Journal of Organometallic Chemistry, 297 (1985) 341–348
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

OXIDATIVE ADDITION OF FURAN TO A TRIOSMIUM CLUSTER. THE CRYSTAL STRUCTURE OF $[HOs_3(CO)_{10}(\mu,\eta^2\text{-}C_4H_3O)]$

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(Received June 27th, 1985)

Summary

$[Os_3(CO)_{10}(NCMe)_2]$ reacts with furan with C–H activation, and oxidative addition of the furan to the decacarbonyltriosmium moiety to give the μ,η^2-furyl cluster compound $[HOs_3(CO)_{10}(\mu,\eta^2\text{-}C_4H_3O)]$. A crystal structure determination has shown this product to be a triosmium cluster with one Os–Os edge bridged simultaneously by a hydride atom and the furyl ligand. The latter is bonded asymmetrically with an Os–C σ-bond to one Os atom, with the second Os atom complexed weakly by one olefinic double bond, resulting in an overall μ,η^2 geometry ($P2_1/n$, a 9.499(1), b 15.515(2), c 12.881(2) Å, β 92.67(1)°, V 1896.3 Å^3, d_{calcd} 3.218 g/cm^3 for $Z = 4$, R_w 0.026 for 253 parameters and 2587 observations).

Introduction

The interactions of hydrocarbon moieties with the triosmium cluster framework have attracted considerable interest because of the possible significance of these reactions for catalytic processes. The weakly stabilized complex $[Os_3(CO)_{10}(NCMe)_2]$ provides a useful synthetic reagent for studying these reactions under mild conditions because of the ease of displacement of the acetonitrile ligand. In particular, C–H bond activation reactions on osmium clusters are well established for a substantial number of organic compounds, e.g. arenes [1–4], olefins [2], aldehydes [5], and trialkylamines [6,7], but the nature of the products is still often unpredictable. This applies especially to a heteroaromatic species like furan, which in principle can oxidatively add to the triosmium cluster in various ways: by coordination of the oxygen atom and *ortho*-metallation to give the μ-2-furyl cluster (**1**), by dehydrogenation in α and β position to give the dihydride (**2**), or by *ortho*-metallation and η^2-coordination of the furyl group (**3**).

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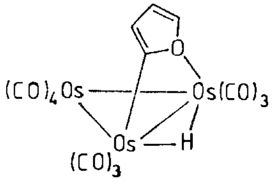

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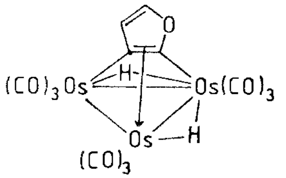

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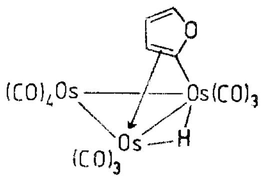
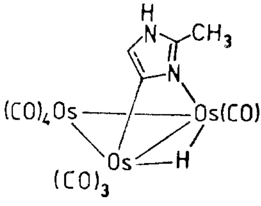


(3)

The structural types **1** and **2** are observed for the 2-methylimidazolyl ligand bound to a triosmium cluster [8] (structure **4**) and the μ_3-pyrrole-2,3-diyltriosmium complex [9] (structure **5**).



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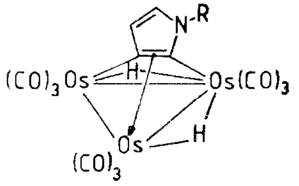

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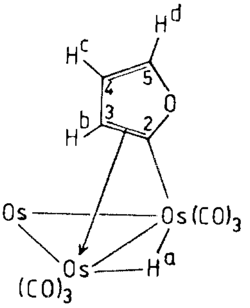
Results and discussion

Reaction of $[Os_3(CO)_{10}(NCMe)_2]$ with an excess of furan (L) at room temperature gave one major product (26% isolated yield), which was shown to have the stoichiometry $[Os_3(CO)_{10}L]$ as indicated by its mass spectrum (parent molecular ion m/e 924 related to ^{192}Os) and elemental analysis. On the basis of spectroscopic data structure **3** was assigned to this product. The IR spectrum is extremely similar to those reported for the μ-vinyl complexes $[Os_3H(CR^1{=}CR^2H)(CO)_{10}]$ [10,11]. Carbonyl region recorded in hexane: 2107w, 2071vs, 2058s, 2023vs, 2009s, 2004m, 2000m, 1992vw, 1986w cm^{-1}.

