Interaction of Cyclohexyl Isocyanate with Oxoruthenium(V) 2-Alkyl-2-Hydroxybutyrates†

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The interaction of the tetra-*n*-propylammonium salts of the oxoruthenium(V) anions $[RuO\{OCEt(R)C(O)O\}_2]^-$ (R = Me or Et) with excess of cyclohexyl isocyanate in toluene or tetrahydrofuran forms salts of the amidoruthenium(IV) anions $[Ru\{NH(C_6H_{11})\}\{OCEt(R)(O)O\}_2]^-$. Interaction of these amido species with dioxygen affords the corresponding paramagnetic imidoruthenium(V) anions. The crystal structure of the amido complex with R = Et has been determined by X-ray diffraction. The Ru atom is trigonal bipyramidally co-ordinated by two chelating $OCEt_2C(O)O$ ligands and a terminal $NH(C_6H_{11})$ ligand; the carboxylate oxygen atoms are axial, while the deprotonated hydroxy groups and the amido ligand are equatorial. The Ru–N–C angle of 132.1° is consistent with an amido ligand; although the amido H atom could not be located crystallographically, its presence is clearly indicated by IR, ^1H NMR and X-ray photoelectron spectroscopy.

We noted previously[1a] that the three known ruthenium complexes with terminal imido groups were characterised only by analyses and spectroscopic methods; recently *tert*-butylimido complexes of osmium(VI) and ruthenium(VI) with porphyrin ligands made by oxidation of Bu^tNH_2 complexes with O_2 have also been characterised spectroscopically.[1b] Our attempts to convert a variety of oxoruthenium complexes into imido species by interaction with RNCO, $RN{=}PMe_3$ or $RNH(SiMe_3)$ (R = alkyl and aryl) were unsuccessful. The interaction of the tetraphenylphosphonium salts of the anions $[RuO_2Cl_3]^-$ and also $[OsO_2Cl_4]^{2-}$ with Bu^tNCO gave the isomorphous nitridoureato anions $[MN\{Bu^tNC(O)NBu^t\}Cl_2]^-$ (M = Ru or Os), other isocyanates or silylamines gave intractable oils.[1a]

Since the 2-hydroxy-2-methylbutyrato complex anion of chromium $[Cr(NBu^t)\{OCMe(Et)C(O)O\}_2]^-$ was obtained[2] as its $[N(PPh_3)_2]^+$ salt, not, however, from the corresponding oxochromium complex but from interaction of $[Cr(NBu^t)Cl_4]^-$ with the hydroxycarboxylic acid in presence of Et_3N, it seemed possible that a ruthenium imido analogue could be obtained by interaction of isocyanates with the oxoruthenium(V) salt $[NPr^n_4][RuO\{OCEt_2C(O)O\}_2]$ described[3] and structurally chacterised[3a] by Griffith and co-workers. We show that the interaction of this complex with $C_6H_{11}NCO$ gives the ruthenium(IV) amido complex $[NPr^n_4][Ru\{NH(C_6H_{11})\}\{OCEt_2C(O)O\}_2]$ **1**, whose X-ray crystal structure has been determined. The corresponding oxo and amido (**2**) complexes with $OCMe(Et)C(O)O^{2-}$ as ligands have also been made. The use of isocyanates other than cyclohexyl gave oils that have eluded crystallisation. Although the oxoosmium analogue $[PPh_4][OsO\{OCEt_2C(O)O\}_2]$ was obtained,[3] interaction of this compound with $C_6H_{11}NCO$ gave only intractable products.

