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The reaction of $Ru_3(\mu_3\text{-}NPh)(\mu\text{-}DPPM)(CO)_8$ (DPPM = diphenylphosphinomethane) with alkynes. Crystal structure of $Ru_2(\mu\text{-}DPPM)(CO)_4$-$(\mu_2\text{-}\eta^3\text{-}HC{=}CPhC(O)NPh)$

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Abstract

The μ_3-nitrene cluster $Ru_3(\mu_3\text{-}NPh)(\mu\text{-}DPPM)(CO)_8$ (**1**) (DPPM = diphenylphosphinomethane) reacts with PhC≡CR (R = H, Ph) to give the binuclear metallapyrrolidone complexes $Ru_2(\mu\text{-}DPPM)(CO)_4(\mu_2\text{-}\eta^3\text{-}RC{=}CPhC(O)NPh)$ (**2**, R = H; **3**, R = Ph)), which are produced by combination of the alkyne with CO and the nitrene ligand. The structure of **2** has been determined crystallographically (**2** is monoclinic, space group $P2_1/n$ (no. 14) with a 11.749(4), b 28.428(5), c 12.586(3) Å, β 109.13(2)°, V 3972(3) Å^3, $Z = 4$, $R = 0.025$ and $R_\omega = 0.027$ for 5150 absorption-corrected reflections having $I \geqslant 3\sigma(I)$). Compounds **2** and **3** are compared with the analogous derivatives obtained by reaction of $Ru_3(\mu_3\text{-}NPh)(CO)_{10}$ with alkynes.

Introduction

We recently reported on the synthesis and crystal structure of $Ru_3(\mu_3\text{-}NPh)(\mu\text{-}DPPM)(CO)_8$ (**1**) (DPPM = diphenylphosphinomethane) [1]. We also studied the reactions of compound **1** with carbon monoxide under a variety of conditions. We found that compound **1** is very robust, giving PhNCO (or $PhNHCO_2Me$ in the presence of methanol) in small amount, and $Ru_3(\mu\text{-}DPPM)(CO)_{10}$ only at 170 °C under 60 atm of carbon monoxide. It is note worthy that the presence of DPPM in cluster **1** does not cause any significant change in the bonding of the triply-bridging imido ligand to the three ruthenium atoms compared with that in $Ru_3(\mu_3\text{-}NPh)(CO)_{10}$ [1].

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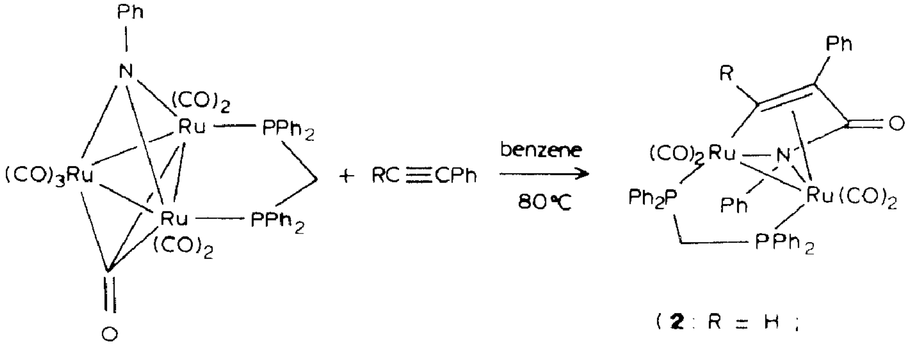
These results allowed us to rule out the possibility that compound **1** is an intermediate in the reductive carbonylation of nitrobenzene catalysed by $Ru_3(\mu\text{-}DPPM)(CO)_{10}$ [2]. While our work on the reactivity of compound **1** and of the related $Ru_3(\mu_3\text{-}NPh)(CO)_{10}$ (a key intermediate in the reductive carbonylation of aromatic nitro compounds catalysed by $Ru_3(CO)_{12}$ in the presence of $NEt_4^+Cl^-$ as co-catalyst [3]) was underway, an interesting report on the reactions of $Ru_3(\mu_3\text{-}NPh)(CO)_{10}$with alkynes under mild conditions appeared [4]. We report here on the related reactions of compound **1** with alkynes, which gave as the main products the metallapyrrolidone complexes $Ru_2(\mu\text{-}DPPM)(CO)_4(\mu_2\text{-}\eta^3\text{-}RC{=}CPhC(O)NPh)$ (**2**, R = H; **3**, R = Ph).

