ELSEVIER

Inorganica Chimica Acta 229 (1995) 47–54

Inorganica Chimica Acta

Coordination and fragmentation of 1,4-dithiacyclohexane by a triosmium cluster ☆

Richard D. Adams *, Linfeng Chen, John H. Yamamoto

Department of Chemistry and Biochemistry, University of South Carolina, Columbia, SC 29208, USA

Received 4 March 1994

Abstract

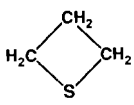
The reactions of 1,4-dithiacyclohexane (1,4-DTCH) with $Os_3(CO)_{10}(NCMe)_2$, $Os_3(CO)_{11}(NCMe)$ and $Os_3(CO)_{12}$ have been investigated. The reaction of 1,4-DTCH with $Os_3(CO)_{11}(NCMe)$ at 25 °C yielded $Os_3(CO)_{11}(\overline{SCH_2CH_2SCH_2CH_2})$ (**1**) in 46% yield. The reaction of 1,4-DTCH with $Os_3(CO)_{10}(NCMe)_2$ at 25 °C yielded $Os_3(CO)_{10}(\overline{SCH_2CH_2SCH_2CH_2})$ (**2**) in 75% yield. Compound **2** was characterized by a single crystal X-ray diffraction analysis. The molecule consists of a triangular triosmium cluster with ten linear terminal carbonyl ligands, and a 1,4-DTCH ligand coordinated as a chelate to only one of the metal atoms. When compound **2** was heated to reflux in cyclohexane solvent four compounds were obtained: $Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C{=}CH_2)(\mu\text{-}H)_2$ (**3**), $Os_2(CO)_6(\mu\text{-}SCH_2CH_2S)$ (**4**), $Os_3(CO)_{10}(\mu\text{-}SCH_2CH_2S)$ (**5**), $Os_3(CO)_8(\mu_3\text{-}\eta^2\text{-}C{=}CH_2)(\overline{SCH_2CH_2SCH_2CH_2})(\mu\text{-}H)_2$ (**6**). The formation of ethylene as a coproduct was observed spectroscopically when the reaction was performed in toluene-d_8 solvent in an NMR tube at 100 °C. The same cluster complexes were obtained from the pyrolysis of **1**, and from the direct reaction of 1,4-DTCH with $Os_3(CO)_{12}$ at 125 °C. Compounds **4** and **5** were characterized by single crystal X-ray diffraction analysis. Both compounds contain a bridging, chelating ethanedithiolato, SCH_2CH_2S, ligand. Compound **4** can be obtained from **5** in good yield by heating to 125 °C in octane solvent. Compound **3** has been reported previously. Compound **6** is a simple 1,4-DTCH derivative of **3**. Crystallographic data for **2**: $Os_3S_2O_{10}C_{14}H_8$, space group, $P2_1/n$, $a=8.641(2)$, $b=25.108(4)$, $c=10.533(1)$ Å, $\beta=113.35(1)°$, $Z=4$, 2064 reflections, $R=0.037$. For **4**: $Os_2S_2O_6C_8H_4$, space group $P2_1/n$, $a=8.612(2)$, $b=16.062(8)$, $c=9.988(4)$ Å, $\beta=98.37(1)°$, $Z=4$, 1295 reflections, $R=0.044$. For **5**: $Os_3S_2O_{10}C_{12}H_4$, space group $P2_1/c$, $a=14.079(2)$, $b=9.383(1)$, $c=15.153(2)$ Å, $\beta=108.20(8)°$, $Z=4$, 1893 reflections, $R=0.030$.

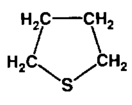
Keywords: Crystal structures; Osmium complexes; Carbonyl complexes; Dithiacyclohexane complexes; Thioether complexes; Cluster complexes

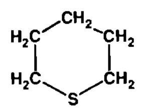
1. Introduction

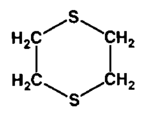
The activation and transformations of cyclic thioethers is of great interest because of their relationship to the important process of hydrodesulfurization that is used in the purification of fossil fuels [1]. Recently, polynuclear metal complexes have been shown to induce the cleavage of carbon–sulfur bonds in cyclic thioethers under mild conditions [2–6].

Much of our recent research has been focused on the ring opening of thietanes (**A**) by the cleavage of carbon–sulfur bonds in osmium [3], ruthenium [4] and rhenium [5] cluster complexes. We have also found that the five-membered ring of tetrahydrothiophene (**B**) can be opened through the cleavage of a carbon–sulfur bond when the molecule is coordinated to a triosmium cluster complex; however, more forcing conditions are required [6]. Our studies of the transformations of thiacyclohexane (**C**) by a triosmium cluster complex have revealed the occurrence of CH bond cleavages on the methylene groups, but C–S bond cleavages were not observed [7].


A


B


C


D

In this report we present the results of our investigations of the transformations of 1,4-dithiacyclohexane (1,4-DTCH) (**D**) with the triosmium cluster complexes $Os_3(CO)_{10}(NCMe)_2$, $Os_3(CO)_{11}(NCMe)$ and $Os_3(CO)_{12}$. There have been very few studies of the reactions of 1,4-DTCH with metal cluster complexes. An early report

---

☆ Dedicated to Professor F.A. Cotton on the occasion of his 65th birthday.

* Corresponding author.

SSDI 0020-1693(94)04225-K

on the reaction of 1,4-DTCH with $Fe_2(CO)_9$ described the formation of the complex $Fe_2(CO)_6(\mu\text{-}SCH_2CH_2S)$ containing an ethanedithiolato ligand formed by fragmentation of the dithiacyclohexane molecule [8]. Our studies support this earlier result and show that the transformations of 1,4-DTCH by the triosmium carbonyl cluster yield complexes containing ethanedithiolato ligands by cleavage of two carbon–sulfur bonds and the elimination of ethylene.

2. Experimental

2.1. General data

Reagent grade solvents were dried with appropriate drying agents and stored over 4 Å molecular sieves. All reactions were performed under a nitrogen atmosphere unless specified otherwise. IR spectra were recorded on a Nicolet 5DXB FTIR spectrophotometer. ^1H NMR spectra were run on either a Brüker AM-300 or AM-500 spectrometer operating at 300 or 500 MHz, respectively. Thin layer chromatographic separations were performed in air on Analtech silica gel (0.25 mm) F_{254} uniplates. Silica gel (70–230 mesh, 60 Å) was purchased from Aldrich. Elemental analyses were performed by Oneida Research Services, Whitesboro, NY. 1,4-Dithiacyclohexane (1,4-DTCH) was purchased from Aldrich (1,4-Dithiane) and was used without further purification. $Os_3(CO)_{11}NCMe$ [9] and $Os_3(CO)_{10}(NCMe)_2$ [10] were prepared by the published procedures.

