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Isolation of a diketone species that is allylically bound to tungsten, and its relationship to a tungsten η^2-ketone complex

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Abstract

The diketone complex $[W(CO)_2(\eta\text{-}C_5H_4Me)\{\eta^3\text{-}\overline{C(O)\text{–}C(Ph)\text{–}C(H)\text{–}C(Ph)\text{–}C}(H)\text{–}C(O)\text{–}C_5Me_5\}]$ (**3**) was isolated from the reaction of PhC_2H with a mixture of $[Ni(CO)I(\eta\text{-}C_5Me_5)]$ and $[W(CO)_3(\eta\text{-}C_5H_4Me)]^-$. Complex **3** contains an organic diketone fragment that is bound in a π-allyl fashion to a tungsten atom. It was fully characterized by standard spectroscopic techniques and by a single-crystal X-ray diffraction study. The relationship of complex **3** to a structurally characterized cyclopentadienyl tungsten η^2-ketone species **1**, and the likelihood that **3** and the methylcyclopentadienyl analog of **1** share common intermediates, are discussed. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Allyl complexes; Ketone; Nickel; Tungsten; Carbon–carbon coupling

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1. Introduction

The exploration of the chemistry of alkynes with organometallic complexes remains a fertile research area [1]. We have reported some of the rich chemistry that Ni–Mo and Ni–W hetero-bimetallic species demonstrate with alkynes [2]. We have also looked into the reactions of mixtures of the monometallic precursors of the hetero-bimetallic compounds with alkynes.

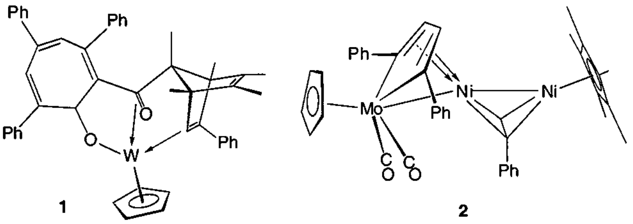

Fig. 1. The structures of complexes **1** and **2**.

When an in situ mixture of $[M(CO)_3(\eta\text{-}C_5H_5)]^-$ (M = Mo, W) and $[Ni(CO)I(\eta\text{-}C_5Me_5)]$ is treated with PhC_2H, unusual products which contain many new carbon–carbon bonds have been isolated [3,4]. Among them is the 16-electron tungsten side-bound η^2-ketone complex **1** [3], which contains a pentamethylcyclopentadiene (C_5Me_5) group that has been the recipient of a Diels–Alder added PhC_2H ligand. This adduct forms one of the two alkyl groups of the η^2-ketone ligand. The other ketonic group is formed by cyclo-oligomerization of three PhC_2H ligands and a CO ligand to form a triphenyltropone species that binds in its enol form, via the oxygen, to the tungsten atom. The trimetal species **2**, isolated from the simultaneous reaction of $[Ni(CO)I(\eta\text{-}C_5Me_5)]$, $[Mo(CO)_3(\eta\text{-}C_5H_5)]^-$ and PhC_2H, shows the likely fate of the Cp* stripped nickel atom [4]. The structures of complexes **1** and **2** are given in Fig. 1.

How complex **1** forms, remains a mystery. Here, we describe the isolation and structural characterization of complex **3**, a molecule that probably shares a common intermediate with the methylcyclopentadienyl analog of **1**, the η^2-ketone complex **1′**. We also indicate that **1′** (and by inference, **1**) as well as the new species **3** require the presence of nickel to form, even though neither species contains this element. The C_5Me_5 ligand trans-

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fer from a nickel atom to form a tungsten complex demonstrates again the relative lability of nickel-bound η^5-C_5Me_5 ligands.

2. Results and discussion

2.1. Synthesis and X-ray analysis of **3**

Complex **3** was isolated in low yield from the reaction of $[W(CO)_3(\eta\text{-}C_5H_4Me)]^-$, $[Ni(CO)I(\eta\text{-}C_5Me_5)]$ and PhC_2H. The spectroscopic data (discussed shortly) precluded its structural assignment; so, a single-crystal X-ray diffraction study was undertaken to establish the structure of **3**. Crystal data and data collection parameters, positional parameters of non-hydrogen atoms and tables of key bond lengths and bond angles are collected in Tables 1–3, respectively. A CHEM 3D® diagram of complex **3**, $[W(CO)_2(\eta\text{-}C_5H_4Me)\{\eta^3\text{ - }\overline{C(O)–\mathit{C}(Ph)–\mathit{C}(H)–\mathit{C}(Ph)–C}(H)–C(O)–C_5Me_5\}]$ (only *ipso*-phenyl carbon atoms are shown for clarity), and a ChemDraw sketch are depicted below (Fig. 2).

