Complexes of the Platinum Metals. Part 25.[1] Reactions of Ruthenium and Osmium Nitrosyls [MH(NO)(PPh$_3$)$_3$] and [M(NO)$_2$(PPh$_3$)$_2$] with Perfluorocarboxylic Acids: *X*-Ray Crystal Structure† Determination of Nitrosyl(trifluoroacetato)(trifluoroacetohydroximato-*OO'*)-bis(triphenylphosphine)osmium(II)–Dichloromethane (1/1)

Esther B. Boyar, Alan Dobson, and Stephen D. Robinson *
Department of Chemistry, King's College, Strand, London WC2R 2LS
Barry L. Haymore and John C. Huffman
Department of Chemistry and Molecular Structure Centre, Indiana University, Bloomington, Indiana 47401, U.S.A.

Ruthenium and osmium hydridonitrosyl complexes, [MH(NO)(PPh$_3$)$_3$], react with perfluorocarboxylic acids RCO$_2$H (R = CF$_3$ or C$_2$F$_5$) to afford the products [Ru(O$_2$CR)$_3$(NO)(PPh$_3$)$_2$] and [OsH(O$_2$CR)$_2$(NO)(PPh$_3$)$_2$] respectively. The reaction intermediates [RuH(O$_2$CR)$_2$(NO)(PPh$_3$)$_2$] and [OsH$_2$(NO)(PPh$_3$)$_3$]$^+$ have been detected in solution by ^{1}H and ^{31}P-{^{1}H} n.m.r.; the latter species has been isolated and characterised as the tetraphenylborate salt. The ruthenium dinitrosyl complex [Ru(NO)$_2$(PPh$_3$)$_2$] reacts with the acids RCO$_2$H in boiling toluene or 2-methoxyethanol to afford the products [Ru(O$_2$CR)$_3$(NO)(PPh$_3$)$_2$]. The corresponding osmium complex [Os(NO)$_2$(PPh$_3$)$_2$] reacts with the same acids in boiling 2-methoxyethanol and boiling toluene to yield the hydrides [OsH(O$_2$CR)$_2$(NO)(PPh$_3$)$_2$] and the novel hydroximate derivatives $[\overline{\mathrm{Os\{ON{=}C(O}})\mathrm{R\}(O_2CR)(NO)}$-(PPh$_3$)$_2$] respectively. Possible mechanisms for these reactions are discussed. The *X*-ray crystal structure of $[\overline{\mathrm{Os\{ON{=}C(O}})\mathrm{CF_3\}(O_2CCF_3)(NO)(PPh_3)_2]{\cdot}CH_2Cl_2}$ has been determined. The crystals are triclinic, space group $P\bar{1}$, with a = 12.709(3), b = 22.694(8), c = 9.662(3) Å, α = 118.28(3), β = 113.59(3), γ = 59.66(4)°, and Z = 2. The structure has been refined to $R(F)$ = 0.051 and $R'(F)$ = 0.049 for 4 730 observed reflections. The complex contains six-co-ordinated osmium(II) bound to a chelate *O,O'*-trifluoroacetohydroximate(2–) ligand, a unidentate trifluoroacetate ligand, a linear nitrosyl group, and a pair of mutually *cis* triphenylphosphine ligands.

Treatment of low oxidation state [ML$_n$] or hydride, [MH$_m$L$_n$] complexes of the platinum group metals (L = PPh$_3$, CO, *etc.*) with perfluorocarboxylic acids has previously been exploited to provide a clean efficient route to the corresponding perfluorocarboxylate complexes.[2–4] These reactions involve protonation at the metal centre followed by elimination of dihydrogen and/or co-ordination of the carboxylate anion. We are now extending these syntheses to include a series of nitrosyl-containing precursors and thus introducing scope for competing reaction modes involving protonation of the nitrosyl ligands.

In this paper we report on the reactions of the ruthenium and osmium hydridonitrosyls [MH(NO)(PPh$_3$)$_3$] and dinitrosyls [M(NO)$_2$(PPh$_3$)$_2$] with some perfluorocarboxylic acids and describe the products isolated. These include novel *O,O'*-chelate trifluoroacetohydroximate complexes, one of which has been characterised by *X*-ray diffraction methods. A preliminary report on the synthesis and structure of the hydroximate complexes has previously been published.[5]

Experimental

Platinum metal salts were supplied by Johnson Matthey; the nitrosyl complexes [MH(NO)(PPh$_3$)$_3$][6,7] and [M(NO)$_2$(PPh$_3$)$_2$][8,9] (M = Ru or Os) were prepared by standard literature procedures. Unless otherwise indicated, reactions were performed under nitrogen and products were worked-up in air. Yields are based on platinum metal content. Analytical results, obtained by the microanalytical laboratory, University College, London, and melting points, taken in sealed tubes under nitrogen, are given in Table 1. I.r. and n.m.r. data, collected using a Perkin-Elmer 457 grating spectrophotometer and Bruker HFX 90 or WM 250 n.m.r. spectrometers respectively, are recorded in Table 2. Proton, ^{19}F, and ^{31}P n.m.r. spectra are referenced to internal SiMe$_4$, internal C$_6$F$_6$, and external 85% H$_3$PO$_4$ respectively; positive values are to low field of the reference in each case.

(A) *Products from the Complexes* [MH(NO)(PPh$_3$)$_3$].—*Nitrosyltris(trifluoroacetato)bis(triphenylphosphine)ruthenium*(II). Trifluoroacetic acid (0.5 cm^3) and [RuH(NO)(PPh$_3$)$_3$] (0.10 g) were mixed together in benzene (8 cm^3) and allowed to stand at room temperature for 30 min. The benzene was removed by evaporation under reduced pressure, and the resultant dark oil was crystallised from dichloromethane–light petroleum (b.p. 40—60 °C) to yield dark yellow crystals. These were filtered off, washed successively with small volumes of methanol, water and methanol, then dried *in vacuo*. Yield 0.08 g (73%).

This reaction afforded the same product when performed in boiling toluene (70% yield) or boiling 2-methoxyethanol (60% yield).