2.2. Reaction of $Os_3(CO)_{11}(NCMe)$ with 1,4-DTCH

50.0 mg (0.054 mmol) of $Os_3(CO)_{11}(NCMe)$ was dissolved in 20 ml of CH_2Cl_2. To this solution was added 8.0 mg (0.067 mmol) of 1,4-DTCH. The solution was then stirred at 25 °C for 1 h. The solvent was removed in vacuo, and the residue was transferred to TLC plates and was separated using a 1/4 CH_2Cl_2/hexane solvent mixture. One major band was isolated; it was determined to be **1** (23.1 mg, 46%). A large insoluble residue, observed at the bottom of the plate, could not be characterized. Spectroscopic data for **1**: IR, ν(CO) (cm^{-1} in hexane): 2109(w), 2056(s), 2037(s), 2023(vs), 2004(m), 1993(m), 1975(w), 1964(w), 1959(w); ^1H NMR (δ in $CDCl_3$): 3.24 (bs, 4H), 2.87 (bs, 4H).

2.3. Reaction of $Os_3(CO)_{10}(NCMe)_2$ with 1,4-DTCH

A 20.0 mg amount of $Os_3(CO)_{10}(NCMe)_2$ (0.022 mmol) and 3.0 mg (0.025 mmol) of 1,4-DTCH were dissolved in 20 ml of CH_2Cl_2 and stirred at 25 °C for 1 h. The solvent was removed in vacuo, and the residue transferred to TLC plates and separated with a 1/1 hexane/CH_2Cl_2 solvent mixture. Two yellow bands were separated that yielded the compounds $Os_3(CO)_{11}(\overline{SCH_2CH_2SCH_2C}H_2)$ (**1**) (1.7 mg, 9%) and $Os_3(CO)_{10}(\overline{SCH_2CH_2SCH_2C}H_2)$ (**2**) (15.0 mg, 75%). Spectroscopic data for **2**: IR, ν(CO) (cm^{-1}): 2092(m), 2040(s), 2001(vs), 1962(m), 1954(m), 1913(w); ^1H NMR (δ in $CDCl_3$): 3.10 (d, J(H–H) = 8.0 Hz), 2.70 (d, J(H–H) = 8.0 Hz); at −60 °C (in $CDCl_3$): 3.22 (s, 2H), 3.15 (s, 2H), 2.90 (s, 2H), 2.45 (s, 2H). *Anal.* Calc. for **2**: C, 17.32; H, 0.82. Found: C, 17.30; H, 0.72%.

2.4. Reaction of $Os_3(CO)_{12}$ with 1,4-DTCH

A 50.0 mg amount of $Os_3(CO)_{12}$ (0.055 mmol) and 13.2 mg 1,4-DTCH (0.110 mmol) were dissolved in 35 ml of octane and the solution was heated to reflux for 24 h. The solvent was removed in vacuo, and the residue transferred to TLC plates and separated with a 1/4 CH_2Cl_2/hexane solvent mixture to yield in order of elution: $Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C{=}CH_2)(\mu\text{-}H)_2$ (**3**) [11] (4.4 mg, 9%); $Os_2(CO)_6(\mu\text{-}SCH_2CH_2S)$ (**4**) (14.6 mg, 29%); $Os_3(CO)_{10}(\mu\text{-}SCH_2CH_2S)$ (**5**) (4.8 mg, 10%); $Os_3(CO)_8(\mu_3\text{-}\eta^2\text{-}C{=}CH_2)(\overline{SCH_2CH_2SCH_2C}H_2)(\mu\text{-}H)_2$ (**6**) (9.6 mg, 19%). Spectroscopic data for **3**: IR, ν(CO) (cm^{-1} in hexane): 2108(w), 2062(vs), 2058(vs), 2030(s), 2017(s), 2009(m), 1992(w), 1984(m); ^1H NMR (δ in $CDCl_3$): 6.49 (s, 1H), 5.95 (s, 1H), −18.07 (d, J(H–H) = 0.96 Hz, 1H), −21.70 (d, J(H–H) = 1.44 Hz, 1H); ^1H NMR (δ in toluene-d_8): 6.06 (s, 1H), 5.53 (s, 1H), −18.20 (d, J(H–H) = 1.41 Hz, 1H), −21.88 (d, J(H–H) = 1.56 Hz, 1H). For **4**: IR, ν(CO) (cm^{-1} in hexane): 2087(m), 2055(vs), 2007(vs), 1992(s), 1983(m); ^1H NMR (δ in $CDCl_3$): 2.19 (s, 4H). *Anal.* Calc. for **4**: C, 14.99; H, 0.62. Found: C, 14.99; H, 0.24%. For **5**: IR, ν(CO) (cm^{-1} in hexane): 2103(w), 2067(s), 2050(w), 2016(vs), 1985(m), 1977(w); ^1H NMR (δ in $CDCl_3$): 3.44 (s, 4H); ^1H NMR (δ in toluene-d_8): 2.59 (s, 4H). *Anal.* Calc. for **5**: C, 15.55; H, 0.42. Found: C, 15.82; H, 0.44%. For **6**: IR, ν(CO) (cm^{-1} in hexane): 2086(m), 2052(vs), 2034(s), 2016(s), 2009(m), 1982(m), 1968(w); ^1H NMR (δ in $CDCl_3$): 6.34 (s, 1H), 5.85 (s, 1H), 3.14 (bs, 4H), 2.87 (bs, 4H), −16.90 (s, 1H), −19.90 (s, 1H); ^1H NMR (δ in toluene-d_8): 6.21 (s, 1H), 5.67 (s, 1H), 2.10 (bs, 4H), 2.04 (bs, 4H) −16.88 (s, 1H), −19.92 (s, 1H). M^+: calc: 948 for three ^{192}Os (found 948), with ions corresponding to the loss of each of eight CO ligands plus combination of CO and 1,4-DTCH.

