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ACTIVATION OF A CARBON–NITROGEN TRIPLE BOND IN THE PRESENCE OF $\text{Ru}_3(\text{CO})_{12}$ AND $\text{H}_4\text{Ru}_4(\text{CO})_{12}$ *

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Summary

The reaction of PhCN with $\text{Ru}_3(\text{CO})_{12}$ in the presence of acetic acid gives $\text{H}_4\text{Ru}_4(\text{CO})_{12}$ (I), $(\mu\text{-H})\text{Ru}_3(\text{CO})_{10}(\mu\text{-N=CHPh})$ (II) and $(\mu\text{-H})\text{Ru}_3(\text{CO})_{10}(\mu\text{-NH-CH}_2\text{Ph})$ (III) as the main products. Reaction under 110 atm of H_2 gives more III and also gives benzylamine. Replacement of acetic acid by H_2 at atmospheric pressure gives only II. When $\text{H}_4\text{Ru}_4(\text{CO})_{12}$ reacts with PhCN alone or in the presence of NaOH, II is formed as the only product.

The structures of II and III have been fully elucidated by X-ray methods. The nitrogen atom of the N=CHPh ligand in II and that of the NHCH_2Ph ligand in III, interact with the isosceles-triangular metal cluster, symmetrically bridging the shortest Ru(1)–Ru(2) edge. A hydride ligand in both II and III bridges the same Ru(1)–Ru(2) edge of the cluster. Under mild conditions acetic acid is an essential requirement for the activation of $\text{Ru}_3(\text{CO})_{12}$ for reaction with PhCN to give III, which cannot be obtained under these conditions from II.

Introduction

In recent years transition metal clusters have attracted increasing attention because of their potential catalytic activity in reactions involving substrates which are not activated by monometallic species [1–4].

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Catalytic hydrogenation of the carbon–nitrogen triple bond is of particular interest, but these compounds have so far been the subject of only a few reports. Various iron carbonyls have been reported to react with some organic nitriles [5–9] and the triosmium cluster compounds $\text{H}_2\text{Os}_3(\text{CO})_{10}$ and $\text{H}_2\text{Os}_3(\text{CO})_9(\text{PMe}_2\text{Ph})$ have been found to react with CF_3CN [10,11], but until recently no reports had appeared on the activation of these substrates by neutral and electronically saturated metal carbonyl clusters.

In a previous communication we reported on the synthesis of $(\mu\text{-H})\text{Ru}_3(\text{CO})_{10}(\mu\text{-NHCH}_2\text{Ph})$ from $\text{Ru}_3(\text{CO})_{12}$ and benzonitrile in the presence of acetic acid, together with its characterisation by X-ray analysis and by spectroscopic measurements [12]. More recently the reaction of $\text{Ru}_3(\text{CO})_{12}$ with benzonitrile in refluxing ligroin under H_2 has been studied [13].

In this paper we describe the reactions of benzonitrile with $\text{Ru}_3(\text{CO})_{12}$ and with $\text{H}_4\text{Ru}_4(\text{CO})_{12}$ in the presence of various reactants.

Results and discussion

The same main products can be obtained from the reaction of PhCN (L) with dodecacarbonyltriruthenium and with tetrahydridododecacarbonyltetraruthenium, but under different conditions.

When L is refluxed for about 1 h with $\text{Ru}_3(\text{CO})_{12}$ in cyclohexane in the presence of acetic acid the solution contains three compounds, of molecular formula $\text{H}_4\text{Ru}_4(\text{CO})_{12}$ (I), $\text{Ru}_3(\text{CO})_{10}(\text{L} + 2\text{H})$ (II), and $\text{Ru}_3(\text{CO})_{10}(\text{L} + 4\text{H})$ (III), as determined by mass spectrometry, in addition to a very polar orange species IV. Infrared and proton nuclear magnetic resonance data for these compounds are listed in Table 1.