Results

(i) Synthesis of complexes 2 and 3

Reaction of $Ru_3(\mu_3\text{-}NPh)(\mu\text{-}DPPM)(CO)_8$ with $PhC{\equiv}CR$ (R = H, Ph), at 80 °C in benzene and under dinitrogen gave the metallapyrrolidone complexes, $Ru_2(\mu\text{-}DPPM)(CO)_4(\mu_2\text{-}\eta^3\text{-}RC{=}CPhC(O)NPh)$ (**2**, R = H; **3**, R = Ph) as the main products (eq. 1):



(1)

(**2** : R = H ;
3 : R = Ph)

As in the case of the reactions of $Ru_3(\mu_3\text{-}NPh)(CO)_{10}$ with alkynes [4], these products are binuclear complexes containing a bridging acrylamide ligand as a part of a metallapyrrolidone ring. Compound **2** has been crystallographically characterized (vide infra). The reaction appears to be highly regioselective, since we abserved no indication of the formation of the isomer with the H and Ph substituents in **2** interchanged. Other minor products formed in reaction **1** have not been characterized. Compounds **2** and **3** show almost identical IR spectra in the carbonyl stretching region, with $\nu(CO)$ 2010(s), 1995(vs), 1930(s) and $\nu(C{=}O)$ 1685(m), cm^{-1} in benzene. The ^{31}P, ^1H and ^{13}C NMR data for these compounds are reported in the Experimental section.

It has been suggested that the intermediate in the reaction of $Ru_3(\mu_3\text{-}NPh)(CO)_{10}$ with alkynes is a trinuclear derivative in which the alkyne acts as a bridging ligand between two ruthenium atoms, by analogy with the formation of similar compounds in the reaction of $Fe_3(\mu_3\text{-}PPh)(CO)_{10}$ with alkynes [4]. A similar intermediate is probably formed in reaction 1, in spite of the fact that there should be a strengthening of the metal–carbon bond to the remaining carbonyls when two of them are replaced by the more basic DPPM ligand [1].

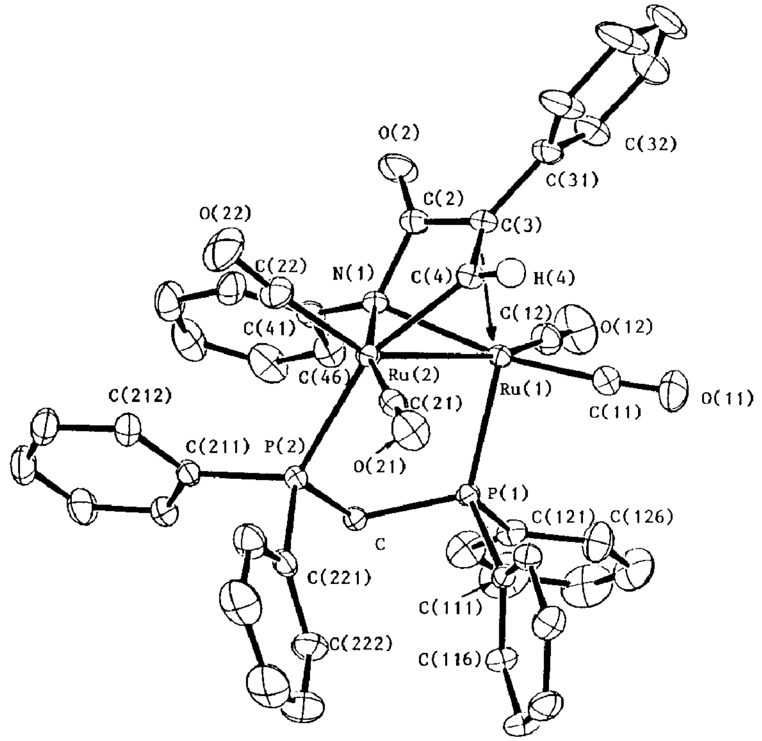


Fig. 1. ORTEP drawing of compound 2. Thermal ellipsoids are drawn at 30% probability.