Results and Discussion

The golden-brown compounds **1** and **2** are stable in air and crystals of **1** suitable for X-ray study were obtained from acetone–hexane (1:1) at −20 °C. As discussed below, while the X-ray study shows the Ru–N–C angle, 132.1°, to be much smaller than in imido compounds[4] and in the region appropriate for amides, the hydrogen atom on the N atom was not located. With the amido formulation the oxidation state of ruthenium is IV. The hydrogen atom has presumably been abstracted from the cyclohexyl ring of the excess of cyclohexyl isocyanate; hydrogen abstraction from a cyclohexyl group of $P(C_6H_{11})_3$ by a ruthenium compound has been recently reported.[5]

There is convincing spectroscopic evidence for the presence of the $Ru\{NH(C_6H_{11})\}$ group. Both compounds **1** and **2** have sharp ^1H NMR spectra consistent with a diamagnetic ruthenium(IV) species having the expected peaks for both cation and anion. The ^1H resonances of the C_6H_{11} groups at 25 °C are consistent with slow ring inversion on the NMR time-scale; the X-ray structure shows that in the solid the C_6H_{11} ring is in the chair form. A similar situation has been reported in ^1H NMR spectra of $W_2(OC_6H_{11})_6$.[6]

The amido NH proton resonances occur at *ca.* δ 13. For other transition-metal amido compounds the amido proton resonances have been observed over a wide range from *ca.* δ 2.2[7a] to *ca.* 16.8.[7b] The variations probably are due to various factors such as anisotropic deshielding,[8a] the possibility of hydrogen bonding to halide atoms when these are present,[8b] the extent of $M\overset{..}{=}N$ bonding and whether the nitrogen atom is sp^2 rather than sp^3.[7a,8c]

For compound **2** variable-temperature NMR studies show that, as recently observed by Templeton and co-workers,[9] there is restricted rotation about the metal–nitrogen bond. Thus on heating to *ca.* 423 K in deuterionitrobenzene the NH peaks coalesce. For **1** at 298 K the doublet at *ca.* δ 13 is also consistent with restricted rotation about the Ru–N bond. Although the NMR spectra are sharp, **1** and **2** show feeble paramagnetism, probably temperature independent, in the solid state (μ *ca.* 1.0 at 298 K); the compounds are EPR silent in frozen solutions (CH_2Cl_2, MeCN). We have been unable to obtain natural-abundance ^{14}N NMR spectra, presumably due to the intrinsically large linewidths associated with the nitrogen atom of the ligands.[10]

The IR spectra of compounds **1** and **2**, which are quite complicated in the 1650–650 cm^{-1} region due to the $OCEt(R)C(O)O$ ligand, show a sharp N–H stretch at *ca.* 3400 cm^{-1}. There is no evidence for a Ru=O stretch[3] as for the starting material but a new band at *ca.* 1090 cm^{-1} can probably be assigned to the $Ru\overset{..}{=}N$ stretch.

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

Non-SI unit employed: eV ≈ 1.60×10^{-19} J.

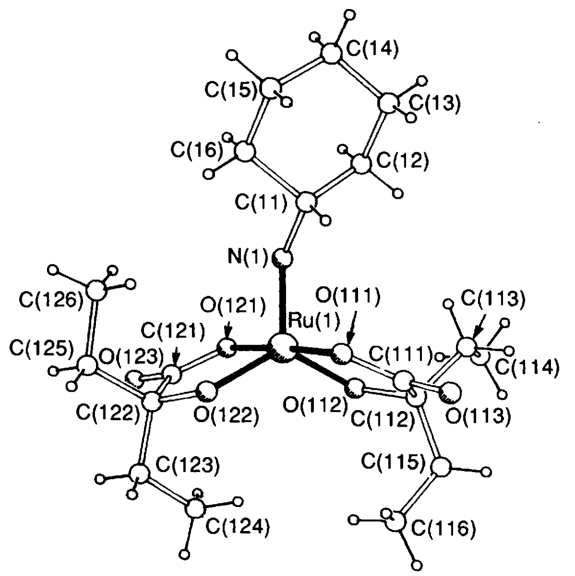

Fig. 1 The structure of one of the anions in $[NPr^n_4][Ru\{NH(C_6H_{11})\}\{OCEt_2C(O)O\}_2]$