Dihydrido(nitrosyl)tris(triphenylphosphine)ruthenium(II) *trifluoroacetate*. An attempt to detect this salt by running the high-field ^{1}H n.m.r. spectrum of a freshly prepared solution of [RuH(NO)(PPh$_3$)$_3$] and trifluoroacetic acid (*ca.* 1:1 mole ratio) in deuteriated benzene was unsuccessful; effervescence

---

† *Supplementary data available* (No. SUP 56115, 10 pp.): full bond lengths and angles, thermal parameters, H-atom co-ordinates. 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 (%) C	H	N
$[Ru(O_2CCF_3)_3(NO)(PPh_3)_2]$	220—221	50.5 (50.7)	3.1 (3.0)	6.8 (6.3)
$[Ru(O_2CC_2F_5)_3(NO)(PPh_3)_2]$	200—202	47.3 (47.2)	2.7 (2.6)	1.2 (1.2)
$[OsH(O_2CCF_3)_2(NO)(PPh_3)_2]$	258—259	49.6 (49.4)	3.4 (3.2)	1.3 (1.4)
$[OsH(O_2CC_2F_5)_2(NO)(PPh_3)_2]$	255—257	47.1 (47.1)	2.9 (2.9)	1.2 (1.3)
$[Os\{ON{=}C(O)CF_3\}(O_2CCF_3)(NO)(PPh_3)_2]$	168—170	48.0 (48.75)	3.2 (3.1)	2.8 (2.85)
$[Os\{ON{=}C(O)C_2F_5\}(O_2CC_2F_5)(NO)(PPh_3)_2]$	159—160	46.9 (46.5)	3.0 (2.8)	2.4 (2.60)
$[OsH_2(NO)(PPh_3)_3][H(O_2CCF_3)_2]$	138	56.6 (56.4)	3.9 (3.8)	1.2 (1.1)
$[OsH_2(NO)(PPh_3)_3][BPh_4]$	228	69.8 (70.5)	4.8 (5.0)	1.1 (1.1)

* Calculated values are in parentheses.

Table 2. Spectroscopic data[a]

$[Ru(O_2CCF_3)_3(NO)(PPh_3)_2]$	$\nu(NO)$ 1 908, $\nu(OCO)_{asym.}$ 1 728, 1 697 N.m.r.: ^1H, $\delta(Ph)$ 7.9 (*o*-H), 7.1 (*m*,*p*-H); ^{19}F, δ 89.32, 87.52; ^{31}P, $\delta(PPh_3)$ 19.37
$[Ru(O_2CC_2F_5)_3(NO)(PPh_3)_2]$	$\nu(NO)$ 1 908, $\nu(OCO)_{asym.}$ 1 719, 1 693 N.m.r.: ^{31}P, $\delta(PPh_3)$ 15.18
$[RuH(O_2CCF_3)_2(NO)(PPh_3)_2]$	N.m.r.: ^1H, $\delta(RuH)$ -3.8, $^2J(PH)_{cis} = 15.9$
$[OsH(O_2CCF_3)_2(NO)(PPh_3)_2]$	$\nu(OsH)$ 2 156, $\nu(NO)$ 1 820, $\nu(OCO)_{asym.}$ 1 721, 1 681 N.m.r.: ^1H, $\delta(OsH)$ -5.41, $^2J(PH)_{cis} = 14.0$; $\delta(Ph)$ 7.89 (*o*-H), 7.05 (*m*,*p*-H); ^{31}P, $\delta(PPh_3)$ 15.35
$[OsH(O_2CC_2F_5)_2(NO)(PPh_3)_2]$	$\nu(OsH)$ 2 160, $\nu(NO)$ 1 817, $\nu(OCO)_{asym.}$ 1 711, 1 681 N.m.r.: ^1H, $\delta(OsH)$ -6.68, $^2J(PH)_{cis} = 14.0$
$[Os\{ON{=}C(O)CF_3\}(O_2CCF_3)(NO)(PPh_3)_2]$	$\nu(NO)$ 1 820, $\nu(C{=}N)$ 1 610, $\nu(OCO)_{asym.}$ 1 700, 1 685, $\nu(OCO)_{sym.}$ *ca.* 1 390 N.m.r.: ^{19}F, δ 94.25, 87.70, $^5J(PF) = 1.25$; ^{31}P, $\delta(PPh_3)$ -7.4, -13.6, $^2J(PP') = 11.9$
$[Os\{ON{=}C(O)C_2F_5\}(O_2CC_2F_5)(NO)(PPh_3)_2]$	$\nu(NO)$ 1 817, $\nu(C{=}N)$ 1 609, $\nu(OCO)_{asym.}$ 1 700, $\nu(OCO)_{sym.}$ *ca.* 1 390
$[OsH_2(NO)(PPh_3)_3][H(O_2CCF_3)_2]$	$\nu(OsH)$ 2 100, 2 010, $\nu(NO)$ 1 770[b], $\nu(OCO)_{asym.}$ 1 770[b] N.m.r.: ^1H[c], -3.98 (m), $^2J(PH)_{cis} = 18.5, 15.5$, $^2J(HH') = 5.4$; -4.25 (m), $^2J(PH)_{cis} = 16.0$, $^2J(PH)_{trans} = 41.0$; ^{31}P, $\delta(PPh_3)$ 7.55 (d), -2.21 (t), $^2J(PP') = 9.8$
$[OsH_2(NO)(PPh_3)_3][BPh_4]$	$\nu(OsH)$ 2 095, 1 990, $\nu(NO)$ 1 755[b], $\nu(OCO)_{asym.}$ 1 755[b] N.m.r.: ^1H[c], -3.99 (m), $^2J(PH)_{cis} = 18.5, 15.5$, $^2J(HH') = 5.4$; -4.23 (m), $^2J(PH)_{cis} = 16.0$, $^2J(PH)_{trans} = 41.0$; ^{31}P, $\delta(PPh_3)$ 7.24 (d), -2.81 (t), $^2J(PP') = 10.3$

[a] I.r. data in cm $^{-1}$. N.m.r.: δ in p.p.m., J in Hz. [b] $\nu(NO)$ and $\nu(OCO)_{asym.}$ superimposed. [c] Analysed by selective decoupling experiments and computer simulation.

(H_2 elimination) was observed on mixing the components and no high-field signal could be detected for the resulting solution.

Hydrido(nitrosyl)bis(trifluoroacetato)bis(triphenylphosphine)ruthenium(II). This complex was not isolated but has been observed in significant concentrations (*ca.* 30—40% total Ru content of solution) and characterised by high-field ^1H n.m.r. spectroscopy (see Table 2). Trifluoroacetic acid (0.1 cm^3) and $[RuH(NO)(PPh_3)_3]$ (0.02 g) were mixed together in deuteriated benzene (1 cm^3) at room temperature and the ^1H n.m.r. spectrum was recorded after *ca.* 10 min. There was slight effervescence on mixing.

Hydrido(nitrosyl)bis(trifluoroacetato)bis(triphenylphosphine)osmium(II). Trifluoroacetic acid (0.2 cm^3) was added to $[OsH(NO)(PPh_3)_3]$ (0.075 g) in 2-methoxyethanol (10 cm^3). After heating under reflux for 1 h, the solution was evaporated under reduced pressure to give an oil. Addition of hexane (5 cm^3) led to precipitation of a yellow solid which was filtered off, washed with hexane, and then dried *in vacuo*. Yield 0.07 g (98%).

When the above procedure was repeated using refluxing toluene as solvent the product mixture, examined in solution by ^1H and ^{31}P-{^1H} n.m.r., was found to consist of dihydrido(nitrosyl)tris(triphenylphosphine)osmium(II) trifluoroacetate (*ca.* 60%) and hydrido(nitrosyl)bis(trifluoroacetato)bis(triphenylphosphine)osmium(II) (*ca.* 40%).

