Electrophilic Behaviour of Nitrosyls: the Reactions of Ketones with Nitrosyls and the Crystal and Molecular Structure of the Product of the Reaction between *trans*-Chloro(nitrosyl)tetra(pyridine)ruthenium and Acetone†

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The reaction between *trans*-$[RuCl(py)_4(NO)]^{2+}$ (py = pyridine) and acetone in the presence of aqueous NH_3 gave the adduct *trans*-$[RuCl(py)_4\{N(OH)CHC(O)CH_3\}]^+$, isolated as the PF_6^- salt. The product was characterised by i.r. and n.m.r. spectroscopies and by *X*-ray diffraction. Crystal data for $[RuCl(py)_4\{N(OH)CHC(O)CH_3\}]PF_6{\cdot}(CH_3)_2CO$ are as follows: space group $P2_1$, $a = 8.712(3)$, $b = 14.272(20)$, $c = 13.169(5)$ Å, $\beta = 104.63(3)°$, $Z = 2$, final $R = 0.057$ for 268 variables and 1 607 observed reflections. The spectroscopic and diffraction data suggest that the predominant tautomer in the ligand is the delocalised form $N(\overset{\cdots}{=}O\cdots H)\overset{\cdots}{=}CH\overset{\cdots}{=}C(\overset{\cdots}{=}O)CH_3$. The product decomposed intramolecularly in aqueous solution to give $[RuCl(py)_4(NCH)]^+$, which in turn reacted further to give an ill defined paramagnetic complex. In CH_3CN solution, $[RuCl(py)_4\{N(OH)CHC(O)CH_3\}]^+$ decomposed cleanly to give $[RuCl(py)_4(NCCH_3)]^+$.

It has been known for many years that $[Fe(CN)_5(NO)]^{2-}$ reacts with ketones, and the reaction is used as a standard test for ketones containing the $CH_3C(O)$– group.[1] Such reactions are also used as a preparative method for the nitrosation of ketones, the final product being an oxime on alkaline and a nitrile on acid hydrolysis [reactions (1) and (2) respectively].[2]

$$[Fe(CN)_5(NO)]^{2-} + R^1C(O)CH_2R^2 + OH^- \longrightarrow [Fe(CN)_5(H_2O)]^{3-} + R^1C(O)CR^2{=}NOH \quad (1)$$

$$[Fe(CN)_5(NO)]^{2-} + R^1C(O)CH_2R^2 + H_2O \longrightarrow [Fe(CN)_5(H_2O)]^{3-} + H^+ + R^2CN + R^1COOH \quad (2)$$

Other nitrosyls such as $[Ru(NH_3)_5(NO)]^{3+}$ and $[RuCl(bipy)_2(NO)]^{2+}$ (bipy = 2,2′-bipyridine) undergo similar reactions.[3,4] The final products of these reactions have been clearly identified but the mechanisms are still obscure, despite several kinetic and spectroscopic investigations.[2,3,5,6] It has been assumed that the first step in the reaction is the nucleophilic attack of a deprotonated ketone on the nitrosyl [reaction (3)]. Subsequent

$$[Fe(CN)_5(NO)]^{2-} + [R^1C(O)CHR^2]^- \longrightarrow [Fe(CN)_5\{N(O)CHR^2C(O)R^1\}]^{3-} \quad (3)$$

deprotonation and/or cyclisation and rearrangement of the ligand $[N(O)CHR^2C(O)R^1]$ leads to the oxime or nitrile.[3,5,6] There is, however, no evidence that the intermediate produced in reaction (3), which may have the tautomeric forms (**I**)—(**III**) or the delocalised form (**IV**) when $R^1 = CH_3$ and $R^2 = H$ (Figure 1), is actually formed. Such an adduct has never been isolated and its structure is unknown. Reaction (3) is an example of the electrophilic behaviour of the nitrosyl ligand in $[Fe(CN)_5(NO)]^{2-}$, a type of reaction which we have studied extensively.[7,8] In continuation of these studies we have searched for an intermediate of the type produced by reaction (3). We sought one which was stable enough to isolate and characterise, but whose decomposition could be followed. We have found such a case in the reaction between *trans*-$[RuCl(py)_4(NO)]^{2+}$ (py = pyridine)[9] and acetone in the presence of aqueous ammonia. We report here on the formation, characterisation, and decomposition of the cation *trans*-$[RuCl(py)_4\{N(OH)CHC(O)CH_3\}]^+$.

