seven-membered ring metallacyclic complexes $[Ir\{ON(CF_3)CF_2CF_2N(CF_3)O\}Cl(CO)L_2]$, $[Ir\{ON(CF_3)CF_2CF_2N(CF_3)O\}\{ON(CF_3)_2\}(CO)(PPh_3)_2]$, and $[Pt\{ON(CF_3)CF_2CF_2N(CF_3)O\}(PPh_3)_2]$ respectively.

THERE is now considerable evidence that some oxidative-addition reactions of low-valent transition-metal complexes occur by a free-radical mechanism.[1] Most of the work reported to date has been concerned with mechanistic studies, and the synthetic uses of this reaction have not been explored to any extent. We recently reported[2] oxidative-addition reactions of the radical bis(trifluoromethyl)amino-oxyl, $(CF_3)_2NO$, and as part of our investigations of the reaction of 'persistent'[3] radicals with transition-metal compounds we now describe some reactions of iridium(I) and platinum(0) complexes with the stable diradical $CF_3N(O)CF_2CF_2N(O)CF_3$.

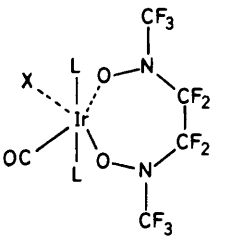
RESULTS AND DISCUSSION

A rapid reaction occurs when a benzene solution of $[Pt(PPh_3)_4]$ is treated with an excess of $CF_3N(O)CF_2CF_2N(O)CF_3$ at room temperature to give the platinum(II) complex (1) as an air-stable white solid, which has characteristic, strong i.r. bands at 1 262, 1 250, 1 237, 1 209, 1 163, and 1 150 [ν(C–F)], 1 052 [ν(N–O)], 890 and 852 cm^{-1} [ν(C–N)] for the dioxyl ligand. Under similar conditions, the iridium(I) complexes *trans*-$[IrCl(CO)L_2]$ (L = PPh_3, $AsPh_3$, or $PMePh_2$) and *trans*-$[Ir\{ON(CF_3)_2\}(CO)(PPh_3)_2]$ gave the adducts (2)—(5). These compounds, which are stable in air for several days, and stable for several months under nitrogen, have been shown by molecular-weight determination to be monomeric in solution. Thus, the $CF_3N(O)CF_2CF_2N(O)CF_3$ moiety is presumed to be present as a *cis*-chelating ligand bound to the metal through the two oxygen atoms. An apparent 1 : 2 : 1 triplet pattern is observed for the methyl group of the $PMePh_2$ ligand in the ^1H n.m.r. spectrum of compound (4). This is usually indicative of strong virtual coupling between *trans* ^{31}P nuclei,[4] although cases of virtual coupling between *cis* phosphine ligands are also known.[5-7] Another diagnostic test for *trans*-arylphosphine ligands is whether the aromatic skeletal i.r. vibration at 1 572 cm^{-1} is of greater intensity than that at 1 586 cm^{-1};[8,9] this is found to be the case for the i.r. spectra of compounds (2), (4), and (5). On this basis the complexes are assigned the stereochemistry shown.

An unusual feature of the i.r. spectra of these iridium(III) complexes is that in every case two strong metal–carbonyl absorptions, rather than the single band expected, are observed in the region 2 035—2 060 cm^{-1}.



(1)



(2) L = PPh_3 X = Cl
(3) L = $AsPh_3$ X = Cl
(4) L = $PMePh_2$ X = Cl
(5) L = PPh_3 X = $ON(CF_3)_2$

Furthermore, the 1 : 2 : 1 triplet for the CF_3 groups in the region −14.5 to −14.7 p.p.m. observed at room temperature in the ^{19}F n.m.r. spectra of compounds (2) and (3) collapses to a single broad peak on cooling the solution to 0 °C. On further cooling to −40 °C this band is resolved into a doublet of doublets [J(F–F) = 24 and 44 Hz]. The iridacycle $Ir\{ON(CF_3)CF_2CF_2N(CF_3)O\}$ must be fluxional, and these complexes appear to be mixtures of two conformational isomers which interconvert rapidly at room temperature. The ^{19}F n.m.r. spectrum of

compound (4) is even more complex and at room temperature the CF_3 groups appear as three triplets of approximately equal intensity at −13.4, −14.3, and −16.0 p.p.m. Fluxional behaviour is also evident in the spectrum of the platinum complex (1), but the rate of equilibration between the conformers is much faster possibly due to the lower steric requirements. Coalescence of the 1 : 2 : 1 triplet for the CF_3 groups does not occur until −60 °C.