Dihydrido(nitrosyl)tris(triphenylphosphine)osmium(II) *hydrogenbis(trifluoroacetate)*. Trifluoroacetic acid (0.2 cm^3) was added to $[OsH(NO)(PPh_3)_3]$ (0.075 g) in benzene (10 cm^3). The mixture was stirred at room temperature for 1 h then evaporated under reduced pressure to yield an oil. Crystallisation from dichloromethane–light petroleum (b.p. 40—60 °C) afforded a yellow powder which was filtered off, washed with light petroleum, and dried *in vacuo*. Yield 0.08 g (83%).

Dihydrido(nitrosyl)tris(triphenylphosphine)osmium(II) *tetraphenylborate*. The oil obtained in the above procedure was dissolved in acetone (5 cm^3). Sodium tetraphenylborate (0.045 g) in acetone (1 cm^3) was added, and the mixture was stirred at room temperature for 30 min. Addition of methanol (3 cm^3) and water (3 cm^3) followed by reduction of the solution to half volume under reduced pressure afforded a pale yellow solid which was then washed with hexane and dried *in vacuo*. Yield 0.06 g (60%).

(*B*) *Products from the Complexes* $[M(NO)_2(PPh_3)_2]$.—*Nitrosyltris(trifluoroacetato)bis(triphenylphosphine)ruthenium*(II). Trifluoroacetic acid (0.5 cm^3) and $[Ru(NO)_2(PPh_3)_2]$ (0.2 g) were heated together under reflux in toluene (5 cm^3) for 30 min. During this time the initial dark brown solution became slightly paler and the evolution of nitric oxide was observed (brown fumes on contact with air). After 30 min the toluene was removed by evaporation under reduced pressure, and the resultant dark oil was crystallised from dichloromethane–light petroleum (b.p. 40—60 °C) to yield dark yellow crystals. These were filtered off, washed successively with small volumes of methanol, water and methanol, then dried *in vacuo*. Yield 0.25 g (87%).

When the reaction was performed on a larger scale (× 2.5) a small yield of hydroxylammonium trifluoroacetate (0.05 g, *ca.* 20%) was isolated from the product mixture.

Nitrosyltris(pentafluoropropionato)bis(triphenylphosphine)-ruthenium(II) was similarly obtained as orange-yellow crystals (68%) using pentafluoropropionic acid.

A parallel series of reactions using 2-methoxyethanol as solvent in place of toluene gave identical products but with rather poorer yields (*ca.* 50—60%).

Hydrido(nitrosyl)bis(trifluoroacetato)bis(triphenylphosphine)osmium(II). Trifluoroacetic acid (1.0 cm^3) and $[Os(NO)_2(PPh_3)_2]$ (0.4 g) were heated together under reflux in 2-methoxyethanol (10 cm^3) for 30 min. During this time the reaction solution lightened in colour from dark brown to pale yellow. After 30 min the solution was evaporated under reduced pressure to leave a dark brown oil. Addition of methanol (5 cm^3) led to rapid precipitation of pale yellow crystals of the required product. These were filtered off, washed successively with small volumes of methanol, water and methanol, then dried *in vacuo*. Yield 0.28 g (56%).

Hydrido(nitrosyl)bis(pentafluoropropionato)bis(triphenylphosphine)osmium(II) was similarly prepared as yellow crystals (65%) using pentafluoropropionic acid.

Nitrosyl(trifluoroacetato)(trifluoroacetohydroximato)bis(triphenylphosphine)osmium(II). Trifluoroacetic acid (1.0 cm^3) was added to a solution of $[Os(NO)_2(PPh_3)_2]$ (0.5 g) in boiling toluene (10 cm^3). The dark orange solution was heated under reflux for 30 min, during which time the solution became significantly paler. The mixture was then evaporated under reduced pressure to produce a dark brown oil which was crystallised from toluene–methanol as orange-brown crystals (0.55 g, 87%).

Nitrosyl(pentafluoropropionato)(pentafluoropropiohydroximato)bis(triphenylphosphine)osmium(II) was similarly prepared as orange crystals (82%) using pentafluoropropionic acid.

Reactions of the Dinitrosyls $[M(NO)_2(PPh_3)_2]$ *with Acids* RCO_2H ($R = CF_3$ *or* C_2F_5) *in Cold Benzene*.—The dinitrosyl (*ca.* 0.5 g) was added to a solution of the acid (0.5 cm^3) in benzene (*ca.* 5 cm^3) and the mixture was shaken for 5 min. The resultant brown (M = Ru) or orange-yellow (M = Os) solution was evaporated under reduced pressure and the residual oil was crystallised from benzene–light petroleum to afford yellow crystals (*ca.* 50—75% yield). These products gave analytical data consistent with the variable stoicheiometry $M(NO)_2(PPh_3)_2(RCO_2H)_n$ (n = 3—5).

X-Ray Structure Analysis of $[\overline{Os\{ON{=}C(O})CF_3\}(O_2CCF_3)(NO)(PPh_3)_2]\cdot CH_2Cl_2$.—Bright orange solvated crystals were grown from dichloromethane–methanol.

A well formed crystal of dimensions 0.12 × 0.13 × 0.13 mm was chosen for the study. The Picker goniostat used in the data collection as well as the low-temperature apparatus and data reduction techniques have been described previously.[10] The crystal was cooled to -160 °C and a systematic search of a limited hemisphere of reciprocal space located no systematic absences or symmetry related peaks, indicating a triclinic space group. Statistical tests and subsequent solution and refinement of the structure indicate the centrosymmetric space group $P\bar{1}$. Cell data are based on a refinement of angular data from 36 reflections.

Crystal data. $C_{40}H_{30}F_6N_2O_5OsP_2\cdot CH_2Cl_2$, $M = 1169.76$, $a = 12.709(3)$, $b = 22.694(8)$, $c = 9.662(3)$ Å, $\alpha = 118.28(3)$, $\beta = 113.59(3)$, $\gamma = 59.66(4)^\circ$, $D_c = 1.720$ g cm^{-3} for $Z = 2$, λ(Mo-K_α) = 0.710 69 Å.

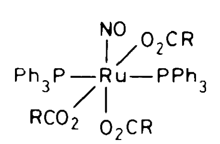
Of the 5 396 unique data collected in the range $6 \geqslant 2\theta \geqslant 45^\circ$, 4 730 were observed using the criteria $I > 2.33\sigma(I)$ and were used in the refinement. Due to the nearly equidimensional size of the crystal, no absorption correction was deemed necessary [μ(Mo-K_α) = 33.7 cm^{-1}]. The structure was solved by a combination of direct methods and Fourier techniques. Hydrogen atoms were included as fixed atom contributors [d(C–H) = 0.95 Å, $B_{iso.}$ = 4.002 Å^2], phenyl carbons were assigned isotropic thermal parameters and all other atoms anisotropic thermal parameters in the full-matrix refinement. Final residuals are $R(F) = 0.051$ and $R'(F) = 0.049$. A final difference Fourier map was essentially featureless, the largest peak being 0.92 e Å^{-3}, located near the Os atom. Fractional atomic co-ordinates are given in Table 3.

