Complexes of the Platinum Metals. Part 23.[1] Synthesis of the Nitrosyl Carboxylate Complexes $[M(O_2CR)_2(NO)(PPh_3)_2]$ (M = Rh or Ir; R = CF_3, C_2F_5, or C_6F_5): Crystal and Molecular Structures† of the Trifluoroacetate Derivatives $[M(O_2CCF_3)_2(NO)(PPh_3)_2]$

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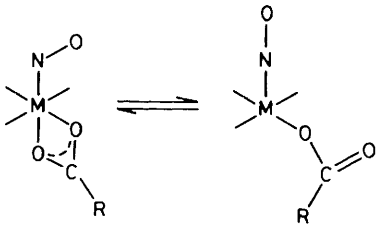
The rhodium complex $[Rh(NO)(PPh_3)_3]$ reacts with perfluorocarboxylic acids, RCO_2H, *in the presence of dioxygen* to afford emerald green complexes $[Rh(O_2CR)_2(NO)(PPh_3)_2]$ (R = CF_3, C_2F_5, or C_6F_5) in good yield. In contrast, the corresponding iridium precursor, $[Ir(NO)(PPh_3)_3]$ reacts with the same acids under aerobic or anaerobic conditions to yield brown complexes $[Ir(O_2CR)_2(NO)(PPh_3)_2]$. The trifluoroacetate derivatives have been examined by *X*-ray diffraction methods and shown to possess dissimilar structures. Crystals of the rhodium complex are monoclinic, space group *Cc*, with $a = 12.593(2)$, $b = 15.466(3)$, $c = 20.479(3)$ Å, $\beta = 100.03(4)°$, and $Z = 4$. The structure, which has been refined to $R = 0.06$ for 2 918 observed reflections, consists of tetragonal-pyramidal molecules with angular apical nitrosyl ligands and *trans* phosphine ligands. Crystals of the iridium complex (solvated with one molecule of acetone) are orthorhombic, space group *Pbcn*, with $a = 19.171(2)$, $b = 22.684(3)$, $c = 20.169(3)$ Å, and $Z = 8$. The structure, which has been refined to $R = 0.081$ for 3 791 observed reflections, consists of trigonal-bipyramidal molecules with linear equatorial nitrosyl groups and axial *trans* phosphine ligands. The angle subtended at the iridium by the co-ordinated oxygen atoms of the unidentate trifluoroacetate ligands is remarkably small [75.0(6)°]. Preliminary calculations performed using a steric energy calculation computer program, EENY2, suggest that in each case the structure adopted corresponds to a stereochemical energy minimum.

Nitric oxide is able to function as a formal one-electron (angular NO) or three-electron (linear NO) donor ligand. Similarly carboxylate anions can co-ordinate as two-electron (unidentate) or four-electron (bidentate) donor ligands. In each case, facile interconversion of bonding modes (linear $\rightleftharpoons$ angular NO)[2] and (unidentate $\rightleftharpoons$ bidentate carboxylate ligands)[3] has been demonstrated. In principle therefore an equilibrium process of the form shown in the Scheme should be feasible. Labile processes of this type involving rapid changes in co-ordination number and oxidation state of the central metal ion could conceivably feature in the substrate co-ordination and electron-transfer steps commonly encountered in reactions catalysed by transition metal complexes. In order to examine this possibility more closely, we have synthesised a range of complexes containing nitrosyl and carboxylate ligands within the same co-ordination sphere. In this paper we describe in detail[4] the preparation and characterisation of a series of rhodium and iridium complexes $[M(O_2CR)_2(NO)(PPh_3)_2]$ (R = CF_3, C_2F_5, or C_6F_5) and report the crystal and molecular structures of the trifluoroacetate derivatives $[M(O_2CCF_3)_2(NO)(PPh_3)_2]$. In the following paper[5] we discuss the mechanism of formation of these complexes, in particular the dioxygen dependence of the rhodium synthesis.



Scheme.

Experimental

Solvents (AnalaR grade) were dried over molecular sieves, perfluorocarboxylic acids were used as purchased (Fluorochem), rhodium trichloride trihydrate and sodium chloroiridate hexahydrate were supplied by Johnson Matthey. Nitrosyl complexes were prepared by literature methods[6,7] and used without further purification. Analyses, by the Microanalytical Laboratory, University College, London, and melting points, taken in sealed tubes under nitrogen on a Buchi apparatus, are given in Table 1. I.r. spectra (Nujol mulls) were recorded on a Perkin-Elmer 457 grating spectrometer; ^{31}P and ^{19}F n.m.r. spectra were obtained using a Bruker HFX90 spectrometer and Fourier-transform facility. Spectroscopic data are reported in Table 2. N.m.r. data are referenced against external 85% H_3PO_4 (^{31}P) and internal C_6F_6 (^{19}F), with positive values to low field of the reference.

