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SYNTHESIS AND REACTIONS OF ARENE–RUTHENIUM COMPLEXES CONTAINING NITROGEN-DONOR LIGANDS; CRYSTAL STRUCTURE OF (p-cymene)$_2$Ru$_2$Cl$_2$(N$_3$)$_2$

RICHARD S. BATES, MICHAEL J. BEGLEY and ANTHONY H. WRIGHT*

Chemistry Department, University of Nottingham, Nottingham NG7 2RD, U.K.

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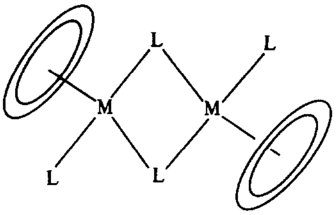
Abstract—A range of nitrogen bases have been reacted with [(arene)RuCl$_2$]$_2$ complexes. The reaction with simple amines to give monomeric addition compounds (arene)RuCl$_2$NR$_3$ has been made rapid and quantitative using ultrasound. Steric factors predominate in determining the extent of the reactions. Trimethylsilylazide has been found to be a particularly suitable source of the azide ligand, generating the new dimer [(arene)Ru(μ-N$_3$)Cl]$_2$ which has been structurally characterized. This complex has been shown to undergo dimer cleavage and halide loss reactions.

The dimeric complexes of type **1** are very common and may be subdivided into two groups depending on whether the bridging ligands contribute two or three electrons.[1]



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The reactivity of the former dimers, such as [CpFe(CO)$_2$]$_2$, is well established.[2] By comparison, the latter group of dimers such as [(arene)RuCl$_2$]$_2$ is much less understood.[3] We have begun a programme investigating the reactivity of these complexes, initially examining the range of different nitrogen-donor ligands that may be introduced to the metal centre.

Extensive investigations of the reactions of these dimers with oxygen-based ligands have been reported,[4] and the reaction with soft nitrogen-based ligands such as pyridine and acetonitrile has been investigated, particularly as sources of the [(arene)Ru]$^{2+}$ fragment.[5]

RESULTS AND DISCUSSION

Reactions with amines

One of the problems associated with using the dimers [(arene)RuCl$_2$]$_2$ (**1**), and especially the benzene-containing dimer, lies in the insolubility of these substrates in non-coordinating solvents. This can be readily overcome by carrying out the reactions at room temperature using a simple ultrasound bath.

Both aliphatic and aromatic primary amines react rapidly with [(C$_6$H$_6$)RuCl$_2$]$_2$ at room temperature when subjected to ultrasound in non-polar solvents (Scheme 1). The products are yellow crystalline solids and the initial product in each case is that of simple addition resulting in dimer cleavage (**2**, **3** and **4**). Analogous products such as (MeC$_6$H$_4$CHMe$_2$)RuCl$_2$(NH$_2$CMe$_3$) (**10**) can be obtained using substrate dimers containing other arenes.

In the case of p-toluidine, addition of excess ligand and longer reaction periods leads to increasing amounts of the product containing two amine ligands (**5**), resulting from subsequent halide substitution. The further substitution that is only observed with aromatic amines, indicates that in these reactions the softness (HSAB theory) of the nucleophile plays a more important role than basicity.

This conclusion is supported by the results of reactions with aliphatic secondary or tertiary

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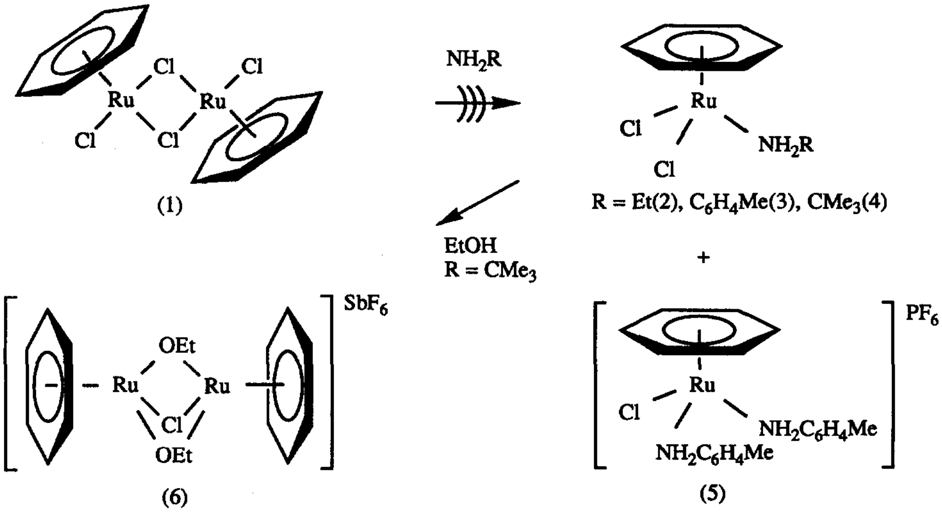
* Author to whom correspondence should be addressed.



