Synthesis and structural characterisation of a novel tris-methylene bridged compound $(NO)_4Fe_2Se(\mu\text{-}CH_2)_3$

Pradeep Mathur [a,*], Bala Manimaran [a], Md. Munkir Hossain [a], Arnold L. Rheingold [b],
Louise M. Liable-Sands [b], Glenn P.A. Yap [b]

[a] *Department of Chemistry, Indian Institute of Technology, Powai, Bombay 400 076, India*
[b] *Department of Chemistry, University of Delaware, Newark, DE 19716, USA*

Received 18 December 1996; revised 1 February 1997

Abstract

The tris-methylene bridged compound $(NO)_4Fe_2Se(\mu\text{-}CH_2)_3$ has been isolated. It has been characterised by IR and ^1H, ^{13}C, and ^{77}Se NMR spectroscopy. Its structure has been determined by single-crystal X-ray diffraction methods. The structure consists of a heavy atom triangle consisting of one Se and two Fe atoms. The Fe–Fe and the two Fe–Se edges are bridged by methylene groups. © 1997 Published by Elsevier Science S.A.

Keywords: Chalcogen; Alkylidene clusters

1. Introduction

The bridging and stabilising nature of chalcogen atoms have been extensively utilised in the cluster growth reactions [1]. Recent literature reveals that chalcogen stabilised cluster compounds are widely used in the reactivity study with organic and inorganic species [2]. The convenient synthesis of homo- and mixed-chalcogenide iron carbonyl clusters has expanded the synthetic developments in the area of mixed metal, mixed chalcogenide clusters [3]. Synthesis and characterisation of metal alkylidene clusters are interesting because these species are known to be intermediates in many catalytic reactions [4]. Possible involvement of methylene groups in carbon monoxide reduction on metal surfaces continues to attract interest in the synthesis of metal complexes containing bridging methylene groups [5]. In previous studies we have used diazomethane as a conveniently prepared reagent for reactions with $(CO)_6Fe_2(\mu\text{-}E_2)$ and $(CO)_9Fe_3(\mu_3\text{-}E)_2$ and have obtained different types of methylene bridged iron carbonyl compounds [6,7]. Typically, diazomethane is prepared from basic solution of N-methyl-N-nitroso-p-toluenesulfonamide. Apart from their use as convenient

sources of carbene, $:C(H)R$ $(R = H$ or $CH_3)$ species, N-alkyl-N-nitrosourea derivatives and N-alkyl-N-nitroso-p-toluenesulfonamide have also been shown to be good nitrosylating agents. For example, the reaction of N-alkyl-N-nitrosourea with $[(CO)_2CoC_5H_5]$ forms the nitrosylated compound $[(CO)(NO)Co_2(C_5H_5)_2]$ [8]. Re-examination of an earlier studied addition of base to N-methyl-N-nitroso-p-toluenesulfonamide in diethyl ether, as a means of generating diazomethane, and addition of the ethereal distillate to $(CO)_9Fe_3(\mu_3\text{-}Se)_2$ shows that in addition to the methylene bridged iron carbonyl compounds $\{(CO)_3Fe(\mu\text{-}CH_2)Se\}_2$, $(CO)_6Fe_2(\mu\text{-}SeCH_3)_2$, $(CO)_6Fe_2(\mu\text{-}SeCH_2Se)$, $(CO)_6Fe_2(\mu\text{-}SeCH_2CH_2Se)$, an unusual tris-methylene bridged iron nitrosyl compound is also produced. Its isolation and complete characterisation are reported here.

2. Experimental

2.1. General procedures

All reactions and other manipulations were performed using standard Schlenk techniques under an atmosphere of pre-purified dry argon. The solvents were purified, dried and distilled under nitrogen atmosphere prior to use, according to the literature methods [9].

* Corresponding author.

