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Preliminary communication

Ansa-[(2,2-bis-η-cyclopentadienyl)propane]-molybdenum and -tungsten chemistry and related studies

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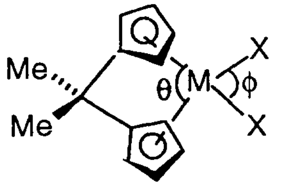
Abstract

The compounds [M(η-C$_5$H$_4$-CMe$_2$μ-C$_5$H$_4$)X$_2$] (where M = Mo and X$_2$ = H$_2$, Cl$_2$, Me$_2$, PhH; M = W and X$_2$ = H$_2$, Cl$_2^*$, Me$_2$, Me(PhCO$_2$), MeH) and [Mo(η-C$_5$H$_4$C(CH$_2$)$_4$-η-C$_5$H$_4$)X$_2$] (X = H, Cl*) are described. For the complexes marked with an asterisk the crystal structures are reported. These *ansa*-bridged compounds exhibit substantially different reactivities from those of the unbridged analogues.

Keywords: Molybdenum; Tungsten; *Ansa*-bridging; 2,2-bis-η-cyclopentadienyl(propane)

Recently there has been considerable interest in the chemistry of the so-called stereorigid, *ansa*-bridged bis-η-cyclopentadienyl derivatives of the Group IV metals [1]; e.g. {*ansa*-M(η-C$_5$H$_4$-ER$_2$-η-C$_5$H$_4$)]Cl$_2$} (where M = Ti, Zr, Hf and E = Si, C [2]), since these compounds are precursors for homogeneous catalyst systems for α-olefin polymerisation [3]. The structural changes associated with the presence of the single atom *ansa*-bridged compounds have been established; for example, a decrease in the bending angle θ. (The bending angle is defined as the angle between the lines from the metal centre normal to the planes of the η-cyclopentadienyl rings.)



Little is known of the electronic consequences of the introduction of such an *ansa* bridge. Smith and Brintzinger have studied the chemistry of the {M[(η-C$_5$H$_4$-(CH$_2$)$_2$-η-C$_5$H$_4$)]}[M = Ti, V] systems and suggested that differences in reactivity between these and the non-bridged Ti(η-C$_5$H$_5$)$_2$ system may reflect the inability of *ansa*-bridged system to achieve a parallel ring structure [4]. Thus, we decided to compare the well-known and very extensive chemistry of the bent bis-η-cyclopentadienyl derivatives of molybdenum and tungsten [5] with that of analogues containing an *ansa*-CR$_2$ system; for example, the derivatives of the moiety M[(η-C$_5$H$_4$)CMe$_2$(η-C$_5$H$_4$)], where M = Mo or W.

Recently the use of the compound [WCl$_4$dme] (dme = 1,2-dimethoxyethane) for the synthesis of bis-η-cyclopentadienyl-tungsten compounds has been described [6]. We have found that treatment of [MoCl$_4$ dme] with [Li(C$_5$H$_4$)CMe$_2$(C$_5$H$_4$)Li] in diethyl ether gives red–brown [Mo(η-C$_5$H$_4$-CMe$_2$-η-C$_5$H$_4$)Cl$_2$] (**1**) in 52% yield. The red–brown tungsten analogue [W(η-C$_5$H$_4$-CMe$_2$-η-C$_5$H$_4$)Cl$_2$] (**2**) was prepared similarly, in 64% yield, using [WCl$_4$dme]. Typically the new *ansa* compounds **1** and **2** were prepared on a 6–8 g scale.

Treatment of **1** and **2** with LiAlH$_4$ in diethyl ether gave the corresponding pale yellow crystalline dihydrides [M(η-C$_5$H$_4$-CMe$_2$-η-C$_5$H$_4$)H$_2$], where M = Mo (**3**) and W (**4**) in ca. 30 and 40% yield respectively. The compounds **1–4** clearly will be synthons for an extensive development of the chemistry of the M(η-C$_5$H$_4$-CMe$_2$-η-C$_5$H$_4$) moiety. We have made a preliminary study of their chemistry and find substantial differences from that of the non-*ansa* analogues.

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Thus, photolysis of a solution of **3** in benzene using a medium pressure mercury lamp for 100 h gave > 80% yield of the phenyl hydrido complex [Mo(η-C_5H_4-CMe_2-η-C_5H_4)PhH], **5**. However, during prolonged photolysis of **4** in benzene for 100 h, monitoring by ^{1}H-NMR spectroscopy showed there was no reaction.