2.5. Thermolysis of 1

A 37.0 mg amount of **1** was dissolved in 35 ml of heptane and was heated to reflux for 46 h. The solvent was removed in vacuo, and the residue transferred to TLC plates and separated using a 1/4 CH_2Cl_2/hexane solvent mixture to yield **3** (1.2 mg, 3%), **4** (7.1 mg, 19%), **5** (3.3 mg, 9%) and **6** (10.3 mg, 28%).

2.6. Thermolysis of 2

A 23.0 mg amount of **2** was dissolved in 35 ml of heptane and was then heated to reflux for 48 h. The solvent was removed in vacuo, and the residue transferred to TLC plates and separated with a 4/1 hexane/CH_2Cl_2 solvent mixture. Four bands were eluted that were identified as **3** (1.3 mg, 6%), **4** (1.4 mg, 6%), **5** (1.4 mg, 6%) and **6** (1.2 mg, 5%).

2.7. Thermolysis of 5

A 6.0 mg amount of **5** was dissolved in 10 ml of octane and heated to reflux for 24 h. The solvent was removed in vacuo, and the residue transferred to TLC plates and separated with pure hexane to give 3.0 mg of **4**, 69% yield.

2.8. Thermolysis of 2 in toluene-d_8 in an NMR tube

A 12.0 mg amount of **2** was dissolved in an NMR tube in 1.5 ml of toluene-d_8. The NMR tube was placed into an oil bath at 100 °C for 2 h. A ^1H NMR spectrum taken of the solution showed the compounds **3**, **5** and **6** plus free ethylene ($\delta = 5.25$ ppm). The solvent was removed in vacuo, and the residue transferred to TLC plates and separated to give **3** (0.5 mg, 4%), **5** (0.5 mg, 4%) and **6** (2.0 mg, 17%).

2.9. Crystallographic analyses

Crystals of **2**, **4** and **5** were grown by slow evaporation of solvent from solutions in hexane/CH_2Cl_2 solvent mixtures. The data crystals were mounted in thin-walled glass capillaries. Diffraction measurements were made on a Rigaku AFC6S fully automated four-circle diffractometer using graphite-monochromated Mo Kα radiation. The unit cells were established and refined from 15 randomly selected reflections obtained by using the AFC6 automatic search, center, index, and least-squares routines. Crystal data, data collection parameters, and results of the analyses are listed in Table 1. All data processing was performed on a Digital Equipment Corp. VAXstation 3520 computer using the TEXSAN structure solving program library obtained from the Molecular Structure Corp., The Woodlands, TX. Neutral atom scattering factors were calculated by the standard procedures [12a]. Lorentz–polarization (Lp) and absorption corrections were applied for each analysis. Anomalous dispersion corrections were used for all non-hydrogen atoms [12b]. Full-matrix least-squares refinements minimized the function: $\Sigma_{hkl} w(|F_o| - |F_c|)^2$, where $w = 1/\sigma(F)^2$, $\sigma(F) = \sigma(F_o^2)/2F_o$ and $\sigma(F_o^2) = [\sigma(I_{raw})^2 + (0.02I_{net})^2]^{1/2}Lp$.

All three compounds crystallized in the monoclinic crystal system. For compounds **2** and **4** the space group $P2_1/n$ was identified uniquely based on the systematic absences observed during the collection of data. For **5** the space group $P2_1/c$ was likewise established. For all three analyses the structures were solved by a combination of direct methods (MITHRIL) and difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic thermal parameters, and all hydrogen atom positions were calculated by assuming idealized geometries. The scattering contributions of the hydrogen atoms were added to the structure factor calculations but their positions were not refined.

3. Results and discussion

The reactions of $Os_3(CO)_{11}(NCMe)$ and $Os_3(CO)_{10}(NCMe)_2$ with 1,4-dithiacyclohexane (1,4-DTCH) (**D**) at 25 °C have yielded the mono- and disubstituted complexes $Os_3(CO)_{11}(\overline{SCH_2CH_2SCH_2CH_2})$ (**1**) and $Os_3(CO)_{10}(\overline{SCH_2CH_2SCH_2CH_2})$ (**2**) in 46 and 75% yields, respectively. A strong similarity of the IR spectrum of **1** to that of the complex, $Os_3(CO)_{11}(\overline{SCH_2CH_2CH_2})$ indicates that both structures are similar and the 1,4-DTCH ligand lies on an equatorial coordination site [3h]. Compound **2** was characterized by a single crystal X-ray diffraction analysis and an ORTEP drawing of its molecular structure is shown in Fig. 1. Final atomic positional parameters are listed in Table 2. Selected bond distances and angles are listed in Table 3. Complex **2** contains a triangular triosmium cluster with ten linear terminal carbonyl ligands distributed among the three metal atoms as shown in Fig. 1. There is one 1,4-DTCH ligand that is a chelating ligand coordinated to the atom Os(1). One of the sulfur atoms S(2) is coordinated in an equatorial site, Os(1)–S(2) = 2.380(4) Å, while the other S(1) is coordinated in an axial site, Os(1)–S(1) = 2.461(5) Å, and the latter is significantly longer than the former. The three metal–metal bonds are not equivalent and the Os(1)–Os(2) bond that lies *trans* to the sulfur atom S(2) is significantly shorter, 2.844(1) Å, than the other two, Os(1)–Os(3) = 2.912(1) Å and Os(2)–Os(3) = 2.914(1) Å. The Os–Os distances in $Os_3(CO)_{12}$ are 2.877(3) Å in length [13]. Structurally, **2** is very similar to the complex $Os_3(CO)_{10}$(s-*cis*-C_4H_6) (**7**) which contains a butadiene ligand with one double bond coordinated in an equatorial position and the other in an axial position [14]. In **7** the Os–Os bond *trans* to the equatorially coordinated double bond is actually 0.021(3) Å longer than the other Os–Os bonds.

