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COMPLEXES OF THE PLATINUM METALS—XXXIV.* SYNTHESIS AND CHARACTERIZATION OF SOME BINUCLEAR RUTHENIUM(I/I) TRIAZENIDO COMPLEXES: X-RAY CRYSTAL STRUCTURE OF TETRACARBONYLBIS (μ-1,3-DI-*p*-TOLYLTRIAZENIDO)BIS(*p*-TOLUIDINE) DIRUTHENIUM(I/I)

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Abstract—The ruthenium(I) triazenido complexes $[Ru(ArNNNAr)(CO)_3]_2$ (Ar = *p*-C_6H_4Me or *p*-C_6H_4Cl) have been prepared by heating $Ru_3(CO)_{12}$ with free triazene in benzene under a carbon monoxide atmosphere, and by heating $[Ru(O_2CMe)(CO)_2]_n$ with free triazene and triethylamine in acetonitrile under carbon monoxide. Reactions of the diruthenium(I/I) triazenido complexes with PPh_3, $P(OMe)_3$ or ArNNNHAr (Ar = *p*-C_6H_4Cl) afford axial substitution products of the general form $[Ru(ArNNNAr)(CO)_2L]_2$. However, with ArNNNHAr (Ar = *p*-C_6H_4Me) cleavage of triazene to generate axial *p*-toluidine ligands occurs. The structure of the *p*-toluidine adduct, $[Ru(ArNNNAr)(CO)_2(NH_2Ar)]_2$ has been determined by X-ray diffraction methods. The compound crystallizes in space group $P\bar{1}$ with $a = 11.350(1)$, $b = 20.582(4)$, $c = 10.371(5)$ Å, $\alpha = 100.75(4)$, $\beta = 104.30(3)$, $\gamma = 84.40(1)°$; $U = 2303.89$ Å^3 and $Z = 2$.

The synthesis of the carboxylates $[Ru(O_2CR)(CO)_2]_n$ and $[Ru(O_2CR)(CO)_2L]_2$ (R = H, Me, Et, $^nC_9H_{19}$; L = CO, PPh_3, $AsPh_3$, py, MeCN) in 1969[2] marked a significant milestone in the development of ruthenium(I) chemistry. In the intervening years these carboxylate derivatives have been extensively studied[3–9] and a number of analogous metal–metal bonded diruthenium(I/I) complexes with other bridging ligands including mercaptobenzothiazolate[10] and pyrazolate[11] anions have been characterized. However, although there is a marked similarity between the structural chemistry of polynuclear metal carboxylates[12] and triazenides,[13] binuclear ruthenium(I) triazenido complexes of the form $[Ru(ArNNNAr)(CO)_3]_2$ do not appear to have been described. We now report the synthesis and axial substitution reactions of some compounds of this type, and the molecular structure of one example $[Ru(ArNNNAr)(CO)_2(NH_2Ar)]_2$ (Ar = *p*-C_6H_4Me).

EXPERIMENTAL

General

Hydrated ruthenium trichloride was supplied by Johnson Matthey plc, 1,3-diaryltriazenes were prepared by a standard literature procedure.[14] Reactions were performed under a nitrogen atmosphere but products were worked up in the open laboratory. IR spectra were recorded on a Perkin–Elmer 983G spectrometer using samples mulled in Nujol between CsI plates. Proton NMR spectra were recorded in $CDCl_3$ solution on a Bruker WM-250 spectrometer at 250.13 MHz and are referenced to internal TMS. Phosphorus-31 spectra were recorded in $CDCl_3$ solution on a Bruker HFX-90 spectrometer at 36.43 MHz and are referenced to external 85%

Dedicated to Professor Sir Geoffrey Wilkinson in recognition of his outstanding achievements in the field of organometallic chemistry.

* For part XXXIII, see ref. 1.

