Notes

Synthesis and Crystal Structures† of $[PPh_4][MN\{Bu^tNC(O)NBu^t\}Cl_2]$ (M = Ru or Os); a New Reaction of *tert*-Butyl Isocyanate. Synthesis of $W[Bu^tNC(O)NBu^t]_2(NHBu^t)_2$

Wa-Hung Leung,[a] **Geoffrey Wilkinson,***[,a] **Bilquis Hussain-Bates**[b] **and Michael B. Hursthouse***[,b]
[a] *Johnson Matthey Laboratory, Chemistry Department, Imperial College, London SW7 2AY, UK*
[b] *Chemistry Department, Queen Mary and Westfield College, Mile End Road, London E1 4NS, UK*

The interaction of the tetraphenylphosphonium salts of the ruthenium- and osmium-(VI) anions $[RuO_2Cl_3]^-$, $[RuO_2Cl_4]^{2-}$ and $[OsO_2Cl_4]^{2-}$ with excess of *tert*-butyl isocyanate in acetonitrile forms the salts of the anions $[MN\{Bu^tNC(O)NBu^t\}Cl_2]^-$, M = Ru or Os. X-Ray diffraction studies have shown the anions to have distorted square-pyramidal geometry with the nitrido groups in axial positions. The metal nitrido groups have been shown to arise by C–N bond cleavage of unisolated *tert*-butylimido intermediates accompanied by cycloelimination of $Me_2C{=}CH_2$ and HCl. Similar reactions using other aryl and alkyl isocyanates gave intractable products. The compound $W[Bu^tNC(O)NBu^t]_2(NHBu^t)_2$ is formed on reaction of $W(NBu^t)_2(NHBu^t)_2$ with Bu^tNCO.

There are only three examples of ruthenium complexes with terminal imido groups and none has been characterised crystallographically. The first known were the ruthenium(V) alkyl compounds, $Ru_2(NR)_2(CH_2SiMe_3)_6$, R = Ph or $SiMe_3$, obtained by interaction of the oxo species $Ru_2O_2(CH_2SiMe_3)_6$ with PhNCO and $Me_3SiN{=}PMe_3$, respectively.[1] Subsequently the very extremely air- and water-unstable ruthenium(VI) compound $Ru(NSiMe_3)(CH_2SiMe_3)_4$ was obtained as oily orange crystals by methylation of $[RuN(CH_2SiMe_3)_4]^-$ with $CF_3SO_3SiMe_3$ in Et_2O.[2] Various cluster[3a] and binuclear[3b] compounds with bridging imido groups, μ_n, n = 2–4, are also known. Attempts to obtain terminal imido complexes by interaction of RuO_4 and other oxoruthenium species [RuO_4^-, $RuO_2Cl_3^-$, $RuO_2Cl_2(py)_2$ (py = pyridine)] with RNCO, $RN{=}PMe_3$ or $RNHSiMe_3$, R = alkyl and aryl, have been unsuccessful. However, the reaction between $[PPh_4][RuO_2Cl_3]$ and Bu^tNCO has led quite unexpectedly to the dichloro(*N,N′*-di-*tert*-butylureato)nitridoruthenate(VI) anion in what we believe to be a unique reaction of *tert*-butyl isocyanate. The corresponding osmium analogue has been made from $[PPh_4]_2[OsO_2Cl_4]$.

Results and Discussion

The interaction of excess of Bu^tNCO with the oxo complexes $[RuO_2Cl_n]^{(n-2)-}$, n = 3 or 4,[4] and $[OsO_2Cl_4]^{2-}$ [5] as the tetraphenylphosphonium salts in refluxing acetonitrile led, on work-up, to the salts $[PPh_4][MN\{Bu^tNC(O)NBu^t\}Cl_2]$ that crystallise from CH_2Cl_2–Et_2O–hexane mixtures as air-stable orange (M = Ru, **1**) or yellow (M = Os, **2**) crystals. Use of a stoichiometric amount of Bu^tNCO in the hope of obtaining $[Ru(NBu^t)_2Cl_3]^-$ gave only a brown, oily, intractable material.

The structure of the isostructural anions as confirmed by X-ray diffraction study is shown in Fig. 1; bond lengths and angles are given in Table 1. The metal atom in both cases has distorted square-pyramidal geometry. The main distortion arises from the restricted bite of the ureato ligand which spans two basal sites with a N–M–N angle of *ca.* 66°. The angles between the axial nitride and the basal Cl and N atoms in both anions lie in the narrow range 105–109°.