Scheme 1. Reactions of $(C_6H_6)_2Ru_2Cl_4$ with amines.

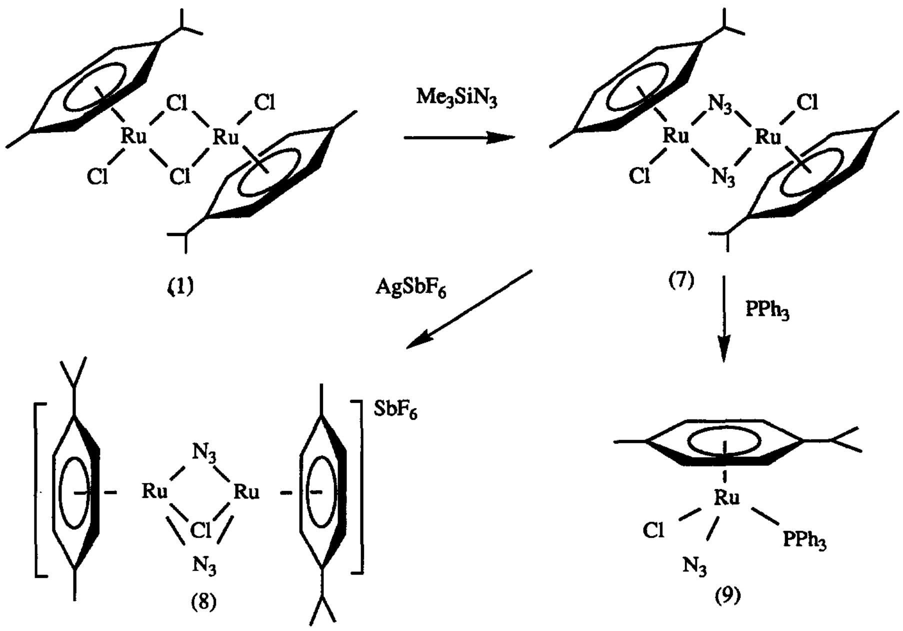
amines in which no addition reactions were observed. This result contrasts with the well-established reactions of the same substrates with tertiary phosphines and indicates that steric factors are much more important with the relative hard amines which are poorer ligands for the ruthenium centre. Softer nitrogen bases such as pyridine undergo the same reaction giving the addition product in the first step.

The recent report of addition reactions of primary aliphatic amines and a range of phosphine nucleophiles to the dimer adds further support for the reactivity pattern described.[6]

The relative weakness of the Ru—N bonds that are formed is illustrated in the reaction of $(C_6H_6)RuCl_2(NH_2CMe_3)$ with $AgSbF_6$ in ethanol, in which the only product that was detected was the triply-bridged cation **6**. In other reactions the only products isolated involve loss of the amine ligand.

Azide ligands

The azide ligand is a non-sterically demanding nitrogen-based pseudohalide. The reagent Me_3SiN_3 provides an excellent source of the azide moiety



Scheme 2. Synthesis and reactions of $(cymene)_2Ru_2Cl_2(N_3)_2$.

and reacts rapidly with $[(cymene)_2RuCl_2]_2$ to give orange crystals of $[(cymene)_2Ru(N_3)Cl]_2$ (**7**).

IR spectra of **7** contain a single absorption assignable to the azide ligand and a single Ru—Cl stretch is observed. The ^1H NMR spectrum contains the absorption associated with a cymene ligand in only one environment. An X-ray crystal structure was carried out to confirm the dimeric nature of the product, Fig. 1.