Compound I is the well known tetrahydridododecacarbonyltetraruthenium [14]. The ^1H NMR spectrum of compound II displays a hydride signal at τ 23.28 as a doublet (J 1.5 Hz); decoupling shows that the signal is long range coupled with a one proton doublet at τ 1.05 (not exchangeable with D_2O), which can be assigned to the $=\text{CH}$ proton. A multiplet at τ 2.35–2.65 is attributable to the five benzene protons. The mass spectrum of II exhibits the molecular ion at m/z 691 and ions

TABLE 1
IR AND ^1H NMR DATA

| Complex | Color | $\nu(\text{CO})^a$ (cm^{-1}) | Chemical shift b (τ) |
|---------|-------------|--|--|
| I | yellow | 2081s, 2067vs, 2030m 2024s, 2009w | 28.0s |
| II | orange | 2101mw, 2064vs, 2054vs 2024vs, 2018s, 2010(sh), 2006ms, 1991vw. | 1.05d (1H), 2.35–2.65m (5H), 23.28d (1H) |
| III | dark yellow | 2100m, 2064vs, 2049vs, 2024vs, 2009s, 1999s 1992m, 1980m, 1965w. | 2.6–2.8m (5H), 4.95br (1H), 6.18d (2H), 23.52d (1H) |
| IV | orange | 2044(sh), 2029vs, 1978s, 1946vs, 1914vw. | |

^a Solvent n-hexane for I, II, III, methanol for IV. ^b Solvent CDCl_3 .

arising from the progressive loss of 10 carbonyl ligands.

Compound II was fully characterized as $(\mu\text{-H})\text{Ru}_3(\text{CO})_{10}(\mu\text{-N}=\text{CHPh})$ by an X-ray analysis. Its structure, together with significant bond distances and angles, is shown in Fig. 1 and consists of an isosceles triangular metal cluster bonded to ten terminal carbonyls. A benzylideneamino ligand, formed by partial reduction of the benzonitrile triple bond with one hydrogen atom, interacts with the cluster only through the nitrogen atom, symmetrically bridging the shortest Ru(1)–Ru(2) edge of the cluster. The second hydrogen atom is a hydride ligand which bridges the same Ru(1)–Ru(2) edge.

Compound III has been previously identified as $(\mu\text{-H})\text{Ru}_3(\text{CO})_{10}(\mu\text{-NH-CH}_2\text{Ph})$ by X-ray analysis and spectroscopic measurements [12]. The ^1H NMR spectrum shows a hydride proton at τ 23.52 as a doublet (J 1.6 Hz), a two proton doublet at τ 6.18 (J 7.2 Hz) due to the benzylic CH_2 , a one proton broad signal at τ 4.95 due to NH (exchangeable with D_2O) and a multiplet at τ 2.6–2.8 for the five benzene protons. Upon decoupling of the NH proton, both doublets collapse to singlets, indicating a $\text{CH}_2\text{-NH-Ru-H}$ sequence. The mass spectrum exhibits the molecular ion at m/z 693 with progressive loss of 10 carbonyl ligands.