Complex **3** gave well separated ^{1}H NMR signals in $CDCl_3$ at 20°C (recorded at 250 MHz): δ 8.40 (H^d, d, J_{cd} 1.8 Hz), 8.05 (H^b, d, J_{bc} 3.2 Hz), 6.31 (H^c, dd, J_{cd} 1.8 Hz, J_{bc} 3.2 Hz), and −15.36 ppm (H^a, s), each being equivalent to one hydrogen atom.

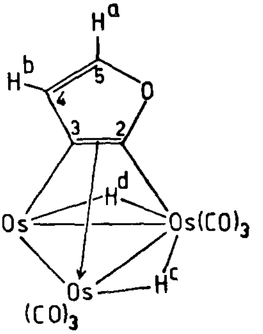


The broadband decoupled ^{13}C NMR spectrum in $CDCl_3$ at 20°C (recorded at 50.8 MHz) shows four signals for the heterocycle which were clearly assigned by a gated decoupling experiment: δ 112.9 (C(4), ddd, $^1J(C-H) \sim 180$ Hz), 127.0 (C(3), d"t", ${}^1J$(C–H) $\sim$ 180 Hz), 160.0 (C(5), ddd, ${}^1J$(C–H) $\sim$ 200 Hz), and 172.2 ppm (C(2), d, ${}^2J$(C–H) $\sim$ 10 Hz). Owing to fluxionality of the CO ligands at room temperature only 4 carbonyl resonances can be distinguished at δ 171.0, 176.4, 178.7, and 181.5 ppm.

Among the products from reactions of heterocycles with triosmium clusters structure type **3** is unprecedented. However, several μ,η^2-vinyltriosmium complexes show similar structures [11,12]. They represent intermediates in the formation of the corresponding dihydrides [13,14].

The obvious prediction that the analogous transformation of **3** into **2** should take place under suitable conditions was confirmed by an NMR tube experiment; anhydrous Me_3NO in excess was added to a solution of **3** in $CDCl_3$ and the mixture was kept at room temperature for 6 h, during which the decarbonylation induced by Me_3NO was assisted by several freeze-pump-thaw cycles.

The ${}^1H$ NMR spectrum (recorded at 200 MHz) at room temperature exhibited 3 additional signals: δ 7.55 (H^a, d, J_{ab} 2.1 Hz), 6.78 (H^b, d, J_{ab} 2.1 Hz), and -19.61 ($H^{c,d}$, s) ppm. The bridging hydride atoms are expected to be fluxional at room temperature.



The ${}^1H$ NMR resonances are therefore consistent with the assumption that **3** is converted into **2** by hydrogen transfer from ligand to metal following abstraction of another CO ligand. To confirm the structural conclusions from the spectra of **3** a single-crystal X-ray structure determination was carried out.

Molecular structure of $[HOs_3(CO)_{10}(\mu,\eta^2\text{-}C_4H_3O)]$

The structure determination (Fig. 1, 2, Table 1) revealed the heavy atom backbone of the compound to consist of the familiar Os_3 cluster forming a nearly isosceles triangle. Two of the Os atoms (Os(1), Os(2)) are each bonded to three terminal CO groups, whereas the third (Os(3)) has four CO ligands. The Os(1)–Os(2) vector between the first two fragments is doubly bridged by the furyl ligand and a hydride atom. The bridging-ligand geometry (Fig. 2) of the furyl group is characterized by a carbon atom (C(11)) adjacent to the furyl oxygen atom (O(11)) which is strongly σ bonded to one Os atom (Os(1)). Furthermore, the double bond involving C(11) (C(11)–C(12)) is bonded asymmetrically by a weak π interaction to Os(2), to give an overall μ,η^2-bridging geometry. This assessment of the bonding characteristics is strongly supported by other structural details. In particular, the Os–furyl σ bond length (Os(1)–C(11) 2.11(1) Å) is virtually identical to those in the stilbenyl complex $[HOs_3(CO)_{10}(CPh{=}CHPh)]$ [15] and the vinyl complexes $[HOs_3(CO)_{10}(CH{=}CHR)]$, R = H [12], Et [16], ${}^tBu$ [11], (Os–C 2.10–2.15 Å), in