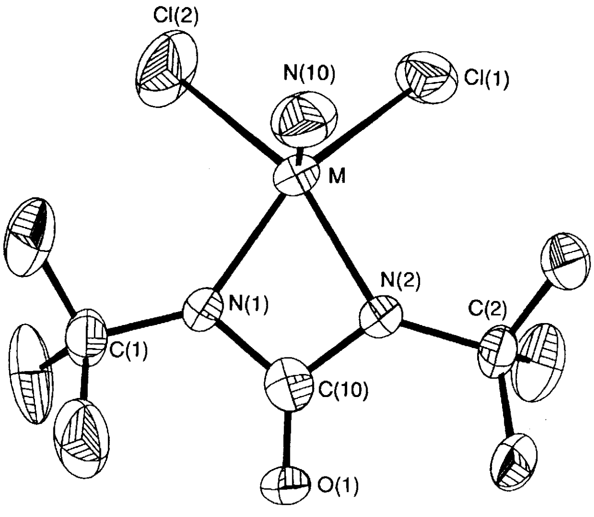

Fig. 1 The structure of the isomorphous ions $[MN\{Bu^tNC(O)NBu^t\}Cl_2]^-$ in the tetraphenylphosphonium salts, M = Ru or Os

The ureato-*N,N′* ligand, $Bu^tNC(O)NBu^t$, is chelating and is symmetrically bonded; the lengths of both the M–N and N–C bonds in the metallacycle suggest a small degree of π delocalisation in the ring. As far as we are aware these are the first chelating ureato-*N,N′* ligands to be structurally characterised. Comparison of the three types of bond in the anions, M–Cl, M≡N and M–N shows that the Ru–Cl bonds are marginally longer than the Os–Cl bonds but that the Ru–N bonds of both types are marginally shorter than the Os–N bonds. The differences are on the borderline of significance, however.

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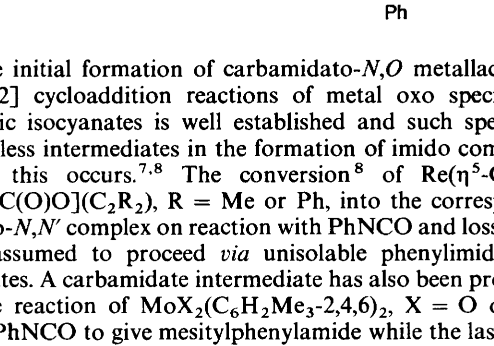
† Tetraphenylphosphonium dichloro(*N,N′*-di-*tert*-butylureato-κ^2N,N')nitrido-ruthenate and -osmate.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

Table 1 Selected bond lengths (Å) and angles (°) for [PPh_4][MN(Bu^{t}NCONBu^t)Cl_2] (M = Ru or Os)

	Compound **1** M = Ru	Compound **2** M = Os
Cl(1)–M	2.367(3)	2.362(4)
Cl(2)–M	2.351(4)	2.344(4)
N(10)–M	1.588(6)	1.629(7)
N(1)–M	1.973(6)	1.980(7)
N(2)–M	1.974(6)	1.977(6)
C(10)–N(1)	1.376(8)	1.388(8)
C(10)–N(2)	1.380(7)	1.384(8)
Cl(2)–M–Cl(1)	83.7(2)	83.0(2)
N(10)–M–Cl(1)	105.5(3)	105.2(3)
N(10)–M–Cl(2)	106.4(3)	106.2(3)
N(1)–M–Cl(1)	144.9(1)	145.2(2)
N(1)–M–Cl(2)	95.2(2)	95.5(2)
N(1)–M–N(10)	108.3(3)	108.5(3)
N(2)–M–Cl(1)	94.5(2)	95.1(2)
N(2)–M–Cl(2)	143.7(1)	143.9(2)
N(2)–M–N(10)	108.9(3)	109.0(3)
N(2)–M–N(1)	66.2(3)	66.1(3)
C(1)–N(1)–M	138.6(3)	138.9(4)
C(2)–N(2)–M	137.4(3)	137.2(4)
C(10)–N(1)–M	95.4(4)	95.4(4)
C(10)–N(2)–M	95.2(4)	95.7(4)
O–C(10)–N(1)	128.6(5)	128.5(6)
O–C(10)–N(2)	128.4(6)	129.1(6)
N(2)–C(10)–N(1)	102.9(4)	102.2(5)
C(10)–N(1)–C(1)	125.7(5)	125.5(6)
C(10)–N(2)–C(2)	127.3(5)	127.0(6)