Table 1
Crystallographic data for $(NO)_4Fe_2Se(\mu\text{-}CH_2)_3$

(a) Crystal parameters	
formula	$C_3H_6Fe_2N_4O_4Se$
formula weight	352.8
crystal system	monoclinic
space group	Cc
a (Å)	12.240(10)
b (Å)	7.438(4)
c (Å)	11.700(10)
β (deg)	103.98(8)
V (Å^3)	1034(1)
Z	4
crystal dimensions (mm^3)	$0.38 \times 0.38 \times 0.42$
crystal colour	orange–red
D_{calc} (g cm^3)	2.267
μ(Mo Kα) (cm^{-1})	63.22
temperature (K)	296
T_{max} / T_{min}	3.26
(b) Data collection	
diffractometer	Siemens P4
monochromator	graphite
radiation	Mo Kα ($\lambda = 0.71073$ Å)
2θ scan range (deg)	4.0–45.0
data collected (h,k,l)	$+13, -8, \pm12$
independent observed reflections $F_o \geq 4\sigma(F_o)$	456
(c) Refinement [a]	
$R(F)$ (%)	8.98
$R(wF)$ (%)	10.70
Δ/σ (max)	0.00
$\Delta(\rho)$ (e Å^{-3})	1.83
N_o / N_v	5.1
GOF	1.54

[a] Quantity minimised $\Sigma w\Delta^2$; $R = \Sigma\Delta / \Sigma(F_o)$; $R(w) = \Sigma\Delta w^{1/2} / \Sigma(F_o w^{1/2})$, $\Delta = |(F_o - F_c)|$.

Infrared spectra were recorded on a Nicolet Impact 400 FT spectrometer as hexane solutions in 0.1 mm path-length NaCl cells. NMR spectra were obtained on a Varian VXR 300S spectrometer in CDCl$_3$. ^{77}Se NMR measurements were made at an operating frequency of 57.23 MHz using 90° pulses with 1.0 s acquisition time and the spectra were referenced to Me$_2$Se ($\delta = 0$). Elemental analysis was carried out using a Carlo Erba automatic analyser. $(CO)_9Fe_3(\mu\text{-}Se)_2$ was prepared as previously reported [10].

2.2. Preparation of $(NO)_4Fe_2Se(\mu\text{-}CH_2)_3$

To a cooled (0 °C) 30 ml diethyl ether solution of N-methyl-N-nitroso-p-toluenesulfonamide (2.14 g) was added a solution of KOH (4 g in 10 ml of 96% ethanol). The ethereal solution was distilled into an ether solution (50 ml) of $(CO)_9Fe_3(\mu_3\text{-}Se)_2$ (0.5 g, 0.86 mmol) and the addition was continued till TLC and IR indicated total consumption of starting material $(CO)_9Fe_3(\mu_3\text{-}Se)_2$. The colour of the solution changed from violet to brown–red.

The reaction mixture was stirred at room temperature for a further 2 h. The solution was filtered through Celite and the solvent was evaporated. The mixture was re-dissolved in hexane and subjected to chromatographic work-up on silica-gel TLC plates using hexane as eluant. This yielded five orange coloured bands. The first four compounds were identified as previously reported $\{(CO)_3Fe(\mu\text{-}CH_2)Se\}_2$ (62 mg, 12%), $(CO)_6Fe_2(\mu\text{-}SeCH_3)_2$ (56 mg, 11%), $(CO)_6Fe_2(\mu\text{-}SeCH_2Se)$ (42 mg, 8%) and $(CO)_6Fe_2(\mu\text{-}SeCH_2CH_2Se)$ (32 mg, 6%) [7]. The fifth orange band was characterised as the new compound $(NO)_4Fe_2Se(\mu\text{-}CH_2)_3$ (72 mg, 23%). IR ($\nu(NO)$, cm^{-1}) 1819 (w), 1784 (s), 1759 (s), 1746 (w). ^{1}H NMR: δ 2.01 (d, $J = 5.1$ Hz), δ 4.42 (d, $J = 5.1$ Hz) ($^2J_{H-Se} = 36.7$ Hz) [FeSe(μ-CH_2)], δ 8.98 (d, $J = 3.3$ Hz), δ 9.77 (d, $J = 3.3$ Hz) [FeFe(μ-CH_2)]. ^{13}C(^{1}H) NMR: δ 22.1 (t, $J_{C-H} = 163.9$ Hz) [FeSe(μ-CH_2)], δ 134.5 (t, $J_{C-H} = 145.4$ Hz) [FeFe(μ-CH$_2$)]. ^{77}Se(^{1}H) NMR: δ −287 (t, $^2J_{Se-H} = 36.8$ Hz). Anal. Found: C, 10.4; H, 1.81; N, 15.9. $C_3H_6Fe_2N_4O_4Se$ Calc.: C, 10.2; H, 1.70; N, 15.9%. M.p. 89–91 °C.