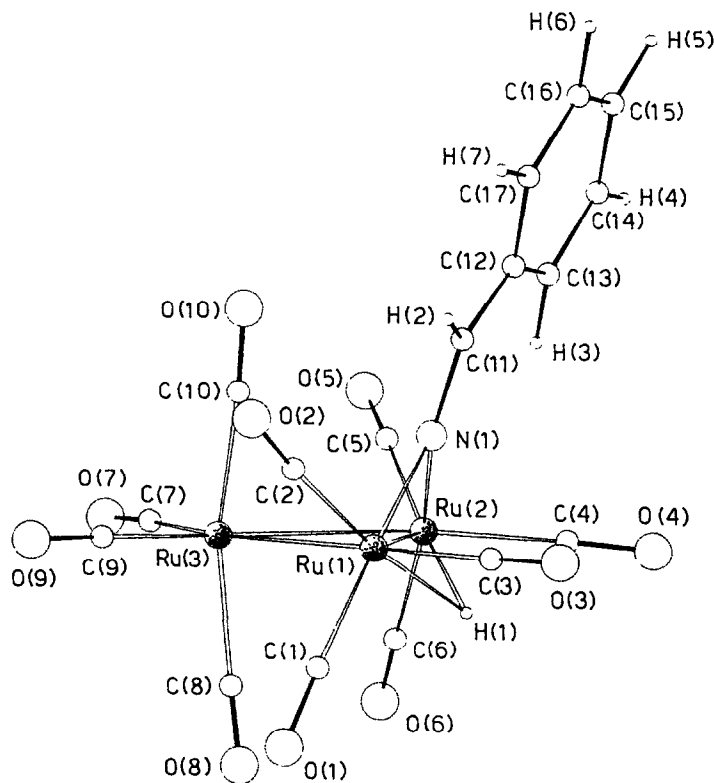
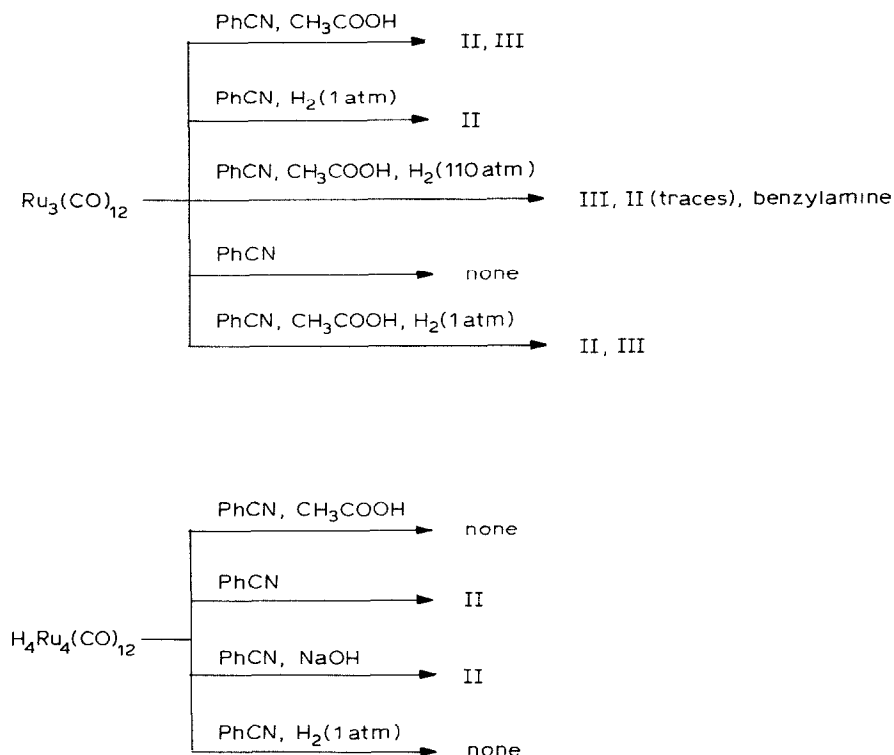


Fig. 1. Molecular structure of the complex $(\mu\text{-H})\text{Ru}_3(\text{CO})_{10}(\mu\text{-N}=\text{CHPh})$ (II) with the atomic numbering scheme. Important bond distances (Å) and bond angles ($^\circ$): Ru(1)–Ru(2) 2.772(3), Ru(1)–Ru(3) 2.819(4), Ru(2)–Ru(3) 2.822(3), Ru(1)–N 2.02(2), Ru(2)–N 2.02 (3), N–C(11) 1.42(3), C(11)–C(12) 1.46(3); Ru(2)–Ru(1)–Ru(3) 60.61(8), Ru(1)–Ru(2)–Ru(3) 60.52(8), Ru(1)–Ru(3)–Ru(2) 58.87(8), Ru(1)–N–Ru(2) 86.6(9), Ru(1)–N–C(11) 127(2), Ru(2)–N–C(11) 146(2), N–C(11)–C(12) 123(3).

The structure of III is very similar to that of II, with the $\text{NH-CH}_2\text{Ph}$ benzyl-amino ligand, formed by complete reduction of the benzonitrile triple bond, replacing the less hydrogenated N=CHPh benzylideneamino ligand. The metal cluster size, the orientation of the 10 carbonyls with respect to the cluster, and the double bridge (through the hydride and the nitrogen atom) on the Ru(1)-Ru(2) edge remain practically unaltered. The Ru(1)-Ru(2) edge in both II and III is shorter than the Ru(1)-Ru(3) and Ru(2)-Ru(3) edges (2.772(3) against 2.819(4) and 2.822(3) Å in II, 2.746(2) against 2.826(2) and 2.830(2) Å in III). The dihedral angles of the N-Ru(1)-Ru(2) and H(1)-Ru(1)-Ru(2) planes with the metal triangle are practically unchanged, 107.6 and 134.2° in II, 108.9 and 126.3° in III. Only the Ru-N bond distances is significantly shorter in II (2.02(2) and 2.02(3) Å) than in III (2.088(5) and 2.105(5) Å). The multiple carbon-nitrogen bond in II (N-C(11) 1.42(3) Å) also affects the C-C_{ph} bonds (C(11)-C(12) 1.46(3) Å) and makes the $\text{Ru(1), Ru(2), N, C(11)}$ atoms exactly coplanar. The corresponding N-C(11) and C(11)-C(12) bond distances in the saturated ligand of III are 1.483(8) and 1.515(9) Å, respectively.