Table 1
Crystallographic data for compounds **2**, **4** and **5**

	2	**4**	**5**
Empirical formula	$Os_3S_2O_{10}C_{14}H_8$	$Os_2S_2O_6C_8H_4$	$Os_3S_2O_{10}C_{12}H_4$
Formula weight	970.93	640.64	942.88
Crystal system	monoclinic	monoclinic	monoclinic
Lattice parameters			
a (Å)	8.641(2)	8.616(2)	14.079(2)
b (Å)	25.108(4)	16.062(8)	9.383(1)
c (Å)	10.533(1)	9.988(4)	15.153(2)
α (°)	90.0	90.0	90.0
β (°)	113.35(1)	98.37(1)	108.20(8)
γ (°)	90.0	90.0	90.0
V (Å^3)	2098.0(6)	1367.4(6)	1901.5(7)
Space group	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)
Z	4	4	4
D_{calc} (g cm^{-3})	3.07	3.11	3.29
μ(Mo Kα) (cm^{-1})	183.8	188.9	202.8
Temperature (°C)	20	20	20
$2\theta_{max}$ (°)	43.0	42.0	43.0
No. observations ($I > 3\sigma(I)$)	2064	1295	1893
No. variables	262	163	244
Residuals: R; R_w	0.037; 0.042	0.044; 0.056	0.030; 0.036
Goodness of fit indicator	2.52	2.25	2.18
Max. shift in final cycle	0.00	0.00	0.00
Largest peak in final difference map (e Å^{-3})	1.49	1.06	3.24
Absorption correction	DiFab	empirical	DiFab

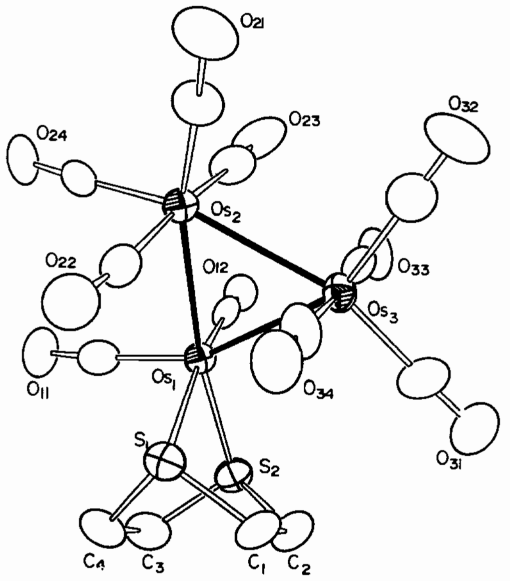
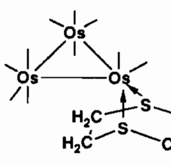
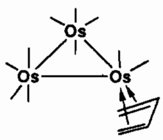


Fig. 1. An ORTEP diagram of the molecular structure of $Os_3(CO)_{10}(\overline{SCH_2CH_2SCH_2CH_2})$ (**2**) showing 50% probability thermal ellipsoids.



2



7

We had observed previously that σ-donors positioned *trans* to osmium–osmium bonds in open triosmium clusters also produced an increase in the osmium–osmium distance [15], thus, the substantial decrease observed in the Os(1)–Os(2) bond in **2** is not explained.

The six-membered ring has adopted the classic 'boat' conformation as a result of the coordination of the two sulfur atoms. All hydrogen atoms are inequivalent according to the solid state structure; however, the ^{1}H NMR spectrum of **2** at room temperature shows only two resonances (doublets) at $\delta = 3.10$ (d, 4H, J(H–H) = 8.0 Hz) and 2.70 (d, 4H, J(H–H) = 8.0 Hz). This indicates the presence of a dynamical process that has averaged the environments of most of the protons. This was confirmed by recording the spectrum at −60 °C. At this temperature the ^{1}H NMR spectrum exhibits four broad singlets of equal intensity at 3.22 (s, 2H), 3.15 (s, 2H), 2.90 (s, 2H), 2.45 (s, 2H) ppm. From this information alone, it is not possible to define the exchange mechanism unambiguously; however, the compounds $Os_3(CO)_{10}$(1,3-cyclohexadiene) [16] and $Os_3(CO)_{10}$(norbornadiene) [17] which are structurally similar to **2** and **7** exhibit similar dynamical activity that leads to an averaging of the double bonds. We believe that the dynamical transformations in **2** are probably similar to those in $Os_3(CO)_{10}$(1,3-cyclohexa-

Table 2
Positional parameters and B_{eq} values for **2**

Atom	x	y	z	B_{eq}
Os(1)	0.47920(08)	0.33342(03)	0.34055(06)	2.20(3)
Os(2)	0.30128(08)	0.37357(03)	0.06868(06)	2.61(3)
Os(3)	0.66258(08)	0.39268(03)	0.20675(07)	2.62(3)
S(1)	0.4710(06)	0.41076(20)	0.4812(04)	2.9(2)
S(2)	0.6671(05)	0.3127(02)	0.5708(04)	3.1(2)
O(11)	0.1577(16)	0.2894(06)	0.3471(13)	5.0(7)
O(12)	0.5459(15)	0.2250(06)	0.2477(12)	3.9(6)
O(21)	0.2059(19)	0.4385(06)	−0.1948(15)	5.9(8)
O(22)	0.1771(18)	0.4630(07)	0.2069(14)	6.0(8)
O(23)	0.4184(18)	0.2791(08)	−0.0539(14)	6.7(8)
O(24)	−0.0383(16)	0.3181(07)	−0.0053(13)	4.9(7)
O(31)	1.0131(18)	0.4145(08)	0.4264(15)	8(1)
O(32)	0.717(02)	0.4377(08)	−0.0427(15)	8(1)
O(33)	0.7760(16)	0.2809(06)	0.1591(14)	4.6(7)
O(34)	0.5423(17)	0.4974(06)	0.2812(14)	4.7(7)
C(1)	0.691(02)	0.4224(07)	0.5886(16)	3.1(8)
C(2)	0.795(02)	0.3722(09)	0.6315(18)	3.8(9)
C(3)	0.534(02)	0.3260(09)	0.6650(17)	4(1)
C(4)	0.423(02)	0.3774(09)	0.6184(17)	3.8(9)
C(11)	0.280(02)	0.3074(08)	0.3497(16)	3.3(8)
C(12)	0.5153(20)	0.2689(09)	0.2753(17)	2.9(8)
C(21)	0.247(02)	0.4187(07)	−0.0927(19)	3.2(8)
C(22)	0.235(02)	0.4286(09)	0.1591(17)	3.2(8)
C(23)	0.379(02)	0.3168(08)	−0.0027(18)	3.6(9)
C(24)	0.088(02)	0.3387(09)	0.0253(17)	4(1)
C(31)	0.882(03)	0.4063(10)	0.3454(19)	5(1)
C(32)	0.695(03)	0.4226(10)	0.049(02)	5(1)
C(33)	0.723(02)	0.3220(09)	0.1729(17)	3.1(8)
C(34)	0.583(02)	0.4569(09)	0.2508(20)	3.5(9)