Table 1 Selected bond lengths (Å) and angles (°) for compound **1**

Anion 1		Anion 2	
Ru(1)–N(1)	1.818(6)	Ru(2)–N(2)	1.812(5)
Ru(1)–O(111)	2.033(3)	Ru(2)–O(211)	2.063(3)
Ru(1)–O(112)	1.848(3)	Ru(2)–O(212)	1.855(3)
Ru(1)–O(121)	2.049(3)	Ru(2)–O(221)	2.041(4)
Ru(1)–O(122)	1.869(3)	Ru(2)–O(222)	1.871(3)
N(1)–C(11)	1.453(10)	N(2)–C(21)	1.400(8)
N(1)–Ru(1)–O(111)	97.5(2)	N(2)–Ru(2)–O(211)	98.6(2)
N(1)–Ru(1)–O(112)	115.1(2)	N(2)–Ru(2)–O(212)	114.7(2)
O(111)–Ru(1)–O(112)	83.4(1)	O(211)–Ru(2)–O(212)	83.2(1)
N(1)–Ru(1)–O(121)	86.0(2)	N(2)–Ru(2)–O(221)	86.4(2)
O(111)–Ru(1)–O(121)	176.3(1)	O(211)–Ru(2)–O(221)	174.8(1)
O(112)–Ru(1)–O(121)	96.4(1)	O(212)–Ru(2)–O(221)	93.3(1)
N(1)–Ru(1)–O(122)	119.5(2)	N(2)–Ru(2)–O(222)	119.3(2)
O(111)–Ru(1)–O(122)	93.2(1)	O(211)–Ru(2)–O(222)	95.0(1)
O(112)–Ru(1)–O(122)	125.2(2)	O(212)–Ru(2)–O(222)	125.6(1)
O(121)–Ru(1)–O(122)	83.9(1)	O(221)–Ru(2)–O(222)	83.9(1)
Ru(1)–N(1)–C(11)	132.3(4)	Ru(2)–N(2)–C(21)	131.8(5)

X-Ray photoelectron spectra of the oxoruthenium(v) complex $[NPr^n_4][RuO\{OCEt_2C(O)O\}_2]$ and **1** have been compared. Due to interference from the high carbon content, the ruthenium $3p_{\frac{3}{2},\frac{1}{2}}$ levels at 460–475 eV had to be used rather than the $3d_{\frac{5}{2}}$ level at 280–286 eV that is normally more accurate for ruthenium oxidation-state determination. For the oxo species the $3p_{\frac{3}{2}}$ level was measured at 464.4 eV and the oxidation state assigned as Ru^V with carbon 1s at 285 eV. For the amido compound **1** the ruthenium $3p_{\frac{3}{2}}$ binding-energy level at 463.8 eV is a definitive shift indicative of a lower oxidation state. The amido compound also shows two nitrogen levels, one at 402.3 eV (as in the oxo compound) due to NPr^n_4 and the other at 399.5 eV due to the N atom of the amido group.

The crystal structure of compound **1** contains two cations and two anions in the asymmetric unit. The cations are of unremarkable structure. The two anions are essentially identical, differing mainly in the dispositions of the ethyl groups. There are some differences in bond lengths and angles between the two anions, several times their estimated standard deviations, but these are not more than 0.03 Å and 3°, and seem to be of no chemical significance. Fig. 1 shows one anion; selected bond lengths and angles are given in Table 1. The amido ligand is terminally bound to a single metal atom. The mean Ru–N–C angle is 132.1°, appropriate for a terminal amido ligand. The hydrogen atom bonded to nitrogen could not be unambiguously located from electron-density maps, so we are unable to determine the planarity or otherwise of the bonding at nitrogen. Nitrogen occupies the expected equatorial substituent site in the chair conformation of the cyclohexyl ring.

The co-ordination geometry of Ru is relatively undistorted trigonal bipyramidal, with equatorial sites occupied by the amido ligand and the deprotonated hydroxy groups of the chelating $OCEt_2C(O)O$ ligands; the carboxylate oxygen atoms occupy the axial sites. The RuO_2C_2 chelate rings are essentially planar [root mean square (r.m.s.) deviations from mean planes are 0.043, 0.006, 0.019 and 0.016 Å for the four independent ligands in two anions].

Normal van der Waals contacts are found between the ions. The amido NH group is not involved in hydrogen bonding, as there are no short intra- or inter-molecular distances involving the nitrogen atoms.

