ELSEVIER

www.elsevier.nl/locate/ica

Inorganica Chimica Acta 294 (1999) 232–239

Inorganica Chimica Acta

Preparation of cyclopentadienyl molybdenum clusters linked by a cyclotetradeca-1,8-diyne ligand

Wen-Yann Yeh [a,*], Ming-Ann Hsu [a], Shie-Ming Peng [b], Gene-Hsiang Lee [b]

[a] *Department of Chemistry, National Sun Yat-Sen University, Kaohsiung 804, Taiwan*
[b] *Department of Chemistry, National Taiwan University, Taipei 106, Taiwan*

Received 30 December 1998

Dedicated to Professor Duward F. Shriver on the occasion of his 65th birthday.

Abstract

The diyne-bridged complexes $Cp_2Mo_2(CO)_4(\mu\text{-}\eta^2\text{-}C_{14}H_{20})$ (**1**) and $[Cp_2Mo_2(CO)_4]_2(\mu,\mu\text{-}\eta^2,\eta^2\text{-}C_{14}H_{20})$ (**2**) have been prepared from the reactions of cyclotetradeca-1,8-diyne ($C_{14}H_{20}$) with $Cp_2Mo_2(CO)_6$ in refluxing toluene, or with $Cp_2Mo_2(CO)_4$ at 25°C. In contrast, $Cp_2Mo_2(CO)_6$ reacts with $Ag^+BF_4^-$ and $C_{14}H_{20}$ to yield $[CpMo^+(CO)(\mu,\mu\text{-}\eta^2,\eta^2\text{-}C_{14}H_{20})]_2(BF_4^-)_2$ (**3-BF4**) through redox cleavage of the Mo–Mo bond. An alternative method to prepare **3-BF4** is via iodide abstraction of $CpMoI(CO)_3$ by $Ag^+BF_4^-$ in the presence of $C_{14}H_{20}$. Compound **3-BF4** reacts with Me_3NO in acetonitrile to afford $[CpMo^+(NCMe)(\mu,\mu\text{-}\eta^2,\eta^2\text{-}C_{14}H_{20})]_2(BF_4^-)_2$ (**4-BF4**). An alkyne–alkyne coupling reaction is achieved by treating **3-BF4** with PPN^+Cl^- to yield the cyclobutadienophane complex $CpMo(CO)Cl(\eta^4\text{-}C_4(C_{10}H_{20}))$ (**5**). Metathesis of **3-BF4** with $Na^+BPh_4^-$ gives $[CpMo^+(CO)(\mu,\mu\text{-}\eta^2,\eta^2\text{-}C_{14}H_{20})]_2(BPh_4^-)_2$ (**3-BPh4**), the crystal structure of which was determined by X-ray diffraction. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Crystal structures; Molybdenum complexes; Cyclobutadienyl complexes; Cycloalkadiyne complexes; Cluster complexes

---

1. Introduction

Reactions of alkyne derivatives with metal carbonyls are known to give a wide variety of organometallic and organic products [1]. In particular, cycloalkadiynes [2] are versatile starting materials for the synthesis of phanes, superphanes and cage compounds [3]. Gleiter et al. [4] have shown the reactions of cycloalkadiynes with $Fe(CO)_5$, $CpCo(CO)_2$ and $Cp^*Co(C_2H_4)_2$ to give metal-capped cyclobutadienophane and cyclobutadienosuperphane complexes. The coordination chemistry of cyclodiynes with transition metal clusters, however, has received less attention. We recently described the synthesis of triosmium and triiron carbonyl clusters containing cyclotetradeca-1,8-diyne ligands [5]. New cyclopentadienyl molybdenum clusters bridged by this cyclodiyne ligand are presented in this paper.

2. Experimental

2.1. General methods

All manipulations were carried out under an atmosphere of purified dinitrogen with standard Schlenk techniques [6]. Cyclotetradeca-1,8-diyne ($C_{14}H_{20}$) [7], $Cp_2Mo_2(CO)_6$ [8], $Cp_2Mo_2(CO)_4$ [9], and CpMo(CO)I [10] were prepared by literature methods. Silver tetrafluoroborate ($Ag^+BF_4^-$), sodium tetraphenylborate ($Na^+BPh_4^-$) and bis(triphenylphosphoranylidene)ammonium chloride (PPN^+Cl^-) from Aldrich were used as received. Trimethylamine oxide (Me_3NO) from Aldrich was sublimed (0.01 torr, 90°C) before use. Solvents were dried over appropriate reagents [11] under dinitrogen and distilled immediately before use. Preparative thin-layer chromatographic (TLC) plates were prepared from silica gel (Merck). IR spectra were recorded with a 0.1 mm path CaF_2 solution cell on a Hitachi I-2001 IR spectrometer. ^1H and ^{13}C NMR

---

[*] Corresponding author. Fax: +886-7-525 3908.

PII: S0020-1693(99)00207-8

spectra were obtained on a Varian VXR-300 spectrometer at 300 and 75.4 MHz, respectively. Fast atom bombardment (FAB) and electron impact (EI) mass spectra were recorded by using a VG Blotch-5022 mass spectrometer. Elemental analyses were performed at the National Science Council Regional Instrumentation Center at the National Chen-Kung University, Tainan, Taiwan.