Nitrosylbis(trifluoroacetato)bis(triphenylphosphine)rhodium.—Nitrosyltris(triphenylphosphine)rhodium (0.2 g, 0.22 mmol) was added to a mixture of trifluoroacetic acid (0.25 cm^3, 3.0 mmol) and acetone (5 cm^3) in an open conical flask. The red suspension was stirred for *ca.* 20 min; during this time it darkened then gradually cleared to form a bright emerald green solution. Dilution with light petroleum (b.p. 40—60 °C; 10 cm^3) followed by slow concentration under reduced pressure gave a green precipitate which was filtered off, washed successively with acetone (2 cm^3) and light petroleum (2 × 5 cm^3), then dried *in*

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† Nitrosylbis(trifluoroacetato)bis(triphenylphosphine)-rhodium and -iridium.

Supplementary data available (No. SUP 56112, 9 pp.): thermal parameters, full lists of bond lengths and angles. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

Table 1. Analytical data and melting points

Complex	M.p. (θ_c/°C)	Analysis[a] (%) C	H	N
$[Rh(O_2CCF_3)_2(NO)(PPh_3)_2]$	225—227	54.2 (54.4)	3.5 (3.4)	1.4 (1.6)
$[Rh(O_2CC_2F_5)_2(NO)(PPh_3)_2]$	212—213	51.0 (51.3)	3.0 (3.1)	1.3 (1.4)
$[Rh(O_2CC_6F_5)_2(NO)(PPh_3)_2]$	180—182	55.8 (55.6)	2.9 (2.8)	1.6 (1.6)
$[Ir(O_2CCF_3)_2(NO)(PPh_3)_2]$[b]	208—210	50.2 (49.9)	3.0 (3.2)	1.2 (1.4)
$[Ir(O_2CC_2F_5)_2(NO)(PPh_3)_2]$	204—205	47.4 (47.0)	2.9 (2.8)	1.2 (1.3)
$[Ir(O_2CCF_3)(NO)(PPh_3)_2][BPh_4]$[c]		63.2 (62.8)	4.5 (4.25)	1.15 (1.2)

[a] Calculated values are in parentheses. [b] Acetone solvate (1/1). [c] P, 5.55 (5.25)%.

Table 2. Spectroscopic data

Complex	ν(NO)/cm^{-1}	ν(OCO)/cm^{-1}	δ(P)	^1J(Rh–P)/Hz
$[Rh(O_2CCF_3)_2(NO)(PPh_3)_2]$[a]	1 671	1 694	20.85 (d)	115
$[Rh(O_2CC_2F_5)_2(NO)(PPh_3)_2]$[b]	1 662	1 688	20.95 (d)	117
$[Rh(O_2CC_6F_5)_2(NO)(PPh_3)_2]$	1 671	1 694	21.68 (d)	120.5
$[Ir(O_2CCF_3)_2(NO)(PPh_3)_2]$	1 793	1 689	13.16 (s)	—
$[Ir(O_2CC_2F_5)_2(NO)(PPh_3)_2]$	1 807	1 687		—
$[Ir(O_2CCF_3)(NO)(PPh_3)_2][BPh_4]$	1 850	1 572	22.44 (s)	—

[a] ^{19}F N.m.r.: 74.85 p.p.m. (s). [b] ^{19}F N.m.r.: −83.95 (t), −119.35 p.p.m. (quartet), ^3J(FF′) = 2 Hz.

vacuo to afford the required product as *emerald green microcrystals* (0.165 g, 86%). The following complexes were prepared similarly: nitrosylbis(pentafluoropropionato)bis(triphenylphosphine)rhodium as emerald green crystals (52%); nitrosylbis(pentafluorobenzoato)bis(triphenylphosphine)rhodium as emerald green crystals (53%).

Attempted synthesis under anaerobic conditions. When the above mixtures were prepared under strictly anaerobic conditions using carefully degassed solvents, no *visible* reaction occurred in the cold or on refluxing the suspension for 2 h. If air was subsequently admitted the red suspensions turned brown over a period of 24 h and gave only a negligible yield of the green complex.

Reaction of Nitrosyltris(triphenylphosphine)rhodium with Dioxygen.—Admission of air to suspensions of complex $[Rh(NO)(PPh_3)_3]$ in acetone led to rapid darkening of the mixture over a period of *ca.* 10 min. Subsequent addition of trifluoroacetic acid failed to produce a colour change to green and examination of the solution by ^{31}P n.m.r. revealed PPh_3O as the only phosphorus-containing species present.

Conversion of Nitrosylbis(trifluoroacetato)bis(triphenylphosphine)rhodium to Nitrosyltris(triphenylphosphine)rhodium.—A solution of $[Rh(O_2CCF_3)_2(NO)(PPh_3)_2]$ (0.10 g, 0.11 mmol) in ethanol (10 cm^3) was treated with potassium hydroxide (0.05 g, 1.0 mmol) and triphenylphosphine (0.10 g, 0.38 mmol). The mixture was heated under reflux for 10 min during which time the colour changed from green to red. The *red precipitate* was collected, washed with n-hexane, and dried *in vacuo* (yield 0.08 g, 77%). It was identified as the required product by spectroscopic (i.r., ^{31}P-{^{1}H} n.m.r.) comparison with an authentic specimen.