2.3. Crystal structure determination of $(NO)_4Fe_2Se(\mu\text{-}CH_2)_3$

Crystal, data collection, and refinement parameters are given in Table 1. Suitable crystals were selected, sectioned, and mounted with epoxy cement on glass fibres. The unit-cell parameters were obtained by the least-squares refinement of the angular settings of 24 reflections ($20° \leq 2\theta \leq 24°$). All inspected crystals were found to be either twinned or multiple. Approximately 15% of the data set was rejected by the learnt-profile routine as spurious diffraction contributions from a minor twin or satellite crystal. The systematic absences

Table 2
Atomic co-ordinates ($\times 10^4$) and equivalent isotropic displacement coefficients (Å$^2 \times 10^3$) for $(NO)_4Fe_2Se(\mu\text{-}CH_2)_3$

Atom	x	y	z	U_{eq}
Se	9432	1364(5)	9192	48(1) *
Fe(1)	11610(6)	1958(7)	10145(5)	42(2) *
Fe(2)	10497(5)	3561(7)	8048(5)	44(2) *
C(1)	11986(42)	2349(63)	8562(41)	56(9)
C(2)	9029(45)	3645(65)	8477(49)	70(12)
C(3)	10155(38)	1849(58)	10747(40)	48(9)
N(4)	12191(30)	−88(48)	10535(29)	47(7)
N(5)	12370(31)	3737(47)	10912(32)	50(8)
N(6)	11000(30)	5643(58)	8414(33)	56(8)
N(7)	10222(36)	2875(56)	6663(35)	63(9)
O(4)	12758(34)	−1355(40)	10919(33)	76(15) *
O(5)	12952(26)	4758(45)	11497(24)	65(12) *
O(6)	11316(42)	7132(51)	8495(33)	85(15) *
O(7)	9972(43)	2802(59)	5554(25)	95(19) *

* Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor.

Table 3
Bond distances (Å) and bond angles (deg) for $(NO)_4Fe_2Se(\mu\text{-}CH_2)_3$

Se–Fe(1)	2.666(7)	Se–Fe(2)	2.647(7)
Se–C(2)	1.904(49)	Se–C(3)	1.855(43)
Fe(1)–Fe(2)	2.773(8)	Fe(1)–C(1)	2.035(53)
Fe(1)–C(3)	2.068(52)	Fe(1)–N(4)	1.695(36)
Fe(1)–N(5)	1.737(34)	Fe(2)–C(1)	1.993(49)
Fe(2)–C(2)	1.980(60)	Fe(2)–N(6)	1.683(42)
Fe(2)–N(7)	1.654(41)	N(4)–O(4)	1.192(47)
N(5)–O(5)	1.148(45)	N(6)–O(6)	1.169(58)
N(7)–O(7)	1.261(49)		
Fe(1)–Se–Fe(2)	62.9(2)	Fe(1)–Se–C(2)	99.4(16)
Fe(2)–Se–C(2)	48.2(18)	Fe(1)–Se–C(3)	50.6(16)
Fe(2)–Se–C(3)	101.5(15)	C(2)–Se–C(3)	105.6(20)
Se–Fe(1)–Fe(2)	58.2(2)	Se–Fe(1)–C(1)	93.8(14)
Fe(2)–Fe(1)–C(1)	45.9(14)	Se–Fe(1)–C(3)	43.9(12)
Fe(2)–Fe(1)–C(3)	92.2(12)	C(1)–Fe(1)–C(3)	135.9(18)
Se–Fe(1)–N(4)	106.0(12)	Fe(2)–Fe(1)–N(4)	135.1(12)
C(1)–Fe(1)–N(4)	101.6(19)	C(3)–Fe(1)–N(4)	102.3(18)
Se–Fe(1)–N(5)	134.3(13)	Fe(2)–Fe(1)–N(5)	102.5(12)
C(1)–Fe(1)–N(5)	98.7(19)	C(3)–Fe(1)–N(5)	104.6(19)
N(4)–Fe(1)–N(5)	114.1(16)	Se–Fe(2)–Fe(1)	58.9(2)
Se–Fe(2)–C(1)	95.4(15)	Fe(1)–Fe(2)–C(1)	47.1(15)
Se–Fe(2)–C(2)	45.8(14)	Fe(1)–Fe(2)–C(2)	94.1(15)
C(1)–Fe(2)–C(2)	139.3(21)	Se–Fe(2)–N(6)	129.4(15)
Fe(1)–Fe(2)–N(6)	95.7(13)	C(1)–Fe(2)–N(6)	95.0(18)
C(2)–Fe(2)–N(6)	101.9(20)	Se–Fe(2)–N(7)	107.2(15)
Fe(1)–Fe(2)–N(7)	132.4(14)	C(1)–Fe(2)–N(7)	96.4(21)
C(2)–Fe(2)–N(7)	106.0(22)	N(6)–Fe(2)–N(7)	120.6(20)
Fe(1)–C(1)–Fe(2)	87.0(22)	Se–C(2)–Fe(2)	85.9(21)
Se–C(3)–Fe(1)	85.4(21)	Fe(1)–N(4)–O(4)	168.3(33)
Fe(1)–N(5)–O(5)	171.8(34)	Fe(2)–N(6)–O(6)	170.2(37)
Fe(2)–N(7)–O(7)	164.4(38)		