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Table 1. Melting points[a] and analytical data[b]

Complex	Ar	M.p. (°C)	C	H	N
$Ru_2(ArNNNAr)_2(CO)_6$	*p*-C_6H_4Me	180–184	50.0(49.8)	3.4(3.4)	10.4(10.2)
$Ru_2(ArNNNAr)_2(CO)_6$	*p*-C_6H_4Cl	206–209	39.7(40.0)	1.6(1.8)	9.1(9.3)
$Ru_2(ArNNNAr)_2(CO)_4(ArNH_2)_2$	*p*-C_6H_4Me	202–205	56.2(55.9)	4.6(4.3)	11.4(12.7)
$Ru_2(ArNNNAr)_2(CO)_4(ArNNNHAr)_2$	*p*-C_6H_4Cl	212-214	45.4(45.3)	2.2(2.5)	11.9(12.2)
$Ru_2(ArNNNAr)_2(CO)_4(PPh_3)_2$	*p*-C_6H_4Me	216–220	63.4(63.4)	4.4(4.5)	6.4(6.5)
$Ru_2(ArNNNAr)_2(CO)_4(PPh_3)_2$	*p*-C_6H_4Cl	247–250	56.3(56.1)	3.3(3.4)	6.0(6.1)
$Ru_2(ArNNNAr)_2(CO)_4\{P(OMe)_3\}_2$	*p*-C_6H_4Me	194–197	45.1(45.1)	4.5(4.6)	8.3(8.3)
$Ru_2(ArNNNAr)_2(CO)_4\{P(OMe)_3\}_2$	*p*-C_6H_4Cl	204–207	37.0(37.4)	3.0(3.1)	7.5(7.7)

[a] M.p. taken in sealed tubes under nitrogen.
[b] Calculated figures in parentheses.

H_3PO_4. Melting points were taken in sealed tubes under nitrogen. Microanalysis were performed in the microanalytical laboratories at King's College and University College London. Melting points and analytical data are collected in Table 1.

*Synthesis of hexacarbonylbis(μ-*1,3-*di-*p-*tolyltriazenido)diruthenium*(I/I)

(a) *From triruthenium dodecarbonyl.* Triruthenium dodecacarbonyl (0.20 g, 0.31 mmol) was added to a solution of 1,3-di-*p*-tolyltriazene (0.2 g, 0.89 mmol) in benzene (20 cm^3) and the mixture was heated under reflux in a carbon monoxide atmosphere for 18 h. After cooling, the dark solution was filtered and the filtrate evaporated under reduced pressure to leave an oil which solidified on trituration with ethanol. The solid was crystallized from dichloromethane–ethanol then washed with ethanol and dried *in vacuo* to afford *orange microcrystals* (0.12 g, 47%).

(b) *From* catena-*acetatodicarbonylruthenium. Catena*-acetatodicarbonylruthenium (0.25 g, 0.59 mmol) and triethylamine (1 g, 10 mmol) were added to a solution of 1,3-di-*p*-tolyltriazene (0.5 g, 2.23 mmol) in acetonitrile (15 cm^3) and the mixture heated under reflux in a carbon monoxide atmosphere for 3 h. The dark solution was allowed to stand under a carbon monoxide atmosphere for 12 h after which time the product was collected by filtration. Crystallization from dichloromethane–ethanol followed by washing with ethanol and drying *in vacuo* afforded *orange microcrystals* (0.21 g, 43.5%).

*Synthesis of hexacarbonylbis(μ-*1,3-*di-*p-*chlorophenyltriazenido)diruthenium*(I/I)

Method (a) gave orange–yellow microcrystals (77.5%). Synthesis by method (b) gave orange–yellow microcrystals (69%).

*Synthesis of tetracarbonylbis(triphenylphosphine) bis(μ-*1,3-*di-*p-*tolyltriazenido)diruthenium*(I/I)

Hexacarbonylbis(*μ*-1,3-di-*p*-tolyltriazenido)diruthenium (0.1 g, 0.12 mmol) was added to a solution of triphenylphosphine (0.15 g, 0.57 mmol) in benzene (15 cm^3) and the mixture was heated under reflux for 1 h. After cooling, the orange solution was filtered and the filtrate evaporated under reduced pressure, the residual oil was then triturated in ethanol to give a solid.

Crystallization from dichloromethane–ethanol followed by washing with ethanol and drying *in vacuo* afforded *bright orange microcrystals* (0.11 g, 71%).

Synthesis of tetracarbonylbis(triphenylphosphine) bis(μ - 1,3 *- di -* p *- chlorophenyltriazenido)diruthenium*(I/I)

Using the same method as above gave bright orange microcrystals (75%).