Attempted Preparation of Nitrosyl(trifluoroacetato)bis(triphenylphosphine)rhodium Tetraphenylborate.—Nitrosyltris(triphenylphosphine)rhodium (0.2 g, 0.22 mmol) was added to a solution of trifluoroacetic acid (0.2 cm^3, 2.5 mmol) in acetone (7 cm^3). The mixture was stirred at ambient temperature for 5 min, after which time a solution of sodium tetraphenylborate (0.07 g) in methanol (1 cm^3) was added. There was no evidence of precipitation within the green solution.

Nitrosylbis(trifluoroacetato)bis(triphenylphosphine)iridium. Trifluoroacetic acid (0.5 cm^3, 0.77 mmol) and $[Ir(NO)(PPh_3)_3]$ (0.3 g, 0.3 mmol) were added successively to acetone (40 cm^3) and the mixture heated under reflux for 40 min. During this time the orange suspension darkened and cleared to give a brown solution which was subsequently cooled, filtered, and then concentrated to *ca.* 30% of its original volume by evaporation under reduced pressure. The concentrated solution was diluted with light petroleum (b.p. 40—60 °C; *ca.* 5 cm^3) then set aside to crystallise. The product which separated as a 1/1 acetone solvate was filtered off and recrystallised from acetone–light petroleum to form *dark brown needles* (0.222 g, 77%). Nitrosylbis(pentafluoropropionato)bis(triphenylphosphine)-iridium was prepared similarly and isolated as dark brown crystals (83%).

Nitrosyl(trifluoroacetato)bis(triphenylphosphine)iridium Tetraphenylborate.—A solution of sodium tetraphenylborate (0.018 g, 0.05 mmol) in methanol (2 cm^3) was added to a suspension of $[Ir(O_2CCF_3)_2(NO)(PPh_3)_2]$ (0.05 g, 0.05 mmol) in methanol (3 cm^3). The sand coloured precipitate which formed immediately was filtered off, washed with methanol (2 × 2 cm^3) and hexane (5 cm^3), then dried *in vacuo* to give the required product as *buff microcrystals* (0.03 g, 52%).

Crystallography.—Crystals were obtained from acetone–light petroleum (b.p. 40—60 °C) solutions.

Crystal data for $[Rh(O_2CCF_3)_2(NO)(PPh_3)_2]$. $C_{40}H_{30}F_6NO_5P_2Rh$, $M = 883.52$, monoclinic, $a = 12.593(2)$, $b = 15.466(3)$, $c = 20.479(3)$ Å, $\beta = 100.03(4)°$, $U = 3\,927.6$ Å^3, space group Cc, $Z = 4$, $D_c = 1.494$ g cm^{-3}, $F(000)$ 1 784, μ(Mo-K_α) = 5.14 cm^{-1}.

Crystal data for $[Ir(O_2CCF_3)_2(NO)(PPh_3)_2]\cdot Me_2CO$. $C_{40}H_{30}F_6IrNO_5P_2\cdot C_3H_6O$, $M = 1\,001.89$, orthorhombic, $a = 19.171(2)$, $b = 22.684(3)$, $c = 20.169(3)$ Å, $U = 8\,771.0$ Å^3, space group $Pbcn$, $Z = 8$, $D_c = 1.517$ g cm^3, $F(000) = 3\,952$, μ(Mo-K_α) = 33.75 cm^{-1}.

Data collection. Intensity data were recorded for both crystals on a Nonius CAD4 diffractometer in a standard manner,[8] using Mo-K_α radiation [graphite monochromatised, λ(Mo-K_α) = 0.710 69 Å] and an $\omega/2\theta$ scan mode with $1.5 \leqslant \theta \leqslant 25.0°$ in

Table 3. Final fractional atomic co-ordinates (× 10^4) for $[Rh(O_2CCF_3)_2(NO)(PPh_3)_2]$