Table 3
Selected intramolecular distances and angles for **2**

Intramolecular distances (Å)			
Os(1)–Os(2)	2.844(1)	S(2)–C(2)	1.82(2)
Os(1)–Os(3)	2.912(1)	S(2)–C(3)	1.82(2)
Os(1)–S(1)	2.461(5)	C(1)–C(2)	1.51(3)
Os(1)–S(2)	2.380(4)	C(3)–C(4)	1.57(3)
Os(2)–Os(3)	2.914(1)	Os–C(av.)	1.90(2)
S(1)–C(1)	1.81(2)	O–C(av.)	1.16(2)
S(1)–C(4)	1.85(2)		
Intramolecular bond angles (°)			
Os(2)–Os(1)–Os(3)	60.82(3)	C(1)–S(1)–C(4)	95.1(8)
Os(2)–Os(1)–S(1)	101.1(1)	Os(1)–S(2)–C(2)	104.7(6)
Os(2)–Os(1)–S(2)	168.9(1)	Os(1)–S(2)–C(3)	101.0(6)
Os(3)–Os(1)–S(1)	92.3(1)	C(2)–S(2)–C(3)	95(1)
Os(3)–Os(1)–S(2)	108.8(1)	S(1)–C(1)–C(2)	114(1)
S(1)–Os(1)–S(2)	74.4(2)	S(2)–C(2)–C(1)	112(1)
Os(1)–Os(2)–Os(3)	60.74(3)	S(2)–C(3)–C(4)	115(1)
Os(1)–Os(3)–Os(2)	58.44(3)	S(1)–C(4)–C(3)	109(1)
Os(1)–S(1)–C(1)	103.3(6)	Os–C(av.)–O	175(2)
Os(1)–S(1)–C(4)	100.4(7)		

E.s.d.s in the least significant figure are given in parentheses.

diene) and $Os_3(CO)_{10}$(norbornadiene) and all of the *exo* ring protons are averaged and all of the *endo* ring protons are averaged. Thus, in the averaged spectrum only two doublets are observed: one for the *exo* hydrogens on the methylene groups and one for the *endo* hydrogens with geminal coupling.

When solutions of $Os_3(CO)_{12}$ and 1,4-DTCH in octane solvent were heated to reflux four compounds identified as $Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C{=}CH_2)(\mu\text{-}H)_2$ (**3**) (9% yield), $Os_2(CO)_6(\mu\text{-}SCH_2CH_2S)$ (**4**) (29% yield), $Os_3(CO)_{10}(\mu\text{-}SCH_2CH_2S)$ (**5**) (10% yield) and $Os_3(CO)_8(\mu_3\text{-}\eta^2\text{-}C{=}CH_2)(\overline{SCH_2CH_2SCH_2CH_2})(\mu\text{-}H)_2$ (**6**) (19% yield) were obtained. When the reaction was performed in an NMR tube in toluene-d_8 solvent, formation of the coproduct ethylene was also observed spectroscopically. Compound **3** has been obtained previously from the reaction of $Os_3(CO)_{12}$ with ethylene [11]. On the basis of its mass spectrum and ^1H NMR spectrum, we believe that compound **6** is simply a 1,4-DTCH derivative of **3**, but on the basis of this information alone it is not possible to determine to which of the three metal atoms the 1,4-DTCH ligand is attached. Compounds **4** and **5** were characterized by single crystal X-ray diffraction analysis. An ORTEP diagram of the molecular structure of **4** is shown in Fig. 2. Final atomic positional parameters are listed in Table 4. Selected bond distances and angles are listed in Table 5. Compound **4** contains only two osmium atoms. Each metal contains three linear terminal carbonyl ligands, and overall, the $Os_2(CO)_6$ unit possesses the classic 'sawhorse' structure. There is an 1,2-

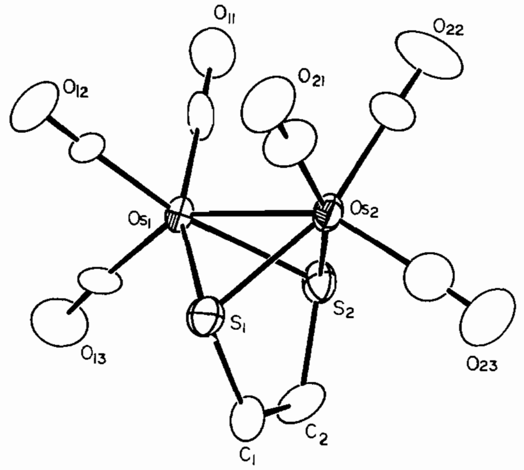


Fig. 2. An ORTEP diagram of the molecular structure of $Os_2(CO)_6(\mu\text{-}SCH_2CH_2S)$ (**4**) showing 50% probability thermal ellipsoids.

Table 4
Positional parameters and B_{eq} values for **4**

Atom	x	y	z	B_{eq}
Os(1)	0.08216(09)	0.31065(05)	0.10788(07)	2.16(4)
Os(2)	0.11984(09)	0.42228(05)	0.31356(07)	2.26(4)
S(1)	0.3119(06)	0.3207(03)	0.2747(05)	2.6(2)
S(2)	0.1616(06)	0.4518(03)	0.0872(05)	2.5(2)
O(11)	−0.251(02)	0.3463(11)	−0.0214(18)	5.1(9)
O(12)	−0.025(02)	0.1491(11)	0.2284(19)	6(1)
O(13)	0.210(02)	0.2391(13)	−0.1369(17)	6(1)
O(21)	0.036(02)	0.3235(11)	0.5501(17)	5.1(9)
O(22)	−0.1937(20)	0.5126(13)	0.2592(15)	5(1)
O(23)	0.321(02)	0.5577(13)	0.4724(18)	7(1)
C(1)	0.449(03)	0.3801(14)	0.192(02)	4(1)
C(2)	0.376(03)	0.4437(15)	0.0926(20)	3(1)
C(11)	−0.123(03)	0.3341(13)	0.023(02)	3(1)
C(12)	0.017(02)	0.2081(13)	0.183(02)	2(1)
C(13)	0.163(02)	0.2612(15)	−0.043(02)	3(1)
C(21)	0.063(03)	0.3599(15)	0.459(02)	4(1)
C(22)	−0.079(03)	0.4790(15)	0.2832(19)	3(1)
C(23)	0.244(03)	0.5077(17)	0.413(02)	4(1)

ethanedithiolato ligand that bridges the two metal atoms with each sulfur atom bonded to both metal atoms. Similarly coordinated 1,2-ethanedithiolato ligands have been observed previously in other cluster complexes [18,19]. The ethanedithiolato ligand observed in **2** exhibits no unusual structural features. The bridging dithiolato ligand serves as a six-electron donor, and in the presence of a metal–metal single bond, Os(1)–Os(2) = 2.710(1) Å, each metal atom achieves the expected 18-electron configuration. In accord with the structural analysis, the ^1H NMR spectrum shows only one resonance, $\delta = 2.19$ ppm, for the four equivalent protons on the two methylene groups.