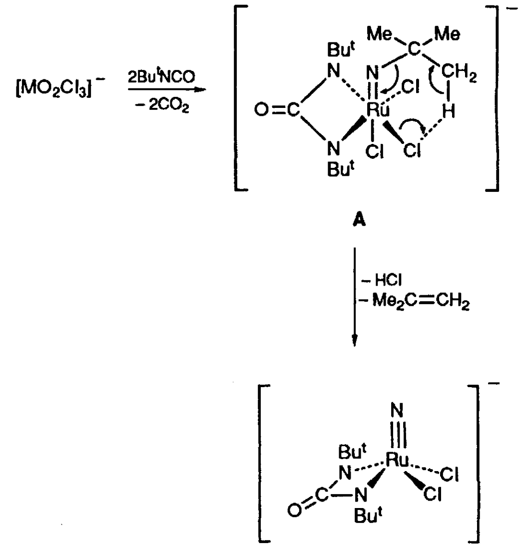
The IR spectra of compounds **1** and **2** are in accord with the structure having ν(C=O, ureato) and ν(M≡N) bands, the latter at 1067 (**1**) and 1104 (**2**) cm^{-1} falling within the normal range for terminal nitrido compounds.[6] The ^{1}H NMR spectra show only the NBu^t singlets and the multiplet for the [PPh_4]$^+$ ion. The formation of the ureato group, which we consider to occur first, is unexceptional [equation (1)].



(1)

The initial formation of carbamidato-*N*,*O* metallacycles in [2 + 2] cycloaddition reactions of metal oxo species with organic isocyanates is well established and such species are doubtless intermediates in the formation of imido compounds when this occurs.[7,8] The conversion[8] of Re(η^5-C_5Me_5)[PhNC(O)O](C_2R_2), R = Me or Ph, into the corresponding ureato-*N*,*N′* complex on reaction with PhNCO and loss of CO_2 was assumed to proceed *via* unisolable phenylimido intermediates. A carbamidate intermediate has also been proposed[9] in the reaction of $MoX_2(C_6H_2Me_3\text{-}2,4,6)_2$, X = O or NPh, with PhNCO to give mesitylphenylamide while the last step of equation (1) was proposed[10] to explain the exchange of imido groups in [Mo(η^5-C_5H_4Me)(NPh)(μ-NPh)]$_2$ on interaction with organic isocyanates.

The course of the present reactions presumably involves transient carbamidato and *tert*-butylimido species and a ureato *tert*-butylimido complex anion, **A**, of equation (2). The M≡N group can then be readily formed in a cycloelimination reaction, involving a bent imido group and hydrogen bonding Cl • • • H–C. This results in N–C bond cleavage and formation of isobutylene (2-methylpropene), $Me_2C{=}CH_2$, and HCl, the latter probably forming a nitrilium salt with MeCN solvent. We have trapped the isobutylene formed by sweeping the gaseous products of the reaction into a solution of bromine in CCl_4 and have identified the resulting $Me_2C(Br)CH_2Br$ by mass and ^{1}H NMR spectra by comparison with an authentic sample. No isobutylene was detected in blank experiments in which the metal complex was omitted.



(2)

There appears to be no precedent for the formation of M≡N groups in reactions of transition-metal complexes and organic isocyanates.[6,9,11] Cleavage of a C–N bond in the hydrolysis[12] of Os(NBu^t)O_3 in concentrated hydrochloric acid which leads to [$OsNCl_5$]$^-$ and Cl_2 has been quoted;[6] no mechanism has been proposed but this also could involve elimination of isobutylene and its rapid reaction with HCl or Cl_2.

The driving force for C–N cleavage of the NBu^t group could be interpreted as arising from the formation of strong M≡N bonds to Ru^{VI} and Os^{VI} associated with the stability of the incipient *tert*-butyl carbonium ion.