The presence of acetic acid is necessary for formation of compounds I, II, III; replacement of acetic acid by molecular hydrogen at atmospheric pressure in the $\text{Ru}_3(\text{CO})_{12}/\text{PhCN}$ system under the same conditions gives only I and II, as shown in Scheme 1. Not even traces of III can be obtained. When a moderate stream of hydrogen is passed through, a solution containing $\text{Ru}_3(\text{CO})_{12}$, PhCN and acetic acid



SCHEME 1. Experimental conditions for synthesis of II and III from $\text{Ru}_3(\text{CO})_{12}$ and $\text{H}_4\text{Ru}_4(\text{CO})_{12}$.

gives the compounds I, II, and III but more slowly. From these results it can be concluded that H_2 at atmospheric pressure can act as a source of hydrogen only for the production of I and II. In contrast, formation of III requires the presence of acetic acid, and the absence of multiple bonds in the coordinated ligand of III suggests that the acid may be a requirement to saturate the carbon–nitrogen triple bond. An important step is likely to be the preliminary interaction of the acid with the nitrile unit of PhCN in the presence of the $Ru_3(CO)_{12}$ cluster. In fact II is not an intermediate in the formation of III, since the reaction of II with acetic acid in cyclohexane does not give III even after prolonged times.

When cyclohexane solutions of $Ru_3(CO)_{12}$, PhCN and acetic acid are heated at about $80^\circ C$ at increasing pressure of H_2 , the proportion of II decreases and that of III increases. At 110 atm H_2 , III is the main product, with only trace amounts of the other complexes, and, interestingly, benzylamine is also formed.

The formation of $H_4Ru_4(CO)_{12}$ along with compounds II and III in the reaction of $Ru_3(CO)_{12}$, PhCN and acetic acid suggested investigation of the possible role of this complex in the reaction. Thus $H_4Ru_4(CO)_{12}$ was treated with benzonitrile and acetic acid in refluxing cyclohexane, but no soluble complexes were formed. This indicates that the interaction of the acetic acid with PhCN is not effective for the reductive coordination of PhCN in the presence of the $H_4Ru_4(CO)_{12}$ cluster.

The lack of reaction of $H_4Ru_4(CO)_{12}$ with PhCN in the presence of acetic acid is in agreement with the observed decrease of the reaction rate in the system containing $Ru_3(CO)_{12}$, PhCN and acetic acid after the addition of H_2 , which is known to react with $Ru_3(CO)_{12}$ to give $H_4Ru_4(CO)_{12}$. In the absence of acetic acid $H_4Ru_4(CO)_{12}$ reacts with PhCN to give II as the only product, and this is again the sole product, but formed more rapidly, when NaOH is present.

In contrast to carbonyliron clusters, which react with benzonitrile to give complexes, such as $Fe_3(CO)_9(PhCN)$, containing the intact nitrile coordinated to Fe_3 cluster [5–8], $Ru_3(CO)_{12}$ reacts with this nitrile only in the presence of acetic acid or molecular hydrogen.

Both the increased yield of III and the formation of benzylamine, observed at higher pressures of hydrogen suggest that III is the probable precursor of benzylamine. Studies of the catalytic hydrogenation of PhCN by this system are in progress.

Experimental

Benzonitrile, analytical grade, and Kieselgel PF(254–366) were from Merck. Glacial acetic acid was from C. Erba. Hydrogen and nitrogen were commercial products, dried before use. Solvents, analytical grade from C. Erba, were redistilled and dried over molecular sieves. $Ru_3(CO)_{12}$ was prepared from $RuCl_3 \cdot xH_2O$ (Johnson–Matthey) by a literature method [15].

IR spectra were recorded on a Perkin–Elmer 580B spectrophotometer. The mass spectra were recorded on a double focusing Kratos MS80 operating with direct inlet system at 70 eV. 1H NMR spectra were recorded at 200.057 MHz on a VARIAN XL-200 spectrometer from $CDCl_3$ solutions. A 5000 Hz sweep width was used with a digital resolution of 0.156 Hz/point. TMS was used as internal reference.

