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Transition metal-cyanocarbon chemistry

VII *. Reactions of mono- and di-cyanoacetylenes with tricarbonylcyclopentadienylmethylthiolatotungsten(II). Formation of phosphorus ylide complex $[(C_5H_5)(CO)_2\overline{W(CH(P(C_6H_5)_3)C}(CN)SCH_3)]$. Crystal structure of $[(C_5H_5)(CO)_2(P(C_6H_5)_3)W(C(O)C(CN)=CHSCH_3)\cdot CH_2Cl_2]$

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Abstract

Reactions of $(C_5H_5)(CO)_3W(SMe)$ with cyano-activated alkynes $RC{\equiv}CCN$ with $R = H$ or CN give heterometallacyclic complexes $(C_5H_5)(CO)_2\overline{W(C(O)C(CN)=C(R)S}Me)$ ($R = H$ (**2**) or CN (**6**)) or for $R = H$, an insertion σ-vinylic complex $[(C_5H_5)(CO)_3W(CH=C(CN)SMe)]$ (**3**). Irradiation of **3** in the presence of PPh_3 in THF gives the ylide complex $(C_5H_5)(CO)_2W(\eta^2\text{-}CH(PPh_3)C(CN)SMe)$ (**5**), whereas **2** under such conditions gives an η^1-acylic complex $[(C_5H_5)(CO)_2PPh_3W(C(O)C(CN)=CHSMe)]$ (**4**). The structure of **4** has been determined by X-ray diffraction.

Introduction

For some years we have been engaged in a systematic study of the behaviour of cyano-substituted alkynes towards organometallic complexes of transition metals. We have observed that the interactions of monocyanoacetylene (mca) and di-

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* For part VI see ref. 2.

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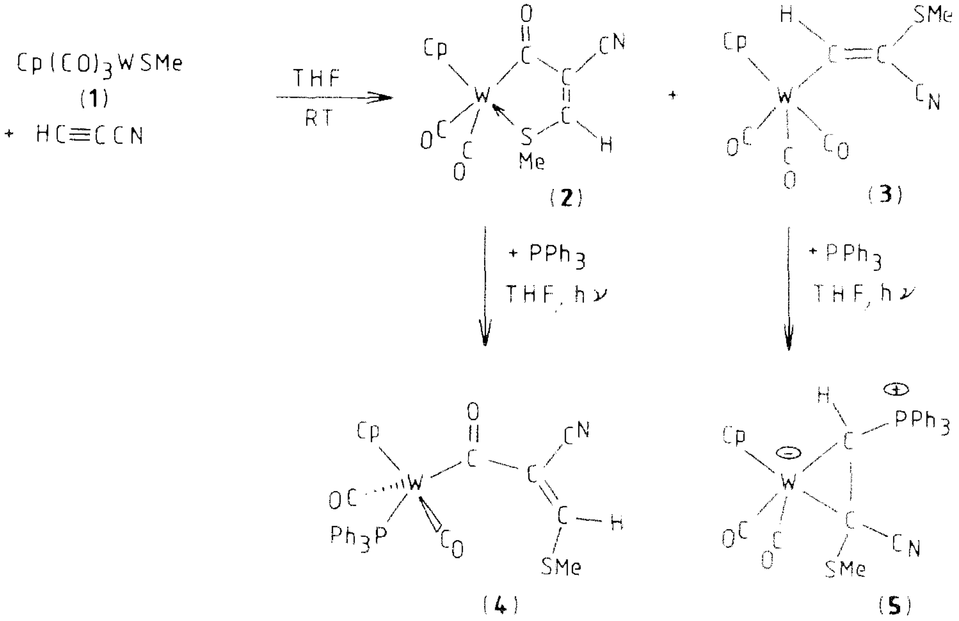
cyanoacetylene (dca) with monocyclopentadienyl hydrides of molybdenum, tungsten [1] and iron [2] and with dicyclopentadienyl hydrides of molybdenum and tungsten [3] always result in insertion of the alkyne into the metal–hydride bonds. An interesting feature of these reactions is their regio- and stereo-specifity.