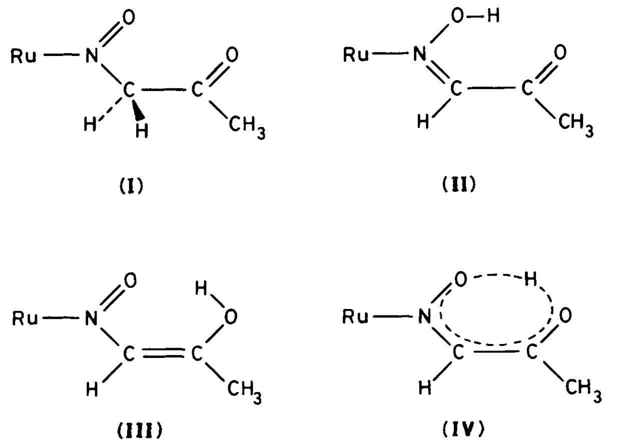

Figure 1. The four possible tautomers of the $RuC_3H_5NO_2$ group

Experimental

The starting material *trans*-$[RuCl(py)_4(NO)]^{2+}$ was prepared as previously described.[9] All other materials were reagent grade. Instruments used were a Hitachi EPI-G2 i.r. and a Hitachi R22 n.m.r. spectrometer. Magnetic moments were by the Gouy method and microanalyses by the Institute of Chemical and Physical Research, Wako, Saitoma 351, Japan and by the Sophia University Analytical Facility.

Formation of trans-$[RuCl(py)_4\{N(OH)CHC(O)CH_3\}]PF_6$.—To a solution of $[RuCl(py)_4(NO)][PF_6]_2$ (0.1 g, 0.129 mmol) in acetone (10 cm^3) was added two drops of concentrated aqueous ammonia. The solution was set aside for 10 min at

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

Table 1. Atomic co-ordinates (× 10^3) for the non-hydrogen atoms of *trans*-$[RuCl(py)_4\{N(O\overline{H)CHC(O})CH_3\}]PF_6\cdot(CH_3)_2CO$, with estimated standard deviations in parentheses

Atom *	*X/a*	*Y/b*	*Z/c*
Ru	484.6(1)	500	116.9(1)
Cl	325.4(5)	357.8(3)	74.3(3)
N(1)	439(1)	496(1)	268(1)
C(1)	294(2)	481(1)	276(1)
C(2)	254(2)	479(1)	373(1)
C(3)	367(2)	487(2)	463(1)
C(4)	524(2)	487(2)	456(1)
C(5)	552(1)	492(2)	360(1)
N(2)	516(1)	507(2)	−38(1)
C(6)	551(2)	417(1)	−80(1)
C(7)	587(3)	422(2)	−179(2)
C(8)	588(2)	517(2)	−227(1)
C(9)	549(2)	589(2)	−183(2)
C(10)	509(2)	580(1)	−90(1)
N(3)	278(1)	580(1)	66(1)
C(11)	241(2)	656(1)	118(1)
C(12)	103(2)	701(1)	92(1)
C(13)	−15(2)	670(1)	6(1)
C(14)	20(2)	599(1)	−51(1)
C(15)	165(2)	554(1)	−20(1)
N(4)	686(1)	415(1)	161(1)
C(16)	687(2)	340(1)	224(1)
C(17)	820(2)	279(2)	255(1)
C(18)	931(3)	290(1)	209(1)
C(19)	942(2)	366(1)	145(2)
C(20)	813(2)	424(1)	126(1)
N(5)	613(1)	618(1)	151(1)
C(21)	754(1)	622(1)	225(1)
C(22)	835(2)	706(1)	252(1)
C(23)	987(2)	697(1)	341(1)
O(1)	801(2)	785(1)	209(1)
O(2)	561(1)	695(1)	101(1)
P	−2.5(5)	3.4(8)	377.5(3)
F(1)	−93(2)	−11(2)	262(1)
F(2)	102(2)	83(1)	351(2)
F(3)	113(3)	−69(1)	357(2)
F(4)	−108(2)	−77(1)	409(1)
F(5)	86(2)	15(2)	494(1)
F(6)	−127(2)	76(1)	398(2)
C(24)	475(4)	747(2)	448(2)
C(25)	407(4)	735(2)	532(2)
C(26)	659(4)	747(2)	466(3)
O(3)	394(3)	745(2)	359(1)