Complex **3** consists of a $[W(CO)_2(\eta\text{-}C_5H_4Me)]$ unit bonded in a η^3-allylic fashion to a 1,3-diketone represented here as RC(=O)R′ [one C=O group is considered as being part of R′]. Both R and R′ are unsaturated groups that are linked to the ketonic CO carbon atom. R is a 2,4-pentamethylcyclopentadiene ligand, while R′ is a five-membered ring formed by the coupling of two PhC_2H ligands, in head to tail fashion, with another carbonyl ligand.

The five-membered $\overline{C(O)–\mathit{C}(Ph)–\mathit{C}(H)–\mathit{C}(Ph)–C}(H)$ ring is ligated to the tungsten atom in an allylic fashion through the italicized carbon atoms [C(1), C(4) and C(5)]. These carbon atoms are in an *exo*- conformation with respect to the η-C_5H_4Me group (the ‘V’ formed by the allylic carbon atoms points towards, and not away from, the η-C_5H_4Me ring. This geometry is commonly seen in the structures of many Group 6 allylic complexes [5]. The central carbon atom in the allylic group (C(5)) forms a much a shorter bond to the tungsten atom than to the other two allylic carbon atoms (W–C(5) = 2.164(6): cf. W–C(1) = 2.345(6); W–C(4) = 2.350(6) Å). While other bond lengths and angles are

Table 1
Crystal data and structure refinement parameters for the complex $[W(CO)_2(\eta\text{ - }C_5H_4Me)\{\eta^3\text{ - }\overline{C(O)–\mathit{C}(Ph)–\mathit{C}(H)–\mathit{C}(Ph)–C}(H)–C(O)–C_5Me_5\}]\cdot CH_2Cl_2$ (**3**·CH_2Cl_2)

Empirical formula	$WO_4C_{36}H_{34}\cdot CH_2Cl_2$
Formula weight	799.45
Temperature (K)	293
Space group	$P2_1/c$ (no. 14)
Unit cell dimensions	
a (Å)	17.278(2)
b (Å)	12.3774(9)
c (Å)	15.331(2)
β (°)	92.372(8)
V (Å^3)	3275(1)
Z	4
Absorption coefficient (cm^{-1})	38.04
2θ range (°)	4.0–45.0
Data collected	4527
Data with $I > 3.0\sigma(I)$	3315
Unique data	4527
[a]R	0.032
[b]R_w	0.040

[a] $R = \Sigma|F_o - F_c|/\Sigma F_o$.

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

Table 2
Selected bond distances (Å) of **3**·CH_2Cl_2 with e.s.d.s in parentheses

Atom 1	Atom 2	Distance
W	C(1)	2.345(6)
W	C(4)	2.350(6)
W	C(5)	2.164(6)
W	C(61)	1.924(7)
W	C(71)	1.943(9)
O(21)	C(2)	1.204(8)
O(30)	C(30)	1.197(7)
O(61)	C(61)	1.174(8)
O(71)	C(71)	1.155(9)
C(1)	C(2)	1.491(9)
C(1)	C(5)	1.419(8)
C(1)	C(11)	1.479(9)
C(2)	C(3)	1.540(9)
C(3)	C(4)	1.550(8)
C(3)	C(30)	1.529(9)
C(4)	C(5)	1.439(8)
C(4)	C(41)	1.503(8)
C(30)	C(31)	1.526(9)