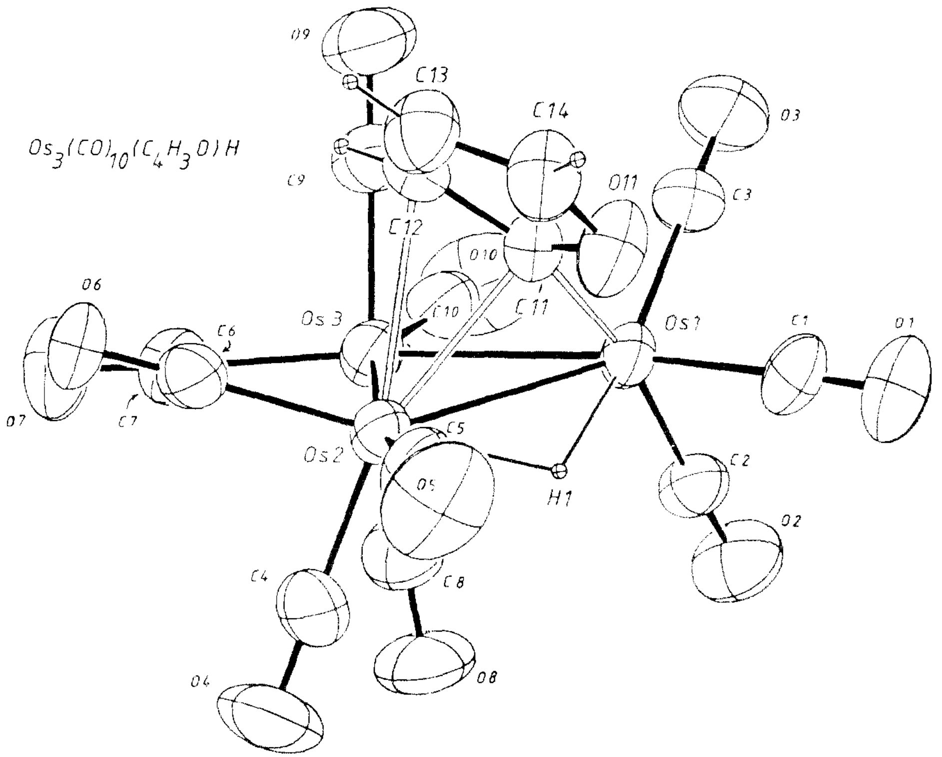


Fig. 1. Molecular geometry of [HOs$_3$(CO)$_{10}$(μ,η^2-C$_4$H$_3$O)] with numbering of principal atoms (ORTEP, thermal ellipsoids at the 50% level, H atoms with arbitrary radii).

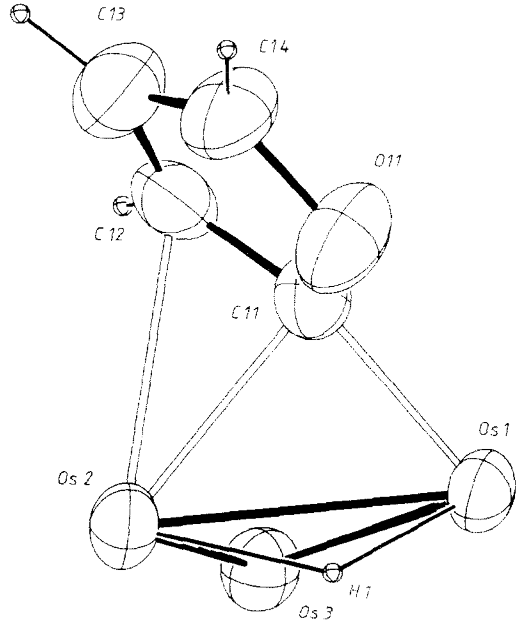


Fig. 2. Bridging ligand geometry in [HOs$_3$(CO)$_{10}$(μ,η^2-C$_4$H$_3$O)] (ORTEP, 50%).

which the bridging ligands are also σ,π bonded. However, in contrast to the situation with those complexes, the π complexation of one furyl double bond to the second Os atom Os(2) is noticeably more asymmetric, as implied by markedly different Os(2)–C(11) and Os(2)–C(12) bond distances (2.34(1) vs. 2.63(1) Å). The weaker η^2-π bonding of the furyl ligand to Os(2) is also reflected in the length of the Os(2)–Os(3) bond (2.866(1) Å) which involves Os(3) of the $Os(CO)_4$ fragment and Os(2) π coordinated with the olefinic double bond. As in the stilbenyl [15] and vinyl complexes [11,12,16], this bond is the longest in the Os_3 triangle.