Atom	*x*	*y*	*z*
Rh(1)	−555	1 528(1)	1 923
N	−597(22)	273(8)	1 871(13)
O	−814(14)	−154(9)	2 187(9)
P(1)	−1 538(6)	1 726(5)	843(3)
C(111)	−2 233(12)	2 790(8)	836(7)
C(112)	−3 356(12)	2 850(8)	707(7)
C(113)	−3 856(12)	3 637(8)	794(7)
C(114)	−3 234(12)	4 362(8)	1 009(7)
C(115)	−2 112(12)	4 301(8)	1 137(7)
C(116)	−1 612(12)	3 515(8)	1 051(7)
C(121)	−2 595(11)	967(9)	548(7)
C(122)	−3 015(11)	918(9)	−128(7)
C(123)	−3 820(11)	318(9)	−359(7)
C(124)	−4 204(11)	−234(9)	86(7)
C(125)	−3 784(11)	−185(9)	762(7)
C(126)	−2 979(11)	415(9)	993(7)
C(131)	−716(10)	1 738(10)	183(7)
C(132)	−609(10)	2 448(10)	−221(7)
C(133)	55(10)	2 394(10)	−698(7)
C(134)	613(10)	1 630(10)	−771(7)
C(135)	506(10)	921(10)	−367(7)
C(136)	−158(10)	974(10)	110(7)
P(2)	498(7)	1 767(6)	3 004(5)
C(211)	1 093(11)	2 791(7)	2980(7)
C(212)	426(11)	3 499(7)	2 784(7)
C(213)	874(11)	4 317(7)	2 742(7)
C(214)	1 989(11)	4 428(7)	2 896(7)
C(215)	2 656(11)	3 721(7)	3 092(7)
C(216)	2 208(11)	2 902(7)	3 134(7)
C(221)	−286(9)	1 776(9)	3 659(6)
C(222)	−362(9)	2 506(9)	4 049(6)
C(223)	−982(9)	2 479(9)	4 550(6)
C(224)	−1 527(9)	1 723(9)	4 662(6)
C(225)	−1 452(9)	993(9)	4 272(6)
C(226)	−831(9)	1 020(9)	3 771(6)
C(231)	1 569(10)	990(9)	3 310(7)
C(232)	1 980(10)	963(9)	3 988(7)
C(233)	2 774(10)	360(9)	4 235(7)
C(234)	3 156(10)	−214(9)	3 805(7)
C(235)	2 745(10)	−187(9)	3 127(7)
C(236)	1 951(10)	415(9)	2 880(7)
O(11)	−2 028(18)	1 555(13)	2 235(11)
O(12)	−2 054(17)	2 867(15)	2 546(11)
C(11)	2 439(17)	2 205(22)	2 439(17)
C(12)	−3 589(15)	2 088(10)	2 552(8)
F(121)	−3 538(15)	1 791(12)	3 172(8)
F(122)	−4 182(14)	1 492(11)	2 181(9)
F(123)	−3 985(13)	2 849(10)	2 705(8)
O(21)	909(15)	1 486(11)	1 587(9)
O(22)	808(16)	2 902(14)	1 395(10)
C(21)	1 266(15)	2 134(18)	1 432(14)
C(22)	2 428(14)	2 091(12)	1 313(9)
F(221)	2 601(14)	1 495(11)	866(8)
F(222)	3 069(14)	2 791(11)	1 417(9)
F(223)	3 109(15)	1 812(12)	1 854(9)

each case. For the rhodium complex 3 849 reflections were recorded, of which 3 611 were unique (merging $R = 0.06$), and 2 918 satisfied the condition $I > 1.5\sigma(I)$. For the iridium complex, the equivalent numbers were 8 564, 7 704, and 3 791 ($R = 0.081$).

Structure solution. Both structures were solved *via* the heavy-atom method and refined by least squares. In both cases problems were encountered with disorder of the CF_3 groups, and in the iridium complex, heavy-atom pseudo-symmetry [x_{Ir}, $x_{P(1)}$, and $x_{P(2)}$ all $\approx \frac{1}{4}$] severely complicated the structure development and refinement. For the iridium complex, both CF_3 groups could be modelled using two F_3 sites, with occupancies normalised to unity. For the rhodium complex, the disorder was more severe and complicated, and the most stable refinement was achieved by including only three fluorine atoms at each site, but with occupancies less than unity. Although a number of residual peaks remained at each CF_3 site, inclusion of additional, fractional atoms did not lead to acceptable refinement. Accordingly we consider that the model with fractional F_3 groups is the best that can be obtained. Fortunately the various other models tried did not lead to any significant changes in parameters defining the co-ordination sphere.

For both structures the final results also included C_6H_5 groups refined as rigid bodies with hexagonal C_6 units and, in the iridium complex, only with isotropic thermal parameters due to the paucity of observed intensity data. For the iridium complex an acetone molecule of solvation was located on a two-fold axis and included with isotropic thermal parameters.

The final *R* values are 0.06 (Rh) and 0.081 (Ir) (unit weights were used in both cases). Final atomic fractional co-ordinates are given in Tables 3 and 4. Details of computers, programs, and atomic scattering factors are in ref. 9.

Results and Discussion

We have previously reported a convenient clean route to some platinum group metal carboxylate complexes based on the reactions of carboxylic[10] acids or perfluorocarboxylic acids[11] with hydride or low-oxidation-state platinum metal phosphine precursors in organic solvents. Extension of this technique to the nitrosyls $[M(NO)(PPh_3)_3]$ (M = Rh or Ir) affords a new series of complexes $[M(O_2CR)_2(NO)(PPh_3)_2]$ (M = Rh, R = CF_3, C_2F_5, or C_6F_5; M = Ir, R = CF_3 or C_2F_5).