Table 3
Selected bond angles (°) of **3**·CH_2Cl_2 with e.s.d.s in parentheses

Atom 1	Atom 2	Atom 3	Angle
C(61)	W	C(71)	83.0(3)
C(2)	C(1)	C(11)	124.0(6)
O(21)	C(2)	C(1)	127.5(6)
C(1)	C(2)	C(3)	107.5(5)
C(2)	C(3)	C(30)	110.4(5)
C(3)	C(4)	C(5)	106.2(5)
C(5)	C(4)	C(41)	116.9(5)
O(30)	C(30)	C(3)	120.6(6)
C(3)	C(30)	C(31)	118.6(6)
W	C(71)	O(71)	175.7(7)
C(2)	C(1)	C(5)	107.6(5)
C(5)	C(1)	C(11)	124.6(5)
O(21)	C(2)	C(3)	124.8(6)
C(2)	C(3)	C(4)	101.7(5)
C(4)	C(3)	C(30)	121.0(5)
C(3)	C(4)	C(41)	121.5(5)
C(1)	C(5)	C(4)	108.8(5)
O(30)	C(30)	C(31)	120.6(6)
W	C(61)	O(61)	175.2(6)

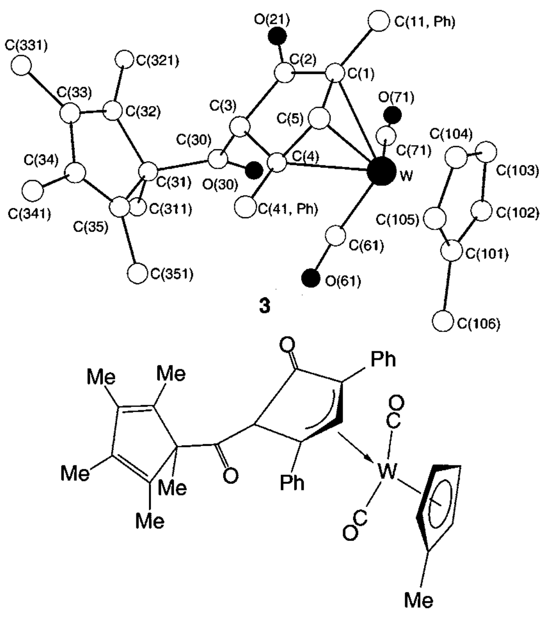

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Fig. 2. X-ray structure of **3**, showing the labeling scheme used, and a sketch of the complex.

appropriate for the bond orders depicted in the sketch and are unremarkable, some further comments about the tungsten–allylic carbon bond lengths are in order.

The *long–short–long* pattern observed for the outer–inner–outer carbon to tungsten distances (respectively) is not necessarily fully explained by steric repulsion effects, despite the fact that C(5) carries a hydrogen atom, while C(1) and C(4), the outer allylic carbon atoms, bear phenyl groups. Asymmetric bonding is not unusual for π-allylic ligands coordinated to various metals [6] and tungsten is no exception. In a γ-lactone species which is linked in a π-allylic fashion to a [W(CO)$_2$(η-C$_5$H$_5$)] unit, for example, the central carbon–tungsten bonds, and the mean terminal carbon-to-tungsten distances are 2.24 and 2.31, respectively, a *long–short–long* bonding pattern [7]. In contrast, the same manuscript describes a related allylic complex which contains a *short–short–long* set of W–C distances (2.252(7), 2.251(6) and 2.321(6), respectively). Two structurally characterized [W(CO)$_2$(substituted allyl)(η-C$_5$H$_5$)] complexes show a *long–short–long* pattern for the W–C$_{\text{allyl}}$ bond lengths; in the other two species reported in the same article, the bonds exhibit a *short–short–long* pattern in one molecule and are approximately equal in the other [8]. In another recent structural report of a substituted allyl moiety, bonded to a [W(CO)$_2$(η-C$_5$H$_5$)] group, the W–C$_{\text{allyl}}$ bonds found in the complex [W$_2$(CO)$_5$(μ-η^1,η^3-CH$_2$C(O)-C$_3$H$_4$)], are statistically the same, averaging around 2.28 Å [9]. As a final example, the electronically very different complex [W$_2$(η^3-C$_5$H$_4$Me)$_2$(NMe$_2$)$_4$] contains shorter central carbon–tungsten distances (2.37 Å, mean) than the other W–C$_{\text{allyl}}$ bonds (2.49 Å, mean) [10]. Clearly, allylic carbon-to-metal bonding distances are highly variable and not easily explained.