In the furyl complex this bond is noticeably shorter, however, than those in the related complexes (2.876(3)–2.917(2) Å) in which the olefinic bonds are much more symmetrically coordinated. The weaker π coordination of the furyl group is probably a result of the presence of the more electronegative O atom adjacent to the complexed double bond; its distances from Os(1) and Os(2) (2.97(1), 3.20(1) Å) are too long for bonding. The μ,η^2-bridging geometry results in an interplane angle of 48.3° between the furyl ring and the Os_3 triangle. The σ bonded Os atom Os(1) in the plane of the furyl ring lies within the standard deviations. The plane Os(2),C(11),Os(1) forms an angle of 113.6° with that through the Os atoms. Its angle with the plane Os(1),H(1),Os(2) is 108.4°. The bridging hydride was found with satisfactory precision in difference maps but was not refined. Its bonding parameters resemble closely those in similar Os_3-hydride compounds [12,17]. The doubly bridged Os(1)–Os(2) bond (2.830(1) Å) is the shortest Os–Os bond in the cluster. Apparently the lengthening effect of the bridging hydride upon metal–metal bonds is more than counterbalanced by the effect of the μ,η^2 furyl group, as was observed for the other alkenyltriosmium complexes mentioned.

The π-bonded double bond of the furyl group is oriented towards the $Os(CO)_4$ fragment. To adopt the nomenclature proposed by Pierpont et al. [15], based upon the orientation of the α substituent of the alkenyl ligand (in this case O(11)) with respect to the $Os(CO)_4$ group, the structure is in an *anti* conformation. It is thus similar to that of the previously mentioned stilbenyl complex [15]. The observed conformation differs, however, from that of the vinyl complexes [11,12,16], which have a *syn* conformation. Furthermore, the structure differs considerably from those of the imidazolyl [18] and 2-methylimidazolyl complexes [8], in which the bridging ligands are bonded by an Os–C σ bond to one Os atom but by an N donor bond to the second one (see structure **4**). Although these structural differences may be rationalized in terms of the HSAB concept (the furyl oxygen atom being too hard for an interaction with the soft Os atom) they probably arise from the stronger donor properties of the imidazolyl sp^2-N atoms.

Experimental

Preparation of $[HOs_3(CO)_{10}(\mu,\eta^2\text{-}C_4H_3O)]$

A solution of anhydrous Me_3NO (0.100 g) in acetonitrile (100 ml) was added during 1 h to a refluxing solution of $Os_3(CO)_{12}$ (0.500 g) in acetonitrile (300 ml). The reaction was monitored by IR until the absorptions due to $Os_3(CO)_{12}$ and $[Os_3(CO)_{11}(NCMe)]$ had disappeared. The solvent was removed under vacuum and furan (100 ml) was added to the dark yellow residue by vacuum transfer. The flask was wrapped in aluminum foil and the mixture was allowed to warm to room temperature. After 12 h stirring at room temperature the solvent was removed from

TABLE 1

PRINCIPAL BOND DISTANCES (Å) AND ANGLES (°) FOR [$HOs_3(CO)_{10}(\mu,\eta^2\text{-}C_4H_3O)$] WITH e.s.d.'s IN UNITS OF THE LAST SIGNIFICANT FIGURE IN PARENTHESES (See Fig. 1 for atom numbering scheme)