* N(1), C(1)—C(5) comprise ring A of Figure 2; N(2), C(6)—C(10) ring B; N(3), C(11)—C(15) ring C; and N(4), C(16)—C(20) ring D. C(24)—C(26) and O(3) are the lattice acetone.

room temperature, during which time the colour changed from orange to dark violet. The solution was filtered and diethyl ether (25 cm^3) added to the filtrate. On setting aside at 5 °C for 30—60 min the purple adduct, $[RuCl(py)_4\{N(O\overline{H)CHC(O})CH_3\}]PF_6$ deposited in crystalline form. It was collected by filtration, washed with ether, and air dried. Yield 0.04 g, 0.058 mmol, 45% (Found: C, 40.7; H, 3.9; Cl, 5.2; N, 11.6; PF_6, 21.6. Calc. for $C_{23}H_{25}ClF_6N_5O_2PRu$: C, 40.3; H, 3.7; Cl, 5.2; N, 10.2; PF_6, 21.2%).

Decomposition of trans-$[RuCl(py)_4\{N(O\overline{H)CHC(O})CH_3\}]PF_6$.—A suspension of *trans*-$[RuCl(py)_4\{N(O\overline{H)CHC(O})CH_3\}]PF_6$ (0.3 g) in water (25 cm^3) was stirred under argon for 72 h at room temperature. During this time the solid changed colour from dark to light brown. The solid was collected by filtration, washed with water, ethanol, and ether and dried *in vacuo*. Yield 0.16 g, 58% {assuming formation of $[RuCl(py)_4(NCH)]PF_6$} (Found: C, 40.2; H, 3.3; N, 10.9. Calc. for $C_{21}H_{21}ClF_6N_6PRu$: C, 40.4; H, 3.4; N, 11.2%). Infrared: 2 050 cm^{-1} (sharp, intense) [ν(N≡C)]. Magnetic moment: $\mu_{eff.}$ = 2.63 at 25 °C. Electronic spectrum: $\lambda_{max.}$ 356, 474 nm.

Formation of $[Ru(NH_3)(py)_4(NO_2)]PF_6$.—To a suspension of $[RuCl(py)_4(NO)][PF_6]_2$ (0.1 g) in water (5 cm^3) was added concentrated aqueous ammonia (5 cm^3). The mixture was warmed gently until a yellow solution was formed. The solution was cooled, filtered and then set aside for 48 h at room temperature. The yellow crystals of $[Ru(NH_3)(py)_4(NO_2)]PF_6\cdot H_2O$ which formed were collected by filtration, washed quickly with water, ethanol, and ether and dried *in vacuo*. Yield 0.03 g, 35% (Found: C, 37.6; H, 3.7; N, 13.0. Calc. for $C_{20}H_{25}F_6N_6O_3PRu$: C, 37.3; H, 3.9; N, 13.1%). Infrared: 1 276, 1 308 cm^{-1} [$\nu(NO_2)$]; 1 380 cm^{-1} [$\delta(NH_3)$]; 3 400 cm^{-1} [ν(N–H)]; 3 675 cm^{-1} [ν(O–H)]. N.m.r.: 8.36 (doublet, $H^{2,6}$), 7.96 (triplet, H^4), 7.39 p.p.m. (t, $H^{3,5}$). The compound was diamagnetic and showed an irreversible oxidation wave at 0.57 V (*versus* $Ag/AgClO_4$) in CH_3CN solution.