EXPERIMENTAL

Infrared spectra were recorded on a Perkin-Elmer 621 spectrophotometer and n.m.r. spectra were recorded on a Perkin-Elmer R10 spectrometer operating at 60 MHz (^1H) and 56.46 MHz (^{19}F; trifluoroacetic acid external reference; chemical shifts to low field of the reference are designated negative). Molecular weights were determined by the vapour-pressure (isopiestic) method using a Perkin-Elmer 115 molecular-weight apparatus. The compounds *trans*-[IrCl(CO)$(PPh_3)_2$],[10] *trans*-[IrCl(CO)$(AsPh_3)_2$],[11] *trans*-[IrCl(CO)$(PMePh_2)_2$],[10] *trans*-[Ir{ON$(CF_3)_2$}(CO)$(PPh_3)_2$],[2] [Pt$(PPh_3)_4$],[12] and perfluoro-*NN'*-dimethylethane-1,2-bis(amino-oxyl) [13] were prepared by previously reported procedures. All reactions were carried out under an atmosphere of dry nitrogen, and all solvents were purified, dried, and de-aerated using standard procedures.

Reactions of Perfluoro-NN'-dimethylethane-1,2-bis(amino-oxyl).—(a) *With* [Pt$(PPh_3)_4$]. Addition of the diradical (0.6 g, 2.0 mmol) to a solution of the platinum complex (0.7 g, 0.56 mmol) in benzene with stirring over 15 min gave [*perfluoro*-NN'-*dimethylethane*-1,2-*bis*(*amino-oxy*)]*bis*(*triphenylphosphine*)*platinum*(II)–*cyclohexane* (1/1) (0.58 g, 0.53 mmol, 94%) as a white solid, m.p. 180—182 °C (decomp.), after recrystallisation from dichloromethane–cyclohexane (1 : 1) (Found: C, 50.6; H, 3.5; F, 16.5; N, 2.1. $C_{40}H_{30}F_{10}N_2O_2P_2Pt{\cdot}C_6H_{12}$ requires C, 50.2; H, 3.7; F, 17.2; N, 2.5%) {N.m.r.: ^1H ($CDCl_3$), δ 2.2 (s, 12, C_6H_{12}) and 7.5 (m, 30, C_6H_5); ^{19}F (CH_2Cl_2), −15.1 [t, 6, J(F–F) = 15 Hz, CF_3] and 32.1 p.p.m. (m, 4, CF_2)}.

(*b*) *With trans*-[IrCl(CO)$(PPh_3)_2$]. The diradical (0.8 g, 2.7 mmol) was added to a solution of *trans*-[IrCl(CO)$(PPh_3)_2$] (0.75 g, 0.96 mmol) in carbon tetrachloride and the mixture was stirred for 15 min at room temperature. Removal of the solvent and unchanged diradical under reduced pressure gave a colourless oil, which on dissolving in benzene and addition of methanol gave *carbonylchloro*-[*perfluoro*-NN'-*dimethylethane*-1,2-*bis*(*amino-oxy*)]*bis*-(*triphenylphosphine*)*iridium*(III)–*benzene* (1/1) (1.1 g, 0.95 mmol, 99%) as a white solid, m.p. 219—240 °C (decomp.) [Found: C, 48.7; H, 3.3; Cl, 4.1; F, 16.6; N, 2.4%; M (C_6H_6) = 981. $C_{41}H_{30}ClF_{10}IrN_2O_3P_2{\cdot}C_6H_6$ requires C, 48.8; H, 3.1; Cl, 3.1; F, 16.5; N, 2.4%; M = 1 154] {N.m.r.: ^1H ($CDCl_3$), δ 7.3 (s, 6, C_6H_6) and 8.2 (m, 30, C_6H_5); ^{19}F (CH_2Cl_2 at 25 °C), −14.5 [t, 6, J(F–F) = 15 Hz, CF_3] and 30.9 p.p.m. (m, 4, CF_2). I.r.: ν(CO) 2 060s and 2 050s cm^{-1}}.