No product involving further substitution of the chlorides has been detected. This result contrasts with the related reaction of $[(C_5Me_5)_2RhCl_2]_2$ with sodium azide, in which the product involving monosubstitution could only be obtained by limiting the amount of nucleophile to a 1 : 1 stoichiometry.[7]

A second difference between the related complexes lies in the thermal instability of the ruthenium complex. When **7** was heated in toluene, rapid loss of the arene ligand occurred (detected by NMR spectroscopy) and a brown product precipitated from solution that detonated on handling.

Unlike the amine ligands, the azide ligands remain in the coordination sphere when simple reactions are carried out. For example, addition of triphenylphosphine leads to simple bridge cleavage and formation of $(cymene)Ru(N_3)Cl(PPh_3)$ (**9**). The ^1H NMR spectrum of the product contains three sets of signals assignable to cymene ligands indicating that the complex exists in non-polar solutions in three conformations and there is steric hindrance to rotation of the arene ring.

Chloride rather than azide loss occurs when dimer **7** is reacted with $AgSbF_6$, leading to formation of the mixed ligand triply-bridged product **8**.

Structure of (p-*cymene*)$_2Ru_2Cl_2(N_3)_2$ (7)

The X-ray crystal structure determination of **7** shows that the molecule is dimeric with the two azide ligands bridging the two metals (Fig. 1), and bond lengths and angles are given in Table 1. The only crystallographically-imposed symmetry is an inversion centre midway between the metal atoms.

The surprising feature of the structure is that the ligating nitrogens are pyramidally coordinated, not planar, with the angles about the nitrogen summing to 351.6°. The ruthenium atoms and ligating nitrogens lie in a plane and N(2) and N(3) lie 0.514(2) and 0.992(3) Å, respectively, out of the plane. An examination of non-bonding interactions and a space filling model of the molecule failed to reveal any steric interactions that might cause the bending. Reactions aimed at exploring any reactivity associated with a lone pair on the ligating nitrogen were, however, unsuccessful. A related rhodium complex also contains a bridging azide ligand and has the same overall geometry, but in this case the angles about the ligating nitrogen do not differ significantly from those required for planarity.[7]

The cymene ring is essentially planar and the distance from the ring to the metal is 1.657(3) Å, a distance very similar to that found in $[(C_6Me_6)RuCl_2]_2$.[8] Likewise, the Ru—Cl distance of 2.395(1) Å is very close to that determined for the hexamethylbenzene complex.

EXPERIMENTAL

All reactions were carried out under nitrogen or argon using standard Schlenk techniques. Characterization of new compounds was achieved by means of elemental analysis, IR and NMR spectroscopy and mass spectrometry. Microanalytical data were obtained from the University of Nottingham's Microanalytical Laboratory. IR spectra were recorded on a Perkin–Elmer 983G spectrometer as Nujol mulls on CsI plates. NMR spectra were recorded on a Bruker 250 MHz spectrometer. A 500 W biological cell disruptor from Sonics and Materials Inc. was used for the experiments involving ultrasound.

Ruthenium trichloride was obtained from Johnson Matthey Chemicals Ltd and $[(C_6H_6)RuCl_2]_2$

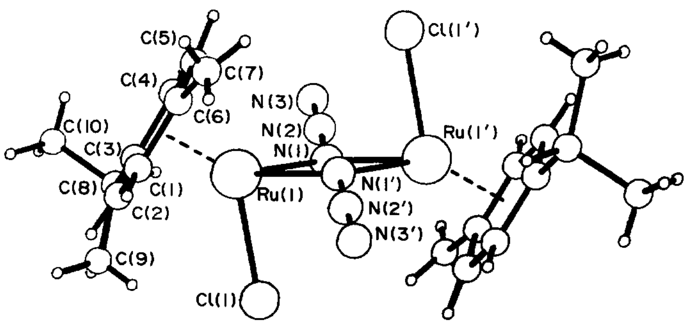


Fig. 1. Molecular structure of $(cymene)_2Ru_2Cl_2(N_3)_2$ showing the principal atomic numbering.