Determination of the Crystal Structure of trans-$[RuCl(py)_4\{N(O\overline{H)CHC(O})CH_3\}]PF_6$ *by* X-*Ray Diffraction*.—Because of the rather narrow range of pH in which the acetone adduct of $[RuCl(py)_4(NO)]^{2+}$ was formed, and its subsequent decomposition, it was very difficult to vary the reaction conditions in order to obtain crystals suitable for *X*-ray diffraction. One attempt led to marginally acceptable crystals whose data were a = 24.11(3), b = 13.88(2), c = 8.882(8) Å, β = 97.22(9)°, space group $P2_1$, Z = 4. From this crystal 1 743 reflection intensities were measured. However, refinement of the structure terminated at R = 0.126, and this value could only be reached by postulating a serious disorder in the crystal. A batch of sponge-like crystals was obtained from another reaction, and the data and refinement reported here were obtained from one of these.

Crystal data. $C_{26}H_{31}ClF_6N_5O_3PRu$, M = 743.1, monoclinic, space group $P2_1$, a = 8.712(3), b = 14.272(20), c = 13.169(5) Å, β = 104.63(3)°, U = 1 583.11 Å^3, Z = 2, D_c = 1.56, D_m = 1.54 Mg m^{-3}, F(000) = 1 504; graphite-monochromated Mo-K_α radiation, λ = 0.710 73 Å, μ(Mo-K_α) = 6.48 mm^{-1}. Because of the shape of the crystal an empirical absorption correction[10] was applied.

The intensities of a unique set of 2 132 reflections with $2\theta < 45°$ were measured by the ω–2θ scan technique on an Enraf-Nonius CAD4 diffractometer at 20 °C. Of these reflections, 1 607 were judged to be observed [$I > 3\sigma(I)$]. After applying the usual corrections to the data, the structure was readily solved by Patterson and Fourier techniques and refined using the SHELX 76 program package.[11] Scattering factors were taken from International Tables[12] and were corrected for both the real and the imaginary parts of the anomalous dispersion where appropriate. The function minimized was $\Sigma w(\Delta F)^2$ with a weighting scheme of the form $w = 1/[\sigma^2(|F|) + k(|F|^2)]$, k being refined. The final refinement used 268 variable parameters. The Ru, Cl, P, and F atoms were refined anisotropically, as were the C, N, and O atoms of both the $N(O\overline{H)CHC(O})CH_3$ ligand and the lattice acetone. All other

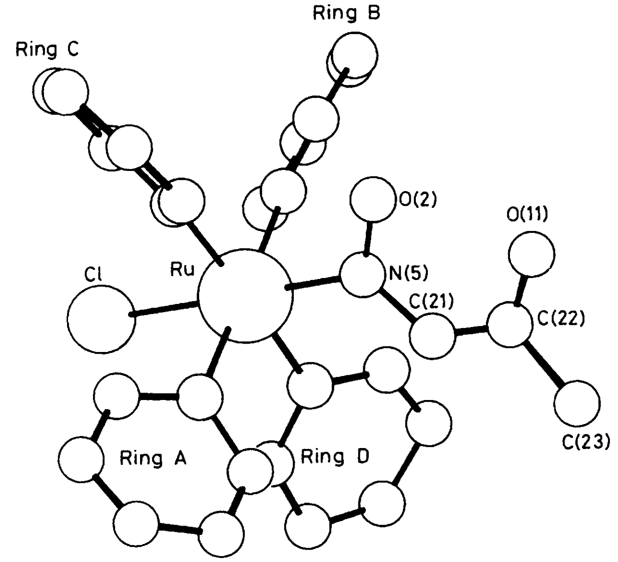


Figure 2. Molecular structure of the cation *trans*-$[RuCl(py)_4\{N(OH)CHC(O)CH_3\}]^+$