Results and Discussion

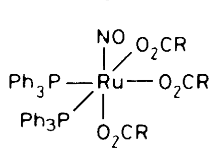
The hydridonitrosyl complexes $[MH(NO)(PPh_3)_3]$ react with perfluorocarboxylic acids RCO_2H ($R = CF_3$ or C_2F_5) in cold or boiling toluene or 2-methoxyethanol to afford species $[Ru(O_2CR)_3(NO)(PPh_3)_2]$ and $[OsH(O_2CR)_2(NO)(PPh_3)_2]$ in excellent yield. The ruthenium products are isolated as air-stable dark yellow crystals and, on the basis of spectroscopic data (Table 2) are assigned stereochemistry (**1a**) analogous to that established for the corresponding halides $[RuX_3(NO)(PPh_3)_2]$.[11] The only possible alternative (**1b**) is stereochemically less favourable, and is excluded by the ^1H n.m.r. spectra which display phenyl-proton resonance patterns (separation between *ortho* and *meta/para* resonances *ca.* 0.8 p.p.m.) indicative of a mutually *trans* pair of triphenylphosphine ligands.[12] The osmium products, which are isolated as air-stable pale yellow crystals are likewise assigned stereochemistry (**2a**). Again the ^1H n.m.r. pattern of the phenyl protons (*ortho–meta/para* separation *ca.* 0.8 p.p.m.) indicates the presence of *trans* triphenylphosphine ligands[12] and this excludes the only feasible alternative stereochemistry (**2b**).

Formation of the ruthenium and osmium products can be rationalised in terms of the reaction sequence shown in Scheme 1. The failure of the osmium system to yield species analogous to the ruthenium products $[Ru(O_2CR)_3(NO)(PPh_3)_2]$ can be attributed to the greater inertness of osmium relative to ruthenium; all attempts to convert $[OsH(O_2CCF_3)_2(NO)(PPh_3)_2]$ to $[Os(O_2CCF_3)_3(NO)(PPh_3)_2]$ by treatment with excess trifluoroacetic acid were unsuccessful.

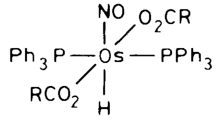
Since the proposed cationic intermediates $[MH_2(NO)(PPh_3)_3]^+$ do not appear to have been reported previously, attempts were made to isolate them as tetraphenylborate salts



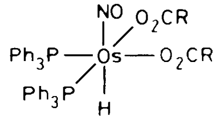
(**1a**)



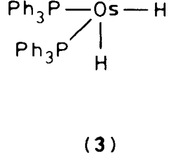
(**1b**)



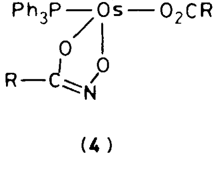
(**2a**)



(**2b**)



(**3**)



(**4**)

Table 3. Fractional atomic co-ordinates (non-hydrogen atoms; × 10^4) for $[\overline{\mathrm{Os\{ON{=}C(O}}\mathrm{)CF_3\}(O_2CCF_3)(NO)(PPh_3)_2}]$

Atom	x	y	z	Atom	x	y	z
Os(1)	4 955.2(3)	2 837(2)	−336.7(2)	C(22)	489(9)	3 610(5)	−1 620(11)
Cl(1)	9 250(4)	1 744(2)	5 010(6)	C(23)	−441(9)	3 453(5)	−2 908(12)
Cl(2)	8 131(5)	720(2)	3 731(6)	C(24)	−300(9)	3 181(5)	−4 458(12)
P(1)	2 859(2)	3 685(1)	−270(3)	C(25)	784(9)	3 065(5)	−4 750(11)
P(2)	4 856(2)	1 693(1)	−2 278(3)	C(26)	1 719(8)	3 214(5)	−3 486(11)
F(1)	4 928(5)	4 375(3)	5 242(7)	C(31)	2 688(8)	4 531(5)	−299(10)
F(2)	6 499(6)	3 438(3)	5 727(7)	C(32)	1 613(8)	4 917(5)	−1 199(11)
F(3)	6 710(6)	4 064(3)	4 847(7)	C(33)	1 490(10)	5 552(6)	−1 255(12)
F(4)	9 680(6)	1 311(4)	−720(10)	C(34)	2 414(9)	5 814(5)	−386(12)
F(5)	9 263(6)	1 833(5)	1 580(9)	C(35)	3 457(9)	5 452(6)	525(12)
F(6)	9 473(7)	2 412(4)	564(12)	C(36)	3 619(9)	4 808(5)	577(11)
O(1)	4 815(6)	3 425(3)	−2 565(8)	C(41)	4 322(8)	1 629(5)	−4 379(10)
O(2)	5 359(5)	3 578(3)	1 883(7)	C(42)	3 418(9)	1 351(5)	−5 444(11)
O(3)	5 049(5)	2 427(3)	1 143(7)	C(43)	3 072(9)	1 306(5)	−7 026(12)
O(4)	6 919(6)	2 306(3)	232(7)	C(44)	3 604(9)	1 528(5)	−7 571(12)
O(5)	7 354(6)	2 262(4)	−1 875(9)	C(45)	4 512(9)	1 802(5)	−6 546(11)
N(1)	4 909(7)	3 162(4)	−1 665(9)	C(46)	4 859(9)	1 849(5)	−4 954(11)
N(2)	5 496(7)	2 760(4)	2 801(9)	C(51)	3 931(8)	1 352(5)	−1 998(11)
C(1)	5 924(9)	3 801(5)	4 719(12)	C(52)	4 406(9)	650(5)	−2 056(11)
C(2)	5 588(8)	3 333(5)	3 002(11)	C(53)	3 651(9)	388(5)	−1 962(12)
C(3)	9 020(9)	1 937(6)	212(14)	C(54)	2 432(9)	838(5)	−1 829(11)
C(4)	7 613(9)	2 207(6)	−572(12)	C(55)	1 964(9)	1 540(5)	−1 787(12)
C(5)	7 898(10)	1 646(6)	4 673(15)	C(56)	2 705(8)	1 802(5)	−1 871(11)
C(11)	2 442(8)	3 918(5)	1 596(11)	C(61)	6 409(8)	968(5)	−2 185(10)
C(12)	2 490(9)	3 389(5)	1 958(11)	C(62)	6 935(9)	524(5)	−3 519(11)
C(13)	2 160(10)	3 562(6)	3 335(12)	C(63)	8 103(9)	−40(5)	−3 402(12)
C(14)	1 774(10)	4 272(6)	4 362(13)	C(64)	8 713(10)	−168(6)	−1 986(12)
C(15)	1 724(10)	4 811(6)	4 017(12)	C(65)	8 190(9)	262(5)	−636(12)
C(16)	2 051(9)	4 644(5)	2 626(11)	C(66)	7 047(9)	829(5)	−718(11)
C(21)	1 599(8)	3 490(5)	−1 906(10)				