Table 1

Crystallographic data

Formula	$C_{44}H_{33}NO_5P_2Ru_2$
FW (amu)	919.85
Crystal system	monoclinic
Space group	$P2_1/n$
a (Å)	11.749(4)
b (Å)	28.428(5)
c (Å)	12.586(3)
β (°)	109.13(2)
U (Å^3)	3972(3)
Z	4
D calcd. (g cm^{-3})	1.538
μ(Mo-K_α) (cm^{-1})	8.694
Min. transmission factor	0.92
Crystal dimensions (mm)	0.15×0.10×0.10
Scan mode	ω
ω-scan width (°)	$1.2+0.35 \tan \theta$
θ-range (°)	3–25
Octants of reciprocal space explored	$\pm h, +k, +l$
Measured reflections	8306
Unique observed reflections with $I > 3\sigma(I)$	5150
Final R and R_w indices [a]	0.025, 0.027
No. of variables	491
e.s.d.'s [b]	1.091

[a] $R = [\Sigma(F_o - k|F_c|)/\Sigma F_o]$, $R_w = [\Sigma w(F_o - k|F_c|)^2/\Sigma w F_o^2]^{1/2}$.

[b] e.s.d.'s $= [\Sigma w(F_o - k|F_c|)^2/(N_{obs} - N_{var})]^{1/2}$ $w = 1/(\sigma(F_o))^2$; $\sigma(F_o) = [\sigma^2(I) + (0.03I)^2]^{1/2}/2F_o\mathrm{Lp}$.

Table 2

Fractional atomic coordinates with their e.s.d.'s in parentheses

Atom	x	y	z
Ru(1)	0.01837(2)	0.13908(1)	−0.15923(2)
Ru(2)	0.19619(2)	0.07463(1)	−0.09167(2)
P(1)	0.09025(7)	0.16694(3)	0.02502(6)
P(2)	0.32365(7)	0.11274(3)	0.07445(6)
O(2)	0.1342(2)	0.1471(1)	−0.3906(2)
O(11)	−0.2228(2)	0.1115(1)	−0.1437(2)
O(12)	−0.0860(3)	0.2325(1)	−0.2654(3)
O(21)	0.1364(2)	−0.00530(9)	0.0376(2)
O(22)	0.3713(3)	0.0155(1)	−0.1619(3)
N(1)	0.1872(2)	0.13524(9)	−0.1960(2)
C	0.2557(3)	0.1700(1)	0.0871(2)
C(2)	0.1168(3)	0.1279(1)	−0.3118(3)
C(3)	0.0151(3)	0.0968(1)	−0.3127(3)
C(4)	0.0390(3)	0.0661(1)	−0.2194(2)
C(11)	−0.1299(3)	0.1225(1)	−0.1459(3)
C(12)	−0.0456(3)	0.1976(1)	−0.2258(3)
C(21)	0.1606(3)	0.0253(1)	−0.0094(3)
C(22)	0.3083(3)	0.0382(1)	−0.1312(3)
C(31)	−0.0876(3)	0.0897(1)	−0.4195(3)
C(32)	−0.1513(4)	0.1267(2)	−0.4812(3)
C(33)	−0.2472(4)	0.1188(2)	−0.5790(4)
C(34)	−0.2791(4)	0.0748(2)	−0.6170(3)
C(35)	−0.2153(4)	0.0377(2)	−0.5592(3)
C(36)	−0.1192(4)	0.0446(2)	−0.4595(3)
C(41)	0.2861(3)	0.1680(1)	−0.1802(3)
C(42)	0.3948(3)	0.1515(1)	−0.1847(3)
C(43)	0.4925(3)	0.1815(2)	−0.1658(3)
C(44)	0.4809(4)	0.2279(2)	−0.1416(4)
C(45)	0.3719(4)	0.2450(1)	−0.1396(4)
C(46)	0.2741(3)	0.2150(1)	−0.1592(3)
C(111)	0.0493(3)	0.1382(1)	0.1371(2)
C(112)	0.0070(3)	0.0923(1)	0.1262(3)
C(113)	−0.0141(3)	0.0701(1)	0.2160(3)
C(114)	0.0067(3)	0.0934(1)	0.3159(3)
C(115)	0.0482(3)	0.1392(1)	0.3282(3)
C(116)	0.0682(3)	0.1615(1)	0.2388(3)
C(121)	0.0406(3)	0.2271(1)	0.0370(3)
C(122)	0.1149(4)	0.2659(1)	0.0549(4)
C(123)	0.0687(5)	0.3106(2)	0.0599(5)
C(124)	−0.0504(5)	0.3165(2)	0.0480(4)
C(125)	−0.1253(4)	0.2783(2)	0.0293(4)
C(126)	−0.0811(3)	0.2336(1)	0.0226(4)
C(211)	0.4790(3)	0.1286(1)	0.0895(3)
C(212)	0.5509(3)	0.0948(1)	0.0636(3)
C(213)	0.6708(3)	0.1037(2)	0.0783(3)
C(214)	0.7188(3)	0.1469(2)	0.1167(3)
C(215)	0.6495(3)	0.1809(2)	0.1408(3)
C(216)	0.5290(3)	0.1720(1)	0.1285(3)
C(221)	0.3456(3)	0.0798(1)	0.2049(3)
C(222)	0.3264(4)	0.0978(2)	0.2995(3)
C(223)	0.3400(4)	0.0686(2)	0.3918(3)
C(224)	0.3748(4)	0.0230(2)	0.3914(4)
C(225)	0.3972(4)	0.0051(2)	0.2993(4)
C(226)	0.3818(3)	0.0332(1)	0.2064(3)
H(4)	−0.021(3)	0.044(1)	−0.222(3)