Oxidation of Compound **1**.—Attempts to remove the hydrogen atom from the amido group by use of the trityl radical or by iodine (*cf.* ref. 9) failed. However, interaction with O_2 in solution at room temperature results in clean oxidation to the corresponding imido complex. Although we have been unable to obtain crystals of X-ray quality, the formulation as the ruthenium(v) complex $[NPr^n_4][Ru\{N(C_6H_{11})\}\{OCEt_2C(O)O\}_2]$ is supported by analytical and spectroscopic data. The X-band EPR spectrum in frozen CH_2Cl_2 very closely resembles that reported[3b] for the corresponding oxoruthenium(v) anions. There is no N–H stretch in the IR and the ^1H NMR lines are broad.

Experimental

Microanalyses were by Pascher, Remagen and University College, London. Instruments and general procedures have been described.[11]

The oxoruthenium(v) complexes were made as described.[3] Solid-state magnetic susceptibilities at 298 K were determined on an Evans balance. The X-ray photoelectron analyses were made at the Johnson Matthey Technology Centre, Sonning Common, Reading. Samples were mounted on double-sided adhesive tape and analysed using Mg-Kα radiation at 130 W using 80/40 eV pass energies and 7 mm slits; binding energy data were referenced to carbon 1s at 285 eV.

The NMR spectra (250 MHz, 25 °C) are in ppm referenced to $SiMe_4$, IR data in cm^{-1} in Nujol mulls. Commercial chemicals were from Aldrich.

Synthesis of Cyclohexylamido Complexes **1** *and* **2**.—To a solution of the oxo complex $[NPr^n_4][RuO\{OCEt(R)C(O)O\}_2]$ (R = Me or Et) (0.25 g, 0.47 mmol) in toluene was added an excess of $C_6H_{11}NCO$ (0.1 cm^3) and the mixture refluxed for 12 h. After evaporation the residue was crystallised from acetone–hexane (1:1) at −20 °C as red-brown needles. Yield: 35–40%.

$[NPr^n_4][Ru\{NH(C_6H_{11})\}\{OCEt_2C(O)O\}_2]$ **1**: m.p. *ca.* 170 °C [Found (required): C, 55.2 (55.8); H, 9.7 (9.4); N, 4.3 (4.3); O, 15.0 (14.9)%]. Mass spectrum (fast atom bombardment using *m*-nitrobenzyl alcohol): *m/z* 462 (anion + 3 H), 647 (anion + cation + 2 H)$^+$ and 832 (anion + 2 cation + H)$^+$. Conductivity (MeCN, 20 °C); Λ_M = 95.2 ohm^{-1} cm^2 mol^{-1}. IR: 3338m, 1655s, 1631s, 1577m, 1538m, 1345s, 1317s, 1270m, 1181m, 1157m, 1091m, 1064w, 1049w, 1013w, 975m, 955m, 893w, 838m, 800m, 772w, 722m, 695m, 652w, 601w, 574w, 527w, 516w, 426w, 372w and 322w cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.5–3.5 (overlapping multiplets, Pr^nN, Et and cyclohexyl protons), 4.4 (m, cyclohexyl methine), 13.0 and 13.1 (NH).

$[NPr^n_4][Ru\{NH(C_6H_{11})\}\{OCMe(Et)C(O)O\}_2]$ **2**: m.p. *ca.* 165 °C [Found (required): C, 54.8 (54.4); H, 9.2 (9.1); N, 4.9 (4.5)%]. IR: 3325m, 1636s, 1340s, 1317s, 1263s, 1197s, 1158s, 1133s, 1088s, 1027s, 993m, 972m, 915s, 826s, 798s, 765m, 710m,