The reactions of organometallic thiolates of iron, molybdenum and tungsten with the strongly electrophilic acetylenes $CF_3C{\equiv}CCF_3$ (hfb) and $MeO_2CC{\equiv}CCO_2Me$ (dmad) as well as the mono-substituted alkyne $CF_3C{\equiv}CH$ (tfp) have been extensively studied [4,5,6] and various products, especially metallacyclic ones, have been isolated. Because of this and because the formation and breakdown of metallacycles is an important branch of organotransition-metal chemistry [7], we thought it of interest to explore the possibility that use of organometallic thiolates might give heterometallacycles derived from (mca) and (dca).

We report here some results of a study of the reactions of (mca) and (dca) towards organometallic thiolates, particularly a methylthiolate complex of tungsten $Cp(CO)_3W(SMe)$ (**1** $Cp = \eta^5\text{-}C_5H_5$).

Results and discussion

Treatment of **1** with about a 50% excess of (mca) in THF at room temperature for 16 h gives the complexes **2** and **3** which were separated by chromatography (Scheme 1). The formulation of these compounds is based on the elemental analyses (see Experimental section) and spectroscopic data (Table 1). Thus, the presence of the nitrile groups in **2** and **3** was confirmed by IR and that of the methylthiol ligand by ^1H NMR spectroscopy.



Scheme 1

The IR and ^{1}H NMR data for **2** (Table 1) agree well with values reported for analogous heterocyclic complexes of iron and tungsten derived from the corresponding organometallic thiolates and from (hfb) or (tfp) [4,5]. Such a structure for **2** and the positions of the substituents on the metallacycle are confirmed by an X-ray structural study of **4** which results from the reaction of **2** with PPh_3 (Scheme 1). The terminal but not cyclic acylic complex **4** separates as a yellow solid upon UV irradiation of **2** in presence of PPh_3 in THF. The higher field resonance of the hydrogen originally attached to the metallacycle and of the hydrogens of SMe ligand in **4**, with respect to **2**, are consistent with the removal of the thiolate from the metal, and so, the rupture of the metallacycle at this part.

An ORTEP drawing of **4** showing the molecular structure is presented in Fig. 1. Relevant interatomic distances and angles are given in Table 2. There are two molecules of solvent (CH_2Cl_2) in the triclinic centrosymmetric cell. The coordination geometry of the tungsten atom can be described as a distorted, tetragonal pyramid with the apical position occupied by the cyclopentadienyl ring. The nucleophilic moieties (PPh_3 and SMe) are *trans* to one another. Both carbonyl ligands are *cis* with respect to the phosphine. The σ-acylic ligand is nearly planar. The greatest deviations (0.10 Å) from the best plane defined by C(26), C(27), C(28) and C(29) atoms are those of O(3) and S atoms. The W–C(28) bond length of 2.240(9) Å is shorter than W–C(sp^2) distance of 2.32 Å found in Cp(CO)$_3$W(σ-Ph) [8] and than W–C(sp^3) distance of 2.321(4) Å in an "enolate" complex Cp(CO)$_3$W(CH$_2$C(O)OEt) [9], but it is practically the same as the Mo–C(O) bond of 2.26(1) Å observed in Cp(CO)$_2$(PPh$_3$)MoC(O)Me [10]; the covalent radii of Mo^{II} and of W^{II} are practically the same [11] owing to the "*f*" contraction in the *5d* block metals. The W–C(28) distance observed in the structure of **4** is consistent with a single W–C(sp^2) bond which is normally 2.19 Å or longer [12]. This distance is longer than the W–C(O) distances observed in η^3-acryloyl complexes