2.2. Reaction of $Cp_2Mo_2(CO)_6$ and $C_{14}H_{20}$

$Cp_2Mo_2(CO)_6$ (50 mg, 0.1 mmol) and $C_{14}H_{20}$ (60 mg, 0.32 mmol) were added to a 100 ml Schlenk flask equipped with a reflux condenser under N_2. Toluene (50 ml) was introduced into the flask and the mixture was heated to reflux for 16 h, resulting in a change of color from red to brown. The solution was cooled to ambient temperature and the volatile materials were removed under vacuum. The residue was dissolved in CH_2Cl_2 and subjected to TLC, eluting with CH_2Cl_2/n-hexane (3:7 v/v). The first brown band afforded $Cp_2Mo_2(CO)_4(\mu\text{-}\eta^2\text{-}C_{14}H_{20})$ (**1**) (9 mg, 14%) and the second brown band afforded $[Cp_2Mo_2(CO)_4]_2(\mu,\mu\text{-}\eta^2,\eta^2\text{-}C_{14}H_{20})$ (**2**) (6 mg, 11%).

2.2.1. Compound *1*

Mass spectrum (FAB): *m*/*z* 626 (M^+; ^{98}Mo), 570 ($M^+ - 2CO$), 505 ($M^+ - 2CO - Cp$). IR (CH_2Cl_2, νCO): 1980s, 1944m, 1920vs, 1906vs, 1828w cm^{-1}. ^{1}H NMR ($CDCl_3$, 23°C): 5.21 (s, 10H, Cp), 2.91 (m, 4H, CH_2–CMo), 2.24 (m, 4H, CH_2–C≡), 1.55 (m, 12H, CH_2) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 23°C): 230.5 (CO), 109.4 (C≡C–Mo), 91.2 (Cp), 80.6 (C≡C), 38.25, 30.2, 28.5, 26.4, 18.0 (CH_2) ppm.

2.2.2. Compound *2*

Mass spectrum (FAB): *m*/*z* 1064 (M^+; ^{98}Mo), 1008 ($M^+ - 2CO$), 952 ($M^+ - 4CO$). IR (CH_2Cl_2, νCO): 1984s, 1946vs, 1928s, 1902vs, 1828w cm^{-1}. ^{1}H NMR ($CDCl_3$, 23°C): 5.16 (s, 20H, Cp), 2.81 (br, 8H, CH_2–CMo), 1.43 (br, 12H, CH_2) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 23°C): 229.2 (CO), 109 (C≡C–Mo), 90.1 (Cp), 30.7, 29.7, 28.6 (CH_2) ppm. *Anal.* Found: C, 47.58; H, 3.90. Calc. for $C_{42}H_{40}Mo_4O_8$: C, 47.76; H, 3.79%.

2.3. Reaction of $Cp_2Mo_2(CO)_4$ and $C_{14}H_{20}$

$C_{14}H_{20}$ (250 mg, 1.33 mmol) was dissolved in toluene (50 ml) under dinitrogen in a 100 ml Schlenk flask. The flask was placed in an ice-bath at 0°C and a solution of $Cp_2Mo_2(CO)_4$ (300 mg, 0.69 mmol) in 5 ml toluene was introduced. The mixture was stirred at 0°C for 5 min and then at ambient temperature for 1 h. The reaction mixture was worked up in a fashion identical to that above. Compounds **1** (201 mg, 47%) and **2** (71 mg, 20%) were obtained after separation by TLC.

2.4. Reaction of $Cp_2Mo_2(CO)_6$ and $C_{14}H_{20}$ in the presence of $AgBF_4$

$C_{14}H_{20}$ (300 mg, 1.6 mmol), $Cp_2Mo_2(CO)_6$ (340 mg, 0.69 mmol) and $AgBF_4$ (300 mg, 1.54 mmol) were placed in a 500 ml Schlenk flask under dinitrogen and CH_2Cl_2 (200 ml) was then added to the flask. The mixture was stirred vigorously at ambient temperature for 30 h, resulting in a color change from red to orange–yellow. The solvent was removed by a rotary evaporator and the residue was washed several times with benzene (3 × 10 ml) to remove the unreacted starting material. The residue was redissolved in CH_3CN (30 ml) and filtered through a Celite column (3 × 5 cm) to yield a clear orange–yellow solution. The solution was then layered with diethyl ether (50 ml) and left to settle at ambient temperature overnight. Yellow needle microcrystals of $[CpMo^+(CO)(\mu,\mu\text{-}\eta^2,\eta^2\text{-}C_{14}H_{20})]_2(BF_4^-)_2$ (**3-BF4**) (304 mg, 47%) were obtained. Mass spectrum (FAB): *m*/*z* 845 ($M^+ - BF_4$; ^{98}Mo, ^{11}B), 780, 752, 724, 696. IR (CH_2Cl_2, νCO): 2040 cm^{-1}. The NMR data indicated the presence of two isomers, **3A** and **3S**, in an approximate 3:2 ratio.

3A: ^{1}H NMR (CD_3CN, 23°C): 5.77 (s, 10H, Cp), 3.40 (m, 8H), 3.22 (m, 8H), 1.73 (m, 16H), 0.92 (m, 4H), 0.15 (m, 4H, CH_2) ppm. $^{13}C\{^1H\}$ NMR (CD_3CN, 23°C): 166.0, 148.2 (C≡C), 102.2 (Cp), 37.6, 33.1, 31.2, 30.8, 29.6 (CH_2) ppm.

3S: ^{1}H NMR (CD_3CN, 23°C): 5.75 (s, 10H, Cp), 3.40 (m, 8H), 3.22 (m, 8H), 1.73 (m, 16H), 0.92 (m, 4H), 0.15 (m, 4H, CH_2) ppm. $^{13}C\{^1H\}$ NMR (CD_3CN, 23°C): 164.5, 149.0 (C≡C), 102.5 (Cp), 37.5, 33.2, 31.4, 30.7, 30.3, 29.9 (CH_2) ppm.