An ORTEP diagram of the molecular structure of **5** is shown in Figure 3. Final atomic positional parameters are listed in Table 6. Selected bond distances and angles are listed in Table 7. Compound **5** consists of a 'open' triosmium cluster having only two osmium–osmium bonds, Os(1)–Os(3) = 2.8804(8) Å and Os(2)–Os(3) = 2.880(1) Å. There are ten linear terminal carbonyl ligands distributed among the metals as shown in Fig. 3, and there is a 1,2-ethanedithiolato ligand bridging the non-bonded pair of metal atoms Os(1) and Os(2), Os(1)···Os(2) = 3.365(1) Å. This non-bonding distance is slightly larger than those found in the related doubly bridged complexes $Os_3(CO)_{10}(\mu\text{-}OMe)_2$ [20] and $Os_3(CO)_{10}(\mu\text{-}Cl)_2$ [21] where the distances are 3.078(3) and 3.233(2) Å, respectively. As in **4** the four hydrogen atoms are equivalent and only a single resonance is observed, $\delta = 3.44$, in the ^1H NMR spectrum. The ethanedithiolato ligand serves as a six-electron donor and all three metal atoms achieve 18-electron configurations in the presence of only two metal–metal bonds.

Table 5
Selected intramolecular distances and angles for **4**

Intramolecular distances (Å)			
Os(1)–Os(2)	2.710(1)	S(1)–C(1)	1.81(2)
Os(1)–S(1)	2.400(5)	S(2)–C(2)	1.84(2)
Os(1)–S(2)	2.386(5)	C(1)–C(2)	1.50(3)
Os(2)–S(1)	2.395(5)	Os–C(av.)	1.91(3)
Os(2)–S(2)	2.388(5)	O–C(av.)	1.14(2)
Intramolecular bond angles (°)			
Os(2)–Os(1)–S(1)	55.5(1)	Os(2)–S(1)–C(1)	103.1(7)
Os(2)–Os(1)–S(2)	55.4(1)	Os(1)–S(2)–Os(2)	69.2(1)
S(1)–Os(1)–S(2)	77.2(2)	Os(1)–S(2)–C(2)	103.2(8)
Os(1)–Os(2)–S(1)	55.7(1)	Os(2)–S(2)–C(2)	104.2(7)
Os(1)–Os(2)–S(2)	55.4(1)	S(1)–C(1)–C(2)	115(2)
S(1)–Os(2)–S(2)	77.3(2)	S(2)–C(2)–C(1)	113(1)
Os(1)–S(1)–Os(2)	68.8(1)	Os–C(av.)–O	176(2)
Os(1)–S(1)–C(1)	104.2(7)		

E.s.d.s in the least significant figure are given in parentheses.

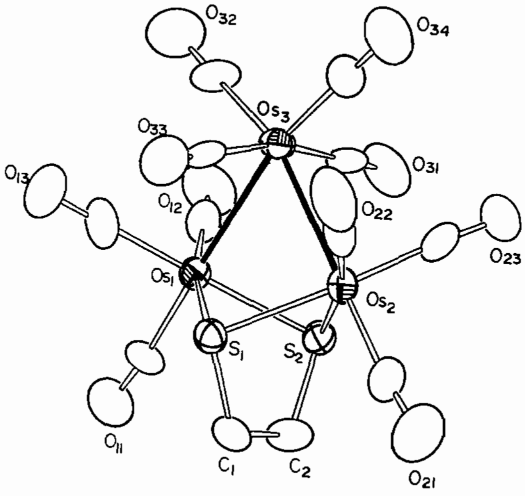


Fig. 3. An ORTEP diagram of the molecular structure of $Os_3(CO)_{10}(\mu\text{-}SCH_2CH_2S)$ (**5**) showing 50% probability thermal ellipsoids.

Compounds **3**, **4**, **5** and **6** were obtained in lower yields in the pyrolyses of **1** and **2** at 97 °C in heptane

Table 6
Positional parameters and B_{eq} values for 5

Atom	x	y	z	B_{eq}
Os(1)	0.31777(05)	0.48829(06)	0.56857(04)	2.33(3)
Os(2)	0.13676(05)	0.25654(06)	0.45960(05)	2.42(3)
Os(3)	0.29671(05)	0.20210(06)	0.62867(05)	2.78(3)
S(1)	0.1360(03)	0.4987(04)	0.5177(03)	2.7(2)
S(2)	0.2627(03)	0.3871(04)	0.4127(03)	2.7(2)
O(11)	0.3539(11)	0.7837(13)	0.5082(10)	5.5(7)
O(12)	0.5388(10)	0.4152(14)	0.6142(11)	5.7(7)
O(13)	0.3433(12)	0.5908(15)	0.7650(10)	6.2(8)
O(21)	−0.0375(13)	0.3020(17)	0.2800(12)	8(1)
O(22)	0.0048(11)	0.1259(13)	0.5636(11)	5.8(7)
O(23)	0.1860(11)	−0.0323(12)	0.3912(09)	5.0(6)
O(31)	0.4222(11)	0.1167(13)	0.5012(11)	5.8(7)
O(32)	0.4728(15)	0.2390(17)	0.7993(13)	8(1)
O(33)	0.1496(11)	0.3393(14)	0.7186(09)	5.2(7)
O(34)	0.2345(14)	−0.1032(15)	0.6506(11)	7.4(9)
C(1)	0.1180(12)	0.5949(15)	0.4083(12)	3.3(7)
C(2)	0.1819(13)	0.5361(17)	0.3518(12)	3.7(8)
C(11)	0.3357(12)	0.6713(16)	0.5261(12)	2.9(7)
C(12)	0.4552(16)	0.4445(17)	0.5965(12)	3.7(8)
C(13)	0.3326(14)	0.5531(17)	0.6901(14)	4.0(9)
C(21)	0.0304(15)	0.2910(18)	0.3486(14)	4.1(9)
C(22)	0.0518(16)	0.1720(18)	0.5230(14)	4.3(9)
C(23)	0.1672(12)	0.0774(19)	0.4192(11)	3.4(8)
C(31)	0.3757(15)	0.1471(16)	0.5475(12)	3.6(8)
C(32)	0.4068(15)	0.2248(19)	0.7332(15)	4.4(9)
C(33)	0.2017(14)	0.2902(17)	0.6869(12)	3.2(7)
C(34)	0.2586(15)	0.0127(18)	0.6434(13)	4.2(9)