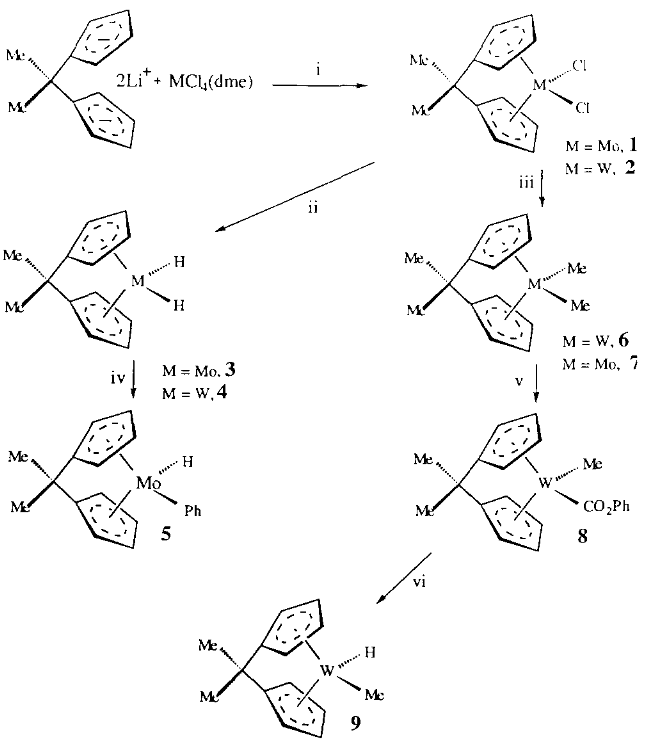
Treatment of a suspension of **1** and **2** in toluene with dimethylzinc gave the expected dimethyl derivatives [W(η-C_5H_4-CMe_2-η-C_5H_4)Me_2] (**6**) and [Mo(η-C_5H_4-CMe_2-η-C_5H_4)Me_2] (**7**) in ca. 45 and 30% yield, respectively. The tungsten derivative was treated with benzoic acid to give [W(η-C_5H_4-CMe_2-η-C_5H_4)Me (CO_2Ph)] (**8**) and this was further treated with Na[$AlH_2(OCH_2CH_2OMe)_2$] to give the methyl hydrido compound [W(η-C_5H_4-CMe_2-η-C_5H_4)MeH] (**9**). When a solution of **9** in benzene was heated for 10 h at 80°C, ^{1}H-NMR spectroscopy showed that no reaction occurred.

There are three striking differences between the reactions of the *ansa*-bridged compounds described above and those of the non-bridged bis-η-cyclopentadienyl analogues. First, photolysis of [Mo(η-C_5H_5)$_2$$H_2$] in benzene gives only the dimer [Mo(η-C_5H_5)(μ-σ,η-C_5H_4)]$_2$ [7]. The phenyl hydrido complex [Mo(η-C_5H_5)$_2$PhH] is not formed, and neither can this compound be made by alternative routes available to the tungsten analogue. Second, photolysis of [W(η-C_5H_5)$_2$$H_2$] in benzene readily gives the phenyl hydrido complex [W(η-C_5H_5)$_2$PhH] [8], whilst under the same conditions **4** is completely unreactive. Third, in contrast to **9**, the methyl hydrido complex [W(η-C_5H_5)$_2$MeH] is thermally unstable above ca. 40°C and decomposes with the evolution of methane and formation of tungstenocene, a reactive intermediate [9] which can insert into carbon–hydrogen bonds [8]. For example, thermolysis of [W(η-C_5H_5)$_2$MeH] in benzene give the phenyl hydrido species [W(η-C_5H_5)$_2$PhH] [9].

The above observations show that the *ansa*-bridged compounds [M(η-C_5H_4-CMe_2-η-C_5H_4)XY] (where M = Mo, XY = H_2 (**3**); PhH (**5**); and M = W, XY = H_2 (**4**); MeH (**9**)) have a much greater stability towards reductive elimination of XY, under either thermal or photochemical conditions as appropriate, than the corresponding non-bridged bis-η-cyclopentadienyl analogues [M(η-C_5H_5)$_2$XY]. The new reactions and structures proposed for compounds **1**–**9** are shown in Scheme 1 [10].