Anion metathesis of **3-BF4** with $NaBPh_4$ was conducted in methanol solution under dinitrogen to afford $[CpMo^+(CO)(\mu,\mu\text{-}\eta^2,\eta^2\text{-}C_{14}H_{20})]_2(BPh_4^-)_2$ (**3-BPh4**). *Anal.* Found: C, 75.72; H, 6.60. Calc. for $C_{88}H_{90}B_2Mo_2O_2$: C, 75.91; H, 6.46%.

2.5. Reaction of $CpMo(CO)_3I$ with $AgBF_4$ and $C_{14}H_{20}$ to give *3-BF4*

$C_{14}H_{20}$ (320 mg, 1.70 mmol), $CpMo(CO)_3I$ (490 mg, 1.32 mmol) and $AgBF_4$ (308 mg, 1.58 mmol) were added to an oven-dried 500 ml Schlenk flask under dinitrogen. Dichloromethane (200 ml) was then introduced into the flask and the resulting mixture was vigorously stirred at room temperature (r.t.) for 30 h. A color change from red–brown to orange–yellow was observed during the reaction. The solvent was removed by a rotary evaporator and the remaining solid was washed several times with benzene to remove the unreacted reactants. The residue was extracted with CH_3CN (100 ml) and the extractant was removed by passing it through a Celite column (3 × 5 cm). The clear filtrate was concentrated to ca. 20 ml and topped with 50 ml of diethyl ether, yielding yellow needle crystals of **3-BF4** (188 mg, 31%).

*2.6. Reaction of **3-BF4** with Me_3NO in acetonitrile solvent*

$[CpMo^+(CO)(\mu,\mu\text{-}\eta^2,\eta^2\text{-}C_{14}H_{20})]_2(BF_4^-)_2$ (**3-BF4**) (30 mg, 0.032 mmol) and CH_3CN (10 ml) were introduced into a 50 ml Schlenk flask under a dinitrogen atmosphere. Me_3NO (5 mg, 0.07 mmol) in CH_3CN solvent (2 ml) was added dropwise into the flask at ambient temperature. The solution was stirred until the IR spectrum showed no νCO absorption at 2040 cm^{-1}. During the reaction, the solution changed color from yellow to light orange–yellow. The reaction mixture was filtered and the volatile materials were removed under vacuum. The residue was crystallized from CH_2Cl_2/n-hexane at −15°C to give orange–yellow crystals of $[CpMo^+(NCMe)(\mu,\mu\text{-}\eta^2,\eta^2\text{-}C_{14}H_{20})]_2(BF_4^-)_2$ (**4-BF4**) (24 mg, 78%). Mass spectrum (FAB): *m*/*z* 871 ($M^+ - BF_4$; ^{98}Mo, ^{11}B). ^1H NMR (CD_2Cl_2, 23°C): 5.51 (s, 10H, Cp), 5.45 (s, 10H, Cp), 3.35–2.90 (m, 16H, CH_2), 2.86 (s, 12H, NCMe), 2.00–1.54 (m, 16H, CH_2), 1.10–0.20 (m, 8H, CH_2) ppm. ^{13}C NMR (CD_2Cl_2, 23°C): 182.5, 180.3, 166.3, 164.3 (C≡C–Mo), 139.9 (CN–Mo), 139.79 (CN–Mo), 102.5, 101.6 (Cp), 38.4, 38.3, 32.0, 31.5, 31.1, 31.0, 30.6, 30.2, 30.0, 29.9, 29.5 (CH_2), 5.3, 5.2 (CH_3) ppm. The NMR data indicated the presence of two isomers, **4A** and **4S**, in an equal quantity.

Table 1
Crystallographic data for **3-BPh4**

Chemical formula	$C_{88}H_{90}B_2Mo_2O_2$
Crystal solvent	$2(CH_3CN)$
FW	1475.21
Crystal system	Triclinic
T (K)	295(2)
Space group	$P\bar{1}$
Unit cell dimensions	
a (Å)	12.7307(1)
b (Å)	13.0087(2)
c (Å)	13.4774(2)
α (°)	65.529(1)
β (°)	78.492(1)
γ (°)	70.451(1)
V ($Å^{3)}$	1909.56(4)
Z	1
D_{calc} (g cm^{-3})	1.283
μ (mm^{-1})	0.379
Radiation (Å)	0.71073
θ Range (°)	1.66–27.48
R_1 [a]	0.0557
wR_2 [a]	0.1261
GOF on F^2	1.006

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = \{\Sigma[w(|F_o|^2 - |F_c|)^2]/\Sigma w|F_o|^4]\}^{1/2}$.

*2.7. Reaction of **3-BF4** and PPN^+Cl^-*

$[CpMo^+(CO)(\mu,\mu\text{-}\eta^2,\eta^2\text{-}C_{14}H_{20})]_2(BF_4^-)_2$ (**3-BF4**) (20 mg, 0.022 mmol) and $(Ph_3P)_2N^+Cl^-$ (PPN^+Cl^-, 48 mg, 0.09 mmol) were placed in a 50 ml Schlenk flask under a dinitrogen atmosphere and CH_2Cl_2 (10 ml) was introduced into the flask by a syringe. The mixture was stirred at r.t. until the suspended particles disappeared (ca. 24 h), forming a clear yellow–green solution. The solvent was removed under vacuum. The residue was extracted with benzene, filtered and dried under vacuum. The extractant was crystallized from CH_2Cl_2/n-hexane at −15°C, affording slightly air-sensitive, green crystals of $CpMo(CO)Cl(\eta^4\text{-}C_4(C_{10}H_{20}))$ (**5**) (17 mg, 93%). Mass spectrum (EI): *m*/*z* 414 (M^+; ^{98}Mo, ^{35}Cl). IR (CH_2Cl_2, νCO): 1930 cm^{-1}. ^1H NMR (C_6D_6, 23°C): 5.10 (s, Cp), 3.70–1.50 (m, CH_2) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6, 23°C): 109.4 (Cp), 98.5 (C_4), 32.2, 23.3, 14.6 (CH_2) ppm.