It may be noted that the analogous Si–N bond is cleaved much more readily and a bridging nitrido complex formed,[13] *e.g.* as in equation (3).

$$V(NSiMe_3)Cl_3 + 2py \longrightarrow [V(\mu\text{-}N)Cl_2(py)_2]_\infty + Me_3SiCl \quad (3)$$

In reactions of the ruthenium dioxohalogeno anions with RNCO, $RN{=}PMe_3$ and $RNHSiMe_3$ having alkyl or aryl R groups that cannot undergo elimination we have obtained only oils or intractable brown materials.

Studies are in progress of reactions between Bu^{t}NCO and other oxohalogeno species, *e.g.* [MoO_2Cl_4]$^{2-}$, to try to establish the criteria required for nitrido complex formation.

Finally, the interaction of W(NBu^t)$_2$(NHBu^t)$_2$[14] with excess of Bu^{t}NCO confirms the direct interaction with a MNBu^t group to give a ureato-*N*,*N′* complex, W[Bu^{t}NC(O)NBu^t]$_2$(NHBu^t)$_2$ **3**. While the yield is good, the very high solubility of **3** in common organic solvents makes recovery in high yield difficult and we have been unable to obtain X-ray-quality crystals. On the basis of analytical and spectroscopic data the formation as **B** seems reasonable.

Experimental

Microanalyses were carried out by Imperial College and University College, London, laboratories. The spectrometers and general techniques have been described.[15] The compounds [PPh$_4$][RuO$_2$Cl$_3$],[4] [PPh$_4$]$_2$[OsO$_2$Cl$_4$][5] and W(NBu^t)$_2$(NHBu^t)$_2$[14] were prepared by literature methods. The ^{1}H NMR spectra (δ) were referenced to SiMe$_4$, the IR spectra were recorded as Nujol mulls.

Tetraphenylphosphonium Dichloro(N,N′-*di*-tert-*butylureato*-κ^{2}N,N′)*nitridoruthenate*(VI) **1**.—To [PPh$_4$][RuO$_2$Cl$_3$] (0.7 g, 1.2 mmol) or an equivalent amount of [PPh$_4$]$_2$[RuO$_2$Cl$_4$] in MeCN (10 cm^3) was added excess of Bu^{t}NCO (*ca.* 1.5 cm^3) and the mixture heated at reflux for 3 h. The brown-orange reaction mixture was filtered and evaporated to dryness. Orange crystals were obtained after recrystallisation from CH$_2$Cl$_2$–Et$_2$O–hexane. Yield *ca.* 30%, m.p. 168–169 °C (Found: C, 56.4; H, 5.4; Cl, 10.5; N, 5.9. C$_{32}$H$_{38}$Cl$_2$N$_3$O$_2$PRu requires C, 56.9; H, 5.4; Cl, 10.2; N, 6.0%). IR: ν(C=O) 1649, ν(Ru≡N) 1067 cm^{-1}. ^{1}H NMR (CDCl$_3$): 1.51 (s, 18 H, NBu^t) and 7.70 (m, 20 H, PPh$_4$).

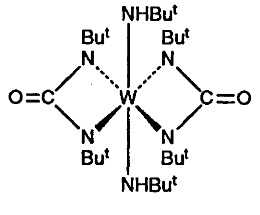
The osmium analogue **2** was prepared similarly from [PPh$_4$]$_2$[OsO$_2$Cl$_4$] (1 g) and Bu^{t}NCO (1 cm^3) in MeCN (10 cm^3). Yellow crystals were obtained after recrystallisation from CH$_2$Cl$_2$–Et$_2$O–hexane. Yield *ca.* 35%, m.p. 159–160 °C (Found: C, 50.4; H, 4.8; Cl, 9.6; N, 5.2. C$_{32}$H$_{38}$Cl$_2$N$_3$O$_2$OsP requires C, 50.5; H, 4.9; Cl, 9.2; N, 5.4%). IR: ν(C=O) 1658, ν(Os≡N) 1104 cm^{-1}. ^{1}H NMR (CDCl$_3$): 1.50 (s, 18 H, NBu^t) and 7.75 (m, 20 H, PPh$_4$).