2.2. Spectroscopic data

The ^{1}H-NMR spectra of solutions of **3** are in accord with its solid-state structure as established by the X-ray diffraction study, but isomers are present in solution. Normal resonances for aromatic η-C$_5$*H*$_4$Me and Ph signals were observed, but six inequivalent methyl resonances were also noted, consistent with a η-C$_5$H$_4$*Me* and five *Me* signals of a C$_5$Me$_5$ group. Some of the latter signals were broad at 20 °C, indicating that dynamic behavior was taking place at ambient temperatures. As the temperature was lowered from 20 to − 30 °C, in ten-degree steps, the chemical shifts of the broad signals shifted slightly as they sharpened. The molecule's dynamic behavior likely arises from the C$_5$Me$_5$ group, which could undergo a series of sigmatropic shifts leading to the observed broadening of its *Me* resonances. The C*H* proton adjacent to the C$_5$Me$_5$ ligand is also broadened, as this proton is coupled to one of the *Me* resonances. Conformational changes of the allylic group (*endo*- and *exo*- with respect to the η-C$_5$H$_4$Me group) are also possible in principle, but this is not believed to occur here, as only the C$_5$Me$_5$ signals undergo changes with temperature.

The mass spectra of **3** showed a parent ion whose *m*/*z* ratio and isotopic envelope were consistent with its formulation as [W(CO)$_4$(PhC$_2$H)$_2$(C$_5$H$_4$Me)(C$_5$Me$_5$)]. IR data indicated that there are two terminal and two low frequency ketonic or acyl CO ligands in the molecule. Shoulders that were observed on some of these ν(CO) bands also suggested that isomers were present in solution.

2.3. Comments on the formation of complexes 1 and 3

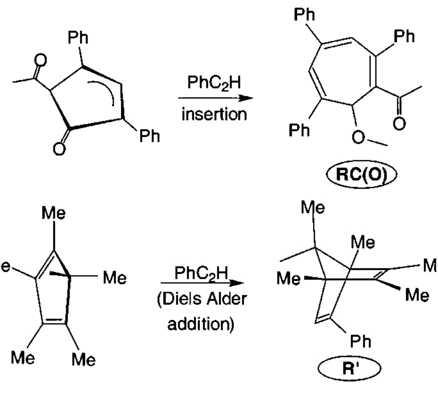
We have no hard kinetic or mechanistic data for the formation of **3**. However, it appears that nickel does play a crucial role in its synthesis as well as that of complex **1** and of its methylcyclopentadienyl analog **1′**. Despite repeated attempts, all reactions of the free hydrocarbon ligand C$_5$Me$_5$H and/or the C$_5$Me$_5^-$ anion with PhC$_2$H and [W(CO)$_3$(η-C$_5$H$_4$Me)]$^-$ in the absence of nickel failed to produce even traces of **1′** or of **3**. Though alkyne–acyl coupling has been previously observed on a tungsten center [11], nickel is well known to be an efficient co-oligomerization catalyst for unsaturated organic species with CO: both linear and cyclic oligomers have been produced from nickel complexes and alkenes, alkynes or nitriles with CO [12]. As nickel appears to be essential in the formation of **1′** and **3**, we believe that the PhC$_2$H–CO coupling reaction is mediated by a nickel species that is formed following the reductive elimination and transfer of a C$_5$Me$_5$ ligand to the tungsten atom.

Complex **3** is structurally related to **1′**, but studies to show that **3** is transformed into **1′**, while negative, are inconclusive; the small quantities of **3** obtained precluded definitive mechanistic studies. While the insertion of another PhC_2H ligand into the cyclopentenyl group of **3** would afford the seven-membered tropone ring system found in **1′**, a likelier scenario would be the involvement of nickel in this process. The five-membered $\overline{C(O)–\mathit{C}(Ph)–\mathit{C}(H)–\mathit{C}(Ph)–C(H)}$ ring seen in complex **3** probably formed part of a nickelacycle: one can speculate that reductive elimination of the organic fragment and of the nickel atom could then take place followed by coordination of the ring onto the tungsten atom as observed in **3**. Insertion of one more PhC_2H ligand into the five-membered ring would afford the tropone group seen in **1′**. If this scenario is correct, then both **1′** and **3** would be derived from a common nickelacycle intermediate. Scheme 1 shows relationships between organic groups present in complexes **1′** and **3**.