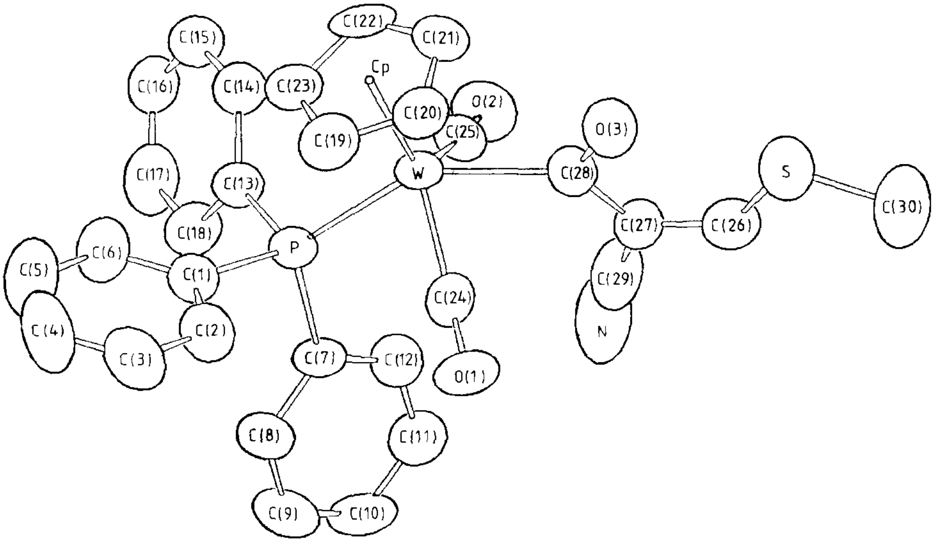


Fig. 1. ORTEP drawing of **4**. CH_2Cl_2 molecule and hydrogen atoms omitted for clarity.

Table 1. IR and ^{1}H NMR data

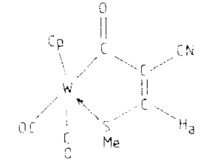
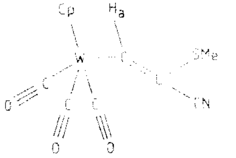
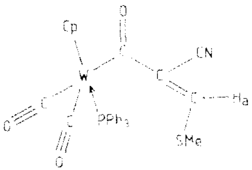
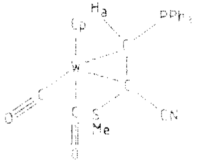
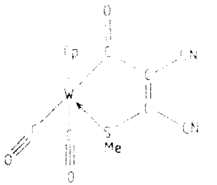
Complex		IR (cm^{-1}) (Nujol)			^{1}H NMR (ppm) (Ref. TMS, solvent CDCl$_3$)			
		ν(CN)	ν(C≡O)	ν(C=O)	δ(C$_6$H$_5$)	δ(C$_5$H$_5$)	δ(H$_a$)	δ(CH$_3$)
	(2)	2220(m)	1960(s) 1880(s)	1570(w)	–	5.40(s)	8.09(s)	3.00(s)
	(3)	2220(m)	2060(s) 2040(s) 1950(s)	–	–	5.62(s)	8.46(s)	2.39(s)
	(4)	2200(w)	1940(s) 1850(s)	1550(s)	7.56(m)	5.13(d) J(P–H) 1.1 Hz	7.00(s)	2.30(s)
	(5)	2200(w)	1910(s) 1810(s)	–	7.60(m)	5.34(s)	2.56(br)	2.20(s)
	(6)	2200(w)	1980(s) 1900(s)	1560(m)	–	5.50(s)	–	3.29(s)

Table 2

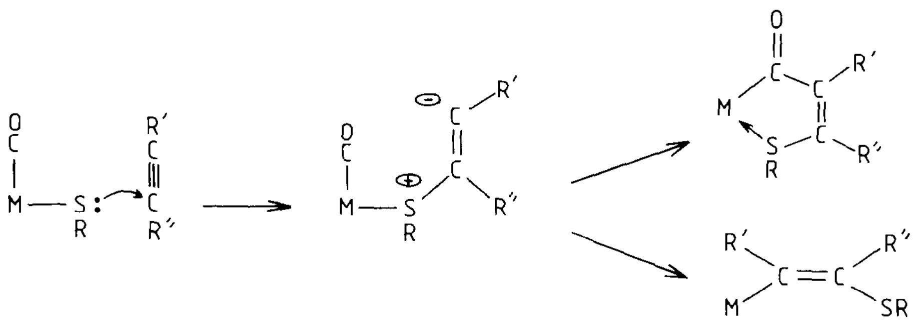
Interatomic distances (Å) and angles (°) for **4**