Table 1. Bond lengths (Å) and angles (°) for $(cymene)_2Ru_2Cl_2(N_3)_2$, with ESDs in parentheses

	Bond lengths		
Ru(1)—Ru(1′)	3.448(1)	N(2)—N(3)	1.148(5)
Ru(1)—Cl(1)	2.395(1)	C(1)—C(2)	1.419(5)
Ru(1)—N(1)	2.165(3)	C(1)—C(6)	1.408(5)
Ru(1)—N(1′)	2.176(3)	C(2)—C(3)	1.409(5)
Ru(1)—C(1)	2.182(3)	C(3)—C(4)	1.412(5)
Ru(1)—C(2)	2.161(3)	C(3)—C(8)	1.518(6)
Ru(1)—C(3)	2.195(3)	C(4)—C(5)	1.409(5)
Ru(1)—C(4)	2.152(3)	C(5)—C(6)	1.409(5)
Ru(1)—C(5)	2.176(3)	C(6)—C(7)	1.495(5)
Ru(1)—C(6)	2.187(3)	C(8)—C(9)	1.534(7)
N(1)—N(2)	1.141(5)	C(8)—C(10)	1.513(7)
	Bond angles		
Cl(1)—Ru(1)—N(1)	85.6(1)	C(2)—C(1)—C(6)	120.2(2)
Cl(1)—Ru(1)—N(1′)	85.4(1)	C(1)—C(2)—C(3)	121.7(1)
Cl(1)—Ru(1)—C(1)	104.2(1)	C(2)—C(3)—C(4)	116.8(2)
Cl(1)—Ru(1)—C(4)	137.3(1)	C(2)—C(3)—C(8)	123.4(2)
N(1)—Ru(1)—N(1′)	74.8(1)	C(4)—C(3)—C(8)	119.7(2)
N(1)—Ru(1)—C(1)	170.0(1)	C(3)—C(4)—C(5)	122.4(2)
N(1)—Ru(1)—C(4)	91.4(1)	C(4)—C(5)—C(6)	120.0(2)
N(1′)—Ru(1)—C(1)	107.4(1)	C(1)—C(6)—C(5)	118.8(2)
N(1′)—Ru(1)—C(4)	134.7(1)	C(1)—C(6)—C(7)	119.9(2)
Ru(1)—N(1)—Ru(1′)	105.2(1)	C(5)—C(6)—C(7)	121.2(2)
Ru(1)—N(1)—N(2)	122.4(1)	C(3)—C(8)—C(9)	109.0(2)
Ru(1′)—N(1)—N(2)	124.1(1)	C(3)—C(8)—C(10)	114.0(2)
N(1)—N(2)—N(3)	177.7(1)	C(9)—C(8)—C(10)	110.8(2)

and $[(cymene)RuCl_2]_2$ were prepared by literature methods.

$(C_6H_6)RuCl_2(NH_2Et)$ (**2**)

$[(C_6H_6)RuCl_2]_2$ (150 mg, 0.3 mmol) was suspended in THF (10 cm^3) and a solution of NH_2Et (100 mg, 2.2 mmol) in THF (5 cm^3) was added and subjected to ultrasound for approximately 90 min. The reaction mixture was allowed to stand at room temperature for 10 min and the yellow precipitate was collected and recrystallized from a dichloromethane–ethanol mixture to give $(C_6H_6)RuCl_2(NH_2Et)$ (71 mg, 40%). Found: C, 31.9; H, 4.3. Calc. for $RuC_8H_{13}Cl_2N$: C, 32.5; H, 4.4%. ν(NH) 3277, 3206 cm^{-1}, ν(RuCl) 273 cm^{-1} (Nujol mull); ^1H NMR ($CDCl_3$) 5.63 (s, 6H, C_6H_6), 3.2 (q, 2H, CH_2), 1.23 (t, 3H, CH_3).

$(C_6H_6)RuCl_2(NH_2C_6H_4Me)$ (**3**)

$[(C_6H_6)RuCl_2]_2$ (150 mg, 0.3 mmol) was suspended in THF (10 cm^3) and a solution of *p*-toluidine ($NH_2C_6H_4Me$) (230 mg, 2.2 mmol) in THF (5 cm^3) was added and subjected to ultrasound for approximately 90 min. The reaction mixture was allowed to stand at room temperature for 10 min and the yellow precipitate was collected and recrystallized from a dichloromethane–ethanol mixture to give $(C_6H_6)RuCl_2(NH_2C_6H_4Me)$ (162 mg, 76%). Found: C, 43.9; H, 4.35. Calc. for $RuC_{13}H_{15}Cl_2N$: C, 43.7; H, 4.2. ν(NH) 3255, 3223 cm^{-1}, ν(RuCl) 276 cm^{-1} (Nujol mull); ^1H NMR ($CDCl_3$) 7.32–7.14 (m, 4H, C_6H_4), 5.33 (s, 6H, C_6H_6), 2.33 (s, 3H, CH_3).