(ii) Description of the structure of compound 2

An ORTEP drawing of compound **2** is shown in Fig. 1. Selected bond distances and angles are listed in Table 3.

The two ruthenium atoms show very distorted octahedral coordination. They are joined by a single Ru–Ru bond bridged by the DPPM ligand and by the μ_2-η^3-HC=CPhC(O)NPh ligand formed by the combination of the nitrene ligand with CO and phenylacetylene, and each bears two terminal CO ligands.

A comparison of **2** with the structurally similar $Ru_2(CO)_6(\mu_2$-η^3-PhC=CPhC(O)NPh) (**4**) [4] reveals small differences in the main framework of the molecule attributable to the presence in **2** of the DPPM ligand viz.:

(i) A lengthening of the Ru–Ru bond (2.698(1) vs. 2.677(1) Å) due to the bite requirements of the bridging DPPM ligand. Consequently, as the Ru(1)–N–Ru(2)

Table 3

Selected bond distances (Å) and angles (deg) with their e.s.d.'s in perentheses and torsion angles (def) within the metallopyrrolidone ring

Ru(1)–Ru(2)	2.698(1)	Ru(1)–N(1)	2.182(2)
Ru(2)–N(1)	2.148(2)	N(1)–C(2)	1.436(4)
C(2)–O(2)	1.207(4)	C(2)–C(3)	1.484(5)
C(3)–C(4)	1.415(4)	Ru(1)–C(3)	2.265(3)
Ru(1)–C(4)	2.249(3)	Ru(2)–C(4)	2.026(3)
Ru(1)–P(1)	2.331(1)	Ru(2)–P(2)	2.395(1)
Ru(1)–C(11)	1.865(4)	C(11)–O(11)	1.145(4)
Ru(1)–C(12)	1.903(4)	C(12)–O(12)	1.141(4)
Ru(2)–C(21)	1.870(3)	C(21)–O(21)	1.139(4)
Ru(2)–C(22)	1.867(4)	C(22)–O(22)	1.140(4)
C(3)–C(31)	1.496(4)	N(1)–C(41)	1.451(4)
P(1)–C	1.844(3)	P(2)–C	1.843(3)
P(1)–C(111)	1.825(3)	P(1)–C(121)	1.829(3)
P(2)–C(211)	1.828(3)	P(2)–C(221)	1.833(3)
C(4)–H(4)	0.93(3)		
Ru(1)–Ru(2)–N(1)	52.03(6)	Ru(1)–N(1)–Ru(2)	77.09(8)
Ru(2)–Ru(1)–N(1)	50.88(6)	Ru(2)–N(1)–C(2)	113.6(2)
N(1)–C(2)–C(3)	106.8(3)	N(1)–C(2)–O(2)	124.9(3)
O(2)–C(2)–C(3)	128.0(3)	C(2)–C(3)–C(4)	114.8(3)
C(3)–C(4)–Ru(2)	117.8(2)	C(4)–Ru(2)–N(1)	76.2(1)
Ru(1)–N(1)–C(2)	87.8(2)	C(2)–C(3)–C(31)	119.8(3)
C(31)–C(3)–C(4)	123.0(3)	Ru(1)–C(11)–O(11)	176.2(3)
Ru(1)–C(12)–O(12)	178.7(3)	Ru(2)–C(21)–O(21)	177.8(3)
Ru(2)–C(22)–O(22)	175.6(3)	C(11)–Ru(1)–C(12)	90.9(1)
Ru(2)–Ru(1)–C(11)	116.7(1)	N(1)–Ru(1)–C(12)	101.8(1)
C(21)–Ru(2)–C(22)	92.1(1)	Ru(1)–Ru(2)–C(21)	113.2(1)
N(1)–Ru(2)–C(22)	100.4(1)	P(1)–Ru(1)–Ru(2)	85.79(2)
P(2)–Ru(2)–Ru(1)	99.55(2)	P(1)–C–P(2)	110.4(1)
P(1)–Ru(1)–C(11)	92.3(1)	P(1)–Ru(1)–C(12)	95.9(1)
P(2)–Ru(2)–C(21)	92.6(1)	P(2)–Ru(2)–C(22)	100.9(1)
C(3)–C(4)–H(4)	116(2)	Ru(2)–C(4)–H(4)	126(2)
C(4)–Ru(2)–N(1)–C(2)	−26.1	N(1)–Ru(2)–C(4)–C(3)	9.6
Ru(2)–N(1)–C(2)–C(3)	35.8	N(1)–C(2)–C(3)–C(4)	−28.1
C(2)–C(3)–C(4)–Ru(2)	7.6		