The compounds [Mo(η-C_5H_4-$C(CH_2)_4$-η-C_5H_4)X_2], X = Cl (**10**) and X = H (**11**) were prepared using [Li(C_5H_4)-$C(CH_2)_4$-(C_5H_4)Li] by a procedure analogous to that used for **1** and **3**.

The crystal structures of [W(η-C_5H_4-CMe_2-η-C_5H_4)Cl_2] (**2**) and [Mo(η-C_5H_4-$C(CH_2)_4$-η-C_5H_4)Cl_2] (**10**) have been determined [11] and distances and angles pertinent to the discussion below are given in Tables 1 and 2, together with related data for [W(η-C_5H_4-CMe_2-η-C_5H_4)H_2] (**4**), [Mo(η-C_5H_4-CMe_2-η-C_5H_4)H_2] (**3**) and for the non-bridged analogues. The structures of **2** and **10** are shown in Fig. 1. The data in Tables 1 and 2 show that, as expected, the bending angle θ is substantially smaller in the *ansa*-bridged compounds than in the non-bridged analogues and, therefore, the structures of intermediate 16-electron fragments M(η-C_5H_4-CMe_2-η-C_5H_4) would be substantially changed from a parallel ring structure found



Scheme 1. Reagents and conditions: (i) in diethyl ether at room temperature; (ii) $LiAlH_4$ in diethyl ether at −78°C, 30–40%; (iii) $ZnMe_2$ in toluene −78°C; (iv) $h\nu$, benzene; (v) $PhCO_2H$ in petroleum ether (b.p. 100–120°C) at reflux; (vi) Na[$AlH_2(OCH_2CH_2OCH_3)_2$] in benzene at room temperature.

Table 1
Selected distances (Å) and angles (°). M = W in **2**; M = Mo in **10**

Compound	**2**	**10**
M–X	2.452(2)	2.4621(4); 2.4694(4)
M–Cp(cent)	1.948	1.957; 1.958
M–Cp(l)	1.939	1.949; 1.950
M–C	2.224–2.452(7) av.	2.226–2.382(2) av.
C–C	1.38(1)–1.462(8) av.	1.390–1.446(3) av.
C(Cp)–C(bridge)	1.526(7)	1.508(2); 1.516(2)
X–M–C(ϕ)	81.85(8)	82.66(2)
X–M–Cp(cent)	110.7 109.4	110.6 109.5 109.6 111.1
Cp(cent)–M–Cp(cent)	126.0	125.3
Bending angle (θ)	115.2	114.6
Cp–Cbr–Cp	93.8(6)	93.6(1)
Conformation	eclipsed	eclipsed

Table 2
Selected distances (Å) and angles (°)

Compound [1]	X–M–X(ϕ)	Bending angle (θ)	Ref.
[$MoCp_2Cl_2$]	82.0(2) 82.0(2)	130.9 130.2	[19]
[$MoCp_2H_2$]	75.5(3)	145.8	[20]
[$Mo\{C(C_4H_8)(C_5H_4)_2\}Cl_2$]	82.66(2)	114.6	[21]
[$Mo\{C(CH_3)_2(C_5H_4)_2\}H_2$]	80.3(2.8)	121	[22]
[$W\{C(CH_3)_2(C_5H_4)_2\}Cl_2$]	81.85(8)	115.2	[21]
[$W\{C(CH_3)_2(C_5H_4)_2\}H_2$]	95.5(4.0)	120.3	[22]

[1] Cp = η-C_5H_5.

for the unbridged [$M(\eta$-$C_5H_5)_2$], where M = Cr, W [12]. In contrast the Cl–M–Cl angles (ϕ) for **1**, **2** and **10** and the non-bridged [$Mo(\eta$-$C_5H_5)_2Cl_2$] are closely similar. Also, in both **2** and **10**, the bond angle at the C(6) atom of ca. 94–97° is significantly below the tetrahedral value of 109.5°. The photoelectron spectrum of [$W(\eta$-C_5H_4-CMe_2-η-$C_5H_4)H_2$] shows that the ionisation energy associated with the d^2 electron is 6.47 eV, and is closely similar to that for the non-bridged analogue [12]. It appears that the changes in electron energies associated with changes of θ [13] are not reflected in the X–M–X grouping. In conclusion, the *ansa*-bridged compounds **3–5** and **9** are much more stable towards reductive elimination reactions than are the related non-bridged compounds. It seems probable that, as suggested by Smith et al. for *ansa*-bis-η-cyclopentadienyltitanium compounds [1], the increased stability reflects the inability of the 16-electron moiety $M(\eta$-C_5H_4-CMe_2-η-$C_5H_4)$ to adopt a parallel ring sandwich structure.