*Synthesis of tetracarbonylbis(trimethylphosphite) bis(μ-*1,3-*di-*p-*tolyltriazenido)diruthenium*(I/I)

Hexacarbonylbis(*μ*-1,3-di-*p*-tolyltriazenido)diruthenium (0.15 g, 0.2 mmol) was added to a solution of trimethylphosphite (0.1 g, 0.81 mmol) in benzene (15 cm^3) and the mixture heated under reflux for 1 h. After cooling, the orange solution was filtered and the filtrate evaporated under reduced pressure. The resulting oil was triturated in ethanol to produce a solid which after crystallization from dichloromethane–ethanol, washing with ethanol and drying *in vacuo* afforded *orange–yellow microcrystals* (0.15 g, 74.5%).

Synthesis of tetracarbonylbis(trimethylphosphite) bis(μ-1,3-di-p-chlorophenyltriazenido)diruthenium(I/I)

Using the same method as above gave orange microcrystals (54%).

Synthesis of tetracarbonylbis(μ-1,3-di-p-tolyltriazenido)bis(p-toluidine)diruthenium(I/I)

Triruthenium dodecacarbonyl (0.3 g, 0.47 mmol) was added to a solution of 1,3-di-*p*-tolyltriazene (0.5 g, 2.2 mmol) in benzene (15 cm^3) and the mixture heated under reflux for 18 h. After cooling, the orange–red solution was filtered and the filtrate evaporated under reduced pressure. The residual oil was triturated in ethanol to produce a solid which after crystallization from dichloromethane–ethanol, washing with ethanol and drying *in vacuo* afforded *orange–brown crystals* (0.21 g, 43%).

Synthesis of tetracarbonylbis(μ-1,3-di-p-chlorophenyltriazenido)bis(1,3-di-p-chlorophenyltriazene) diruthenium(I/I)

Triruthenium dodecacarbonyl (0.2 g, 0.31 mmol) was added to a solution of 1,3-di-*p*-chlorophenyltriazene (0.5 g, 1.89 mmol) in benzene (20 cm^3) and the mixture heated under reflux for 18 h. After cooling, the orange–red solution was filtered and the filtrate evaporated under reduced pressure. The residual oil was triturated to give a solid which after crystallization from dichloromethane–methanol and drying *in vacuo* afforded *deep red crystals* (0.19 g, 44.5%).

X-ray crystal structure of $[Ru(ArNNNAr)(CO)_2(NH_2Ar)]_2$ ($Ar = p\text{-}C_6H_4Me$)

Crystal data. $C_{46}H_{46}N_8O_4Ru_2$, $M = 977.06$. Triclinic, $a = 11.350(1)$, $b = 20.582(4)$, $c = 10.371(5)$ Å, $\alpha = 100.75(4)$, $\beta = 104.30(3)$, $\gamma = 84.40(1)°$, $U = 2303.89$ Å^3. Space group $P\bar{1}$, $Z = 2$, $D_c = 1.41$ g cm^{-3}, $F(000) = 996.06$, $\mu(\text{Mo-}K_\alpha) = 6.90\ cm^{-1}$.

Data collection. Intensity data were recorded on a Nonius CAD4 diffractometer in a standard manner using Mo-K_α radiation, graphite monochromatized, (Mo-K_α) = 0.71069 Å and a $\omega/2\theta$ scan mode with $1.5 < \theta < 25$.[15] A total of 8844 reflections were recorded, of which 8110 were unique (merging $R = 0.04$) and 6958 satisfied the condition $I > 1.5\sigma(I)$.

Structure solution and refinement. The structure was solved via the heavy atom method and refined by least squares, with non-hydrogen atoms anisotropic and hydrogens inserted in idealized positions with group μ_{iso} values. The final R values are $R = 0.0395$, $R_g = 0.0485$.