Rhodium Complexes $[Rh(O_2CR)_2(NO)(PPh_3)_2]$.—Mixtures of the red complex $[Rh(NO)(PPh_3)_3]$ and a perfluorocarboxylic acid in an organic solvent (acetone or benzene) show no visible evidence of reaction in the absence of air; on subsequent admission of dioxygen the solution rapidly turns brown. In contrast, acetone solutions containing $[Rh(NO)(PPh_3)_3]$ and a perfluorocarboxylic acid rapidly turn emerald green when allowed to stand at ambient temperature in the presence of an abundant supply of dioxygen. Products of stoicheiometry $[Rh(O_2CR)_2(NO)(PPh_3)_2]$ are readily isolated from these solutions in high yield as emerald green, air-stable, crystalline solids. Admission of air to the $[Rh(NO)(PPh_3)_3]$ suspension prior to addition of the acid leads to a rapid degeneration of the rhodium complex and, on subsequent addition of the acid, a much reduced or zero yield of the desired product. Gas uptake measurements reveal that dioxygen participation in the $[Rh(NO)(PPh_3)_3]/CF_3CO_2H$ reaction is stoicheiometric rather than catalytic; each mole of rhodium precursor consumes one mole of dioxygen. Phosphorus-31 n.m.r. studies establish that 1:2 solutions of $[Rh(NO)(PPh_3)_3]:CF_3CO_2H$ in deuteriobenzene freshly prepared under anaerobic conditions contain unchanged $[Rh(NO)(PPh_3)_3]$ as the major rhodium-bearing constituent. Admission of air leads to rapid quantitative conversion to $[Rh(O_2CCF_3)_2(NO)(PPh_3)_2]$. The role of dioxygen in this and some related reactions is discussed in the following paper.[5]

The rhodium products, $[Rh(O_2CR)_2(NO)(PPh_3)_2]$, which were isolated as air-stable, emerald green, crystalline solids, display i.r. bands at *ca.* 1 660—1 670 cm^{-1} and *ca.* 1 685—1 695 cm^{-1} which we assign to $\nu(NO)$ and $\nu(OCO)_{asym}$ respectively.

Table 4. Final fractional atomic co-ordinates (× 10^4) for $[Ir(O_2CCF_3)_2(NO)(PPh_3)_2]$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ir	2 523(1)	1 517(0.1)	314(0.5)	C(21)	4 029(22)	1 601(20)	1 994(13)
N	1 617(9)	1 528(12)	271(15)	P(2)	2 594(4)	2 559(3)	300(3)
O	1 032(11)	1 520(12)	241(16)	C(211)	2 700(7)	2 868(7)	1 128(6)
O(1)	3 427(9)	1 401(8)	−309(8)	C(212)	2 362(7)	2 608(7)	1 667(6)
C(1)	3 360(12)	1 556(11)	−883(11)	C(213)	2 434(7)	2 850(7)	2 299(6)
O(11)	2 878(12)	1 801(10)	−1 180(10)	C(214)	2 843(7)	3 351(7)	2 393(6)
C(11)	3 991(16)	1 344(17)	−1 329(14)	C(215)	3 181(7)	3 611(7)	1 855(6)
P(1)	2 499(5)	469(3)	314(3)	C(216)	3 110(7)	3 370(7)	1 223(6)
C(111)	1 699(8)	198(7)	644(9)	C(221)	3 326(7)	2 839(7)	−173(7)
C(112)	1 461(8)	437(7)	1 239(9)	C(222)	3 225(7)	3 267(7)	−661(7)
C(113)	820(8)	261(7)	1 499(9)	C(223)	3 798(7)	3 514(7)	−984(7)
C(114)	416(8)	−154(7)	1 163(9)	C(224)	4 472(7)	3 333(7)	−820(7)
C(115)	654(8)	−394(7)	567(9)	C(225)	4 573(7)	2 905(7)	−333(7)
C(116)	1 295(8)	−218(7)	308(9)	C(226)	4 000(7)	2 658(7)	−10(7)
C(121)	2 593(9)	−191(7)	−524(6)	C(231)	1 797(7)	2 898(7)	1(8)
C(122)	2 152(9)	424(7)	−1 008(6)	C(232)	1 426(7)	3 314(7)	369(8)
C(123)	2 138(9)	177(7)	−1 641(6)	C(233)	815(7)	3 558(7)	113(8)
C(124)	2 565(9)	−303(7)	−1 790(6)	C(234)	574(7)	3 385(7)	−510(8)
C(125)	3 006(9)	−536(7)	−1 306(6)	C(235)	945(7)	2 969(7)	−878(8)
C(126)	3 020(9)	−289(7)	−673(6)	C(236)	1 556(7)	2725(7)	−622(8)
C(131)	3 201(8)	146(8)	803(9)	F(111)	4 538(19)	1 673(15)	−1 235(17)
C(132)	3 062(8)	−240(8)	1 325(9)	F(112)	3 886(18)	1 338(15)	−1 944(17)
C(133)	3 610(8)	−477(8)	1 694(9)	F(113)	4 227(18)	874(16)	−1 204(17)
C(134)	4 297(8)	−328(8)	1 542(9)	F(221)	4 538(22)	1 509(20)	1 726(21)
C(135)	4 437(8)	58(8)	1 020(9)	F(222)	3 913(22)	1 902(19)	2 426(22)
C(136)	3 889(8)	295(8)	651(9)	F(223)	4 050(22)	1 133(19)	2 419(23)
O(2)	3 383(9)	1 556(9)	969(7)	O(101)	0	1 231(23)	2 500
C(2)	3 329(14)	1 387(11)	1 584(14)	C(101)	0	1 749(29)	2 500
O(21)	2 799(11)	1 201(9)	1 834(10)	C(102)	578(25)	2 142(21)	2 218(23)