*2.8. Structural determination of **3-BPh4***

A crystal of $[CpMo^+(CO)(\mu,\mu\text{-}\eta^2,\eta^2\text{-}C_{14}H_{20})]_2(BPh_4^-)_2$ (**3-BPh4**, ca. 0.30 × 0.20 × 0.07 mm) was mounted on a thin-walled glass capillary and aligned on a Siemens SMART-CCD diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The θ range for data collection is 1.66 to 27.48°. A total of 23 592 reflections were measured and 8739 reflections ($R_{int} = 0.0554$) were unique. Sadabs absorption correc-

Table 2
Selected atomic coordinates (× 10^4) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **3-BPh4**

Atom	*x*	*y*	*z*	U_{eq}
Mo	12787(1)	4164(1)	3168(1)	44(1)
O(1)	14504(3)	4508(4)	4284(4)	102(1)
C(1)	13893(4)	4373(4)	3878(4)	71(1)
C(2)	11867(3)	3096(3)	4368(3)	49(1)
C(3)	12471(3)	3247(3)	4896(3)	50(1)
C(4)	12891(4)	2924(4)	5972(3)	64(1)
C(5)	12125(4)	2399(4)	6930(3)	65(1)
C(6)	11051(3)	3295(3)	7100(3)	53(1)
C(7)	10300(4)	2778(4)	8081(3)	61(1)
C(8)	9277(3)	3718(4)	8307(3)	61(1)
C(9)	8432(3)	4261(3)	7486(3)	50(1)
C(10)	7887(3)	4083(3)	6907(3)	53(1)
C(11)	7762(4)	3209(4)	6520(4)	71(1)
C(12)	8796(6)	2820(5)	5781(5)	108(2)
C(13)	9127(4)	3700(4)	4816(4)	71(1)
C(14)	9921(4)	3242(5)	4014(4)	82(1)
C(15)	11083(4)	2452(4)	4380(4)	61(1)
C(16)	13016(4)	4272(4)	1322(3)	61(1)
C(17)	14057(3)	4091(4)	1680(3)	62(1)
C(18)	14328(4)	2969(4)	2506(4)	66(1)
C(19)	13456(4)	2464(4)	2671(4)	72(1)
C(20)	12602(4)	3307(4)	1958(4)	66(1)

tion [12] were carried out with $T_{\min} = 0.8471$ and $T_{\max} = 0.9280$. The structure was solved by the direct method and refined by full-matrix least-squares on F^2. The program used was the SHELXTL package. The data collection and refinement parameters are given in Table 1. Selected atomic positional parameters are collected in Table 2.

3. Results and discussion

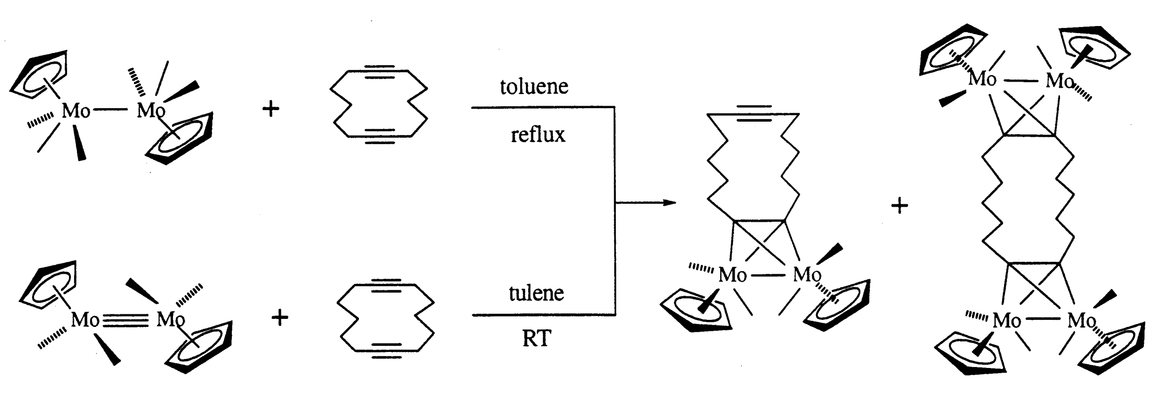
*3.1. Preparation and characterization of **1** and **2***

Cyclotetradeca-1,8-diyne ($C_{14}H_{20}$) reacts with $Cp_2Mo_2(CO)_6$ in refluxing toluene to form 1:1 and 1:2 adducts of $Cp_2Mo_2(CO)_4(\mu\text{-}\eta^2\text{-}C_{14}H_{20})$ (**1**) and $[Cp_2Mo_2(CO)_4]_2(\mu,\mu\text{-}\eta^2,\eta^2\text{-}C_{14}H_{20})$ (**2**) in 14 and 11% yield, respectively, in which the alkyne ligand acts as a four-electron donor, bridging the Mo–Mo bond. Low yields of **1** and **2** are due to the harsh reaction conditions necessary for the decarbonylation of $Cp_2Mo_2(CO)_6$ during diyne addition, resulting in considerable decomposition of the products. Thus, the molybdenum–molybdenum triple-bonded species $Cp_2Mo_2(CO)_4$ readily reacts with $C_{14}H_{20}$ at r.t. to afford **1** (47%) and **2** (20%) in better yields (Scheme 1). Alkyne-bridged dimolybdenum complexes of the type $L_2M_2(CO)_4(\mu\text{-}\eta^2\text{-}C_2RR')$ (L = Cp, indenyl; M = Mo, W; R, R′ = alkyl, aryl) [13] via thermal or photochemical reaction of $L_2M_2(CO)_n$ ($n = 4$ or 6) with RC≡CR′ are well known, while the double-bridged cyclodiyne cluster **2** is rare.