in the diffraction data are consistent for space groups Cc and $C2/c$. Although the E-statistics suggested the non-centrosymmetric option, the centrosymmetric space group was also explored but abandoned because of chemically unreasonable results of refinement. The structure was solved using direct methods, completed by subsequent difference Fourier syntheses and refined by full-matrix least-squares procedures. Semi-empirical absorption corrections were applied. Selenium, iron and oxygen atoms were refined with anisotropic displacement coefficients. Hydrogen atoms were treated as idealised contributions. The largest remaining peak in the difference map ($1.8\,e\,Å^{-3}$) occurs at a chemically unreasonable position and was considered as noise. Atomic co-ordinates, bond distances and bond angles are given in Tables 2 and 3.

All software and sources of the scattering factors are contained in the SHELXTL PLUS (4.2) program library (G. Sheldrick, Siemens XRD, Madison, WI).

3. Results and discussion

An ethereal solution of N-methyl-N-nitroso-p-toluenesulfonamide and an ethanolic solution of potas-

sium hydroxide were mixed at 0 °C and distilled at 35 °C into a flask containing an ethereal solution of $(CO)_9Fe_3(\mu\text{-}Se)_2$. Room temperature stirring for 2 h yielded the previously reported compounds $\{(CO)_3Fe(\mu\text{-}CH_2)Se\}_2$, $(CO)_6Fe_2(\mu\text{-}SeCH_3)_2$, $(CO)_6Fe_2(\mu\text{-}SeCH_2Se)$, $(CO)_6Fe_2(\mu\text{-}SeCH_2CH_2Se)$ and the new tris-methylene compound $(NO)_4Fe_2Se(\mu\text{-}CH_2)_3$. The new compound was characterised by IR and ^1H, ^{13}C and ^{77}Se NMR spectroscopy. Its IR spectrum showed the presence of only terminally bonded nitrosyl groups. ^1H and ^{13}C NMR spectra confirmed the presence of two types of CH_2 groups and the proton-coupled ^{77}Se NMR spectrum showed a triplet for the Se atom bonded to two equivalent CH_2 groups. Elemental analysis confirmed the molecular formula of $(NO)_4Fe_2Se(\mu\text{-}CH_2)_3$.