angle is the same in both structures (77.1(1) and 77.0(1)°), a slight lengthening of the Ru–N bonds is observed in **2**.

(ii) A shortening of the Ru(1)–C(3) (2.265(3) vs. 2.296(3) Å), of the Ru(1)–C(4) (2.249(3) vs. 2.299(3) Å) and of the Ru(2)–C(4) (2.026(3) vs. 2.073(3) Å) bonds is related to the smaller *trans*-influence of the diphosphine ligand than of CO.

The metallapyrrolidone ring is only slightly puckered, as can be inferred from the torsion angles listed in Table 3. Deviations from the best plane passing through the five-membered ring are: Ru(2) 0.116(1), N(1) −0.212(3), C(2) 0.216(4), C(3) −0.069(3), C(4) −0.052(3) Å. The pattern of bond distances and angles within the system is very close to that found in (4).

Experimental

The reactions were carried out under dinitrogen with magnetic stirring. The complex $Ru_3(\mu_3\text{-}NPh)(\mu\text{-}DPPM)(CO)_8$ was prepared as previously described [1]. All solvents were dried, purified, and stored under nitrogen. Infrared spectra were recorded on a Beckman 4210 and a FT Nicolet MX-1 spectrophotmeter. The ^{1}H, ^{31}P and ^{13}C NMR spectra were recorded on a Bruker VP 80 and a Bruker AC 200 spectrometer. Elemental analyses were carried out in the analytical laboratories of Milan University. Crystals of compound **2** suitable for the X-ray study were obtained by slow diffusion of n-hexane into a chloroform solution of **2** kept under dinitrogen.

$Ru_2(\mu\text{-}DPPM)(CO)_4(\mu_2\text{-}\eta^3\text{-}HC{=}CPhC(O)NPh)$ (2)

To compound **1** (0.218 g, 0.22 mmol) were added benzene (30 ml) and PhC≡CH (0.05 ml, 0.46 mmol). The solution was kept at 80 °C and gradually changed from yellow to dark brown. After 5 h at 80 °C IR spectroscopic monitoring (absorption at 2060 cm^{-1}) showed that some unchanged compound (**1**) was still present, and an additional 0.03 ml of PhC≡CH was added. After 3 h compound **1** had almost disappeared from the solution, which was cooled to room temperature, then evaporated to dryness in vacuo (15 mmHg). The residue was purified by column chromatography on alumina; elution with toluene and with a 1/1 mixture of toluene/methylene chloride gave small amounts of uncharacterized by-products and traces of $Ru_3(CO)_{12}$. Elution with methylene chloride gave a crystalline orange compound which did not contain nitrogen; ν(CO) 2040(s), 2005(vs), 1995(sh) and 1950(br) cm^{-1}. This compound was not further investigated. Elution with a 2/1 mixture of methylene chloride/acetone gave a brown solution, which was evaporated to dryness in vacuo. The residue was washed several times with a little benzene and dried in vacuo the give the yellow product (32% yield) in pure form. Elemental analysis: Found: C, 61.3; H, 4.0; N, 1.5. $Ru_2C_{44}H_{33}NO_5P_2 \cdot C_6H_6$ calcd.: C, 62.5; H, 3.9; N, 1.4%; the presence of C_6H_6 was confirmed by thermogravimetric analysis. ^{31}P NMR spectrum in $CDCl_3$: δ(P(1)) 27(d), δ(P(2)) −1.2(d) ppm; J(P(1)–P(2)) 57 Hz (with respect to external H_3PO_4 85% in water). ^{1}H NMR spectrum in $CDCl_3$: δ(=CH) 9.38 ppm (as a quartet due to coupling with two different phosphorus atoms, J(H–P(1)) 1 Hz, J(H–P(2)) 1.7 Hz); $\delta(CH_2)$ 4.04 and 3.6 ppm, each signal being split into six lines. (J(H–H) 12.7 Hz; J(H–P(1)) 9.5 Hz; J(H–P(2)) 11.1 Hz). P(1) and P(2) do not necessarily refer to P(1) and P(2) in Fig. 1 since it was impossible to make definite assignments to the ^{31}P resonances. ^{13}C