(a) *Reaction of PhCN and glacial acetic acid with $Ru_3(CO)_{12}$.* In a typical experiment 180 mg (0.282 mmol) of $Ru_3(CO)_{12}$ were stirred with 0.150 ml (1.44

mmol) of PhCN and 0.16 ml (2.79 mmol) of glacial acetic acid in 100 ml of cyclohexane under N_2 stream for 15 min. The solution was heated under reflux for 1 h, then cooled under N_2 , filtered, and concentrated under reduced pressure. Separation by preparative TLC (using light petroleum and diethyl ether 19/1 v/v as eluent on Kieselgel) gave four bands corresponding to compounds I, II, III and IV. After further purification by TLC I, II and III were crystallized from n-hexane at $-10^\circ C$ and IV was from methanol at $-10^\circ C$.

The same results were obtained when the same quantity of $Ru_3(CO)_{12}$ was treated, in cyclohexane, with 0.60 ml (5.74 mmol) of PhCN and 0.60 ml (10.5 mmol) of glacial acetic acid.

(b) *Reaction of glacial acetic acid with $Ru_3(CO)_{12}$.* $Ru_3(CO)_{12}$, 120 mg (0.188 mmol) and 0.12 ml (2.09 mmol) of glacial acetic acid were used in 100 ml of cyclohexane as in (a). I and trace amounts of $Ru_3(CO)_{12}$ were found.

(c) *Reaction of II with glacial acetic acid.* Treatment of II, 10.0 mg (0.0145 mmol), with 0.050 ml (0.87 mmol) of glacial acetic acid in 20.0 ml of cyclohexane, as in (a), caused extensive decomposition.

(d) *Reaction of PhCN and glacial acetic acid with $Ru_3(CO)_{12}$ under a H_2 stream.* A solution prepared as described in (a) was refluxed for 3 h under a stream of hydrogen. Separation, purification and crystallization of compounds were carried out as in (a) to give II and III.

When the same reaction was carried out under 110 atm of H_2 , III was obtained along with only trace amounts of II. Benzylamine was also formed. At 12 atm of H_2 , mainly III, but also small quantities of II, were found.

(e) *Reaction of PhCN and H_2 with $Ru_3(CO)_{12}$.* A mixture of $Ru_3(CO)_{12}$ and PhCN in 1/5 molar ratio in cyclohexane was first stirred under N_2 , then refluxed in cyclohexane at $80^\circ C$ in a stream of H_2 for 90 min. Only II, separated as in (a), was obtained.

(f) *Reaction of PhCN with $H_4Ru_4(CO)_{12}$.* A cyclohexane solution of $H_4Ru_4(CO)_{12}$, 120 mg (0.161 mmol), and PhCN, 0.080 ml (0.772 mmol) was treated as described in (a) for 2 h. Only compound II was obtained. Initial addition of 0.12 ml of a 3% solution of NaOH (0.09 mmol) halved the reaction time, and again only II was formed.

(g) *Reaction of PhCN with $H_4Ru_4(CO)_{12}$ under H_2 stream.* $H_4Ru_4(CO)_{12}$, 120 mg (0.161 mmol) and PhCN, 0.12 ml (1.16 mmol), were kept in refluxing cyclohexane under a H_2 stream as in (d). No reaction occurred.

(h) *Reaction of PhCN and glacial acetic acid with $H_4Ru_4(CO)_{12}$.* A mixture of $H_4Ru_4(CO)_{12}$, 120 mg (0.161 mmol) PhCN, 0.12 ml (1.16 mmol), and glacial acetic acid, 0.12 ml (2.09 mmol), were allowed to react in cyclohexane as in (a); IV was the sole product.