atoms were refined isotropically. The hydrogen atoms, with the exception of H(101) [the hydrogen atom bonded to O(1) and O(2) of the $N(OH)CHC(O)CH_3$ ligand], were refined as riding on the carbon atoms with a C–H distance of 0.96 Å and the appropriate sp^2 or sp^3 hybridization. The hydrogen atom H(101) was observed in a difference Fourier map. Its position was refined in a preliminary run, and it was then fixed during final refinement. All hydrogen atoms were given the isotropic thermal parameters of the atoms to which they were attached. Refinement converged at $R = 0.057$, $R' = 0.061$ and R_g (including unobserved) = 0.076. The maximum residual intensity was 0.82 e $Å^{-3}$ and the minimum -0.62 e $Å^{-3}$. The maximum was *ca.* 1.5 Å from the ruthenium atom. Table 1 lists the atomic positional parameters obtained from the last cycle of the refinement. Important distances are given in Table 2 and angles in Table 3. The numbering scheme is given in Figure 2.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

Results and Discussion

Formation of trans-$[RuCl(py)_4\{N(OH)CHC(O)CH_3\}]^+$.—Addition of aqueous NH_4OH or NH_4SH to a solution of *trans*-$[RuCl(py)_4(NO)][PF_6]_2$ in acetone resulted in a colour change from orange to purple and, on adding ether, precipitation of the deprotonated adduct *trans*-$[RuCl(py)_4\{N(OH)CHC(O)CH_3\}]PF_6$ [equation (4)]. The nature and concentration of

$$[RuCl(py)_4(NO)]^{2+} + (CH_3)_2CO + OH^- \longrightarrow H_2O + [RuCl(py)_4\{N(OH)CHC(O)CH_3\}]^+ \quad (4)$$

the base required careful control. Use of aqueous NaOH gave only $[RuCl(py)_4(NO_2)]$; use of a large excess of NH_4OH gave $[Ru(NH_3)(py)_4(NO_2)]^+$. Formation of $[RuCl(py)_4(NO_2)]$ from $[RuCl(py)_4(NO)]^{2+}$ and OH^- has been reported previously.[9] The formation of the deprotonated adduct and of the nitro complexes are further examples of nucleophilic attack at the co-ordinated nitrosyl ligand.[7]

In the reaction between $[Fe(CN)_5(NO)]^{2-}$ and $(CH_3)_2CO$ the adduct isolated was the doubly deprotonated form $[Fe(CN)_5\{N(O)CHC(O)CH_3\}]^{4-}$. The counterpart of this in the present case would be $[RuCl(py)_4\{N(O)CHC(O)CH_3\}]$, but this was not observed. Protonation of $[Fe(CN)_5\{N(O)CHC(O)CH_3\}]^{4-}$ to give $[Fe(CN)_5\{N(OH)CHC(O)CH_3\}]^{3-}$ has been noted. Decomposition of the deprotonated adduct gave $[Fe(CN)_5(H_2O)]^{3-}$.[13]

Structure of the $N(OH)CHC(O)CH_3$ *Ligand in* trans-$[RuCl(py)_4\{N(OH)CHC(O)CH_3\}]^+$.—The nature of the ligand formed from acetone and the nitrosyl group was elucidated principally by *X*-ray crystallography. The analysis conclusively established the framework of the ligand as one of the tautomers (**I**)—(**IV**). The distances and angles within the ligand (which is planar) are not compatible with tautomer (**I**), and indicate that the delocalised form (**IV**) is the best description (see Tables 2 and 3). However, the errors in the distances and angles are rather large (because of the unavoidably poor quality of the crystal) and tautomers (**II**) and (**III**) could be accommodated within these error limits. The hydrogen atom, whose position changes depending on the tautomer involved, was located between the oxygen atoms in a difference Fourier map, but its position could not be refined to give a clear preference for a particular tautomer. Hence we sought spectroscopic confirmation of the tautomer involved.