Compounds **1** and **2** form air-stable, reddish–brown crystalline solids, the FAB mass spectra of which present molecular ions at m/z 629 and 1065 for ^{98}Mo, respectively. Their IR absorption patterns in the carbonyl region are almost identical, suggesting a similar coordination environment surrounding the Mo_2 units, while the broad peak at 1828 cm^{-1} might indicate the presence of a bridging or semi-bridging CO ligand [14] for **1** and **2**. The molecular structures determined for the analogous complexes $Cp_2Mo_2(CO)_4(\mu\text{-}\eta^2\text{-}C_2R_2)$ (R = H, Et, Ph) [13c] show that the alkyne C≡C bond is perpendicular to the Mo–Mo vector, which contains a quasi-tetrahedral $[Mo_2C_2]$ core. The ^1H NMR spectra of **1** and **2** show sharp singlets for the Cp groups at 5.21 and 5.16 ppm, respectively, and complex multiplets for the diyne methylene protons. The $^{13}C\{^1H\}$ NMR spectrum of **1** displays a resonance at 91.2 ppm for the Cp carbons, five resonances in the range 38.3–18.0 ppm for the methylene carbons and two resonances at 109.4 and 80.6 ppm for the coordinated and free alkyne carbons, respectively. This would indicate a time-averaged C_s symmetry for **1** in solution. A more simple $^{13}C\{^1H\}$ NMR spectrum is recorded for **2**, showing one Cp carbon resonance at 90.1 ppm, one coordinated-alkyne carbon resonance at 109.0 ppm and three methylene carbon resonances at 30.7, 29.7 and 28.6 ppm, suggesting a time-averaged C_{2v} symmetry for **2** in solution.

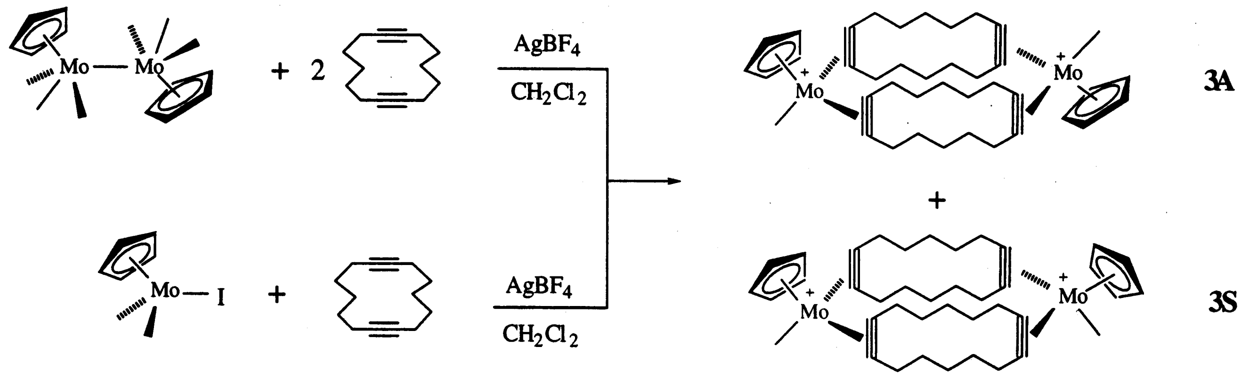
*3.2. Preparation and characterization of **3-BF4** and **4-BF4***

Despite the formation of **1** and **2**, treating $Cp_2Mo_2(CO)_6$ with $C_{14}H_{20}$ and $Ag^+BF_4^-$ leads to oxidative-cleavage of the Mo–Mo bond to form the bis(diyne) complex $[CpMo^+(CO)(\mu,\mu\text{-}\eta^2,\eta^2\text{-}C_{14}H_{20})]_2(BF_4^-)_2$ (**3-BF4**) in a 47% yield. An alternative route to **3-BF4** is through iodide abstraction of $CpMoI(CO)_3$ by $Ag^+BF_4^-$ in the presence of $C_{14}H_{20}$ (Scheme 2). The latter synthetic method has been established for the preparation of cationic molybdenum



1 **2**

Scheme 1.

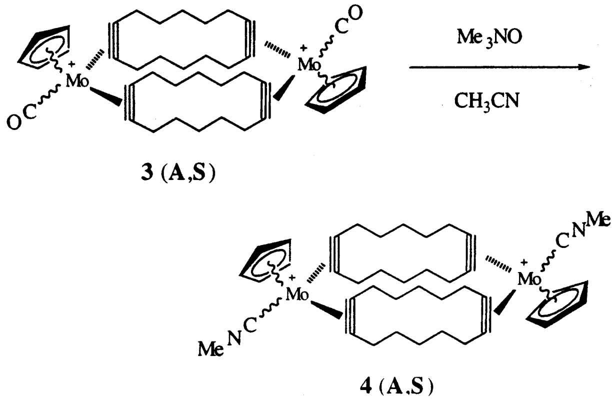


Scheme 2.