Os(1)-Os(2)	2.830(1)	C(11)-O(11)	1.42(1)
Os(1)-Os(3)	1.846(1)	C(14)-O(11)	1.36(1)
Os(2)-Os(3)	2.866(1)	C(11)-C(12)	1.38(2)
		C(12)-C(13)	1.43(2)
Os(1)-C(11)	2.11(1)	C(13)-C(14)	1.32(2)
Os(2)-C(11)	2.34(1)		
Os(2)-C(12)	2.63(1)		
Os(1)..O(11)	2.97(1)		
Os(2)..O(11)	3.20(1)		
Os(1)-H(1)	1.71 [a]		
Os(2)-H(1)	1.77 [a]	Os(1)-H(1)-Os(2)	109 [a]
Os(1)-Os(2)-Os(3)	60.0(1)	O(11)-C(11)-C(12)	103.1(9)
Os(2)-Os(1)-Os(3)	60.6(1)	C(11)-C(12)-C(13)	111(1)
Os(1)-Os(3)-Os(2)	59.4(1)	C(12)-C(13)-C(14)	106(1)
Os(1)-C(11)-Os(2)	78.9(3)	C(13)-C(14)-O(11)	111(1)
Os(1)-C(11)-O(11)	113.3(6)		
Os(1)-C(11)-C(12)	143.6(8)		
Os(2)-C(11)-O(11)	114.5(7)		
Os(2)-C(11)-C(12)	86.1(6)		

[a] Distances and angles for the unrefined H atom H(1) are as taken from the difference synthesis. See Experimental Part for details.

the orange-red solution, and the residue was subjected to column chromatography on silica with pentane as eluant. The orange-red main band yielded [$HOs_3(CO)_{10}$-(μ,η^2-C_4H_3O)] as orange powder. Recrystallization from pentane gave the pure product as orange needles. M.p. 118°C. Yield: 0.130 g (26%). Found: C, 18.52; H, 0.49. $C_{14}H_4O_{11}Os_3$ (918.78) calcd.: C, 18.30; H, 0.44%.

X-ray structure determination

Crystal data: $C_{14}H_4O_{11}Os_3$, $fw = 918.78$, monoclinic, space group $P2_1/n$, a 9.499(1), b 15.515(2), c 12.881(2) Å, β 92.67(1)°, V 1896.3 Å^3, d_{calcd} 3.218 g/cm^3 for $Z = 4$, T 21°C, μ(Mo-K_α) 201.3 cm^{-1}, $F(000) = 1616$.

A suitable orange single crystal (crystal dimensions 0.10 × 0.12 × 0.40 mm^3, from pentane) was sealed into a Lindemann capillary under an atmosphere of argon at dry ice temperature. Diffractometer measurements indicated a monoclinic unit cell which was confirmed by axial photographs. The space group was uniquely determined by the systematic absences. Reduced cell calculations (TRACER) did not indicate any higher symmetry. The exact cell dimensions were obtained by a least squares fit of the parameters of the orientation matrix to the setting angles of 15 high angle reflections from various parts of reciprocal space accurately centered on the diffractometer.

The integrated intensities of two forms of data ($+h, +k, \pm l$; $-h, +k, \pm l$) were measured at room temperature on a computer controlled four-circle diffractometer ($h = \pm 11$, $k = +18$, $l = \pm 15$, $(\sin\vartheta/\lambda)_{\max}$ 0.595, ω scans, $\Delta\omega$ 0.9°, scan speed 0.8–29.3°/min, Mo-K_α radiation, λ 0.71069 Å, Syntex P2_1). The data were corrected empirically for absorption by recording scans at intervals of 10° around the

TABLE 2

FRACTIONAL ATOMIC COORDINATES AND EQUIVALENT ISOTROPIC THERMAL PARAMETERS ($U_{eq.} = (U_1 \cdot U_2 \cdot U_3)^{1/3}$, where U_1, U_2, U_3 are the Eigenvalues of the U_{ij} Matrix. E.s.d.'s in Parentheses)