The i.r. spectrum (KBr disc) of the adduct showed a number of absorption bands of interest: an intense, moderately sharp band at 3 400 cm^{-1}, shifted to 2 500 cm^{-1} when $(CD_3)_2CO$ was used to prepare the adduct complex; a medium intensity, sharp band at 1 710 cm^{-1}, unshifted on deuteriation or on using $[RuCl(py)_4(^{15}NO)][PF_6]_2$ as starting material; an intense, broad absorption at 1 600 cm^{-1}, partially shifted to 1 550 cm^{-1} on deuteriation and partially shifted to 1 585 cm^{-1} on using ^{15}NO; an intense band also appeared at 1 460 cm^{-1} on deuteriation, and this must be derived from the band at 1 600 cm^{-1} also; a weak sharp band at 1 320 cm^{-1}, shifted to 1 250 cm^{-1} on deuteriation; an intense band at 1 220 cm^{-1}, shifted to 1 190 cm^{-1} on using ^{15}NO but unshifted on deuteriation; a medium intensity band at 1 130 cm^{-1} which shifted to 1 090 cm^{-1} on deuteriation; and a sharp band at 910 cm^{-1} which only appeared on deuteriation. Other bands were assigned to pyridine or PF_6, or to the CH_3 group.

The band at 3 400 cm^{-1}, which shifted appropriately on deuteriation, can only be assigned to ν(O–H) and its presence eliminates tautomer (**I**) from consideration. The band at 1 710 cm^{-1}, which was unshifted when ^{15}N was present, must be assigned to ν(C=O). The shifts in the bands at 1 600 and 1 220 cm^{-1} when ^{15}N is present suggest that these should be assigned to ν(C=N) and ν(N–O) or ν(N=O) and ν(C–N). The broad absorption at 1 600 cm^{-1} also contains contributions from pyridine vibrations. Hence the i.r. spectrum supports tautomers (**II**) and/or (**IV**) as the major contributions to the structure.

The ^{13}C n.m.r. spectrum, although of poor quality due to the decomposition of the ligand, also supports the assignment of the major tautomer as (**IV**). In addition to resonances assignable to co-ordinated pyridine there were signals at 168.9 p.p.m., assigned to C(22) (see Figure 2), at 147.7 p.p.m., assigned to C(21), and at 20.0 p.p.m. assigned to the methyl C(23). All of these resonances disappeared on recrystallisation of the sample, or with time in the n.m.r. tube. The ^1H n.m.r. showed resonances at 1.90 and 7.93 p.p.m., assigned to the methyl C(23) hydrogens and the olefinic C(21) hydrogen respectively.

Molecular Structure of trans-$[RuCl(py)_4\{N(OH)CHC(O)CH_3\}]PF_6$.—The *X*-ray analysis established the *trans*-octahedral arrangement of Cl, four pyridines, and the $N(OH)CHC(O)CH_3$ ligand around the ruthenium atom. The delocalisation in the $N(OH)CHC(O)CH_3$ ligand extends to the

Table 2. Important bond distances (Å) in the *trans*-[RuCl(py)$_4$-{N(OH)CHC(O)CH$_3$}]$^+$ cation, with estimated standard deviations in parentheses

Ru-N(1)	2.122(10)	N(5)-O(2)	1.297(16)
Ru-N(2)	2.121(10)	N(5)-C(21)	1.362(16)
Ru-N(3)	2.098(11)	C(21)-C(22)	1.389(23)
Ru-N(4)	2.092(11)	C(22)-C(23)	1.539(20)
Ru-N(5)	2.009(13)	C(22)-O(1)	1.257(22)
Ru-Cl	2.442(4)	O(1) ··· O(2)	2.556(21)