RESULTS AND DISCUSSION

The new binuclear ruthenium(I/I) triazenido complexes $[Ru(ArNNNAr)(CO)_3]_2$ have been prepared from $Ru_3(CO)_{12}$ and free 1,3-diaryltriazenes in a reaction which parallels that used in the original synthesis of the binuclear ruthenium(I/I) carboxylates.[2] They can also be obtained by treatment of the latter species with free triazenes in the presence of excess triethylamine, and were isolated as orange–yellow air-stable microcrystals. The IR and ^1H NMR data (Table 2) recorded for these products, in particular the presence of four strong $\nu(CO)$ stretches in the region 2100–2000 cm^{-1}, (ref. 7) are entirely consistent with the highly symmetrical structure (**I**). Unlike their carboxylate analogues which spontaneously lose carbon monoxide to form O-bridged polymers $[Ru(O_2CR)(CO)_2]_n$ the triazenido products, $[Ru(ArNNNAr)(CO)_3]_2$, are stable with respect to carbon monoxide dissociation at normal temperature and pressure. This difference in behaviour presumably reflects stronger Lewis basicity of the triazenide ligand relative to the carboxylate ligand, resulting in higher electron density on the metal centre and consequently a greater degree of synergic d_π–p_π bonding from metal t_{2g} to carbonyl π^* orbitals in the triazenido complexes. Support for this hypothesis is provided by the $\nu(CO)$ values recorded which are on average 30–35 cm^{-1} lower for the triazenido complexes than they are for the corresponding acetate.[2] Similar reluctance to lose axial carbonyl ligands has recently been reported for the closely related pyrazolato-bridged diruthenium(I/I) species $[Ru(pyrazolate)(CO)_3]_2$,[11] which display $\nu(CO)$ frequencies virtually identical to those recorded for the triazenido complexes.

However, carbonyl ligands are readily lost from the complexes $[Ru(ArNNNAr)(CO)_3]_2$ on treatment with P-donor ligands to give axial substitution products, $[Ru(ArNNNAr)(CO)_2L]_2$ [$L = PPh_3$, $P(OMe)_3$]. The $^{31}P\{^1H\}$ NMR spectra of these complexes each show a singlet consistent with the proposed axial disubstituted structure (**II**). The ^1H NMR spectra of the $P(OMe)_3$ substituted complexes each contain a three-line pattern characteristic of the $A_nA'_n$ part of an $A_nA'_nXX'$ spectrum[16] and thus provide a further example of virtual coupling between $P(OMe)_3$ ligands across a binuclear metal centre.[17]

When a large excess of di-*p*-chlorophenyl triazene was allowed to react with $Ru_3(CO)_{12}$, the isolated

Table 2. Spectroscopic data

Complex	Ar	Infrared spectra[a] ν(CO) (cm^{-1})				Nuclear magnetic resonance spectra[b] δH(aromatic) (ppm)				δH(methyl) (ppm)		δP (ppm)
$Ru_2(ArNNNAr)_2(CO)_6$	p-C_6H_4Me	2089(s)	2062(s)	2024(s)	2010(s)	7.16(s)	7.05(d)	—	—	2.31(s)	—	—
$Ru_2(ArNNNAr)_2(CO)_6$	p-C_6H_4Cl	2093(s)	2067(s)	2029(s)	2016(s)	7.25(d)	7.15(d)	—	—	—	—	—
$Ru_2(ArNNNAr)_2(CO)_4(ArNH_2)_2$	p-C_6H_4Me	2093(m) 1979(s)	2073(s) 1958(s)	2036(s) 1936(s)	2022(s)	7.27(d)	7.21(d)	6.95(d)[c]	6.43(d)[c]	2.31(s)	2.22(s)[d]	—
$Ru_2(ArNNNAr)_2(CO)_4(ArNNNHAr)_2$	p-C_6H_4Cl	2070(s)	2011(s)	—	—	7.35(d)	7.23(d)	7.13(d)	6.94(d)	—	—	—
$Ru(ArNNNAr)_2(CO)_4(PPh_3)_2$	p-C_6H_4Me	2015(sh)	1989(s)	1951(s)	—	7.16(m)	7.06(m)	6.69(d)	6.61(d)	2.24(s)	—	25.23(s)
$Ru(ArNNNAr)_2(CO)_4(PPh_3)_2$	p-C_6H_4Cl	2018(sh)	1988(m)	1951(s)	—	7.21(m)	7.10(m)	6.81(m)	6.46(d)	—	—	25.47(s)
$Ru_2(ArNNNAr)_2(CO)_4\{P(OMe)_3\}_2$	p-C_6H_4Me	2028(m)	1997(s)	1963(s)	—	6.99(d)	6.91(d)	—	—	3.43(t)	2.30(s)	129.8(s)
$Ru_2(ArNNNAr)_2(CO)_4\{P(OMe)_3\}$	p-C_6H_4Cl	2031(sh)	2001(s)	1965(s)	—	7.08(d)	6.90(d)	—	—	3.45(t)	—	128.7(s)

[a] IR spectra : s = strong, m = medium, sh = shoulder.