The C_5Me_5 group in **3** is primed to undergo a Diels–Alder reaction with phenylacetylene to form the C_5Me_5–PhC_2H Diels–Alder adduct seen in **1** and **1′**. We and others have noted the surprising relative lability of η-C_5Me_5 ligands on nickel and on other metals [4,13]. In addition to references cited earlier [4], a η^1-C_5Me_5 platinum species that resulted from η^5-C_5Me_5 ligand slippage has been structurally characterized, and Pt(η^3-C_5Me_5) intermediates were spectroscopically observed [13]. Indeed, the isolation of species such as **1**, **1′**, **2** and **3**, all of which result from η^5-C_5Me_5 to η^0-C_5Me_5 transformations, attests to the ease of such processes.

3. Conclusions

The diketone species **3** was isolated from the reaction of excess PhC_2H with $[W(CO)_3(\eta$-$C_5H_4Me)]^-$ and $[Ni(CO)I(\eta$-$C_5Me_5)]$. Complex **3** was never obtained in the absence of nickel. It contains a five membered ring formed by coupling two PhC_2H ligands with a CO ligand: this ring is linked to a ketonic carbonyl group, which in turn is bonded to a C_5Me_5 moiety. The source of this ligand must have been the nickel atom; this reaction thus affords another example of η-C_5Me_5 ligand lability. Complex **3** and the tungsten η^2-ketone complex **1′** probably share a common intermediate.



Scheme 1. Relationships between organic groups present in complex **3** (left) and in complexes **1** and **1′** (right). R and R′ are the two groups that make up the ketone in **1** and **1′**.

4. Experimental

4.1. General techniques

All manipulations were carried out under an N_2 atmosphere using standard Schlenk tube techniques and flame-dried glassware. Toluene, hexanes, THF, and Et_2O were distilled from blue or purple Na–benzophenone ketyl solutions while methylene chloride was distilled over CaH_2. Deuterated NMR solvents were stored over molecular sieves, and were subjected to three freeze–thaw degassing cycles prior to use. Reagent grade chemicals were used; PhC_2H and $KBHEt_3$ were purchased from Aldrich and used as received. $[Ni(CO)I(\eta$-$C_5Me_5)]$ [14] and $[W(CO)_3(\eta$-$C_5H_4Me)]_2$ [15] were synthesized using standard procedures.

4.2. Spectroscopic measurements

IR spectra were obtained on an IBM IR-32 FT spectrometer. Mass spectra were obtained on JEOL JMS-AX505 HA using chemical ionization (CI) with isobutane as the ionization source. ^1H- and ^{13}C-NMR spectra were recorded on a G.E. GN-300 instrument at 300 and 75 MHz, respectively; $[Cr(acac)_3]$ (≈ 0.01 M) was added to ^{13}C-NMR samples as a shiftless relaxation agent.

4.3. Synthesis of **3**

A THF solution of freshly prepared $K^+[W(CO)_3(\eta$-$C_5H_4Me)]^-$ (from reductive cleavage of $[W(CO)_3(\eta$-$C_5H_4Me)]_2$ (410 mg, 0.59 mmol) with $KHBEt_3$ (1.20 ml of 1.00 M THF) solution) was added dropwise to a toluene suspension of freshly prepared $[Ni(CO)I(\eta$-$C_5Me_5)]$ (412 mg, 1.18 mmol) at −78 °C. Excess PhC_2H (0.5 ml) was added and the now dark-brown mixture was warmed to room temperature (r.t.) and reduced to dryness in vacuum. The residue was extracted with toluene, filtered through a Celite pad and passed through a silica gel column. Two major reddish-brown bands containing the previously reported [2e] nickelacycle complex $[(\eta$-$C_5Me_5\overline{Ni–\{\mu\text{-}C(H)=C(Ph)–C}(O)\}W(CO)_2(\eta$-$C_5H_4Me)]$ (Ni–W) and the dimetallacycle species $[(\eta\text{-C5Me5})\overline{\text{Ni–C(Ph)=C(H)–C(O)–W}}\text{-}(CO)_2(\eta\text{-}C_5H_4Me)]$ (Ni–W), respectively, were eluted with toluene. A yellow band, which contained **3**, was collected using a toluene–ether mixture. At least three other minor bands followed: **1′** (purple–grey), the μ-alkyne complex $[(\eta\text{-}C_5Me_5)Ni(\mu\text{-}\eta^2,\eta^2\text{-}PhC_2H)W(CO)_2\text{-}(\eta\text{-}C_5H_4Me)]$ (Ni–W), and traces of other unidentified products. Orange microcrystals of **3** were obtained from a toluene–hexane mixed solvent system at −20 °C (51 mg, 6%). Anal. Expt (calc.) for $C_{36}H_{34}O_4W$: C, 60.55 (60.43), H, 4.79 (4.45)%.