Ru atom since the Ru-N(5) distance of 2.009(13) Å is much shorter than the distances to the four pyridine nitrogens which average 2.108(10) Å. The Ru-pyridine distances are comparable to those in the parent *trans*-[RuCl(py)$_4$(NO)][PF$_6$]$_2$[14] [average 2.109(8) Å]. The π bonding between ruthenium and the N(OH)CHC(O)CH$_3$ ligand is less than between Ru and NO, as expected; Ru-NO in *trans*-[RuCl(py)$_4$(NO)][PF$_6$]$_2$ is 1.766(8) Å[14] compared to 2.009(13) Å in *trans*-[RuCl(py)$_4$-{N(OH)CHC(O)CH$_3$}]PF$_6$. The nature of the Ru-N bond is also reflected in the Ru-Cl distances *trans* to the ligand of interest. In *trans*-[RuCl(py)$_4$(NO)]$^{2+}$ this distance is 2.315(3) Å; in [RuCl$_5$(NO)]$^{2-}$ it is 2.357(1) Å;[15] in *trans*-[RuCl-(py)$_4$(O)]$^+$ it is 2.419(4) Å;[16] and in *trans*-[RuCl(py)$_4$-{N(OH)CHC(O)CH$_3$}]$^+$ it is 2.442(4) Å. The nitrosyl ligand is an excellent π acceptor but poor σ donor. Therefore it does not compete for the σ orbitals of the metals and allows a σ donor such as Cl *trans* to it to form a strong, short bond.[15,17,18] The above series of Ru^{II}-Cl distances therefore represent an increasing σ-donor capability of the ligand in the order NO < O < N(OH)CHC(O)CH$_3$.

Decomposition of trans-[RuCl(py)$_4${N(OH)CHC(O)-CH$_3$}]$^+$.—The acetone adduct was extremely unstable with respect to decomposition in solution (water, aqueous acetone, or CHCl$_3$) and it could not be recrystallised without a change in its spectroscopic properties. The ultimate product(s) of the decomposition was not well defined. Therefore possible modes of decomposition will be related to the observations during the decomposition. One possible decomposition of the ligand is reaction (5), which is simple reversal of the formation of the

$$[\mathrm{RuCl(py)_4\{N(OH)CHC(O)CH_3\}}]^+ + \mathrm{H_3O^+} \longrightarrow [\mathrm{RuCl(py)_4(NO)}]^{2+} + \mathrm{(CH_3)_2CO} + \mathrm{H_2O} \quad (5)$$

adduct by reaction (4). This reversal did not appear to occur. There was no i.r. evidence for any nitrosyl complex at any stage in the decomposition under any conditions. The formation reaction (4) showed no evidence of being an equilibrium, and the only side products observed were nitro complexes.

Table 3. Important bond angles (°) in the *trans*-[RuCl(py)$_4$-{N(OH)CHC(O)CH$_3$}]$^+$ cation, with estimated standard deviations in parentheses

N(1)-Ru-N(2)	176.5(4)	Ru-N(5)-C(21)	123.2(1.1)
N(3)-Ru-N(4)	176.6(4)	Ru-N(5)-O(2)	119.4(8)
N(5)-Ru-Cl	179.3(3)	O(2)-N(5)-C(21)	117.4(1.3)
		N(5)-C(21)-C(22)	121.8(1.4)
		C(21)-C(22)-C(23)	114.1(1.4)
Average *cis* N-Ru-N or *cis* N-Ru-Cl	90.0(5)	C(21)-C(22)-O(1)	127.7(1.3)
Range	87.7—93.9	O(1)-C(22)-C(23)	118.2(1.5)

Two modes of decomposition of the adducts between ketones and nitrosyls have been discussed in the literature. The first is hydrolysis, giving an oxime [see equation (1)],[2,5,13] and this would be represented in the present case by equation (6). No

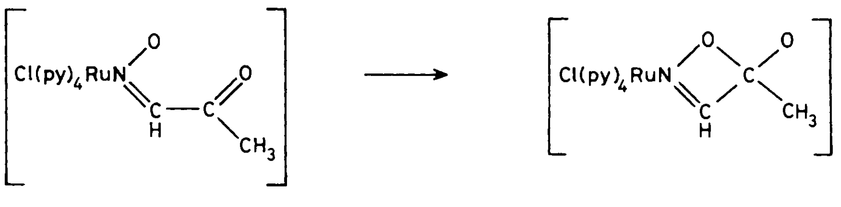
$$[\mathrm{RuCl(py)_4\{N(OH)CHC(O)CH_3\}}]^+ + \mathrm{H_2O} \longrightarrow [\mathrm{RuCl(py)_4(H_2O)}]^+ + \mathrm{CH_3(O)CH{=}NOH} \quad (6)$$

oxime was observed in the reaction product(s), and we therefore discount this pathway. The second mode of decomposition is intramolecular cyclisation and rearrangement giving a nitrile complex,[2,3] which would be represented by reactions (7)—(9)