[b] NMR spectra : δ values relative to TMS (^1H) or 85% H_3PO_4 (^{31}P), s = singlet, d = doublet, t = triplet, m = multiplet.

[c] Half integral intensity of resonances at 7.27 and 7.21 ppm.

[d] Half integral intensity of resonance at 2.31 ppm.

product gave analytical and spectroscopic data consistent with the formation of a bis(triazene) axial substitution complex $[Ru(ArNNNAr)(CO)_2(ArNNNHAr)]_2$ (Ar = p-C_6H_4Cl) formally analogous to the recently reported[7,8] carboxylic acid adduct $[Ru(O_2CPh)(CO)_2(PhCO_2H)]_2$. The ^1H NMR data, which indicate the presence of p-C_6H_4Cl groups in two different environments (ratio 1 : 1), are consistent with the proposed structure (**III**) if we assume that the A_2B_2 patterns arising from the aromatic protons in the two p-C_6H_4Cl groups of the axial triazene ligands are identical. This situation could be coincidental or might indicate the occurrence of a labile fluxional N(1), N(3) interchange at the axial positions. However, in a similar synthesis involving excess 1,3-di-p-tolyltriazene cleavage of triazene molecules and coordination of p-toluidine fragments leading to formation of the axial substitution product, $[Ru(ArNNNAr)(CO)_2(NH_2Ar)]_2$ (Ar = p-C_6H_4Me) occurs. Fragmentation of 1,3-diaryltriazenes under acid conditions with concomitant coordination of the ArN_2^+ moiety is well-known, and has been used as an efficient route to certain aryldiazo complexes.[18] However, to the best of our knowledge there has been no previously reported example involving coordination of the amine, NH_2Ar, fragment formed in such reactions. The axial N-donor ligands in the complexes $[Ru(ArNNNAr)(CO)_2(ArNNNHAr)]_2$ (Ar = p-C_6H_4Cl) and $[Ru(ArNNNAr)(CO)_2(NH_2Ar)]_2$ (Ar = p-C_6H_4Me) are readily displaced by carbon monoxide, triphenylphosphine and trimethylphosphite to yield products of the form $[Ru(ArNNNAr)(CO)_2L]_2$ (L = CO, PPh_3 and $P(OMe)_3$, respectively).

In order to characterize the binuclear triazenido-bridged diruthenium(I/I) structure and to confirm the nature of the axial p-toluidine ligands an X-ray diffraction study was performed on a crystal of $[Ru(ArNNNAr)(CO)_2(NH_2Ar)]_2$ (Ar = p-C_6H_4Me). The molecular structure is shown in Fig. 1, selected bond lengths and bond angles are given in Table 3. The structure is similar in general form to those previously determined for related carboxylato-bridged diruthenium(I/I) complexes. The two ruthenium atoms are linked by a Ru—Ru bond and a *cis* pair of bridging triazenide ligands. The coordination sphere about each ruthenium is completed by a pair of terminal carbonyl ligands in the equatorial sites and a p-toluidine ligand in the axial position. The coordination geometry about each ruthenium centre is essentially octahedral with bond angles subtended at ruthenium by *cis* ligand pairs ranging from 80.5° [$\angle$ Ru(2)—Ru(1)—N(1)] to 97.4° [$\angle$ N(7)—Ru(1)—C(1)]. The N—Ru—Ru—N axis is approximately linear with