(*c*) *With trans*-[IrCl(CO)$(AsPh_3)_2$]. Under similar conditions the diradical (0.3 g, 1.0 mmol) and *trans*-[IrCl(CO)$(AsPh_3)_2$] (0.4 g, 0.46 mmol) in benzene (20 cm^3) gave *carbonylchloro*[*perfluoro*-NN'-*dimethylethane*-1,2-*bis*(*amino-oxy*)]*bis*(*triphenylarsine*)*iridium*(III) (0.35 g, 0.3 mmol, 65%) as a white solid, m.p. 131—136 °C (decomp.), which was recrystallised from dichloromethane–methanol. [Found: C, 42.6; H, 2.4; F, 15.6%; M (CH_2Cl_2) = 1 166. $C_{41}H_{30}As_2ClF_{10}IrN_2O_3$ requires C, 42.2; H, 2.6; F, 16.3%; M = 1 081] {N.m.r.: ^1H ($CDCl_3$), δ 8.3 (m, C_6H_5); ^{19}F (CH_2Cl_2 at 25 °C), −14.7 [t, 6, J(F–F) = 15 Hz, CF_3] and 32.1 p.p.m. (m, 4, CF_2). I.r.: ν(CO) 2 060s and 2 043s cm^{-1}}.

(*d*) *With trans*-[IrCl(CO)$(PMePh_2)_2$]. Treatment of *trans*-[IrCl(CO)$(PMePh_2)_2$] (0.8 g, 1.2 mmol) in benzene (20 cm^3) with the diradical (0.5 g, 1.6 mmol) gave, after 15 min at room temperature, *carbonylchlorobis*(*methyldiphenylphosphine*)[*perfluoro*-NN'-*dimethylethane*-1,2-*bis*(*amino-oxy*]*iridium*(III) (0.57 h, 0.6 mmol, 49%) as a white solid, m.p. 125—128 °C (decomp.), which was recrystallised from benzene–methanol (1 : 1) [Found: C, 39.2; H, 2.9; F, 19.9; N, 2.9%; M (C_6H_6) = 1 065. $C_{31}H_{26}ClF_{10}IrN_2O_3P_2$ requires C, 39.0; H, 2.8; F, 19.9; N, 2.9%; M = 954] {N.m.r.: ^1H ($CDCl_3$), δ 2.76 [apparent 1 : 2 : 1 triplet, 6, apparent J(P=H) = 5 Hz, CH_3] and 8.2 (m, 20, C_6H_5); ^{19}F (CH_2Cl_2 at 25 °C), −14.7 [t, 6, J(F–F) = 15 Hz, CF_3] and 30.2 p.p.m. (m, 4, CF_2). I.r.: ν(CO) 2 048s and 2 035(sh) cm^{-1}}.

(*e*) *With trans*-[Ir{ON$(CF_3)_2$}(CO)$(PPh_3)_2$]. Reaction between the diradical (0.3 g, 1.0 mmol) and *trans*-[Ir{ON$(CF_3)_2$}(CO)$(PPh_3)_2$] (0.3 g, 0.33 mmol) in carbon tetrachloride over 5 min at room temperature gave *carbonyl*-[*perfluoro*-NN'-*dimethylethane*-1,2-*bis*(*amino-oxy*)][*bis*-(*trifluoromethyl*)*amino-oxy*]*bis*(*triphenylphosphine*)*iridium*(III)–*cyclohexane* (1/0.6) (0.25 g, 0.19 mmol, 60%) as a white solid, m.p. 189—192 °C (decomp.), which was recrystallised from dichloromethane–cyclohexane (Found: C, 44.2; H, 3.2; F, 23.6; N, 3.1. $C_{43}H_{30}F_{16}IrN_3O_4P_2{\cdot}0.6C_6H_{12}$ requires C, 44.3; H, 3.0; F, 24.1; N, 3.3%) {N.m.r.: ^1H ($CDCl_3$), δ 2.1 (s, 12, C_6H_{12}) and 8.2 (m, 4.8, C_6H_5); ^{19}F (CH_2Cl_2 at 25 °C), −14.5 [s, 6, $(CF_3)_2NO$], −15.0 [t, 6, J(F–F) = 15 Hz, $CF_3N(O)$], and 26.5 p.p.m. (m, 4, CF_2). I.r.: ν(CO) 2 059s cm^{-1}}.

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