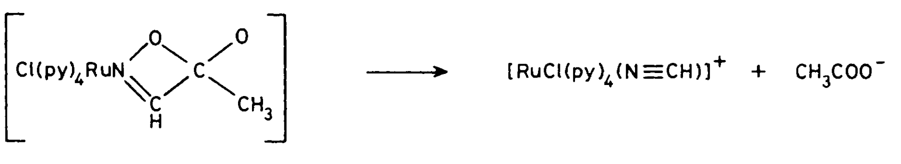
$$[\mathrm{RuCl(py)_4\{N(OH)CHC(O)CH_3\}}]^+ + \mathrm{OH^-} \rightleftharpoons [\mathrm{RuCl(py)_4\{N(O)CHC(O)CH_3\}}] + \mathrm{H_2O} \quad (7)$$

in the present case. The product, [RuCl(py)$_4$(NCH)]$^+$, is analogous to [Ru(NH$_3$)$_5$(NCH)]$^{2+}$ obtained as the PF$_6^-$ salt by Ford[19] and by Isied and Taube.[20] This appears to be the only complex of HCN known. It showed ν(N≡C) at 2 080 cm^{-1}, but was unstable in solution. It first rearranged to [Ru(NH$_3$)$_5$-(CNH)]$^{2+}$, which lost a proton and a *trans* NH$_3$ ligand; a polymer, [{Ru(NH$_3$)$_4$(μ-CN)}$_n$][PF$_6$]$_n$ was ultimately formed.[20]

When [RuCl(py)$_4${N(OH)CHC(O)CH$_3$}]PF$_6$ was hydrolysed the solid obtained showed a sharp, intense band at 2 050 cm^{-1} in addition to bands assignable to pyridine and PF$_6$ in the i.r. spectrum. None of the bands attributable to N(OH)CHC(O)CH$_3$ which were discussed earlier was present. The 2 050 cm^{-1} band is assigned to ν(N≡C). The final product was paramagnetic, even when the decomposition took place in



(8)



(9)

the dark and under argon. Microanalytical results were inconsistent but close to those expected for '$[RuCl(py)_4(NC)]PF_6$'. We have not been able to characterise this ultimate product(s) of the decomposition of *trans*-$[RuCl(py)_4\{N(OH)CHC(O)CH_3\}]^+$ in aqueous solution further. In CH_3CN as solvent the decomposition was slow but a single product, $[RuCl(py)_4(NCCH_3)]PF_6$, was obtained cleanly. This ruthenium(II) product was diamagnetic. The evidence clearly indicates that *trans*-$[RuCl(py)_4\{N(O\overline{H)CHC(O}) CH_3\}]^+$ decomposed intramolecularly to $[RuCl(py)_4(NCH)]^+$ which then underwent further reaction, possibly by intramolecular oxidation to give $[RuCl(py)_4(CN)]PF_6$.

Conclusions

The initial product of the attack of acetone on *trans*-$[RuCl(py)_4(NO)]^{2+}$ in basic solution was *trans*-$[RuCl(py)_4\{N(O\overline{H)CHC(O})CH_3\}]^+$. It is believed that a planar $MN(OH)CR^1C(O)R^2$ unit is initially formed in all reactions between ketones and nitrosyls. *trans*-$[RuCl(py)_4\{N(O\overline{H)CHC(O})CH_3\}]^+$ decomposed by intra-ligand cyclisation to give $[RuCl(py)_4(NCH)]^+$ which underwent further reaction.

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