Table 3. Selected bond lengths and bond angles for $C_{46}H_{46}N_8O_4Ru_2$

Bond lengths (Å)			
Ru(2)—Ru(1)	2.665	N(1)—Ru(1)	2.159(6)
N(6)—Ru(1)	2.150(5)	N(7)—Ru(1)	2.332(6)
C(1)—Ru(1)	1.844(7)	C(2)—Ru(1)	1.853(7)
N(3)—Ru(2)	2.162(6)	N(4)—Ru(2)	2.143(5)
N(8)—Ru(2)	2.286(5)	C(3)—Ru(2)	1.861(7)
C(4)—Ru(2)	1.858(6)	N(2)—N(1)	1.294(5)
C(11)—N(1)	1.445(5)	N(3)—N(2)	1.300(6)
C(31)—N(3)	1.437(5)	N(5)—N(4)	1.296(5)
C(41)—N(4)	1.444(5)	N(6)—N(5)	1.293(5)
C(61)—N(6)	1.446(5)	C(21)—N(7)	1.421(6)
C(51)—N(8)	1.430(6)	C(1)—O(11)	1.140(7)
C(2)—O(21)	1.141(8)	C(3)—O(31)	1.143(8)
C(4)—O(41)	1.140(7)		

Bond angles (°)			
N(1)—Ru(1)—Ru(2)	80.5(2)	N(6)—Ru(1)—Ru(2)	82.6(2)
N(6)—Ru(1)—N(1)	87.8(2)	N(7)—Ru(1)—Ru(2)	166.0(1)
N(7)—Ru(1)—N(1)	89.8(2)	N(7)—Ru(1)—N(6)	86.9(2)
C(1)—Ru(1)—Ru(2)	92.6(2)	C(1)—Ru(1)—N(1)	89.0(3)
C(1)—Ru(1)—N(6)	174.6(2)	C(1)—Ru(1)—N(7)	97.4(3)
C(2)—Ru(1)—Ru(2)	93.5(2)	C(2)—Ru(1)—N(1)	172.5(2)
C(2)—Ru(1)—N(6)	96.0(3)	C(2)—Ru(1)—N(7)	96.9(3)
C(2)—Ru(1)—C(1)	86.8(3)	N(3)—Ru(2)—Ru(1)	83.7(2)
N(4)—Ru(2)—Ru(1)	80.7(2)	N(4)—Ru(2)—N(3)	86.7(2)
N(8)—Ru(2)—Ru(1)	168.4(1)	N(8)—Ru(2)—N(3)	89.3(2)
N(8)—Ru(2)—N(4)	89.7(2)	C(3)—Ru(2)—Ru(1)	92.5(2)
C(3)—Ru(2)—N(3)	174.9(2)	C(3)—Ru(2)—N(4)	89.4(3)
C(3)—Ru(2)—N(8)	94.0(3)	C(4)—Ru(2)—Ru(1)	94.3(2)
C(4)—Ru(2)—N(3)	94.1(3)	C(4)—Ru(2)—N(4)	174.8(1)
C(4)—Ru(2)—N(8)	95.4(3)	C(4)—Ru(2)—C(3)	89.5(3)
N(2)—N(1)—Ru(1)	126.7(4)	C(11)—N(1)—Ru(1)	119.3(3)
C(11)—N(1)—N(2)	110.2(4)	N(3)—N(2)—N(1)	116.1(4)
N(2)—N(3)—Ru(2)	123.5(3)	C(31)—N(3)—Ru(2)	124.9(3)
C(31)—N(3)—N(2)	110.4(4)	N(5)—N(4)—Ru(2)	126.7(3)
C(41)—N(4)—Ru(2)	120.5(3)	C(41)—N(4)—N(5)	110.7(4)
N(6)—N(5)—N(4)	115.6(4)	N(5)—N(6)—Ru(1)	123.6(3)
C(61)—N(6)—Ru(1)	124.2(3)	C(61)—N(6)—N(5)	110.1(4)
C(21)—N(7)—Ru(1)	122.3(4)	C(51)—N(8)—Ru(2)	117.9(4)
O(11)—C(1)—Ru(1)	178.2(6)	O(21)—C(2)—Ru(1)	176.3(4)
O(31)—C(3)—Ru(2)	179.3(4)	O(41)—C(4)—Ru(2)	177.0(4)
C(22)—C(21)—N(7)	119.8(4)	C(26)—C(21)—N(7)	120.2(4)
C(52)—C(51)—N(8)	119.1(3)	C(56)—C(51)—N(8)	120.8(4)