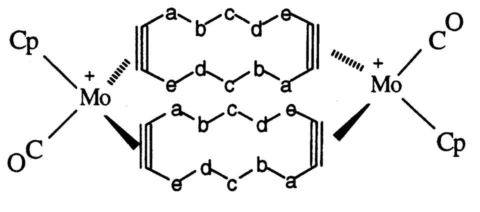
bis(alkyne) complexes $CpMo^+(CO)(\eta^2\text{-}C_2RR')$ [15], which exhibit a rich chemistry of ligand-coupling processes [16].

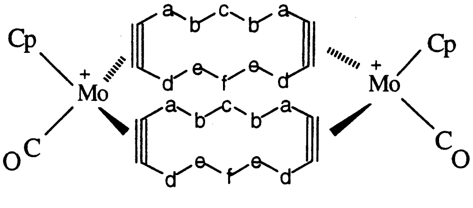
Since terminal CO and neutral cyclopentadienyl groups are normally considered as two- and five-electron donors, respectively, the remaining two alkyne ligands in **3-BF4** must supply six electrons, presumably from two π (||) orbitals and one π (⊥) orbital, to the cationic Mo^+ atom to satisfy the 18-electron rule. Compound **3-BF4** forms air-stable, yellow needle crystals. The FAB mass spectrum shows the highest ion peak at *m*/*z* 845 for ^{98}Mo, corresponding to loss of a BF_4^- species from the mother molecule. The IR spectrum gives only one absorption at 2040 cm^{-1} for the carbonyl groups. However, the ^1H and $^{13}C\{^1H\}$ NMR spectra clearly indicate the presence of two isomers in ca. 3:2 quantity. Since the four alkyne C≡C bonds are approximately parallel (see below), the two CO (and Cp) ligands can be on the same (*syn*, **3S**) or opposite side (*anti*, **3A**) of the molecule. On the basis of the structural symmetry (see below), **3A** is expected to display five ^{13}C resonances for the methylene carbons and **3S** to display six. Thus, the major isomer showing five equal intensity ^{13}C resonances in the range 37.6–29.6 ppm is assigned as **3A**, while the minor isomer **3S** presents six ^{13}C resonances in a 2:2:2:1:1:2 pattern in the same region.

Treatment of **3-BF4** with 2 equiv. of Me_3NO in CH_3CN solution effects displacement of two CO ligands by solvent molecules to generate $[CpMo^+(NCMe)(\mu,\mu\text{-}\eta^2,\eta^2\text{-}C_{14}H_{20})]_2(BF_4^-)_2$ (**4-BF4**) in 78% yield (Eq. (1)). The analogous acetonitrile complexes $[CpMo^+(NCMe)(\eta^2\text{-}C_2RR')]$ are accessible via acetonitrile reflux of $[CpMo^+(CO)(\eta^2\text{-}C_2RR')]$ in the presence of RC≡CR′ [17]. The FAB mass spectrum of **4-BF4** presents the highest mass at *m*/*z* 871 for ^{98}Mo, corresponding to the fragment of the mother molecule minus a BF_4^- group. Except different signals for the CO and NCMe ligands, the ^1H and $^{13}C\{^1H\}$ NMR patterns of **4-BF4** are in good agreement with those for **3-BF4**, while two isomers (**4A** and **4S**) are produced in approximately equal quantities.



(1)


anti **3A**


syn **3S**

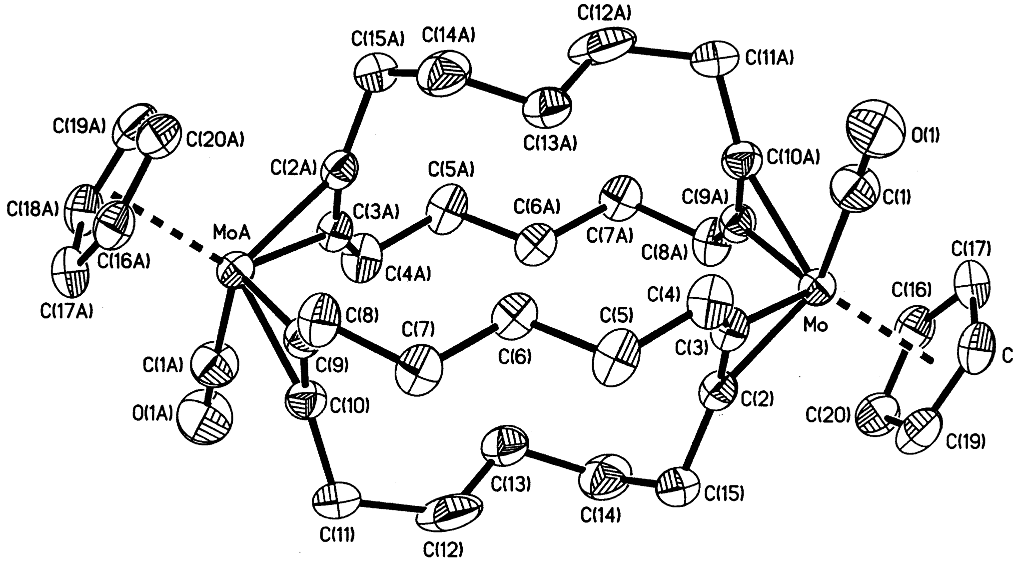


Fig. 1. Molecular structure of [CpMo$^+$(CO)(μ,μ-η^2,η^2-C$_{14}$H$_{20}$)]$_2$(BPh$_4^-$)$_2$ (**3-BPh4**). The hydrogen atoms and the tetraphenylborate groups have been artificially omitted for clarity.