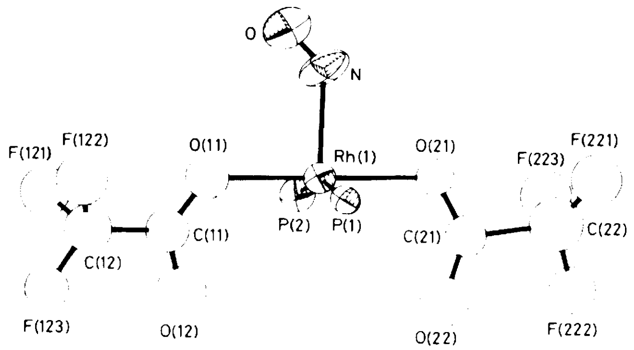


Figure 1. Molecular structure of $[Rh(O_2CCF_3)_2(NO)(PPh_3)_2]$

The reverse assignment cannot be rigorously excluded but leads to marginally less plausible values for ν(NO) and $\nu(OCO)_{asym}$. The ^{31}P n.m.r. spectrum of each complex consists of a doublet, δ *ca.* 21.0 p.p.m., $^1J(RhP)$ *ca.* 116 Hz; the ^{19}F n.m.r. spectrum of the trifluoroacetate shows a singlet (CF_3), that of the pentafluoropropionate displays a quartet (CF_2) and a triplet (CF_3) with a small coupling $^3J(FF')$ = *ca.* 2 Hz.

These data are consistent with a tetragonal-pyramidal structure with apical bent nitrosyl ligand for each complex, similar to that previously established for the corresponding dichloro-derivative $[RhCl_2(NO)(PPh_3)_2]$ [ν(NO) = 1 630 cm^{-1}].[12] However, in view of the dioxygen-dependent nature of the synthesis, an *X*-ray diffraction study of the trifluoroacetate derivative was undertaken to confirm the proposed stoicheiometry and structure of the rhodium complexes. The rhodium complex $[Rh(O_2CCF_3)_2(NO)(PPh_3)_2]$ has a tetragonal-pyramidal structure (Figure 1) with an apical angular nitrosyl ligand [Rh–N–O, 130(2)°] not dissimilar in form and molecular dimensions (Table 5) to that found for the corresponding dichloride, $[RhCl_2(NO)(PPh_3)_2]$.[12] However, it differs from the latter complex in one important aspect. Whereas in most tetragonal-pyramidal nitrosyl complexes, including $[RhCl_2(NO)(PPh_3)_2]$, the N–O vector is coplanar with one of the basal metal–ligand vectors; in the present complex it is coplanar with the bisector of the Rh–O and Rh–P vectors. A rather similar situation has been reported previously for the tetragonal-pyramidal complex *cis*-$[RhBr_2(NO)\{P(OPh)_3\}_2]$ where the N–O vector is coplanar with the bisector of the Rh–P vectors and hence apparently points towards the most crowded part of the molecule.[13] The two carboxylate groups are clearly monodentate with the non-bonded oxygen atoms lying some 3.1 Å from the metal.

Iridium Complexes $[Ir(O_2CR)_2(NO)(PPh_3)_2]$.—In marked contrast to the rhodium system, the reaction of $[Ir(NO)(PPh_3)_3]$ with perfluorocarboxylic acids appears to be essentially independent of dioxygen and goes smoothly to completion under aerobic or anaerobic conditions to yield the species $[Ir(O_2CR)_2(NO)(PPh_3)_2]$ (R = CF_3 or C_2F_5) as air-stable, brown, crystalline solids. These products show i.r. bands at *ca.* 1 685—1 690 cm^{-1} and *ca.* 1 800 cm^{-1} which we attribute to $\nu(OCO)_{asym}$ and ν(NO) respectively. The reverse assignment cannot be rigorously excluded but seems unlikely since it implies an exceptionally high value for $\nu(OCO)_{asym}$. The nitrosyl frequencies assigned for the iridium perfluorocarboxylate complexes differed very substantially from those reported for the corresponding dihalides $[IrX_2(NO)(PPh_3)_2]$ [ν(NO) *ca.* 1 550—1 565 cm^{-1}].[14] This unexpected observation led to speculation that the iridium complexes $[Ir(O_2CR)_2(NO)(PPh_3)_2]$ did not possess tetragonal-pyramidal structures analogous to those found for the corresponding rhodium complex $[Rh(O_2CCF_3)_2(NO)(PPh_3)_2]$ and for the related rhodium and iridium dichloro-complexes $[MCl_2(NO)(PPh_3)_2]$.[12,15] In view of the close correspondence between the ν(NO)