W-P	2.491(2)	P-W-C(28)	141.2(3)
W-C(28)	2.240(9)	P-W-C(24)	79.2(4)
W-C(24)	1.97(1)	P-W-C(25)	82.0(3)
W-C(25)	1.961(9)	P-W-CP	112.1(3)
W-CP [a]	2.014(9)	C(24)-W-C(25)	107.8(4)
C(24)-O(1)	1.127(11)	C(24)-W-C(28)	75.3(4)
C(25)-O(2)	1.148(10)	C(25)-W-C(28)	78.7(3)
C(28)-O(3)	1.219(10)	W-C(28)-O(3)	122(1)
C(28)-C(27)	1.495(13)	W-C(28)-C(27)	125.5(6)
C(27)-C(29)	1.416(14)	C(28)-C(27)-C(29)	126.0(9)
C(29)-N	1.163(15)	C(28)-C(27)-C(26)	120.3(9)
C(26)-C(27)	1.366(13)	C(27)-C(29)-N	176(1)
S-C(26)	1.670(11)	C(27)-C(26)-S	129.1(8)
S-C(30)	1.807(14)	C(26)-S-C(30)	99.7(6)
P-C(1)	1.824(8)	C(1)-P-C(7)	102.5(4)
P-C(7)	1.833(8)	C(1)-P-C(13)	103.0(4)
P-C(13)	1.847(9)	C(7)-P-C(13)	100.5(4)
C(31) [b]-C(11)	1.78(4)	W-P-C(1)	112.7(2)
C(31)-C(12)	1.75(4)	W-P-C(7)	117.9(5)
		W-P-C(13)	117.9(2)
		C(11)-C(31)-C(12)	117(2)

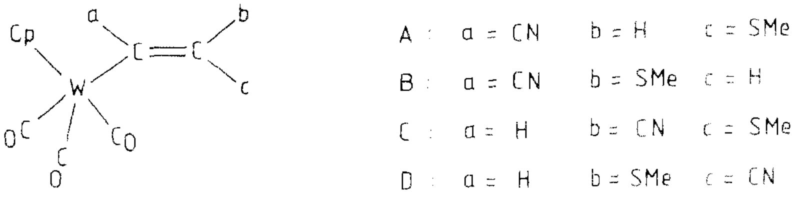
[a] CP is the gravity center of C(19)-C(23) atoms. [b] C(31), C(11) and C(12) is CH_2Cl_2 molecule.

$Cp(CO)LWC(O)C(CF_3){=}C(CF_3)H$ (L = CO, W-C 2.112(5) Å; L = $P(OMe)_3$, W-C 2.091(5) Å [13]), in which the electron delocalisation in the η^3-acryloyl ligand may increase the order of the tungsten-carbon (carbonyl) bond. Other structural parameters for **4** are normal, and will not be discussed in details.

A plausible mechanism of the formation of heterocyclic complexes (such as **2**) and vinyl compounds, which involves initial nucleophilic attack of the sulphur atom of the starting thiolate complex at an acetylenic carbon to give a dipolar intermediate, has been proposed by Davidson [4] (Scheme 2). This mechanism readily accounts for the formation of **2**, but the spectroscopic data for **3** do not seem to agree with the expected formulation, i.e. $Cp(CO)_3W{-}C(CN){=}CH(SMe)$. There are four possible isomers of **3**, differing in the positions of substituents on the σ-alkenyl ligand (Scheme 3).