Orange–red, air stable crystals of $(NO)_4Fe_2Se(\mu\text{-}CH_2)_3$ were grown from CH_2Cl_2/hexane solution at 0 °C, and an X-ray analysis was undertaken. The two different views of the molecular structure of $(NO)_4Fe_2Se(\mu\text{-}CH_2)_3$ are shown in Fig. 1. The core geometry of $(NO)_4Fe_2Se(\mu\text{-}CH_2)_3$ consists of a heavy atom triangle composed of one Se and two Fe atoms. The Fe–Fe $(2.773(8)\,Å)$ and the Fe–Se $(2.666(7), 2.647(7)\,Å)$ bond distances in the three-membered Fe_2Se core of $(NO)_4Fe_2Se(\mu\text{-}CH_2)_3$ are longer than the Fe–Fe and Fe–Se bond distances observed in related compounds: Fe–Fe bond distance in $(CO)_6Fe_2(\mu\text{-}SeCH_2Se)$, $2.527(1)\,Å$; $(CO)_6Fe_2(\mu\text{-}SeCH_3)_2$, $2.563(5)\,Å$ [11]; $(CO)_6Fe_2\{\mu\text{-}SeC(Ph)=C(H)Se\}$, $2.512(1)\,Å$ [12]; $(CO)_6Fe_2\{\mu\text{-}SeC(Ph)C(H)Se\}Pt(PPh_3)_2$, $2.534(2)\,Å$ [13] and $(CO)_5(PPh_3)Fe_2\{\mu\text{-}SeC(CH_2OH)=C(H)Se\}$,
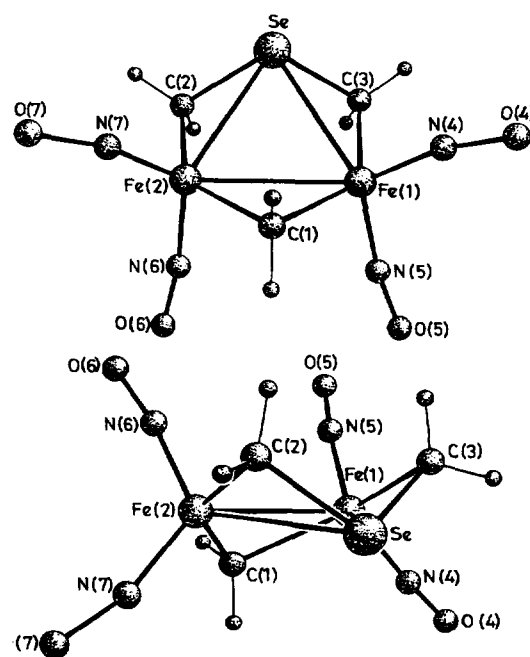

Fig. 1. Two different views of the molecular structure of $(NO)_4Fe_2Se(\mu\text{-}CH_2)_3$.

2.533(3) Å [14]; Fe–Se bond distances in $\{(CO)_3Fe(\mu\text{-}CH_2)Se\}_2$ (2.418 Å) [7], $(CO)_6Fe_2Se_2(\mu\text{-}C(H)CH_3)_2$ (2.424 Å) [15], $(CO)_6Fe_2(\mu\text{-}SeCH_2Se)$ (2.379 Å), $(CO)_6Fe_2(\mu\text{-}SeCH_2CH_2Se)$ (2.361 Å), $(CO)_6Fe_2(\mu\text{-}SeCH_3)_2$ (2.381 Å), $(CO)_6Fe_2\{\mu\text{-}SeC(Ph)=C(H)Se\}$ (2.385 Å), $\{(CO)_6Fe_2(\mu\text{-}Se)_2\}_2C(Ph)–C(H)$ (2.368 Å) [12] and $(CO)_6Fe_2(\mu\text{-}Se_2)Pt(PPh_3)_2$ (2.401 Å) [16]. The Fe–N–O bond angles range from 164(4)° to 172(3)°, consistent with their function as three-electron donors.

Formation of $(NO)_4Fe_2Se(\mu\text{-}CH_2)_3$ represents the first example of incorporation of three methylene groups into a chalcogen bridged iron carbonyl compound. Although there are many examples of compounds containing one or two methylene groups, tris-methylene bridged compounds are rare, a previous example of one such compound being $Ru_2(CH_2)_3(PMe_3)_6$ [17]. For the formation of $(NO)_4Fe_2Se(\mu\text{-}CH_2)_3$, either N-methyl-N-nitroso-p-toluenesulfonamide or some other NO-containing species must have co-distilled along with the ether solution of CH_2N_2. The formal replacement of the carbonyl ligands by nitrosyl groups further demonstrates that indeed, in addition to the use of N-methyl-N-nitroso-p-toluenesulfonamide as a convenient diazomethane precursor, it can be used as a mild nitrosylating agent.

Acknowledgements

References

[1] K.H. Whitmire, J. Coord. Chem. 17 (1988) 95; L. Linford, H.G. Raubenheimer, Adv. Organomet. Chem. 32 (1991) 1; N.A. Compton, R.J. Errington, N.C. Norman, Adv. Organomet. Chem. 31 (1990) 91.

[2] D. Seyferth, G.B. Womack, Organometallics 5 (1986) 2360; D. Seyferth, G.B. Womack, R.S. Henderson, M. Cowie, B.M. Hames, Organometallics 5 (1986) 1568; D. Seyferth, R.S. Henderson, L.-C. Song, G.B. Womack, J. Organomet. Chem. 292 (1985) 9.