$$[\mathrm{MH(NO)(PPh_3)_3}] \xrightarrow{\mathrm{RCO_2H}} [\mathrm{MH_2(NO)(PPh_3)_3}][\mathrm{O_2CR}]$$

$$[\mathrm{MH_2(NO)(PPh_3)_3}][\mathrm{O_2CR}] \xrightarrow{\mathrm{H_2}} [\mathrm{M(O_2CR)(NO)(PPh_3)_2}] + \mathrm{PPh_3}$$

$$[\mathrm{M(O_2CR)(NO)(PPh_3)_2}] \xrightarrow{\mathrm{RCO_2H}} [\mathrm{MH(O_2CR)_2(NO)(PPh_3)_2}]$$

$$[\mathrm{RuH(O_2CR)_2(NO)(PPh_3)_2}] \xrightarrow[\mathrm{H_2}]{\mathrm{RCO_2H}} [\mathrm{Ru(O_2CR)_3(NO)(PPh_3)_2}]$$

Scheme 1.

or, failing that, to observe and characterise them in solution by high-field ^{1}H n.m.r. Addition of CF_3CO_2H (1 mol equiv.) to a cold solution of $[RuH(NO)(PPh_3)_3]$ in deuteriobenzene leads to immediate effervescence (H_2 evolution) and loss of all high-field ^{1}H n.m.r. signals. It therefore appears that the cation $[RuH_2(NO)(PPh_3)_3]^+$ is unstable with respect to reductive elimination of dihydrogen and formation of a 16-electron complex ion $[Ru(NO)(PPh_3)_3]^+$. To date we have been unable to isolate or characterise the latter species which is presumably attacked by the carboxylate counter anion to form $[Ru(O_2CCF_3)(NO)(PPh_3)_2]$. This product in turn would be expected to undergo rapid oxidative addition of a second molecule of acid to form $[RuH(O_2CCF_3)_2(NO)(PPh_3)_2]$, the ruthenium analogue of the final osmium product. When 2 mol equiv. of acid were added this species was indeed observed by ^{1}H n.m.r. spectroscopy (see Table 2).

However, in contrast to the ruthenium complex, the analogous osmium species $[OsH(NO)(PPh_3)_3]$ reacts under similar conditions to form the hitherto unknown cation $[OsH_2(NO)(PPh_3)_3]^+$ in essentially quantitative yield. This cation, which is isoelectronic with the well known carbonyl $[OsH_2(CO)(PPh_3)_3]$[13] and the more recently prepared rhenium nitrosyl $[ReH_2(NO)(PPh_3)_3]$,[14,15] can be identified and assigned stereochemistry (**3**) on the basis of its ^{31}P-{^{1}H}, ^{1}H, and ^{1}H-{^{31}P} n.m.r. spectra (Table 2). It crystallises from solution as the salt $[OsH_2(NO)(PPh_3)_3][H(O_2CCF_3)_2]$ containing the H-bonded $[CF_3CO_2\text{-}H\cdots O_2CCF_3]^-$ anion[16] or can be precipitated as $[OsH_2(NO)(PPh_3)_3][BPh_4]$ by addition of sodium tetraphenylborate.

The ruthenium complex, $[RuH(NO)(PPh_3)_3]$, in contrast to its osmium analogue, reacts readily with dioxygen. Passage of O_2 gas into freshly prepared ^{1}H n.m.r. samples containing the ruthenium complex dissolved in C_6D_6 led to the rapid disappearance of the high-field signal, presumably due to formation of a hydroperoxy species by insertion of dioxygen into the Ru–H bond. Examples of this reaction have previously been reported for other platinum group metal systems.[17,18] Formation of this hydroperoxy complex opens the way for an alternative, dioxygen-mediated pathway for formation of $[Ru(O_2CR)_3(NO)(PPh_3)_2]$ complexes under aerobic conditions (Scheme 2). Qualitative comparisons of rates of reaction under anaerobic and aerobic conditions suggest that the hydroperoxy mechanism may contribute to the reaction under the latter circumstances.

$$[\mathrm{RuH(NO)(PPh_3)_3}] \xrightarrow{\mathrm{O_2}} [\mathrm{Ru(OOH)(NO)(PPh_3)_2}] + \mathrm{PPh_3}$$

$$[\mathrm{Ru(OOH)(NO)(PPh_3)_2}] + \mathrm{PPh_3} \longrightarrow [\mathrm{Ru(OH)(NO)(PPh_3)_2}] + \mathrm{PPh_3O}$$

$$[\mathrm{Ru(OH)(NO)(PPh_3)_2}] \xrightarrow[\mathrm{H_2O}]{\mathrm{RCO_2H}} [\mathrm{Ru(O_2CR)(NO)(PPh_3)_2}]$$

$$[\mathrm{Ru(O_2CR)(NO)(PPh_3)_2}] \xrightarrow{\mathrm{RCO_2H}} [\mathrm{RuH(O_2CR)_2(NO)(PPh_3)_2}]$$

$$[\mathrm{RuH(O_2CR)_2(NO)(PPh_3)_2}] \xrightarrow[\mathrm{H_2}]{\mathrm{RCO_2H}} [\mathrm{Ru(O_2CR)_3(NO)(PPh_3)_2}]$$

Scheme 2.

Table 4. Selected bond lengths (Å) and angles (°) for $[\overline{\mathrm{Os\{ON{=}C(O}}\mathrm{)CF_3\}(O_2CCF_3)(NO)(PPh_3)_2}]$

Os(1)–N(1)	1.726(7)	Os(1)–P(2)	2.406(2)	F(5)–C(3)	1.339(11)	O(4)–C(4)	1.271(11)
Os(1)–O(3)	1.984(6)	F(1)–C(1)	1.332(11)	F(6)–C(3)	1.314(11)	O(5)–C(4)	1.218(11)
Os(1)–O(2)	2.063(6)	F(2)–C(1)	1.319(11)	O(1)–N(1)	1.209(9)	N(2)–C(2)	1.277(11)
Os(1)–O(4)	2.115(6)	F(3)–C(1)	1.342(11)	O(2)–C(2)	1.310(10)	C(1)–C(2)	1.511(13)
Os(1)–P(1)	2.375(2)	F(4)–C(3)	1.311(12)	O(3)–N(2)	1.420(9)	C(3)–C(4)	1.548(13)