Table 2 Atomic coordinates (× 10^4) for compound **1**

Atom	*x*	*y*	*z*
Ru(1)	3664.1(3)	2052.5(2)	2502.3(2)
Ru(2)	1320.9(3)	2831.0(2)	6912.6(2)
N(1)	4495(4)	1715(3)	1836(3)
C(11)	5627(6)	1977(5)	1840(4)
C(12)	6272(6)	1200(5)	1863(5)
C(13)	7450(7)	1481(8)	1865(5)
C(14)	7542(7)	1861(6)	1177(5)
C(15)	6875(10)	2602(6)	1103(8)
C(16)	5709(8)	2353(6)	1106(6)
O(111)	4870(3)	2811(2)	3341(2)
O(112)	3610(2)	1365(2)	3232(2)
O(113)	5761(3)	2872(2)	4540(2)
C(111)	5091(3)	2500(3)	3964(2)
C(112)	4452(3)	1598(3)	3931(2)
C(113)	5245(4)	918(3)	3905(3)
C(114)	4730(5)	−15(3)	3854(4)
C(115)	3930(4)	1612(3)	4611(2)
C(116)	3227(5)	2326(4)	4709(3)
O(121)	2378(3)	1331(2)	1687(2)
O(122)	2872(3)	2986(2)	2369(2)
O(123)	779(3)	1488(2)	984(2)
C(121)	1629(4)	1786(3)	1460(3)
C(122)	1844(4)	2768(3)	1815(3)
C(123)	959(5)	2995(4)	2218(4)
C(124)	772(6)	2415(5)	2774(4)
C(125)	1893(6)	3319(4)	1187(4)
C(126)	2817(8)	3185(6)	789(5)
N(2)	860(5)	2892(3)	5913(3)
C(21)	−180(5)	2877(4)	5457(4)
C(22)	−212(7)	3660(4)	5034(4)
C(23)	−1344(6)	3642(4)	4598(4)
C(24)	−1721(5)	2836(4)	4020(4)
C(25)	−1621(5)	2034(4)	4367(4)
C(26)	−482(7)	2023(4)	4807(5)
O(211)	−114(2)	2977(2)	7248(2)
O(212)	1801(3)	3910(2)	7565(2)
O(213)	−810(3)	3911(2)	8013(2)
C(211)	−59(4)	3690(3)	7738(2)
C(212)	1052(4)	4269(3)	7984(3)
C(213)	932(5)	5190(3)	7832(3)
C(214)	435(5)	5202(4)	7006(3)
C(215)	1533(4)	4274(3)	8833(3)
C(216)	2697(6)	4732(5)	9131(4)
O(221)	2811(3)	2717(2)	6683(2)
O(222)	1435(2)	1732(2)	7186(2)
O(223)	4095(3)	1851(2)	6805(2)
C(221)	3185(4)	2025(3)	6848(3)
C(222)	2432(3)	1387(3)	7130(3)
C(223)	2984(4)	1254(4)	7927(3)
C(224)	3280(5)	2090(5)	8517(3)
C(225)	2161(4)	501(3)	6575(3)
C(226)	1674(6)	560(4)	5756(4)
N(3)	988(3)	8764(2)	1383(2)
C(311)	769(4)	7774(3)	1100(3)
C(312)	978(4)	7446(3)	321(3)
C(313)	743(5)	6448(3)	122(3)
C(321)	188(4)	9221(3)	895(3)
C(322)	−985(4)	8984(4)	891(3)
C(323)	−1667(5)	9585(5)	483(4)
C(331)	887(4)	8925(3)	2212(2)
C(332)	1007(5)	9873(3)	2602(3)
C(333)	1038(5)	9931(4)	3442(3)
C(341)	2111(3)	9129(3)	1333(3)
C(342)	3029(4)	8724(4)	1761(4)
C(343)	4092(6)	9113(7)	1647(7)
N(4)	4050(3)	5787(2)	3160(2)
C(411)	4016(4)	6706(3)	3597(3)
C(412)	2899(4)	6988(3)	3499(3)
C(413)	2984(5)	7947(3)	3836(3)
C(421)	3285(4)	5103(3)	3365(3)
C(422)	3507(4)	5015(3)	4200(3)
C(423)	2540(5)	4469(4)	4337(3)
C(431)	5217(4)	5612(3)	3377(3)
C(432)	5481(4)	4782(3)	2931(3)
C(433)	6613(5)	4632(4)	3285(4)
C(441)	3681(4)	5735(3)	2305(3)
C(442)	4329(5)	6371(4)	1965(3)
C(443)	3950(7)	6177(5)	1107(4)

641m, 599w, 576m, 502w, 473w and 424w cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 0.5–3.4 (overlapping muliplets, Pr^{n}N, Et, Me and cyclohexyl protons), 4.4 (cyclohexyl methine) and 13.3 (NH).