Table 5. Selected bond lengths and angles for $[Rh(O_2CCF_3)_2(NO)(PPh_3)_2]$

(*a*) Bond lengths (Å)

Rh(1)-N	1.944(14)	N-O	1.00(2)
Rh(1)-P(1)	2.359(9)	Rh(1)-P(2)	2.403(11)
Rh(1)-O(11)	2.07(2)	Rh(1)-O(21)	2.08(2)
C(11)-O(11)	1.24(4)	C(21)-O(21)	1.17(3)
C(11)-O(12)	1.14(4)	C(21)-O(22)	1.32(4)

(*b*) Bond angles (°)

N-Rh(1)-P(1)	94.2(8)	N-Rh(1)-P(2)	102.0(8)
N-Rh(1)-O(11)	91(1)	N-Rh(1)-O(21)	88(1)
P(1)-Rh(1)-P(2)	163.6(1)	O(11)-Rh(1)-O(21)	179(1)
Rh(1)-N-O	130(2)		

Table 6. Selected bond lengths and angles for $[Ir(O_2CCF_3)_2(NO)(PPh_3)_2]$

(*a*) Bond lengths (Å)

Ir-N	1.74(2)	N-O	1.12(2)
Ir-P	2.378(8)	Ir-P(2)	2.369(8)
Ir-O	2.16(2)	Ir-O(2)	2.12(2)
C(1)-O(1)	1.22(2)	C(2)-O(2)	1.30(3)
C(1)-O(11)	1.23(2)	C(2)-O(21)	1.30(3)

(*b*) Bond angles (°)

N-Ir-P(1)	90(1)	N-Ir-P(2)	92(1)
N-Ir-O(1)	141(1)	N-Ir-O(2)	144(1)
P(1)-Ir-P(2)	177.7(3)	O-N-Ir	178(2)
O(1)-Ir-O(2)	75.0(6)		

frequencies recorded for the complexes $[Ir(O_2CR)_2(NO)(PPh_3)_2]$ (*ca.* 1 800 cm^{-1}) and those reported for the salts $[IrX(NO)(PPh_3)_2]Y$ (X = OH, Cl, I, Me, or OEt; Y = ClO_4, BF_4, or PF_6) [ν(NO) *ca.* 1 830—1 900 cm^{-1}],[16] we performed conductivity and precipitation experiments to ascertain if our products are salts of the form $[Ir(O_2CR)(NO)(PPh_3)_2][O_2CR]$. Such species could contain four-co-ordinate square-planar cations, isoelectronic with Vaska's complex $[IrCl(CO)(PPh_3)_2]$; or, alternatively, five-co-ordinated trigonal-bipyramidal cations with bidentate carboxylate ligands. Conductivity measurements (10^{-3} mol dm^{-3} solution in nitrobenzene) establish that, although the iridium complex is a marginally better conductor than its rhodium analogue, neither can be formulated as an ionic salt. On addition of sodium tetraphenylborate to methanol suspensions of the complexes $[M(O_2CCF_3)_2(NO)(PPh_3)_2]$ the rhodium compound showed no evidence of reaction but the iridium analogue rapidly deposited a tetraphenylborate salt, $[Ir(O_2CCF_3)(NO)(PPh_3)_2][BPh_4]$, in good yield. These results led us to conclude[4] that the iridium complexes are partially ionised in polar solvents. However, they do not explain the high values of ν(NO) observed in the *solid-state* i.r. spectra of the iridium complexes.

An alternative explanation for the anomalous ν(NO) values recorded for the iridium complexes $[Ir(O_2CR)_2(NO)(PPh_3)_2]$ is indicated by recent spectroscopic and structural studies on some related tetragonal-pyramidal rhodium nitrosyl complexes $[RhBr_2(NO)(PR_3)_2]$ (R = Ph or OPh).[13] This work establishes that replacement of PPh_3 by $P(OPh)_3$ is accompanied by a change of stereochemistry from *trans* to *cis* within the basal plane, and a concomitant increase in ν(NO) from *ca.* 1 630 to *ca.* 1 750 cm^{-1}. Thus, if the iridium complex were to adopt a tetragonal-pyramidal structure, with axial, non-linear nitrosyl bonding, and *cis* perfluorocarboxylate ligands, a high value of ν(NO) might be anticipated. Therefore, in order to determine the overall stereochemistry of the iridium complexes and to ascertain the origin of the anomalously high ν(NO) frequency, an *X*-ray diffraction study was performed on the trifluoroacetato-derivative $[Ir(O_2CCF_3)_2(NO)(PPh_3)_2]$.