3.3. Crystal structure of **3A-BPh4**

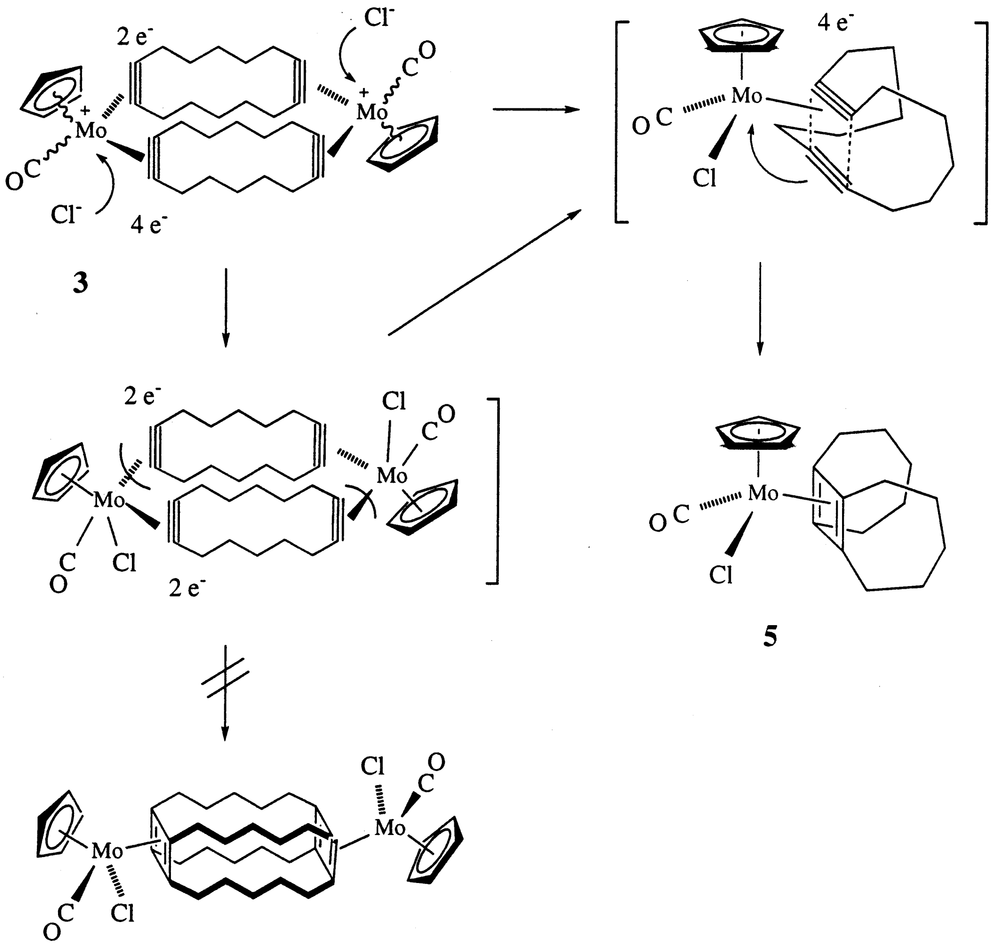
Attempts to grow single crystals of **3-BF4** in either isomeric form were unsuccessful. Fortunately, metathesis of BF$_4^-$ anions by the bulkier BPh$_4^-$ species affords **3-BPh4**, the crystals of which, grown from a saturated acetonitrile solution at −10°C, were found suitable for an X-ray diffraction study.

The crystal contains an order array of discrete monomeric molecule units which are mutually separated by normal van der Waals distances. An ORTEP diagram is shown in Fig. 1, where the hydrogen atoms and the BPh$_4^-$ groups are artificially omitted for clarity. Selected bond distances and bond angles are collected in Table 3. A crystallographically-imposed center of inversion is present; with the CO (and Cp) ligands in the *anti*-position, this structure corresponds to the **3A** isomer.

3A consists of two [(η^5-C$_5$H$_5$)Mo$^+$(CO)] units bridged by two cyclotetradeca-1,8-diyne ligands, characteristic of a three-legged 'piano-stool' configuration. Taking the centers of the alkynes, the center of the cyclopentadienyl ligand and the terminal CO ligand (Mo–C(1)–O(1) = 178.7(4)°), the coordination about each molybdenum atom can be described as a distorted tetrahedron. The parallel alkyne C≡C vectors are tilted towards the WCO group (5.9° to C(3)–C(2) and 5.6° to C(10A)–C(9A)); this gives rise to slight differences between the upper and lower C–W distances, such that Mo–C(3) = 2.158(4), Mo–C(2) = 2.096(4), Mo–C(10A) = 2.116(4) and Mo–C(9A) = 2.075(4) Å. The alkyne C≡C lengths are only slightly different, with C(2)–C(3) = 1.255(5) and C(9A)–C(10A) = 1.271(5) Å. The cyclopentadienyl group is bonded asymmetrically to the Mo atom, with the Mo–C distances ranging from 2.325(4) to 2.410(4) Å.