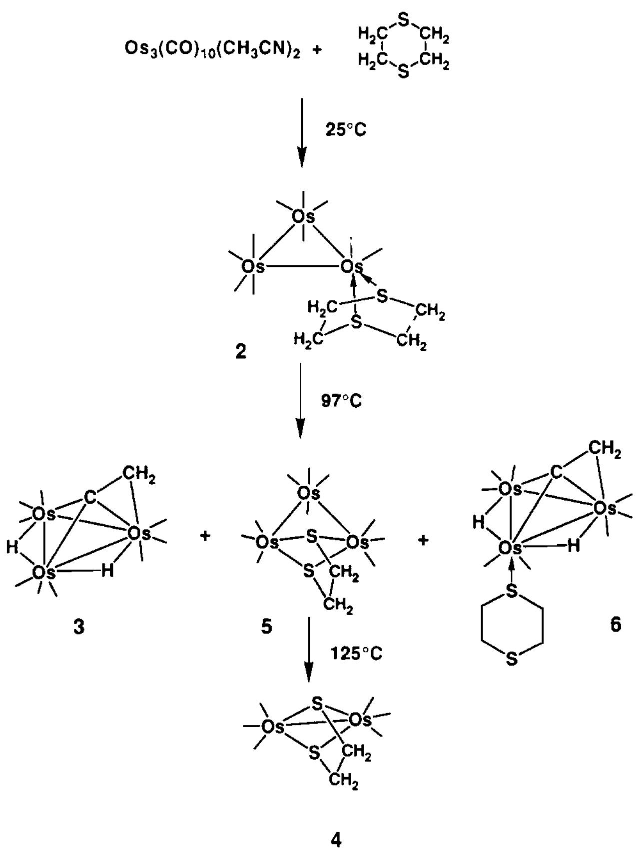
Table 7
Selected intramolecular distances and angles for 5

Intramolecular distances (Å)			
Os(1)–Os(3)	2.8804(8)	S(1)–C(1)	1.83(2)
Os(1)–S(1)	2.433(4)	S(2)–C(2)	1.86(2)
Os(1)–S(2)	2.436(4)	C(1)–C(2)	1.53(2)
Os(2)–Os(3)	2.880(1)	Os–C(av.)	1.91(2)
Os(2)–S(1)	2.438(4)	O–C(av.)	1.15(2)
Os(2)–S(2)	2.437(4)	Os(1)–Os(2)	3.365(1)
Intramolecular bond angles (°)			
Os(3)–Os(1)–S(1)	86.32(9)	Os(1)–S(1)–C(1)	98.1(5)
Os(3)–Os(1)–S(2)	84.85(9)	Os(2)–S(1)–C(1)	98.5(5)
S(1)–Os(1)–S(2)	74.0(1)	Os(1)–S(2)–Os(2)	87.4(1)
Os(3)–Os(2)–S(1)	86.2(1)	Os(1)–S(2)–C(2)	98.6(6)
Os(3)–Os(2)–S(2)	84.9(1)	Os(2)–S(2)–C(2)	97.8(5)
S(1)–Os(2)–S(2)	73.8(1)	S(1)–C(1)–C(2)	113(1)
Os(1)–Os(3)–Os(2)	71.49(2)	S(2)–C(2)–C(1)	112(1)
Os(1)–S(1)–Os(2)	87.4(1)	Os–C(av.)–O	178(2)

E.s.d.s in the least significant figure are given in parentheses.

solvent. When a solution of compound **5** was heated to reflux in octane solvent for 24 h, compound **4** was formed in 69% yield indicating that **5** is probably a precursor to **4** in all of these reactions.

A summary of our studies of the synthesis and transformations of compound **2** is presented in Scheme 1. Compound **2** is formed simply by the displacement of the two labile NCMe ligands in $Os_3(CO)_{10}(NCMe)_2$ and the coordination of the two sulfur atoms to one of the metal atoms. A CO ligand shift must have occurred since the NCMe ligands in $Os_3(CO)_{10}(NCMe)_2$ are coordinated to different metal atoms [22]. When heated one equivalent of ethylene is expelled and the 1,2-ethanethiolato complex **5** is formed. Some of the ethylene that is formed reacts with some of **2** to yield the vinylidene complex **3** by displacement of the 1,4-DTCH ligand. The related compound **6** could be made similarly by a process that does not lead to complete loss of the 1,4-DTCH ligand or by an independent reaction of **3** with 1,4-DTCH. The coordination position of the 1,4-DTCH ligand in **6** was not established. Compound **4** is also formed in the initial reaction. We have found that **4** can be obtained directly from **5** by heating and suspect that all of **4** is probably obtained via the intermediate **5**. Compound **2** is probably traversed as an intermediate in the pyrolysis of **1** and the reaction of $Os_3(CO)_{12}$ with 1,4-DTCH at 125 °C.



Scheme 1.

Our results demonstrate that cleavage of carbon–sulfur bonds in 1,4-DTCH is certainly more facile than that of monothiacyclohexane and is probably facilitated by the elimination of the stable molecule ethylene. It is possible that ethylene elimination from 1,4-DTCH will prove to be a convenient and general route to the formation of ethanedithiolato ligands in polynuclear metal complexes. Indeed, ethylene elimination may be a characteristic fragmentation pathway for a variety of 1,4-dithiacycloalkanes. In this regard, we note the recent report that the reaction of $Ru_3(CO)_{12}$ with 1,4,7-trithiacyclononane yielded the trithiaheptane complex $Ru_3(CO)_9(\mu\text{-}\eta^3\text{-}1,4,7\text{-SCHCHCCHCHS})$ by the apparent loss of an ethylene group from the 1,4,7-trithiacyclononane molecule [23].