∠N(7)—Ru(1)—Ru(2) and ∠N(8)—Ru(2)—Ru(1) equal to 166.0 and 168.4°, respectively. The ruthenium–ruthenium distance (2.665(1) Å) is typical for Ru—Ru bond lengths in complexes of the general form $Ru_2(bridge)_2(CO)_4L_2$ which range from a rather exceptional 3.056(1) Å in $[Ru\{Si(Me)_2CH_2PPh_2\}(CO)_3]_2$[19] to a more usual 2.630(2) Å in $[Ru_2(O_2CBu^{sec})_2(CO)_4(sec\text{-}BuCO_2H)]_2$[7,8] and is similar to the values recorded for a number of binuclear diruthenium(I/I) carboxylates including $[Ru(O_2CPr)(CO)_2(PBu^t_3)]_2$ (2.728(1) Å),[5] $[Ru_2(O_2CC_6H_4F\text{-}4)_2(CO)_5(H_2O)]$ (2.649(2) Å),[7] $[Ru(O_2CPh)(CO)_2(PhCO_2H)]_2$ (2.637(2) Å)[7,8] and $[Ru_2(O_2CBu^{sec})_2(CO)_4(sec\text{-}BuCO_2H)]_2$ (2.630(2) Å).[7,8] Bond lengths and bond angles associated with the bridging triazenide ligands have values similar to those found in other triazenido-bridged complexes.[13] Likewise, the Ru—C and C—O bond lengths found for the carbonyl ligands in the triazenido-bridged com-

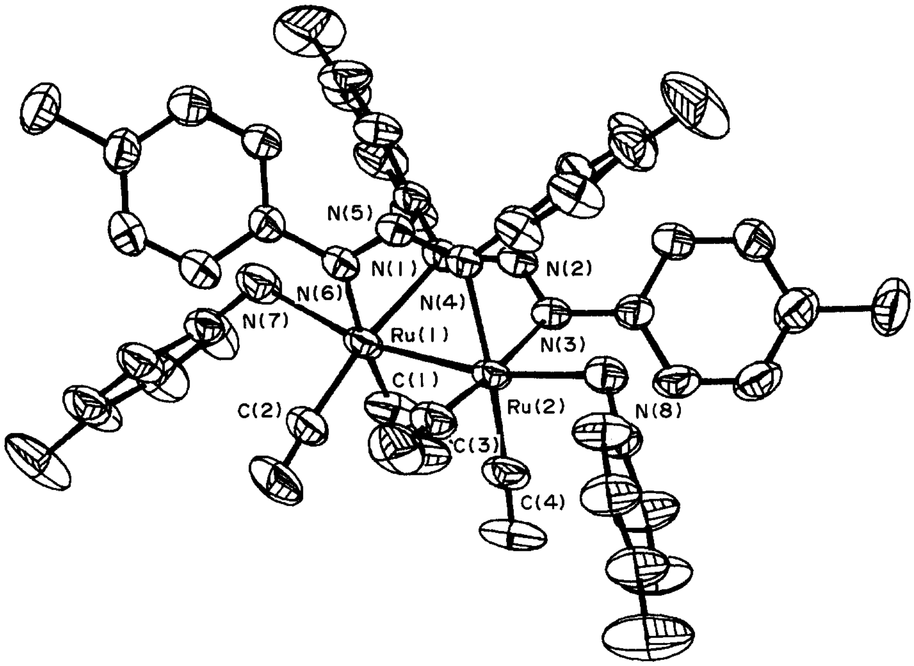

Fig. 1. General view of $[Ru(ArNNNAr)(CO)_2(NH_2Ar)]_2$ (Ar = p-C_6H_4Me) showing the atom labelling scheme. Atoms are represented by their thermal ellipsoids at the 50% probability level. Hydrogen atoms have been omitted for clarity.

plex are very similar to those recorded for related carboxylato-bridged diruthenium(I/I) complexes.[7,8] Finally, the relatively long Ru—N distances [2.332(6) and 2.286(5) Å] found for the axial *p*-toluidine groups are in keeping with the ease with which these ligands are replaced.

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