Table 2 Crystal data, details of intensity measurements and structure refinement

Compound	**1**	**2**
M	695.63	784.76
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a/Å	9.739(2)	9.737(2)
b/Å	12.346(4)	12.241(5)
c/Å	14.227(2)	14.241(2)
α/°	86.18(2)	86.82(1)
β/°	91.31(2)	93.45(2)
γ/°	104.07(2)	104.11(3)
U/Å^3	1655.54	1656.43
Z	2	2
D_c/g cm^{-3}	1.396	1.573
μ/cm^{-1}	6.37	40.93
F(000)	720	780
Total no. of reflections	4857	5029
No. of unique reflections	4608	4617
No. of reflections used [$F > 3\sigma(F)$]	3857	4614
No. of parameters	331	331
Weighting scheme parameter g in $w = 1/[\sigma^2(F) + gF^2]$	0.0002	0.0011
Final R	0.0407	0.030
Final R'	0.0421	0.033

Bis(tert-*butylamido*)*bis*(N,N′-*di*-tert-*butylureato*-κ^{2}N,N′)-*tungsten*(VI) **3**.—To a solution of W(NBu^t)$_2$(NHBu^t)$_2$ (0.47 g, 1 mmol) in hexane (15 cm^3) was added excess of Bu^{t}NCO (1 cm^3) and the mixture heated at reflux for 4 h. After removal of the volatiles, the residue was extracted with hexane. Concentration (to *ca.* 5 cm^3) and cooling (−78 °C) of the hexane extract afforded colourless crystals, which were collected and washed with a small amount of hexane at −78 °C. Yield 20%, m.p. 127–129 °C (Found: C, 46.2; H, 8.3; N, 12.3. C$_{26}$H$_{56}$N$_6$O$_2$W requires C, 46.7; H, 8.3; N, 12.6%). ^{1}H NMR (CDCl$_3$): 1.30 (s, 36 H, NBu^{t}CO), 1.33 (s, 18 H, NH*Bu^t*) and 4.15 (s br, 2 H, NH). IR: ν(N–H) 3354, ν(C=O) 1642 cm^{-1}. Mass spectrum (electron impact): m/z 668 (M^+), 653 ([M − Me]$^+$), 554 ([M − Me − Bu^{t}NCO]$^+$), 455 ([M − Me − 2Bu^{t}NCO]$^+$) and 383 ([M − 2Bu^{t}NCO − NHBu^t]$^+$).

X-Ray Crystallography.—Crystals of the ruthenium and osmium compounds were mounted under argon in thin-walled glass capillaries. Unit-cell parameters and intensity data were obtained using a CAD4 diffractometer and graphite-monochromated Mo-Kα radiation following previously detailed procedures.[16] The data were corrected for absorption on the basis of azimuthal scan profiles. The ruthenium structure was solved and developed *via* the heavy-atom method and refined by full-matrix least squares. The osmium structure was refined using the coordinates for the ruthenium structure as a starting point. Non-hydrogen atoms were refined anisotropically. Hydrogens were included in idealised positions only for the phenyl rings of the PPh$_4$$^+$ ion; the phenyl rings themselves



B

Table 3 Fractional atomic coordinates (× 10^4) for [PPh$_4$][RuN(Bu^{t}NCONBu^t)Cl$_2$]

Atom	x	y	z
Ru	664.5(4)	1 692.6(3)	2 685.7(2)
Cl(1)	182(2)	2 877(1)	1 409(1)
Cl(2)	2 581(2)	1 582(2)	1 752(1)
N(10)	−486(5)	544(3)	2 612(3)
N(1)	1 682(4)	1 636(3)	3 897(3)
N(2)	71(4)	2 552(3)	3 657(2)
C(2)	−983(5)	3 209(4)	3 751(3)
C(123)	−2 275(5)	2 697(5)	3 139(4)
C(122)	−340(7)	4 432(5)	3 417(5)
C(121)	−1 489(6)	3 123(5)	4 784(4)
C(1)	2 645(5)	1 006(4)	4 362(4)
C(112)	4 141(6)	1 777(6)	4 409(6)
C(111)	2 184(8)	642(6)	5 405(5)
C(113)	2 607(9)	−29(6)	3 822(5)
C(10)	1 057(5)	2 362(4)	4 320(3)
O	1 352(4)	2 784(3)	5 075(2)
P	6 339(1)	2 886(1)	8 602(1)
C(11)	5 742(3)	3 689(2)	7 655(2)
C(12)	6 482(3)	4 797(2)	7 460(2)
C(13)	6 009(3)	5 450(2)	6 746(2)
C(14)	4 796(3)	4 997(2)	6 228(2)
C(15)	4 057(3)	3 889(2)	6 423(2)
C(16)	4 530(3)	3 235(2)	7 137(2)
C(21)	5 101(3)	1 558(3)	8 763(3)
C(22)	5 481(3)	612(3)	8 478(3)
C(23)	4 502(3)	−424(3)	8 533(3)
C(24)	3 145(3)	−514(3)	8 872(3)
C(25)	2 765(3)	433(3)	9 157(3)
C(26)	3 743(3)	1 468(3)	9 102(3)
C(31)	8 009(3)	2 662(3)	8 321(2)
C(32)	8 821(3)	2 324(3)	9 052(2)
C(33)	10 093(3)	2 058(3)	8 854(2)
C(34)	10 552(3)	2 131(3)	7 925(2)
C(35)	9 739(3)	2 468(3)	7 194(2)
C(36)	8 468(3)	2 734(3)	7 392(2)
C(41)	6 573(3)	3 629(3)	9 653(2)
C(42)	5 638(3)	3 316(3)	10 407(2)
C(43)	5 837(3)	3 941(3)	11 202(2)
C(44)	6 971(3)	4 878(3)	11 244(2)
C(45)	7 906(3)	5 190(3)	10 490(2)
C(46)	7 707(3)	4 566(3)	9 695(2)