Scheme 2

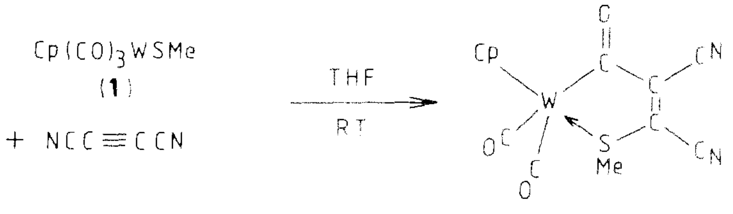


A : a = CN b = H c = SMe
B : a = CN b = SMe c = H
C : a = H b = CN c = SMe
D : a = H b = SMe c = CN

Scheme 3

Structure **A** expected on the basis of Davidson's mechanism does not seem to be consistent with the spectroscopic data, which favour a configuration **D**. In *Z*(*trans*) and *E*(*cis*) isomers of (CN)HC=CH(SMe) a hydrogen bound to the carbon atom bearing the SMe group resonates at 7.3–7.5 ppm, which is intermediate between the value of 8.09 ppm for **2** and that of 7.00 ppm for **4**. In this last compound the H_a and SMe ligands are attached to a terminal C_γ carbon atom. The CH_3 resonances in **3** and **4** are close to each other (Table 1), but those of H_a differ by about 1.5 ppm. This suggests that the H_a atom is attached to a C_α carbon atom rather than to the expected C_β one, and thus that the possible isomers **A** and **B** (Scheme 3) can be ruled out. Moreover, the chemical shifts of protons bound to the C_β carbon atom in some σ-alkenyl complexes of tungsten fall in the region of 6.0 to 6.8 ppm [1,3,14,15]. Those linked to the C_α carbons (with respect to the metal) are deshielded (8.3–8.7 ppm) [1,3]. The structure we propose for the insertion complex **3** is thus of the **C** or **D** type (Scheme 3). As an indirect argument in favour of this view we note the existence of the (tpf) insertion compound $Cp(CO)_2Fe{-}C(CF_3){=}CH_a(SMe)$, formed in a Davidson process, in which the H_a hydrogen resonates at 7.12 ppm [15].

We have shown previously that irradiation of complexes containing σ-alkenyl ligands containing nitrile substituents in the presence of phosphines gives phosphorus ylide complexes [1,16]. Thus we carried out an analogous reaction with the insertion complex **3**. Irradiation of **3** in the presence of PPh_3 in THF gave after work-up complex **5**. An ylide type structure for **5** is proposed on the basis of the analytical (see Experimental section) and spectroscopic data (Table 1). The IR spectrum shows a band at 2200 cm^{-1} attributable to ν(CN), and two bands at 1910 and 1810 cm^{-1} due to the terminal carbonyls. These two last bands are shifted by about 150 cm^{-1} to lower frequencies with respect to the complex **3**, suggesting an ylide structure; a shift of about 100 cm^{-1} would be expected from simple substitution of PPh_3 for CO. The ^{31}P chemical shift of 31.6 ppm is close to the values for analogous ylides of molybdenum (32.1 ppm) and tungsten (34.2 ppm) [1], thus



(6)

Scheme 4

supporting the ylide structure of **5**. Finally, a set of resonances in ^1H NMR spectrum centered at 7.6(m), 5.34(s), 2.56(br) and 2.20(s) ppm in the integration ratio 15/5/1/3, confirms the structure. A broadening of the resonance at 2.56 ppm ($\Delta\nu_{1/2}$ 4 Hz) must be due to a low resolution of a doublet resulting from the coupling of the corresponding proton with phosphorus atom ($^2J(PH) < 4$ Hz); the corresponding ^2J value in $Cp(CO)_2\overline{W(\eta^2\text{-}CH(PPh_3)}CH(CN)$ is 3.7 Hz [1].

Addition of dicyanoacetylene (dca) to the solution of **1** in THF at room temperature leads to an immediate change of colour from yellow to blue and the acylic heterometallacyclic complex **6** can be isolated (Scheme 4). This is in a good agreement with the results obtained by other workers [4–6] for the reactions of organometallic thiolates with the symmetric alkynes.

Experimental

The reactions were performed under nitrogen by use of Schlenk tube techniques. Solvents were purified by standard methods and purged with nitrogen before use. $Cp(CO)_3WSMe$ (**1**) [17], (mca) and (dca) [18] were prepared by the published methods. ^1H and ^{31}P NMR spectra were recorded on a JEOL-JNM-FX100 spectrometer and IR spectra on a Pye-Unicam SP2000 spectrophotometer.