4. Supplementary material

Tables of hydrogen atom positional parameters and anisotropic thermal parameters (10 pages) are available from author R.D.A.

Acknowledgements

Acknowledgment is made to the donors of The Petroleum Research Fund, administered by the American Chemical Society, and the Office of Basic Energy Sciences of the US Department of Energy for support of this research.

References

[1] (a) R.J. Angelici, *Acc. Chem. Res., 21* (1988) 387; (b) C.M. Friend and J.T. Roberts, *Acc. Chem. Res., 21* (1988) 394; (c) E.J. Markel, G.L. Schrader, N.N. Sauer and R.J. Angelici, *J. Catal., 116* (1989) 11; (d) R. Prins, V.H.N. De Beer and G.A. Somorjai, *Catal. Rev. Sci. Eng., 31* (1989) 1; (e) N.N. Sauer, E.J. Markel, G.L. Schrader and R.J. Angelici, *J. Catal., 117* (1989) 295; (f) H. Kwart, G.C.A. Schuit and B.C. Gates, *J. Catal., 61* (1980) 128; (g) J.T. Roberts and C.M. Friend, *J. Am. Chem. Soc., 108* (1986) 7204; (h) S. Kolboe, *Can. J. Chem., 47* (1969) 352; (i) J.F. Lang and R.I. Masel, *Surf. Sci., 183* (1987) 44; (j) W.R. Moser, G.A. Rossetti, J.T. Gleaves and J.R. Ebner, *J. Catal., 127* (1991) 190.

[2] (a) U. Riaz, O. Curnow and M.D. Curtis, *J. Am. Chem. Soc., 113* (1991) 1416; (b) M.D. Curtis, J.E. Penner-Hahn, J. Schwank, O. Beralt, D.J. McCabe, L. Thompson and G. Waldo, *Polyhedron, 7* (1988) 2411; (c) A.E. Ogilvy, M. Draganjac, T.B. Rauchfuss and S.R. Wilson, *Organometallics, 7* (1988) 1171; (d) L. Luo, A.E. Ogilvy, T.B. Rauchfuss, A.L. Rheingold and S.R. Wilson, *Organometallics, 10* (1991) 1002, and refs. therein.

[3] (a) R.D. Adams, *J. Cluster Sci., 3* (1992) 263; (b) R.D. Adams, J.A. Belinski and M.P. Pompeo, *Organometallics, 10* (1991) 2539; (c) R.D. Adams and M.P. Pompeo, *Organometallics, 11* (1992) 1460; (d) *J. Am. Chem. Soc., 113* (1991) 1619; (e) R.D. Adams and J.A. Belinski, *Organometallics, 11* (1992) 2488; (f) R.D. Adams, J.A. Belinski and M.P. Pompeo, *Organometallics, 11* (1992) 3129; (g) R.D. Adams and M.P. Pompeo, *Organometallics, 11* (1992) 103; (h) *11* (1992) 2281; (i) R.D. Adams, J.A. Belinski and M.P. Pompeo, *Organometallics, 11* (1992) 2016.

[4] R.D. Adams, J.A. Belinski and M.P. Pompeo, *Organometallics, 11* (1992) 3422.

[5] (a) R.D. Adams, J.E. Cortopassi and S.B. Falloon, *J. Organomet. Chem., 463* (1993) C5; (b) *Organometallics, 11* (1992) 3794; (c) R.D. Adams, J.A. Belinski and J.A. Schierlmann, *J. Am. Chem. Soc., 113* (1991) 9004.

[6] R.D. Adams, M.P. Pompeo, J.H. Yamamoto and W. Wu, *J. Am. Chem. Soc., 115* (1993) 8207.

[7] R.D. Adams, J.E. Cortopassi, J.H. Yamamoto and W. Wu, *Organometallics, 12* (1993) 4955.

[8] A. Shaver, P.J. Fitzpatrick, K. Steliou and I.S. Butler, *J. Am. Chem. Soc., 101* (1979) 1313.

[9] B.F.G. Johnson, J. Lewis and D. Pippard, *J. Organomet. Chem., 160* (1978) 263; *213* (1981) 249.

[10] J.N. Nicholls and M.D. Vargas, *Inorg. Synth., 28* (1989) 232.

[11] A.J. Deeming and M. Underhill, *J. Chem. Soc., Dalton Trans.,* (1974) 1415.

[12] *International Tables for X-ray Crystallography*; Vol. IV, Kynoch, Birmingham, UK, 1975; (a) pp. 99–101, Table 2.2B; (b) pp. 149–150, Table 2.3.1.

[13] M.R. Churchill and B.G. DeBoer, *Inorg. Chem., 16* (1977) 878.

[14] C.G. Pierpont, *Inorg. Chem., 17* (1978) 1976.

[15] R.D. Adams, I.T. Horváth, B.E. Segmüller and L.-W. Yang, *Organometallics, 2* (1983) 144.

[16] E.G. Bryan, B.F.G. Johnson and J. Lewis, *J. Chem. Soc., Dalton Trans.,* (1977) 144.

[17] M. Tachikawa, S.I. Richter and J.R. Shapley, *J. Organomet. Chem., 128* (1977) C9.

[18] R.D. Adams, G. Chen, S. Sun and T.A. Wolfe, *J. Am. Chem. Soc., 112* (1990) 868.

[19] (a) M. McKenna, L.L. Wright, D.J. Miller, L. Tanner, R.D. Haltiwanger and M. Rakowski DuBois, *J. Am. Chem. Soc., 105* (1983) 5329; (b) M.Rakowski DuBois, R.D. Haltiwanger, D.J. Miller and G. Glatzmaier, *J. Am. Chem. Soc., 101* (1979) 5245.

[20] V.F. Allen, R. Mason and P.B. Hitchcock, *J. Organomet. Chem., 140* (1977) 297.

[21] F.W.B. Einstein, T. Jones and K.G. Tyers, *Acta Crystallogr., Sect. B, 38* (1982) 1272.

[22] P.A. Dawson, B.F.G. Johnson, J. Lewis, J. Puga, P.R. Raithby and M.J. Rosales, *J. Chem. Soc., Dalton Trans.,* (1982) 233.

[23] S. Rossi, K. Kallinen, J. Pursiainen, T.T. Pakkanen and T.A. Pakkanen, *J. Organomet. Chem., 440* (1992) 367.