NMR spectrum in $CDCl_3$: $\delta(N{-}\overset{*}{C}{=}O)$ 177.8 ppm (as a quartet owing to coupling with two different phosphorus atoms; J_3(C–P(1)) 3 Hz, J_3(C–P(2) 9 Hz); δ(=CH) 157 ppm (doublet due to the coupling with P(1) atom; J_2(C–P(1) 57 Hz); $\delta(HC{=}\overset{*}{C}{-}Ph)$ 92.4 ppm(d) having $J_3(C{-}P) = 12$ Hz.

Between 192 and 205 ppm, 4 resonances are present, at δ 192(d), 198(dd), 202(d) and 205(d) ppm, corresponding to the four terminal CO ligands of the rigid system, having J_2(C–P) between 5 and 14 Hz. More precise assignment of the carbonyl region (on the basis of ref. 5,6,7) would be very difficult.

$Ru_2(\mu\text{-}DPPM)(CO)_4(\mu_2\text{-}\eta^3\text{-}PhC{=}CPhC(O)NPh)$ (3)

To compound **1** (0.14 g, 0.14 mmol) were added benzene (20 ml) and PhC≡CPh (0.03 g, 0.168 mmol). The solution was kept at 80 °C and gradually changed from yellow to red orange. After 10 h the solution was evaporated to dryness (15 mmHg), and the residue was purified by column chromatography on silica. Elution with toluene, gave small amounts of several by-products. Elution with methylene chloride gave the yellow product in pure form. Analysis: Found: C, 62.1; H, 3.9; N, 1.5. $Ru_2C_{50}H_{37}NO_5P_2$ calcd.: C, 60.3; H, 3.7; N, 1.4%.

^{31}P NMR in $CDCl_3$: δ(P(1)) 27(d), δ(P(2)) −0.6(d) ppm, J(P(1)–P(2)) 57 Hz (with respect to 85% H_3PO_4 in water). P(1) and P(2) do not refer to P(1) and P(2) in Fig. 1 because it was impossible to make definite assignments of the ^{31}P resonances. ^1H NMR spectrum in $CDCl_3$: $\delta(CH_2)$ broad multiplet between 4.2 and 3.4 ppm.

X-Ray data collection and structure determination

Crystal data and experimental details are summarized in Table 1. An Enraf–Nonius CAD-4 diffractometer was used at room temperature with Mo-K_α radiation (λ 0.71073 Å). The calculations were performed with a PDP11/73 computer using the SDP-Plus Structure Determination Package [8]. The diffracted intensities were corrected for Lorentz, polarization, and absorption (empirical correction) [9], but not for extinction. Scattering factors and anomalous dispersions corrections for scattering factors of non-hydrogen atoms were taken from ref. 10. The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares, minimizing the function $\Sigma w(F_o - k\,|F_c|)^2$.

Anisotropic thermal factors were refined for all the non-hydrogen atoms. All the hydrogen atoms were introduced at calculated positions with C–H 0.95 Å and not refined, except for hydrogen atom H(4), which was refined with an acceptable thermal parameter and position. The final difference Fourier syntheses showed maxima residuals of 0.2 e/Å^3. The atomic coordinates are listed in Table 2. A table of thermal parameters and lists of observed and calculated structure factors are available from the authors.

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