[3] P. Mathur, D. Chakrabarty, Md.M. Hossain, R.S. Rashid, J. Organomet. Chem. 420 (1991) 79; P. Mathur, D. Chakrabarty, Md.M. Hossain, J. Organomet. Chem. 401 (1991) 167; P. Mathur, P. Sekar, C.V.V. Satyanarayana, M.F. Mahon, Organometallics 14 (1995) 2115.

[4] R.C. Brady, R. Pettit, J. Am. Chem. Soc. 102 (1980) 6181; R.H. Grubbs, in G. Wilkinson, F.G.A. Stone, E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, vol. 9, Pergamon Press, Oxford, 1982, Chap. 54, p. 499; L.R. Gilliom, R.H. Grubbs, J. Am. Chem. Soc. 108 (1986) 733; W.J. Feast, V.C. Gibson, K.J. Ivin, A.M. Kenwright, E. Khosravi, J. Chem. Soc., Chem. Commun. (1994) 1399; T.J. Katz, S.J. Lee, J. Am. Chem. Soc. 102 (1980) 422; A.F. Dyke, S.A.R. Knox, P.J. Naish, G.E. Taylor, J. Chem. Soc., Chem. Commun. (1980) 203; M. Brookhart, J.R. Tucker, G.R. Hush, J. Am. Chem. Soc. 105 (1983) 258; L.F. Cannizo, R.H. Grubbs, J. Org. Chem. 50 (1985) 2316; L.E. Clawson, S.L. Buchwald, R.H. Grubbs, J. Am. Chem. Soc. 25 (1984) 5733.

[5] C. Zheng, Y. Apeloig, R. Hoffmann, J. Am. Chem. Soc. 110 (1988) 749; C.P. Casey, J.D. Audett, Chem. Rev. 86 (1986) 339; J.E. Hahn, Progr. Inorg. Chem. 31 (1984) 205.

[6] P. Mathur, V.D. Reddy, J. Organomet. 387 (1990) 193; P. Mathur, V.D. Reddy, R. Bohra, J. Organomet. Chem. 401 (1991) 339; P. Mathur, V.D. Reddy, K. Das, U.C. Sinha, J. Organomet. Chem. 409 (1991) 255; P. Mathur, B. Manimaran, Md.M. Hossain, R. Shanbag, J. Murthy, I.S. Saranathan, C.V.V. Satyanarayana, M.M. Bhadbhade, J. Organomet. Chem. 490 (1995) 173; P. Mathur, B. Manimaran, Md.M. Hossain, C.V.V. Satyanarayana, V.G. Puranik, S.S. Tavale, J. Organomet. Chem. 493 (1995) 251.

[7] P. Mathur, B. Manimaran, R. Trivedi, Md.M. Hossain, M. Arabatti, J. Organomet. Chem. 515 (1996) 155.

[8] W.A. Herrmann, I. Bernal, Angew. Chem., Int. Ed. Engl. 16 (1977) 172.

[9] A.I. Vogel, Textbook of Practical Organic Chemistry, ELBS, Longman, 4th ed., 1984.

[10] P. Mathur, D. Chakrabarty, Md.M. Hossain, R.S. Rashid, V. Rugmini, A.L. Rheingold, Inorg. Chem. 31 (1992) 1106.

[11] P. Mathur, R. Trivedi, Md.M. Hossain, S.S. Tavale, V.G. Puranik, J. Organomet. Chem. 491 (1995) 291.

[12] P. Mathur, Md.M. Hossain, Organometallics 12 (1993) 2398.

[13] P. Mathur, Md.M. Hossain, K. Das, U.C. Sinha, J. Chem. Soc., Chem. Commun. (1993) 46.

[14] P. Mathur, Md.M. Hossain, S. Umbarkar, C.V.V. Satyanarayana, V.G. Puranik, J. Organomet. Chem. 506 (1996) 313.

[15] P. Mathur, B. Manimaran, C.V.V. Satyanarayana, B. Varghese, J. Organomet. Chem. 527 (1997) 83.

[16] V.W. Day, D.A. Lesch, T.B. Rauchfuss, J. Am. Chem. Soc. 104 (1982) 1290.

[17] R.A. Andersen, R.A. Jones, G. Wilkinson, M.B. Hursthouse, K.M.A. Malik, J. Chem. Soc., Chem. Commun. (1977) 865.