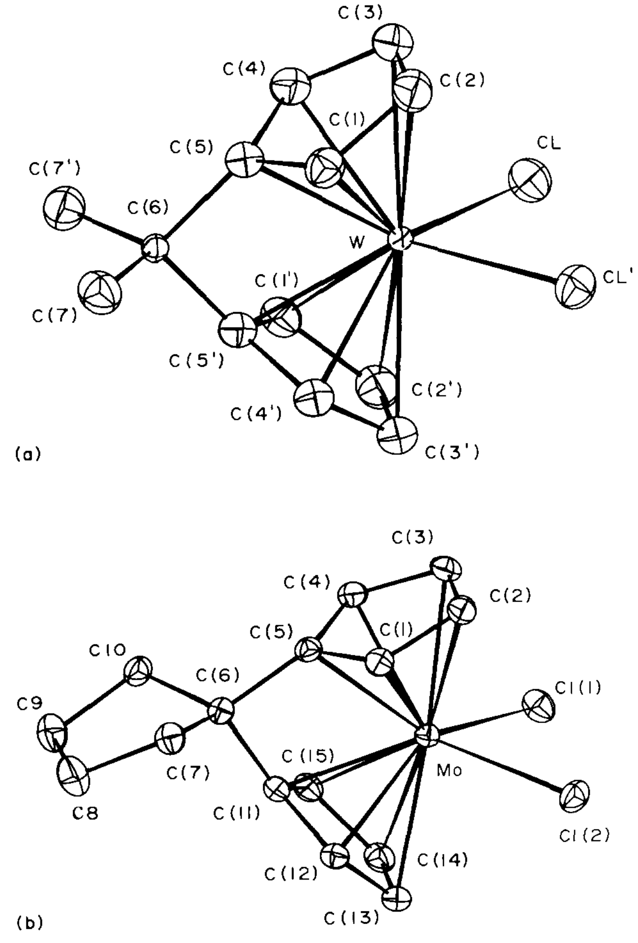


Fig. 1. Molecular structure of (a) **2** and (b) **10**.

Acknowledgements

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[10] Selected spectroscopic data: NMR data recorded at 300 Mz (^1H) or at 75 MHz ($^{13}C\{^1H\}$) and given as δ relative to $SiMe_4$. Mass spectra (MS) measured using electron-impact techniques. Satisfactory microanalysis have been obtained for all new compounds.

Selected NMR, MS and IR data:

1 [$Mo\{C(CH_3)_2(C_5H_4)_2\}Cl_2$]: ^1H, CD_2Cl_2: 6.24 (4H, m, C_5H_4), 5.02 (4H, m, C_5H_4), 0.89 (6H, s, CH_3). IR: Mo–Cl, 320m, 300m, 270m.

2 [$W\{C(CH_3)_2(C_5H_4)_2\}Cl_2$]: ^1H, CD_2Cl_2: 5.93 (4H, m, C_5H_4), 5.43 (4H, m, C_5H_4), 0.83 (6H, s, CH_3). MS: 426 (M^+). IR: W–Cl, 320m, 300m, 270m.

3 [$Mo\{C(CH_3)_2(C_5H_4)_2\}H_2$]: ^1H, C_6D_6: 4.96 (4H, m, C_5H_4), 4.08 (4H, m, C_5H_4), 0.54 (6H, s, CH_3), −4.77 (2H, s). ^{13}C, C_6D_6: 88.6. (s; C_5H_4), 70.7 (s; C_5H_4), 51.3 (s; C_5H_4), C_{ipso}), 33.7 (s; $C(CH_3)_2$), 21.7 (s; CH_3). IR: W–H, 1760s, 1750s.

4 [$W\{C(CH_3)_2(C_5H_4)_2\}H_2$]: ^1H, C_6D_6 ppm: 4.89 (4H, m, C_5H_4), 4.02 (4H, m, C_5H_4), 0.46 (6H, s, CH_3), −7.33 (2H, s, *J*(WH) = 92). ^{13}C, C_6D_6: 86.6. (s; C_5H_4), 64.8 (s; C_5H_4), 43.3 (s; C_5H_4). C_{ipso}), 33.2 (s; $C(CH_3)_2$, 22.1 (s; CH_3). MS: 355 (M^+–H_2). IR: W–H, 1833s, 1823s.