N(1)–Os(1)–O(3)	177.8(3)	O(4)–Os(1)–P(1)	163.9(2)	F(1)–C(1)–C(2)	112.1(8)
N(1)–Os(1)–O(2)	103.4(3)	O(4)–Os(1)–P(2)	89.0(2)	F(3)–C(1)–C(2)	110.6(8)
N(1)–Os(1)–O(4)	96.3(3)	P(1)–Os(1)–P(2)	106.3(1)	N(2)–C(2)–O(2)	126.9(8)
N(1)–Os(1)–P(1)	87.0(2)	C(2)–O(2)–Os(1)	108.9(5)	N(2)–C(2)–C(1)	116.5(8)
N(1)–Os(1)–P(2)	96.8(2)	N(2)–O(3)–Os(1)	115.9(4)	O(2)–C(2)–C(1)	116.4(8)
O(3)–Os(1)–O(2)	78.1(2)	C(4)–O(4)–Os(1)	122.0(6)	F(4)–C(3)–F(6)	107.7(9)
O(3)–Os(1)–O(4)	82.3(2)	O(1)–N(1)–Os(1)	176.1(6)	F(4)–C(3)–F(5)	105.3(9)
O(3)–Os(1)–P(1)	94.8(2)	C(2)–N(2)–O(3)	109.3(7)	F(4)–C(3)–C(4)	112.7(9)
O(3)–Os(1)–P(2)	81.5(2)	F(2)–C(1)–F(1)	108.4(8)	F(6)–C(3)–F(5)	106.8(10)
O(2)–Os(1)–O(4)	79.8(2)	F(2)–C(1)–F(3)	106.0(8)	F(6)–C(3)–C(4)	110.7(9)
O(2)–Os(1)–P(1)	84.1(2)	F(2)–C(1)–C(2)	112.9(8)	F(5)–C(3)–C(4)	113.2(8)
O(2)–Os(1)–P(2)	157.8(2)	F(1)–C(1)–F(3)	106.6(8)		

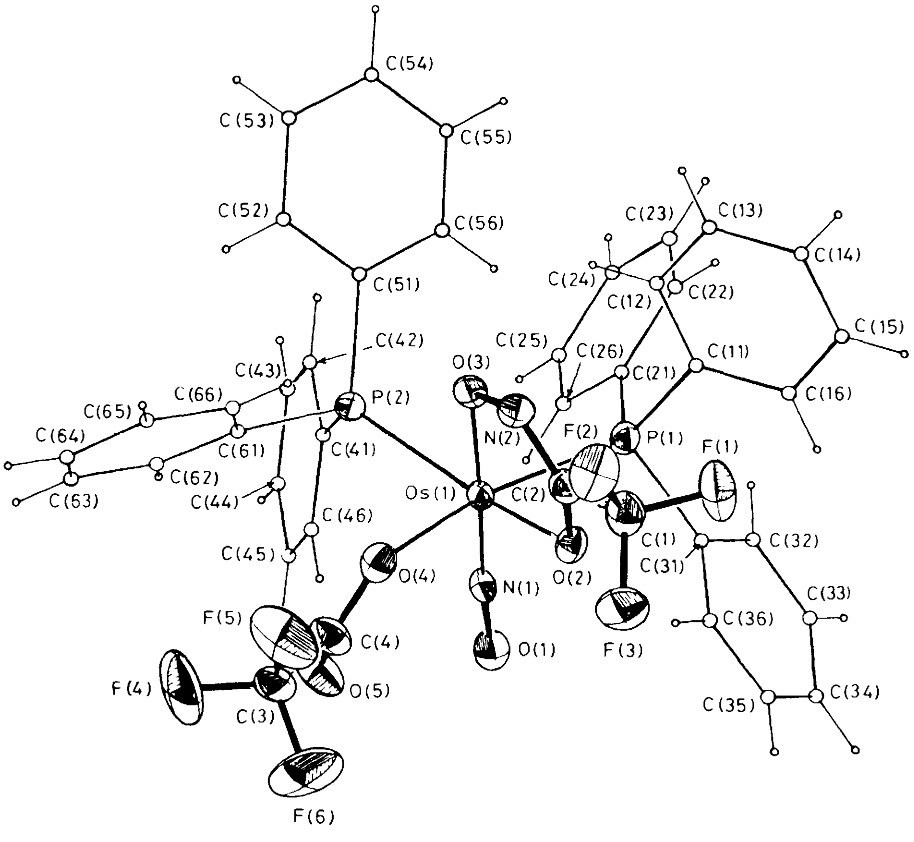
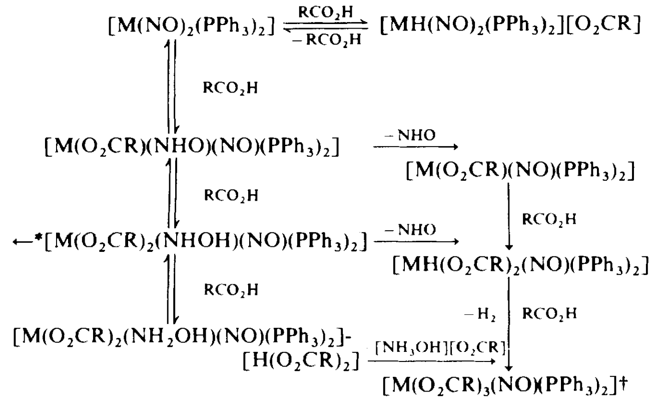


Figure. Molecular structure of $[\overline{\mathrm{Os\{ON{=}C(O}}\mathrm{)CF_3\}(O_2CCF_3)(NO)(PPh_3)_2}]$

The dinitrosyl complexes $[M(NO)_2(PPh_3)_2]$ react with perfluorocarboxylic acids RCO_2H (R = CF_3 or C_2F_5) in refluxing 2-methoxyethanol to afford the products $[Ru(O_2CR)_3(NO)(PPh_3)_2]$ and $[OsH(O_2CR)_2(NO)(PPh_3)_2]$, identical to those described above. When the ruthenium reactions were performed using boiling toluene as solvent in place of 2-methoxyethanol the same products were obtained in improved yield. However, use of boiling toluene as solvent in the osmium reactions leads to formation of a radically different type of complex. The new osmium species, which were isolated in essentially quantitative yield as orange air-stable crystals, could not be characterised on the basis of their spectroscopic data (Table 2). One example (R = CF_3) was therefore recrystallised from dichloromethane–methanol and examined by *X*-ray diffraction methods. The crystal was found to contain molecules of a neutral six-co-ordinate osmium(II) hydroximate complex, $[\overline{\mathrm{Os\{ON{=}C(O}}\mathrm{)CF_3\}(O_2CCF_3)(NO)(PPh_3)_2}]$ (**4**) and dichloromethane solvent in 1 : 1 ratio. The salient details of the osmium complex structure are illustrated in the Figure; the most significant bond lengths and bond angles are listed in Table 4. The most interesting features are the *O,O'*-chelating