Table 4 Fractional atomic coordinates (× 10^4) for $[PPh_4][OsN(Bu^tNCONBu^t)Cl_2]$

Atom	*x*	*y*	*z*
Os	662.5(2)	1 686.7(2)	2 312.1(2)
Cl(1)	209(2)	2 870(2)	3 585(1)
Cl(2)	2 586(3)	1 594(2)	3 241(2)
N(10)	−514(6)	510(4)	2 412(4)
N(1)	1 662(5)	1 618(4)	1 094(3)
N(2)	46(5)	2 528(4)	1 331(3)
C(1)	2 658(6)	1 020(5)	637(4)
C(2)	−1 004(6)	3 203(5)	1 244(4)
C(121)	−1 509(8)	3 100(7)	211(5)
C(122)	−335(8)	4 420(5)	1 541(6)
C(123)	−2 271(7)	2 723(6)	1 856(5)
C(111)	2 176(9)	641(7)	−395(6)
C(112)	4 131(8)	1 803(7)	606(7)
C(113)	2 610(12)	−21(7)	1 187(7)
C(10)	1 041(6)	2 359(4)	667(4)
O	1 345(4)	2 789(4)	−82(3)
P	6 341(1)	2 888(1)	6 395(1)
C(11)	5 748(3)	3 682(3)	7 337(3)
C(12)	6 494(3)	4 785(3)	7 536(3)
C(13)	6 021(3)	5 434(3)	8 247(3)
C(14)	4 802(3)	4 980(3)	8 760(3)
C(15)	4 057(3)	3 877(3)	8 562(3)
C(16)	4 530(3)	3 228(3)	7 851(3)
C(21)	5 108(3)	1 568(3)	6 232(3)
C(22)	5 471(3)	622(3)	6 534(3)
C(23)	4 488(3)	−410(3)	6 475(3)
C(24)	3 142(3)	−496(3)	6 116(3)
C(25)	2 778(3)	450(3)	5 814(3)
C(26)	3 761(3)	1 482(3)	5 873(3)
C(31)	8 000(4)	2 656(4)	6 674(2)
C(32)	8 805(4)	2 314(4)	5 945(2)
C(33)	10 074(4)	2 044(4)	6 143(2)
C(34)	10 539(4)	2 116(4)	7 070(2)
C(35)	9 734(4)	2 458(4)	7 799(2)
C(36)	8 464(4)	2 728(4)	7 601(2)
C(41)	3 404(5)	6 371(4)	4 658(3)
C(42)	4 327(5)	6 680(4)	5 418(3)
C(43)	4 110(5)	6 055(4)	6 214(3)
C(44)	2 971(5)	5 121(4)	6 252(3)
C(45)	2 049(5)	4 812(4)	5 492(3)
C(46)	2 265(5)	5 437(4)	4 695(3)

were constrained to idealised geometry. Crystal data and other experimental details are given in Table 2, final atomic positional parameters in Tables 3 (Ru) and 4 (Os). All computations were made on a T800 transputer hosted by a 286-AT clone using programs referred to in ref. 16.

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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