5 [$Mo\{C(CH_3)_2(C_5H_4)_2\}(H)(C_6H_5)$]: ^1H, $(CD_3)_2CO$: 7.59 (2H, d, C_6H_5), 7.36 (1H, m, C_6H_5), 6.67 (2H, m, C_6H_5), 5.48

(2H, m, C_5H_4), 5.13 (2H, m, C_5H_4), 4.45 (2H, m, C_5H_4), 4.27 (2H, m, C_5H_4), 1.20 (3H, s, $C(CH_3)_2$, 0.87 (3H, s, $C(CH_3)_2$, −4.60 (1H, s). ^{13}C, $(CD_3)_2CO$: 148.8 (s; C_6H_5); 128.5 (s; C_6H_5); 125.9 (s; C_6H_5); 123.2 (s; C_6H_5); 107.6 (s; C_5H_4), 90.2 (s; C_5H_4), 76.6 (s; C_5H_4), 71.2 (s; C_5H_4), 58.6 (s; C_5H_4), C_{ipso}), 22.3 (s; $C(CH_3)_2$), 22.2 (s; $C(CH_3)_2$). IR, Mo–H 1790. MS: 343 (M^+).

6 $[W\{C(CH_3)_2(C_5H_4)_2\}(CH_3)_2]$: ^1H, C_6D_6: 4.46 (4H, m, C_5H_4), 4.10 (4H, m, C_5H_4), 0.44 (6H, s, $C\{(CH_3)_2\}$, 0.17 (6H, s, CH_3) ^{13}C, C_6D_6: 104.8 (s; C_5H_4), 67.8 (s; C_5H_4), 52.2 (s; C_5H_4, C_{ipso}), 30.9 (s; $C(CH_3)_2$), 22.7 (s; $C(CH_3)_2$), −22.7 (s; CH_3). MS: 386 (M^+).

7 $[Mo\{C(CH_3)_2(C_5H_4)_2\}(CH_3)_2]$: ^1H, C_6D_6: 4.48 (4H, m, C_5H_4), 4.11 (4H, m, C_5H_4), 0.51 (6H, s, $C(CH_3)_2$, 0.13 (6H, s, CH_3). ^{13}C, C_6D_6: 106.3 (s; C_5H_4), 73.4 (s; C_5H_4), 59.2 (s; C_5H_4 C_{ipso}), 31.6 (s; $C(CH_3)_2$, 21.9 (s; $C(CH_3)_2$), −10.7 (s; CH_3).

8 $[W\{C(CH_3)_2(C_5H_4)_2\}(CH_3)(O_2CPh)]$: ^1H, C_6D_6: 8.48 (2H, d, C_6H_5), 7.20 (3H, m, C_6H_5), 5.32 (2H, m, C_5H_4), 5.15 (2H, m, C_5H_4), 4.82 (2H, m, C_5H_4), 3.99 (2H, m, C_5H_4), 0.55 (3H, s, $C(CH_3)_2$, 0.46 (3H, s, $C(CH_3)_2$, −0.01 (3H, s, CH_3). ^{13}C, C_6D_6, ppm: 173.5 (s; CO_2Ph); 135.6 (s; C_6H_5); 130.7 (s; C_6H_5); 130.4 (s; C_6H_5); 130.2 (s; C_6H_5); 114.1 (s; C_5H_4), 106.7 (s; C_5H_4), 74.7 (s; C_5H_4), 70.1 (s; C_5H_4), 59.5 (s; C_5H_4), C_{ipso}), 29.9 (s; $C(CH_3)_2\}$ 22.4 (s; $C(CH_3)_2$, 21.6 (s; $C(CH_3)_2$), −20.5 (s; CH_3).

9 $[W\{C(CH_3)_2(C_5H_4)_2\}(CH_3)H]$: ^1H, C_6D_6: 5.13 (2H, m, C_5H_4), 4.41 (4H, m, C_5H_4), 3.79 (2H, m, C_5H_4), 0.57 (3H, s, $C(CH_3)_2$, 0.28 (3H, s, $C(CH_3)_2$, 0.12 (3H, s, CH_3), −6.30 (1H, s, $J(WH) = 62$). ^{13}C, C_6D_6: 104.5 (s; C_5H_4), 86.6 (s; C_5H_4), 70.5 (s; C_5H_4), 63.3 (s; C_5H_4), 47.7 (s; C_5H_4), C_{ipso}), 31.9 (s; $C(CH_3)_2$), 22.4 (s; $C(CH_3)_2$), 22.3 (s; $C(CH_3)_2$, −37.1 (s; CH_3). MS: 370 (M^+).