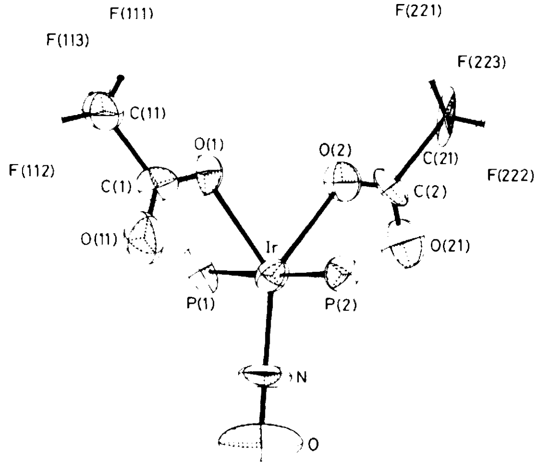
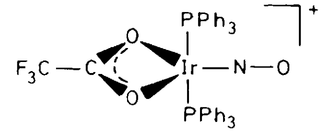


Figure 2. Molecular structure of $[Ir(O_2CCF_3)_2(NO)(PPh_3)_2]$

The structure found is shown in Figure 2 with selected bond lengths and angles given in Table 6. The co-ordination geometry about the metal atom is essentially trigonal bipyramidal, with axial triphenylphosphine ligands and equatorial linear nitrosyl and unidentate carboxylate groups. The structure contrasts strongly with those of the corresponding dichloride $[IrCl_2(NO)(PPh_3)_2]$[15] and the rhodium complex described above.

The most interesting feature of the structure is the very acute angle [75.0(6)°] subtended at the iridium by the co-ordinated oxygen atoms of the two unidentate carboxylate ligands. A very similar trigonal-bypyramidal structure with axial triphenylphosphine ligands and an equatorial linear nitrosyl group has recently been reported by Tiripicchio *et al.*[17] for the dication $[Ir(phen)(NO)(PPh_3)_2]^{2+}$ (phen = 1,10-phenanthroline). In this complex the angle subtended at the iridium by the two nitrogen atoms of the phen ligand is also very acute (75.8°). The presence of this small angle was attributed to geometric constraints arising from a combination of long Ir–N(phen) distances (induced by the high *trans* influence of the linear nitrosyl ligand) and the restricted small bite of the 1,10-phenanthroline chelate ligand. A similar trigonal-bipyramidal structure, proposed for $[Ir(C_2F_4)(NO)(PPh_3)_2]$,[18] if correct, would also be expected to possess a very small subtended angle (C–Ir–C) at iridium, but again because of restraints imposed by the geometry of the metallocycle. However, in the present complex, which displays an even smaller subtended angle at iridium, similar factors are clearly not operative since only non-chelate ligands are involved and it is interesting in our case to consider whether electronic or steric factors are more important in defining the particular structure found. Therefore, in an attempt to assess the relative importance of steric interactions in determining the geometry adopted by the rhodium and iridium complexes, the two structures are being investigated using the potential energy program EENY2.[19,20] This program calculates the potential energy sum for non-bonded interactions either for a static structure, *e.g.* as found from crystal structure analysis, or for a dynamic situation, *i.e.* one in which the structure is changing by forced variations in torsion or bond angles, and permits the energy sum to be minimised as a function of changes in these angles. Preliminary results obtained from these calculations suggest that for each complex the structure found by diffraction methods corresponds to a steric energy minimum. Further calculations are in progress and a full report on this aspect of our work will appear elsewhere.

The Iridium Salt $[Ir(O_2CCF_3)(NO)(PPh_3)_2][BPh_4]$.—The tetraphenylborate salt $[Ir(O_2CCF_3)(NO)(PPh_3)_2][BPh_4]$ displays i.r. bands at 1 850 [ν(NO)] and 1 572 cm^{-1} [ν(OCO)$_{asym}$]. The ^{31}P n.m.r. spectrum comprises a singlet δ 22.44 p.p.m. These data are consistent with the presence of a trigonal-bipyramidal cation containing a linear nitrosyl moiety and a chelate trifluoroacetate ligand (see below).



The proposed stereochemistry about the iridium is therefore similar to that existing in $[Ir(O_2CCF_3)_2(NO)(PPh_3)_2]$, $[Ir(phen)(NO)(PPh_3)_2][PF_6]_2$,[17] and, probably, $[Ir(C_2F_4)(NO)(PPh_3)_2]$.[18]

The structures found for the rhodium and iridium complexes $[M(O_2CCF_3)_2(NO)(PPh_3)_2]$ offer a possible explanation for the differing behaviour of their species toward tetraphenylborate anions. Conversion of the tetragonal-pyramidal rhodium complex $[Rh(O_2CCF_3)_2(NO)(PPh_3)_2]$ to a four- or five-co-ordinate cation $[Rh(O_2CCF_3)(NO)(PPh_3)_2]^+$ would require some reorganisation of the rhodium co-ordination sphere, rearrangement of nitrosyl ligand (angular→linear co-ordination), and removal of a trifluoroacetate ligand situated *trans* to a ligand of poor labilising power. Taken singly these factors are unlikely to pose an insuperable barrier to rearrangement. However, together they could well prove to be an insurmountable obstacle. In contrast the trigonal-bipyramidal iridium complex can readily rearrange to the salt form, as shown above, without recourse to any stereochemical alteration of the iridium co-ordination geometry.

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