$[(C_6H_6)RuCl_2(NH_2CMe_3)] \cdot NH_2CMe_3$ (**4**)

Yield, 207 mg, 87%. Found: C, 42.3; H, 7.7. Calc. for $RuC_{14}H_{28}Cl_2N_2$: C, 42.4; H, 7.1%. ν(NH) 3273, 3215 cm^{-1}, ν(RuCl) 275 cm^{-1} (Nujol mull); ^1H NMR ($CDCl_3$) 5.72 (s, 6H, C_6H_6), 1.34 [s, 9H, $C(CH_3)_3$ (coord)], 1.11 [s, 9H, $C(CH_3)_3$ (free)].

$[(C_6H_6)RuCl(NH_2C_6H_4Me)_2]PF_6$ (**5**)

This product may also be isolated from the reaction described for **3**. The yield is increased if NH_4PF_6 is added to the reaction mixture to give $[(C_6H_6)RuCl(NH_2C_6H_4Me)_2]PF_6$. ν(NH) 3028 cm^{-1} (Nujol mull); ^1H NMR ($CDCl_3$) 7.34–7.06

(m, 8H, C_6H_4), 5.01 (s, 6H, C_6H_6), 2.29 (s, 6H, CH_3).

$(MeC_6H_4CHMe_2)RuCl_2(NH_2CMe_3)$ (**10**)

This compound was made using the method described for **2** (104 mg, 85%). Found: C, 44.2; H, 6.8. Calc. for $RuC_{14}H_{25}Cl_2N$: C, 44.3; H, 6.64%. ν(NH) 3266, 3209 cm^{-1}, ν(RuCl) 273 cm^{-1} (Nujol mull); ^1H NMR ($CDCl_3$) 5.50–5.43 (m, 4H, C_6H_4), 3.05 (sept, 1H, CH), 2.26 (s, 3H, $C_6H_4CH_3$), 1.33 (s, 9H, $C(CH_3)_3$), 1.29 and 1.26 (d, 3H, $CH(CH_3)_2$).

$[(C_6H_6)_2Ru_2Cl(OEt)_2]SbF_6$ (**6**)

$[(C_6H_6)RuCl_2(NH_2CMe_3)]\cdot NH_2CMe_3$ (300 mg, 0.76 mmol) was dissolved in MeCN (20 cm^3) and a solution of $AgSbF_6$ (286 mg, 0.84 mmol) in MeCN (5 cm^3) was added and the mixture stirred for 30 min. The precipitated AgCl was removed by filtration and the product precipitated as an orange solid by the gradual addition of EtOH to give $[(C_6H_6)_2Ru_2Cl(OEt)_2]SbF_6$ (96 mg, 35%). Found: C, 26.5; H, 3.1. Calc. for $Ru_2C_{16}H_{22}ClF_6O_2Sb$: C, 26.7; H, 3.1%. ν(RuCl) 258 cm^{-1} (Nujol mull).

$[(MeC_6H_4CHMe_2)_2Ru_2Cl_2(N_3)_2]$ (**7**)

$[(MeC_6H_4CHMe_2)RuCl_2]_2$ (200 mg, 0.33 mmol) was dissolved in dichloromethane (5 cm^3) and N_3SiMe_3 (530 mg, 4.6 mmol) was added dropwise and the mixture stirred for 30 min. An orange crystalline solid was obtained by addition of hexane and reduction of the volume under reduced pressure. Recrystallization was carried out from CH_2Cl_2–EtOH to give $[(MeC_6H_4CHMe_2)_2Ru_2Cl_2(N_3)_2]$ (186 mg, 90%). Found: C, 37.9; H, 4.5. Calc. for $Ru_2C_{20}H_{28}Cl_2N_6$: C, 38.4; H, 4.5%. ν(NN) 2057 cm^{-1}, ν(RuCl) 281 cm^{-1} (Nujol mull); ^1H NMR ($CDCl_3$) 5.33–5.22 (m, 4H, C_6H_4), 2.92 (sept., 1H, CH), 2.24 (s, 3H, $C_6H_4CH_3$), 1.28 and 1.25 (d, 3H, $CH(CH_3)_2$).