Reaction of 1 with HC≡CCN (mca)

About 15 mmol of freshly prepared (mca) was condensed into a solution of 4.0 g (10.5 mmol) of **1** in THF frozen in liquid nitrogen. The mixture was allowed to warm to room temperature and then stirred for 16 h. The solvent was removed under vacuum and the residue dissolved in a small amount of CH_2Cl_2 and chromatographed on a Florisil column. Elution with 3/1 CH_2Cl_2/hexane gave a yellow band (15% yield) of **3** and that with 95/5 CH_2Cl_2/THF a red band containing **2** (40% yield).

Complex **2**: Found: C, 33.4; H, 2.0; N, 3.3; W, 41.1. $C_{12}H_9NO_3SW$ calcd.: C, 33.4; H, 2.1; N, 3.3; W, 42.7%.

Complex **3**: Found: C, 33.4; H, 2.0; N, 3.2; W, 42.3. $C_{12}H_9NO_3SW$ calcd.: C, 33.4; H, 2.1; N, 3.3; W, 42.6%.

Reaction of 1 with NCC≡CCN (dca)

Addition of a slight excess (0.12 g, 2.8 mmol) of (dca) in THF to the solution of 1 g (2.6 mmol) of **1** in THF caused an immediate change of color from yellow to blue. After five minutes stirring the solvent was evaporated and the residue dissolved in CH_2Cl_2 and chromatographed on Florisil. Elution with CH_2Cl_2 gave **6** in 90% yield.

Complex **6**: Found: C, 34.5; H, 1.9; N, 6.3; W, 39.5. $C_{13}H_8N_2O_3SW$ calcd.: C, 34.2; H, 1.8; N, 6.1; W, 40.3%.

Reaction of 2 with PPh_3

A solution of 0.57 g (0.8 mmol) of **2** and 0.6 g (2.2 mmol) of PPh_3 in THF was irradiated for 24 h. The yellow-light precipitate was filtered off (40% yield).

Complex **4**: Found: C, 51.2; H, 3.4; N, 1.9; P, 4.2; W, 25.6. $C_{30}H_{24}NO_3PSW$ calcd.: C, 52.0; H, 3.5; N, 2.0; P, 4.5; W, 26.5%.

Reaction of **3** *with PPh*$_3$

A solution of 0.8 g (1.85 mmol) of **3** and 1.2 g (4.5 mmol) of PPh$_3$ in THF was irradiated for 48 h. The solvent was evaporated and the residue was dissolved in CH$_2$Cl$_2$ and chromatographed on Florisil. Elution with 95/5 CH$_2$Cl$_2$/THF gave a yellow band, which yielded the crude complex **5**. Recrystallization from CH$_2$Cl$_2$/hexane gave pure **5** in 40% yield.
Complex **5**: Found: C, 52.4; H, 3.6; N, 2.1; P, 4.4; W, 26.0. C$_{29}$H$_{24}$NO$_2$PSW calcd.: C, 52.3; H, 3.6; N, 2.1; P, 4.6; W, 27.6%.

X-Ray structure analysis of **4**

A crystal suitable for X-ray analysis of dimensions 0.08 × 0.24 × 0.16 mm was grown from CH$_2$Cl$_2$/pentane solution and mounted on an Enraf–Nonius CAD4 diffractometer for measurements of cell parameters (25 randomly selected reflections) and diffraction intensities in an ω–2θ scan (θ_{min} 2°, θ_{max} 28°).
Crystal data for **4**: C$_{31}$H$_{26}$Cl$_2$NO$_3$PSW, FM 778.3, Triclinic, a 8.073(5), b 13.603(2), c 15.582(3) Å, α 68.95(1), β 80.24(3), γ 82.71(3)°, U 1570 Å^3. Space group $P\bar{1}$, $Z = 2$, D_c 1.58 g cm^{-3}, μ(Mo-K_α) 39.9 cm^{-1}. λ(Mo-K_α) 0.71069 Å.