*4.4. Spectroscopic data for complex **3***

MS; *m/e*(CI using isobutane) : 715 ($[M]+H^+$), 686 ($([M]-CO)^+$). IR (cm−1): *ν*(CO) 1991 (w, sh), 1973 (s), 1928 (w, sh), 1908 (s), 1712 (w), 1683 (w, sh), 1676 (m). ^{1}H-NMR (Acetone-d_6, 20 °C): δ 7.63, 7.30–7.12 (m, Ph), 5.87 (d, C*H*, $J_{HH}=0.77$ Hz), 5.65 (C*H*, v br), 5.47 (m, H, C_5H_4Me), 5.43 (br, H, C_5H_4Me), 5.37 (m, H, C_5H_4Me), 4.95 (v br, H, C_5H_4Me), 1.84 (br, Me), 1.80 (v br, 2*Me*), 1.78 (br, *Me*), 1.71 (br, *Me*), 1.04 (br., *Me*). (Acetone-d_6, −30 °C): *δ* 7.63, 7.29, 7.16 (m, Ph), 5.87 (d, C*H*, $J_{HH}=0.77$ Hz), 5.63 (d, C*H*, $J_{HH}=0.77$ Hz), 5.52 (m, *H*, C_5H_4Me), 5.47 (m, 2H, C_5H_4Me), 4.93 (m, *H*, C_5H_4Me), 1.82 (m, *Me*), 1.78 (m, *Me*), 1.73 (C_5H_4Me), 1.72 (m, *Me*), 1.00 (*Me*), 0.94 (br m, *Me*). ^{13}C-NMR ($CHCl_3$-d_1, −30 °C): *δ* 223.7, 221.5 (W*C*O), 206.8 (*C*O), 193.7 (*C*O), 139.9, 139.7, 139.5, 138.6 (olefinic *C*Me), 135.1, 134.9, (C_{ipso}, Ph), 129.4, 128.3, 127.6, 125.5 (*C*(2), *C*(3), Ph), 126.7, 126.6 (*C*(4), Ph), 109.0 (C(1), C_5H_4Me), 96.2, 92.3, 92.1, 90.7 (C_5H_4Me, other aromatic *C*), 72.4 (C(O)*C*HC(O)), 66.3 ($J_{WC}=$ 12.7 Hz), 65.0 (*C*Ph, $J_{WC}=9.5$ Hz), 61.4 (*C*H, $J_{WC}=$ 14.2 Hz), 59.3 (aliphatic *C*Me), 15.8, 13.5, 12.2, 11.6, 11.0 (*Me*), 9.6 (C_5H_4Me).

4.5. X-ray data collection

An orange brick of **3**, recrystallized from a CH_2Cl_2–hexane mixture, was mounted in a glass capillary tube on an Enraf–Nonius CAD4 diffractometer equipped with a graphite crystal incident beam monochromator [16]. Cell constants and an orientation matrix were obtained from least-squares refinement of 25 reflections with $19<\theta<21°$, measured by the computer-controlled diagonal slit method of centering. Systematic absences of $h0l$, $l=2n$ and $0k0$, $k=2n$ followed by successful least-squares refinement confirmed the space group as $P2_1/c$ (#14).

Lorentz and polarization corrections and an empirical absorption correction were applied [17]. Hydrogen atoms were located and added to the structure factor calculations but were not refined. The structure was refined in full-matrix least-squares where the function minimized was $\Sigma w(|F_o|-|F_c|)^2$ with the weight w having terms between 0.020 and 1.0 [18]. Scattering factors were from Cromer and Waber [19]; anomalous dispersion effects [16,20] were included in F_c. All calculations were performed on a VAX computer using SDF/VAX software [21].

5. Supplementary material

Crystallographic data for the structural analysis (excluding structure factor listings) have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 159536 for compound **3**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

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