Synthesis of $[NPr^n_4][Ru\{N(C_6H_{11})\}\{OCEt_2C(O)O\}_2]$ **3**.—Through a solution of the amido complex **1** (*ca.* 0.25 g) in CH_2Cl_2 (10 cm^3) was slowly passed oxygen for *ca.* 20 min. After evaporation the residue was washed with toluene (2 × 30 cm^3) and hexane (30 cm^3) and dried in vacuum for 24 h. Yield: essentially quantitative [Found (required): C, 55.3 (55.9); H, 9.1 (9.2); N, 4.4 (4.3)%]. EPR, X-band (CH_2Cl_2, *ca.* 90 K): g = 2.073, 1.974 and 1.911; these values are very similar to those given in ref 3*b*. IR: 1627s, 1346s, 1317s, 1272m, 1264m, 1176m, 1147m, 1134m, 1086m, 1059w, 1046m, 1008w, 971m, 941s, 890w, 832s, 802m, 764m, 718m, 698m, 642m, 593w, 566m, 515w, 510w, 427w, 382w and 371w cm^{-1}.

X-Ray Crystallography.—Crystal data for compound **1**. $C_{30}H_{60}N_2O_6Ru$, M = 645.9, triclinic, space group $P\bar{1}$, a = 12.707(4), b = 15.574(5), c = 18.215(7) Å, α = 99.49(3), β = 102.18(2), γ = 95.72(3)°, λ(Cu-Kα) = 1.541 84 Å, μ = 4.07 mm^{-1}, $F(000)$ = 1380, T = 240 K.

Data collection and treatment. Measurements were made on a Stoe-Siemens diffractometer equipped with a Cryostream cooler.[12] Cell parameters were refined from 2θ values (20–45°) of 28 reflections measured at ±ω. The dark red crystal, of size 0.16 × 0.20 × 0.48 mm, was mounted on a glass fibre. Intensities were measured with on-line profile fitting[13] and ω–θ scans, scan parameters being automatically optimised for each reflection. One unique set of data ($2\theta_{max}$ = 120°, maximum indices 14,17,20) was collected, together with a few equivalent reflections. Three standard reflections showed no significant intensity variation. Semiempirical absorption corrections[14] were applied; transmission factors were in the range 0.294–0.403. Of 11 139 measured reflections, 10 176 were unique, and 9045 with $F > 4\sigma_c(F)$ (σ_c from counting statistics only) were used for structure determination (R_{int} = 0.049).

Structure solution and refinement.[14] Atoms were located from Patterson and difference syntheses, and refined anisotropically to minimise $\Sigma w\Delta^2$ [$\Delta = |F_o| - |F_c|$; $w^{-1} = \sigma^2(F) = \sigma_c^2(F) + 16 + 17G + 42G^2 - 33H + 21H^2 - 40GH$; $G = F_o/F_{max}$, $H = \sin\theta/\sin\theta_{max}$].[15] Hydrogen atoms were constrained [C–H 0.96 Å, H–C–H 109.5°; U(H) = $1.2U_{eq}$(C)]. An isotropic extinction parameter x refined to 1.1(1) × 10^{-6}, whereby $F_c' = F_c(1 + xF_c^2/\sin 2\theta)^{\frac{1}{4}}$. Atomic scattering factors were taken from ref. 16. At convergence, R = 0.0499, $R' = (\Sigma w\Delta^2/\Sigma wF_o^2)^{\frac{1}{2}}$ = 0.0535, S = 1.04 for 752 parameters, maximum (shift/e.s.d.) = 0.074. All features in a final difference synthesis were within ±1.31 e Å^{-3}; the largest peaks were close to Ru atoms. Although there were several peaks around the amido N atoms, it was not possible to assign positions clearly for the H atoms attached to them. Refined atomic coordinates are given in Table 2.

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

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