3003 reflections with $I > 3\sigma(I)$ were used in the solution and refinement of the structure (361 variables). All calculations were carried out using the Enraf–Nonius SDP programs [19]. Neutral atom scattering factors and anomalous dispersion corrections applied to all non-hydrogen atoms were those given by Cromer and Waber [20]. The structure was solved and refined by conventional three-dimensional Patterson, difference Fourier, and full-matrix least-squares methods. All non-hydrogen atoms were refined with anisotropic thermal parameters. The positions of all hydrogen atoms were calculated by the SDP "Hydro" program with B_{iso} fixed at

Table 3

Positional parameters and their estimated standard deviations

Atom	x	y	z	Atom	x	y	z
W(1)	0.24005(4)	0.34858(3)	0.20584(3)	C(9)	0.657(2)	−0.0322(9)	0.4103(9)
S(1)	0.0699(5)	0.6266(3)	0.3873(2)	C(10)	0.747(2)	0.028(1)	0.4360(8)
Cl(1)	0.392(1)	0.2972(8)	−0.3551(7)	C(11)	0.744(2)	0.1360(9)	0.3927(8)
Cl(2)	0.302(1)	0.236(1)	−0.1474(9)	C(12)	0.646(1)	0.1833(8)	0.3236(8)
P(1)	0.4319(3)	0.1922(2)	0.1990(2)	C(13)	0.602(1)	0.2113(7)	0.1000(7)
O(1)	0.197(1)	0.2100(7)	0.4137(5)	C(14)	0.581(1)	0.2935(8)	0.0168(7)
O(2)	0.5731(9)	0.4618(6)	0.1472(6)	C(15)	0.708(2)	0.3060(9)	−0.0583(8)
O(3)	0.062(1)	0.5259(6)	0.2725(5)	C(16)	0.844(1)	0.2414(8)	−0.0527(8)
N	0.581(2)	0.377(1)	0.385(1)	C(17)	0.867(1)	0.1600(9)	0.0287(9)
C(1)	0.321(1)	0.0861(7)	0.1940(7)	C(18)	0.743(1)	0.1440(9)	0.1051(8)
C(2)	0.191(2)	0.0457(9)	0.2618(8)	C(19)	0.010(1)	0.2956(9)	0.1643(8)
C(3)	0.102(2)	−0.0344(9)	0.262(1)	C(20)	−0.040(1)	0.3885(8)	0.1851(7)
C(4)	0.147(2)	−0.077(1)	0.195(1)	C(21)	0.051(1)	0.4708(8)	0.1172(8)
C(5)	0.275(2)	−0.039(1)	0.126(1)	C(22)	0.153(1)	0.4301(9)	0.0555(7)
C(6)	0.364(2)	0.0426(9)	0.1239(8)	C(23)	0.134(1)	0.3197(9)	0.0864(7)
C(7)	0.552(1)	0.1238(7)	0.2961(7)	C(24)	0.222(1)	0.2604(8)	0.3383(7)
C(8)	0.559(2)	0.0145(9)	0.3423(8)	C(25)	0.454(1)	0.4162(7)	0.1726(7)
C(29)	0.451(2)	0.420(1)	0.3660(9)	C(26)	0.241(1)	0.5423(9)	0.3945(8)
C(30)	0.100(3)	0.684(1)	0.471(1)	C(27)	0.292(1)	0.4732(8)	0.3480(7)
C(31)	0.314(3)	0.335(2)	−0.257(3)	C(28)	0.187(1)	0.4640(8)	0.2814(7)

5.0 Å^2. The final residuals were $R = 0.044$, $R_w = 0.060$, GOF = 1.59. The weighting scheme employed was $w^{-1} = \sigma^2(F) = \frac{1}{4}[\sigma(I)/(I) + 0.06^2(I)]$. The final atomic coordinates are listed in Table 3.

Lists of hydrogen atom positions, thermal parameters and structure factors are available from the authors (R.K. or M.M.K.).

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