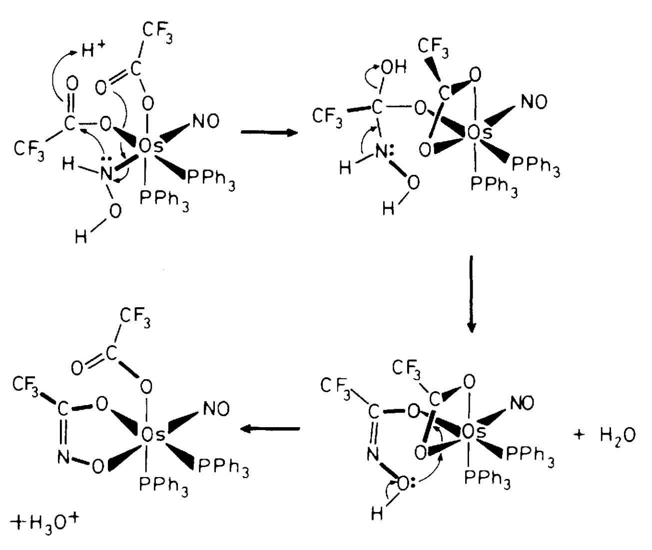


Scheme 3. * See Scheme 4. † Forms for ruthenium only

trifluoroacetohydroximate(2−) ligand and the *cis* disposition of the two bulky triphenylphosphine ligands [P(1)–Os(1)–P(2) = 106.3(1)°]. The hydroximate ligand is unequivocally bound through both oxygen atoms. The N and O atoms originating from one nitrosyl ligand are situated *trans* to the remaining, intact nitrosyl ligand. The C=N double bond length in the hydroximate ligand [1.277(11) Å] is very close to the expected value and its presence explains the i.r. absorption observed at *ca.* 1 609 cm^{-1} which can now be attributed to ν(C=N).[19] The band at *ca.* 1 820 cm^{-1} is consistent with the presence of the linear nitrosyl ligand,[20] and the bands at *ca.* 1 690 and *ca.* 1 390 cm^{-1} are typical of unidentate carboxylate ligands.[21] The presence of a pair of relatively bulky triphenylphosphine ligands in mutually *cis* co-ordination sites is a rather unexpected feature of the structure. However, similar arrangements are not unknown, and a very pertinent example is provided by the closely related osmium carboxylate complex $[Os(O_2CCF_3)_2(MeOH)(CO)(PPh_3)_2]$ and its ruthenium analogue, the latter having been characterised by diffraction methods.[22]

Attempts to convert the osmium trifluoroacetohydroximate to the isomer having *trans* phosphines by heating in toluene at 125 °C for 2 h gave only unchanged starting material.

Formation of the products $[Ru(O_2CR)_3(NO)(PPh_3)_2]$ and $[OsH(O_2CR)_2(NO)(PPh_3)_2]$ from the dinitrosyls $[M(NO)_2(PPh_3)_2]$ can be rationalised in terms of the reaction sequence given in Scheme 3. The initial step could involve protonation at the metal centre, to form the hydrido-cations $[MH(NO)_2(PPh_3)_2]^+$, or on a nitrosyl ligand, to yield the species $[M(O_2CR)(NHO)(NO)(PPh_3)_2]$. Formation of the osmium cation $[OsH(NO)_2(PPh_3)_2]^+$ by protonation of $[Os(NO)_2(PPh_3)_2]$ with HCl has previously been reported[9] but no details have been given. However, bearing in mind the nature of the final products, it appears more probable that the present reactions involve successive protonations of a nitrosyl ligand to yield the intermediates $[M(O_2CR)(NHO)(NO)(PPh_3)_2]$, $[M(O_2CR)_2(NHOH)(NO)(PPh_3)_2]$ and finally $[M(O_2CR)_2(NH_2OH)(NO)(PPh_3)_2][H(O_2CR)_2]$. These could then react further by loss of NHO or NH_2OH, as indicated in Scheme 3, to yield the observed products. Protonation of nitrosyl ligands leading to formation of co-ordinated NHO, NHOH, and NH_2OH groups is a well established phenomenon in platinum metal chemistry; relevant examples are afforded by the reactions of $[OsCl(NO)(CO)(PPh_3)_2]$ and $[Os(NO)_2(PPh_3)_2]$ with HCl to yield $[OsCl_2(NHO)(CO)(PPh_3)_2]$ and $[OsCl_2(NHOH)(NO)(PPh_3)_2]$ respectively.[23] Loss of NHO ligands under mild conditions has also been observed.[23] The isolation of $[NH_3OH][O_2CCF_3]$, albeit in small yield, from the reaction of $[Ru(NO)_2(PPh_3)_2]$ with CF_3CO_2H in boiling toluene lends further support to the proposed mechanism.



Scheme 4.

Failure of the osmium reactions in 2-methoxyethanol to proceed beyond the $[OsH(O_2CR)_2(NO)(PPh_3)_2]$ stage can be attributed to the reluctance of these products to react further with excess acid, RCO_2H (see above), and the tendency of the final protonated intermediate $[Os(O_2CR)_2(NH_2OH)(NO)(PPh_3)_2][H(O_2CR)_2]$, if formed, to revert to $[Os(O_2CR)_2(NHOH)(NO)(PPh_3)_2]$ by loss of acid, RCO_2H, rather than form $[Os(O_2CR)_3(NO)(PPh_3)_2]$ by reacting with more acid and eliminating the salt $[NH_3OH][H(O_2CR)_2]$.

To account for the formation of the hydroximate complexes $[\overline{Os\{ON=C(O})R\}(O_2CR)(NO)(PPh_3)_2]$ in boiling toluene we propose that the $[Os(NO)_2(PPh_3)_2]$ precursor undergoes successive protonations to yield $[Os(O_2CR)(NHO)(NO)(PPh_3)_2]$ and $[Os(O_2CR)_2(NHOH)(NO)(PPh_3)_2]$ as in Scheme 3, and that the latter intermediate then dehydrates (Scheme 4) to afford the final product. The toluene solvent possibly promotes this particular course of reaction by removing liberated water as a toluene–water azeotrope. Although quantitative gas evolution studies have not been performed, sampling of the gas over the reaction mixture indicated that water was produced in the reaction and that dihydrogen was absent.