10 $[Mo\{C(C_4H_8)(C_5H_4)_2\}Cl_2]$: ^1H, CD_2Cl_2: 6.24 (4H, m, C_5H_4), 4.95 (4H, m, C_5H_4), 1.69 (4H, m, CH_2), 1.37 (4H, m, CH_2).

11 $[Mo\{C(C_4H_8)(C_5H_4)_2\}H_2]$: ^1H, C_6D_6: 4.98 (4H, m, C_5H_4), 4.08 (4H, m, C_5H_4), 1.42 (4H, m, CH_2), 1.07 (4H, m, CH_2), −4.74 (2H, s). ^{13}C, C_6D_6, 88.7 (s; C_5H_4), 71.8 (s; C_5H_4), 50.6 (s; C_5H_4), C_{ipso}), 45.7 (s; $C\{C_4H_8\}$), 33.4 (s; CH_2), 23.1 (s; CH_2).

Crystal data for **2**. $C_{13}H_{14}Cl_2W$, $M = 425.01$, monoclinic, $a = 12.2010(9)$, $b = 10.7608(5)$, $c = 9.8770(8)$ Å, $\beta = 110.62(1)$, $V = 1213.7(2)$ Å^3, space group $C2/c$, $Z = 4$, $D_c = 2.33$ g cm^{-3}, $F(000) = 800$, $\mu = 101.37$ cm^{-1}. Crystal dimensions ca. 0.03 × 0.19 × 0.43 mm^3. 2923 measured reflections ($1.0 < \theta < 34°$, $-h$, h, $-l$, k, $-l$, l), 2473 unique (merging $R = 0.055$), 2043 with the $I > 4\sigma(I)$ in refinement (74 variables, observ./variab. = 27.6, weighting coefficients 15.0, −9.7, 10.5), maximum and minimum peaks in the final difference map 1.07 and −1.23 eÅ^{-3}, $R = 0.053$, $R_w = 0.060$.

Crystal data for **10**. $C_{15}H_{16}Cl_2Mo$, $M = 363.14$, triclinic, $a = 8.1632(8)$, $b = 8.3435(4)$, $c = 10.4484(4)$ Å, $\alpha = 70.58(1)$, $\beta = 75.99(1)$, $\gamma = 84.65(1)$, $U = 651.1(1)$ Å^3, space group $P\bar{1}$, $Z = 2$, $D_c = 1.85$ g cm^{-3}, $F(000) = 364$, $\mu = 13.76$ cm. Crystal dimensions ca. 0.06 × 0.16 × 0.34 mm^3. 3297 measured reflections ($1.0 < \theta < 27°$, $-h$, h, $-k$, k, $-l$, l), 2820 unique (merging $R = 0.012$), 2531 with the $I > 3\sigma(I)$ in refinement (163 variables, observ./variab. = 15.5, weighting coefficients 5.6, −2.5, 4.6), maximum and minimum peaks in the final difference map 0.40 and −0.36 eÅ^{-3}, $R = 0.019$, $R_w = 0.023$.

Data were collected at room temperature on an Enraf-Nonius CAD4 diffractometer (ω-2θ mode with the ω scan width = 0.77–0.79 + 0.34 tan θ, ω scan speed 1.4–10.1° min^{-1}, the ratio of the scanning rates $\omega/\theta = 1.2$, graphite-monochromated MoKα radiation, $\lambda = 0.71069$ Å).

For both structures corrections for Lorentz and polarization effects as well as empirical correction for absorption [14] based on azimuthal scan data were applied. The structures of **2** and **10** were solved by direct methods and refined by full-matrix least-squares technique with all non-hydrogen atoms in anisotropic approximation. In **10** all hydrogen atoms were located in the difference Fourier maps, in **2** all H-atoms were placed geometrically. For both structures, hydrogen atoms were included in the refinement with the fixed positional and thermal parameters. Chebyshev weighting scheme was applied [15]. Anomalous dispersion contributions were included in the calculated structure factors. An empirical absorption correction using the DIFABS [16] program was applied after isotropic convergence. Crystallographic calculations were carried out using the CRYSTALS [17] program package on Micro VAX 3800 computer. Neutral atom scattering factors were taken from the usual sources [18]. Additional material available from Cambridge Crystallographic Data Centre comprises atom coordinates, thermal parameters and remaining bond lengths and angles.

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