Atom	y	x	y	$z\,U_{eq.}$
Os(1)	0.2342(0)	0.1565(0)	0.3301(0)	0.040
Os(2)	0.4539(0)	0.1705(0)	0.1901(0)	0.041
Os(3)	0.1750(0)	0.1257(0)	0.1147(0)	0.043
C(1)	0.2831(11)	0.1871(6)	0.4703(9)	0.052
O(1)	0.3093(10)	0.2082(6)	0.5556(6)	0.076
C(2)	0.0942(11)	0.2469(6)	0.3201(8)	0.046
O(2)	0.0149(8)	0.2992(6)	0.3187(6)	0.066
C(3)	0.0997(13)	0.0707(6)	0.3630(9)	0.054
O(3)	0.0148(10)	0.0235(6)	0.3794(6)	0.080
C(4)	0.4521(13)	0.2705(9)	0.1098(10)	0.062
O(4)	0.4570(11)	0.3330(6)	0.0611(9)	0.086
C(5)	0.6280(13)	0.1966(8)	0.2633(10)	0.062
O(5)	0.7317(11)	0.2144(6)	0.3044(9)	0.096
C(6)	0.5330(10)	0.1126(6)	0.0772(8)	0.047
O(6)	0.5801(9)	0.0796(5)	0.0079(6)	0.061
C(7)	0.2089(13)	0.1103(8)	−0.0294(9)	0.064
O(7)	0.2265(12)	0.0971(6)	−0.1146(6)	0.091
C(8)	0.1560(13)	0.2513(9)	0.1028(9)	0.061
O(8)	0.1429)10)	0.3220(5)	0.0973(6)	0.070
C(9)	0.1904(11)	0.0056(8)	0.1502(9)	0.055
O(9)	0.1874(9)	−0.0664(6)	0.1664(9)	0.071
C(10)	−0.0228(13)	0.1114(8)	0.1154(10)	0.066
O(10)	−0.1432(10)	0.1014(6)	0.1166(9)	0.092
O(11)	0.5063(8)	0.0841(5)	0.4139(6)	0.064
C(11)	0.4121(11)	0.0752(6)	0.3256(8)	0.047
C(12)	0.4770(12)	0.0136(6)	0.2666(8)	0.048
C(13)	0.6088(12)	−0.0117(8)	0.3154(9)	0.061
C(14)	0.6179(12)	0.0297(8)	0.4051(9)	0.058
H(1)	0.3767(0)	0.2172(0)	0.2995(0)	0.050
H(12)	0.4382(0)	−0.0095(0)	0.2014(0)	0.050
H(13)	0.6771(0)	−0.0517(0)	0.2879(0)	0.050
H(14)	0.6946(0)	0.0223(0)	0.4564(0)	0.050

diffraction vectors of 9 selected reflections near χ 90° (Syntex XTL). After Lorentz polarisation (Lp) corrections a total of 6968 measured structure factors was averaged to 3349 unique data ($R_{int} = 0.038$, SHELX 76) of which 757 with $F_o \leqslant 4.0\ \sigma\ (F_o)$ were considered statistically insignificant. The structure was solved by Patterson methods which clearly revealed the Os_3 fragment. Subsequent difference Fourier syntheses gave the remainder of the molecule with exception of the H atoms. After exhaustive anisotropic refinement of these atoms the position of the oxygen atom in the furyl ring was confirmed by refinements in which all ring atoms were assigned scattering factors of carbon. This resulted in temperature factors of the (presumed) oxygen atom substantially lower than those for the remainder of the ring atoms. Furthermore, in difference syntheses peaks at reasonable H atom positions showed up near the carbon atoms, whereas there were essentially no spurious peaks near the oxygen atom. In these syntheses the highest peak repeatedly had a stereochemistry plausible for a bridging hydride. It was therefore included in the final refinement cycles as a fixed atom contribution, whereas the other H atoms were held constant at idealized geometrical positions (C–H 0.95 Å). Refinement converged at $R = 0.032$, $R_w = 0.026$, $w = k/\sigma^2(F_o)$, $k = 1.86$ in the last cycle, for 253 refined parameters (SHELX 76). In the final refinement cycles 5 structure factors were suppressed which had shown abnormally large F_o/F_c differences believed to be due to failure of the absorption correction for these reflexions. The final difference map was essentially featureless with the maxima near the Os atoms, $\Delta\rho_{max} = +0.86/-1.06$ e/Å^3. Table 1 lists important distances and angles, Table 2 contains the atomic coordinates and the equivalent isotropic temperature factors. Figures 1 and 2 depict the molecular structure. Further crystal structure data as well as tables of the anisotropic T factors and observed and calculated structure factors have been deposited [19].

Acknowledgements

Part of this work was carried out during a post-doctoral stay of D.H. at the University of California, Berkeley. We thank the DAAD (German Academic Exchange Service) for the award of a NATO fellowship (to D.H.). D.H. is indebted to the late Professor E.L. Muetterties for suggesting the topic and for support and helpful discussions.

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19 Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen. Any request should be accompanied by the depository number CSD 51464, the names of the authors and the full citation of the journal.