N.m.r. studies on $[M(NO)_2(PPh_3)_2]/CF_3CO_2H/C_6D_6$ solutions provided some support for these hypotheses. The ^1H n.m.r. spectra of solutions prepared by addition of CF_3CO_2H (*ca.* 1—4 mol equiv.) to the complexes $[M(NO)_2(PPh_3)_2]$ in cold benzene indicate the absence of hydride ligands but display a broad weak signal at *ca.* 1.6 (M = Ru) or *ca.* 5.06 p.p.m. (M = Os) which sharpens and moves progressively to *ca.* 8—9 p.p.m. (the 'free' acid value) as the acid concentration is increased. We attribute this signal to the protons of co-ordinated NHO, NHOH, and NH_2OH ligands which are exchanging rapidly with each other and with the protons of the excess acid. A rapid exchange process of this type is entirely feasible since the stepwise protonation of co-ordinated nitric oxide to afford NH_2OH is readily reversible.[23] $^{31}P-\{^1H\}$ N.m.r. spectra of the $[Ru(NO)_2(PPh_3)_2]/CF_3CO_2H/C_6D_6$ solutions reveal singlets attributable to the precursor $[Ru(NO)_2(PPh_3)_2]$ (δ *ca.* 48.9 p.p.m.), the product $[Ru(O_2CCF_3)_3(NO)(PPh_3)_2]$ (δ *ca.* 19.8 p.p.m.), and three intermediates (δ *ca.* 13, 25, and 28—39 p.p.m.). The last signal is particularly acid dependent, showing progressive drift as the acid concentration is increased. Selective decoupling of aromatic protons confirms that none of these species contains hydride ligands and we therefore conclude that they are intermediates (Scheme 3; M = Ru) formed by successive protonations of a nitrosyl ligand.

Proton-decoupled ^{31}P n.m.r. spectra of $[Os(NO)_2(PPh_3)_2]/CF_3CO_2H/C_6D_6$ solutions display singlets attributable to $[Os(NO)_2(PPh_3)_2]$ (δ *ca.* 14.8 p.p.m.) and three intermediates (*ca.* −9.9, 0—11, and 32—36 p.p.m.), together with an AB pattern [*ca.* −8.4 and −11.7 p.p.m., $^2J(PP') = 11.8$ Hz] assigned to a fourth intermediate. The AB pattern differs from that observed for the final product $[\overline{Os\{ON{=}C(O}\text{)}CF_3\}(O_2CCF_3)(NO)(PPh_3)_2]$, which appears only when more forcing conditions are applied. Again some of the signals show marked acid-concentration dependence. Selective decoupling experiments (aromatic protons only decoupled) confirm the absence of hydride species. It seems probable that the three singlets and the AB pattern are attributable to the intermediates shown in Schemes 3 and 4 respectively. The singlet at δ *ca.* −9.9 p.p.m. has a chemical shift similar to that recorded for the known species $[OsCl_2(NHOH)(NO)(PPh_3)_2]$ (δ −8.7 p.p.m.), prepared from $[Os(NO)_2(PPh_3)_2]$ and HCl, and is therefore tentatively assigned to $[Os(O_2CCF_3)_2(NHOH)(NO)(PPh_3)_2]$.

Attempts to isolate characterisable compounds from these solutions were unsuccessful. Yellow crystalline solids of apparent stoicheiometry $M(NO)_2(PPh_3)_2(RCO_2H)_n$ (n = 3—5) were obtained in good yield but gave irreproducible analytical data. These products were probably mixtures containing some of the protonated intermediates postulated in Scheme 3. Their stoicheiometry was probably further complicated by the presence of H-bonded counter anions $[H(O_2CR)_2]^-$ in the ionic salts.

The foregoing discussion offers no explanation for the liberation of nitric oxide (detected as brown fumes of NO_2 on admission of air) observed during the reaction of $[Ru(NO)_2(PPh_3)_2]$ with acids in toluene. Possible sources include decomposition of nitrogenous by-products (*i.e.* NH_2OH or NHOH), the presence of unidentified side-reactions, or the thermal decomposition of $[Ru(NO)_2(PPh_3)_2]$. The high yield of product obtained suggests that the second explanation is incorrect and the failure to detect evolution of NO from solutions of $[Ru(NO)_2(PPh_3)_2]$ in boiling toluene implies that the third alternative is also not operative.

Acknowledgements

We thank the S.E.R.C. for financial support (to E. B. B. and A. D.), Johnson Matthey p.l.c. for the loan of platinum metal salts, and the Marshall M. Wrubel Computing Centre at Indiana University for computing time.

References

1 Part 24, E. B. Boyar, D. S. Moore, S. D. Robinson, B. R. James, M. Preece, and I. Thorburn, preceding paper.

2 S. D. Robinson and M. F. Uttley, *J. Chem. Soc., Chem. Commun.*, 1972, 1047.

3 A. Dobson, S. D. Robinson, and M. F. Uttley, *J. Chem. Soc., Dalton Trans.*, 1975, 370.

4 A. Dobson, S. D. Robinson, and M. F. Uttley, *Inorg. Synth.*, 1977, **17**, 124.

5 B. L. Haymore, J. C. Huffman, A. Dobson, and S. D. Robinson, *Inorg. Chim. Acta*, 1982, **65**, L231.

6 S. T. Wilson and J. A. Osborn, *J. Am. Chem. Soc.*, 1971, **93**, 3068.

7 J. S. Bradley and G. Wilkinson, *Inorg. Synth.*, 1977, **17**, 73.

8 N. Ahmad, J. J. Levison, S. D. Robinson, and M. F. Uttley, *Inorg. Synth.*, 1974, **15**, 45.

9 K. R. Grundy, K. R. Laing, and W. R. Roper, *Chem. Commun.*, 1970, 1500.

10 J. C. Huffman, L. N. Lewis, and K. G. Caulton, *Inorg. Chem.*, 1980, **19**, 2755.

11 B. L. Haymore and J. A. Ibers, *Inorg. Chem.*, 1975, **14**, 3060.

12 D. S. Moore and S. D. Robinson, *Inorg. Chim. Acta*, 1981, **53**, L171.

13 L. Vaska, *J. Am. Chem. Soc.*, 1966, **88**, 4100.

14 D. Guisto, G. Ciani, and M. Manassero, *J. Organomet. Chem.*, 1976, **105**, 91.

15 T. S. Cameron, K. R. Grundy, and K. N. Robertson, *Inorg. Chem.*, 1982, **21**, 4149.

16 P.-C. Kong and D. M. Roundhill, *Inorg. Chem.*, 1972, **11**, 1437.

17 G. Strukul, R. Ros, and R. A. Michelin, *Inorg. Chem.*, 1982, **21**, 495.

18 M. T. Atlay, M. Preece, G. Strukul, and B. R. James, *J. Chem. Soc., Chem. Commun.*, 1982, 406; *Can. J. Chem.*, 1983, **61**, 1332.

19 L. J. Bellamy, 'The Infrared Spectra of Complex Molecules,' 3rd edn., Chapman and Hall, London 1975, p. 295.

20 B. F. G. Johnson and J. A. McCleverty, *Prog. Inorg. Chem.* 1966, **7**, 277.

21 S. D. Robinson and M. F. Uttley, *J. Chem. Soc., Dalton Trans.*, 1973, 1912.

22 M. B. Hursthouse, unpublished work, cited in A. Dobson and S. D. Robinson, *Inorg. Chem.*, 1977, **16**, 137.

23 K. R. Grundy, C. A. Reed, and W. R. Roper, *Chem. Commun.*, 1970, 1501.

Received 30th January 1984; *Paper* 4/170