X-Ray data collection, structure determination and refinement of II

The orange crystals of II were of poor quality and mostly twinned. A roughly shaped fragment, cleaved from a larger crystal, having approximate dimensions $0.15 \times 0.20 \times 0.25$ mm was selected and mounted on a Philips PW 1100 diffractometer in a random orientation. Unit cell parameters were obtained by least-squares refinement of the θ values of 20 carefully centered reflections chosen from diverse regions of the reciprocal space. Intensity data were collected at 295 K in the range $3 < \theta < 24^\circ$ (θ - 2θ scan) using the graphite monochromated Mo- K_α radiation. Of

the total 1824 independent collected reflections, 1446, having $I \geq 3\sigma(I)$, were used for the solution and refinement of the structure. Corrections were applied for Lorentz, polarization and absorption effects, this last by a semi-empirical method [16] (maximum and minimum transmission factors 1.4865 and 1.0051 respectively). Crystal data: $C_{17}H_7NO_{10}Ru_3$, $M = 688.45$, monoclinic, a 13.127(8), b 9.296(5), c 9.624(6) Å, β 111.41(3)°, V 1093(1) Å³, $Z = 2$, D_c 2.091 g cm⁻³, $F(000) = 656$, space group $P2_1$, $\mu(\text{Mo-K}\alpha)$ 20.58 cm⁻¹.

The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares using the SHELX system of computer programs [17] with initially isotropic and then anisotropic thermal parameters for the Ru, O, N and C of the carbonyls. The phenyl group was treated as a rigid group with C–C distances of 1.395 Å. The hydridic hydrogen was clearly located in a ΔF map, the others were placed at their geometrically calculated positions and included in the final structure factor calculations. The atomic scattering factors used, corrected for the anomalous dispersion of the Ru atoms, were taken from ref. 18. The function minimized in the

TABLE 2

FRACTIONAL ATOMIC COORDINATES ($\times 10^4$) WITH e.s.d.'s IN PARENTHESES FOR THE NON-HYDROGEN ATOMS

| Atom | x/a | y/b | z/c |
|-------|----------|-----------|-----------|
| Ru(1) | 2519(2) | 1680(3) | –1303(2) |
| Ru(2) | 1763(2) | 0 | 498(2) |
| Ru(3) | 1745(2) | –1120(3) | –2236(2) |
| N | 3271(21) | 652(25) | 650(27) |
| O(1) | 853(25) | 2914(35) | –4231(26) |
| O(2) | 4324(26) | 1313(35) | –2573(34) |
| O(3) | 3267(27) | 4642(27) | 24(37) |
| O(4) | 1688(19) | 1719(31) | 3196(23) |
| O(5) | 2204(27) | –3006(27) | 1757(33) |
| O(6) | –635(20) | –704(29) | –495(34) |
| O(7) | 800(25) | –4118(28) | –2341(33) |
| O(8) | –489(18) | 408(31) | –3647(28) |
| O(9) | 2114(25) | –1337(39) | –5168(24) |
| O(10) | 4104(19) | –1994(29) | –432(29) |
| C(1) | 1549(32) | 2466(41) | –3120(32) |
| C(2) | 3643(32) | 1458(36) | –2172(39) |
| C(3) | 2969(27) | 3540(34) | –473(28) |
| C(4) | 1743(21) | 1065(37) | 2202(33) |
| C(5) | 2077(24) | –1922(42) | 1328(39) |
| C(6) | 255(26) | –427(34) | –151(36) |
| C(7) | 1160(34) | –3046(48) | –2227(41) |
| C(8) | 283(31) | –128(36) | –3170(42) |
| C(9) | 1987(27) | –1251(38) | –4055(32) |
| C(10) | 3242(27) | –1629(37) | –1060(38) |
| C(11) | 4404(25) | 662(37) | 1528(37) |
| C(12) | 4863(18) | 5(29) | 3005(22) |
| C(13) | 4346(18) | –632(29) | 3884(22) |
| C(14) | 4967(17) | –1160(29) | 5297(22) |
| C(15) | 6105(18) | –1051(29) | 5832(22) |
| C(16) | 6622(18) | –414(29) | 4953(22) |
| C(17) | 6002(18) | 114(29) | 3540(22) |

least-squares calculations was $\sum w|\Delta F|^2$; unit weights were chosen in the first stages of the refinement, then weights were applied according to $w = K/[\sigma^2(F_0) + gF_0^2]$ with $K = 0.339$ and $g = 0.0343$. Refinement converged to $R = 0.076$ and $R_w = 0.080$.

Final atomic coordinates for the non-hydrogen atoms are given in Table 2. Tables of the calculated coordinates for the hydrogen atoms, of the thermal parameters and a list of the structure factors are available from the authors on request.

All calculations were carried out on the CYBER 76 computer of the Centro di Calcolo Elettronico dell'Italia Nord-Orientale, Bologna, with financial support from the University of Parma.

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