$[(MeC_6H_4CHMe_2)_2Ru_2Cl(N_3)_2]SbF_6$ (**8**)

$[(MeC_6H_4CHMe_2)_2Ru_2Cl_2(N_3)_2]$ (250 mg, 0.4 mmol) was dissolved in MeCN (10 cm^3) and $AgSbF_6$ (151 mg, 0.44 mmol) in MeCN, was added. The solution was stirred and then filtered to remove the AgCl precipitate. The product was crystallized by addition of ethanol to give $[(MeC_6H_4CHMe_2)_2Ru_2Cl(N_3)_2]SbF_6$ (208 mg, 63%). Found: C, 28.9; H, 3.5. Calc. for $Ru_2C_{20}H_{28}ClF_6N_6Sb$: C, 29.1; H, 3.4%. ν(NN) 2062 cm^{-1} (Nujol mull); ^1H NMR ($CDCl_3$) 5.57–5.36 (m, 4H, C_6H_4), 2.75 (sept., 1H, CH), 2.23 (s, 3H, $C_6H_4CH_3$), 1.29 and 1.28 (d, 3H, $CH(CH_3)_2$).

$[(MeC_6H_4CHMe_2)RuCl(N_3)PPh_3]$ (**9**)

PPh_3 (450 mg, 1.7 mmol) in CH_2Cl_2 (15 cm^3) was added dropwise to a stirred solution of $[(MeC_6H_4CHMe_2)_2Ru_2Cl_2(N_3)_2]$ (150 mg, 0.24 mmol) in CH_2Cl_2 (15 cm^3). A red solid was collected after treatment of the reaction mixture with hexane and the volume reduced under reduced pressure giving $[(MeC_6H_4CHMe_2)RuCl(N_3)PPh_3]$ (234 mg, 85%). Found: C, 58.8; H, 5.1. Calc. for $RuC_{28}H_{29}ClN_3P$: C, 58.5; H, 5.1%. ν(NN) 2039 cm^{-1}, ν(RuCl) 294 cm^{-1} (Nujol mull); ^1H NMR ($CDCl_3$) 5.50–4.80 (m, 4H, C_6H_4), 2.82 (sept., 1H, CH), 1.86–1.81 (s, 3H, $C_6H_4CH_3$), 1.29–1.08 (d, 6H, $CH(CH_3)_2$).

Crystal data

$C_{20}H_{28}Cl_2N_6Ru_2$, $M = 625.52$ g mol^{-1}, triclinic, $a = 7.586(2)$, $b = 8.376(2)$, $c = 9.689(2)$ Å, $\alpha = 101.40(1)$, $\beta = 87.00(1)$, $\gamma = 102.54(2)°$, $U = 589.07(3)$ $Å^3$, space group $P\bar{1}$ (No. 2), $Z = 1$, $D_c = 1.76$ g cm^{-3}, $F(000) = 312$, graphite-monochromated Mo-K_α radiation, $\lambda = 0.71069$ Å, μ(Mo-K_α) = 14.97 cm^{-1}, crystal dimensions $0.5 \times 0.25 \times 0.05$ mm.

Structure determination

Cell dimensions and their standard deviations were obtained by least-squares refinement of diffractometer setting angles for 12 centred reflections close to 13° in θ. Intensities of 3442 independent reflections ($1° < \theta < 25°$) were measured on a Hilger and Watts Y290 diffractometer in a ω–2θ scan mode.

The structure analysis used 3203 reflections with $I < 3\sigma(I)$ after correction for Lorentz and polarization factors. No correction was made for absorption.

Solution by Patterson and difference syntheses was followed by full-matrix least-squares refinement with anisotropic thermal parameters for all atoms except hydrogen using the CRYSTALS suite of programs. All the hydrogen atoms were located in difference maps and included, but not refined. The refinement for 192 parameters converged to $R = 0.039$ and $R_w = 0.046$, employing a weighting scheme based on Chebyshev polynomials. A final difference map contained no significant features. Complex neutral-atom scattering factors were calculated from the analytical approximation and the coefficients given in ref. 9.*

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* Atomic coordinates, thermal parameters, full bond length and angle data and structure factor values have been deposited as supplementary material with the Editor, from whom copies are available on request. Atomic coordinates have also been deposited with the Cambridge Crystallographic Data Centre.

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