Table 3
Selected bond distances and bond angles for **3-BPh4**

Bond distances (Å)			
Mo–C(1)	1.994(5)	Mo–C(9A)	2.075(4)
Mo–C(2)	2.096(4)	Mo–C(10A)	2.116(4)
Mo–C(3)	2.158(4)	Mo–C(17)	2.325(4)
Mo–C(18)	2.340(4)	Mo–C(16)	2.397(4)
Mo–C(20)	2.407(4)	Mo–C(19)	2.410(4)
C(1)–O(1)	1.131(5)	C(2)–C(3)	1.255(5)
C(2)–C(15)	1.496(5)	C(3)–C(4)	1.490(5)
C(9)–C(10)	1.271(5)	C(9)–C(8)	1.483(5)
C(10)–C(11)	1.496(6)	C(16)–C(17)	1.413(6)
C(16)–C(20)	1.400(6)	C(17)–C(18)	1.400(6)
C(18)–C(19)	1.408(7)	C(19)–C(20)	1.432(7)
Bond angles (°)			
C(1)–Mo–C(9A)	110.9(2)	C(1)–Mo–C(2)	109.3(2)
C(2)–Mo–C(9A)	102.6(1)	C(1)–Mo–C(10A)	76.2(2)
C(10A)–Mo–C(9A)	35.3(2)	C(2)–Mo–C(10A)	109.6(1)
C(1)–Mo–C(3)	75.1(2)	C(9A)–Mo–C(3)	113.3(1)
C(2)–Mo–C(3)	34.3(1)	C(10A)–Mo–C(3)	99.0(2)
C(1)–Mo–C(17)	91.0(2)	C(9A)–Mo–C(17)	103.3(2)
C(2)–Mo–C(17)	138.3(2)	C(10A)–Mo–C(17)	110.5(2)
C(3)–Mo–C(17)	143.4(2)	C(1)–Mo–C(18)	85.9(2)
C(9A)–Mo–C(18)	137.0(2)	C(2)–Mo–C(18)	108.7(2)
C(10A)–Mo–C(18)	141.3(2)	C(3)–Mo–C(18)	109.2(2)
C(17)–Mo–C(18)	34.9(2)	C(1)–Mo–C(16)	124.5(2)
C(9A)–Mo–C(16)	81.8(2)	C(2)–Mo–C(16)	120.5(2)
C(10A)–Mo–C(16)	106.4(2)	C(3)–Mo–C(16)	150.8(2)
C(17)–Mo–C(16)	34.8(1)	C(18)–Mo–C(16)	57.2(2)
C(1)–Mo–C(20)	143.7(2)	C(9A)–Mo–C(20)	95.7(2)
C(2)–Mo–C(20)	87.3(2)	C(10A)–Mo–C(20)	129.6(2)
C(3)–Mo–C(20)	117.2(2)	C(17)–Mo–C(20)	58.1(2)
C(18)–Mo–C(20)	58.0(2)	C(16)–Mo–C(20)	33.9(2)
C(1)–Mo–C(19)	114.4(2)	C(9A)–Mo–C(19)	130.3(2)
C(2)–Mo–C(19)	80.9(2)	C(10A)–Mo–C(19)	162.5(2)
C(3)–Mo–C(19)	97.3(2)	C(17)–Mo–C(19)	57.5(2)
C(18)–Mo–C(19)	34.5(2)	C(16)–Mo–C(19)	56.2(2)
C(20)–Mo–C(19)	34.6(2)	Mo–C(1)–O(1)	178.7(4)
Mo–C(2)–C(3)	75.6(3)	Mo–C(2)–C(15)	136.1(3)
Mo–C(3)–C(4)	141.5(3)	C(2)–C(3)–C(4)	147.8(4)
C(3)–C(2)–C(15)	147.7(4)	Mo(A)–C(9)–C(10)	74.1(2)
Mo(A)–C(9)–C(8)	139.0(3)	C(9)–C(10)–C(11)	145.7(4)
Mo(A)–C(10)–C(11)	143.7(3)	C(10)–C(9)–C(8)	146.0(4)



Scheme 3.

3.4. Reaction of **3-BF4** and PPN^+Cl^-

Treatment of **3-BF4** with PPN^+Cl^- in dichloromethane solvent at ambient temperature results in a neutral, slightly air-sensitive cyclobutadienophane complex CpMo(CO)Cl(η^4-$C_4(C_{10}H_{20})$) (**5**) in 94% yield after recrystallization from n-hexane/dichloromethane at − 15°C. There is no evidence to support the formation of a dimolybdenum cyclobutadienosuperphane complex. It is likely that nucleophilic attack of a Cl^- anion at each cationic Mo^+ center is concomitant with dissociation of one alkyne ligand to give [CpMo(CO)Cl(η^2-$C_4(C_{10}H_{20})$)], followed by an intramolecular alkyne–alkyne coupling process to afford **5** (Scheme 3). However, initial formation of an adductive intermediate [CpMo(CO)Cl(μ,μ-η^2,η^2-$C_{14}H_{20}$)]$_2$ is also plausible due to the ability of alkyne ligands to act as two- and four-electron donors [18].

The FAB mass spectrum of **5** presents the molecular ion at *m*/*z* 414 for ^{98}Mo and ^{35}Cl. The terminal CO stretching frequency at 1930 cm^{-1} for **5** is red-shifted by 110 cm^{-1} from that of **3-BF4** (2040 cm^{-1}), indicating an increase in the Mo → CO back-donation as the metal charge change from + 1 to 0. The ^{1}H NMR spectrum of **5** displays a singlet at 5.10 ppm for the Cp protons and a complicated multiplet at 3.70–1.50 ppm for the methylene protons. Its $^{13}C\{^1H\}$ NMR spectrum displays one resonance at 109.4 ppm for the Cp carbons and one resonance at 98.5 ppm for the cyclobutadiene ring carbons, while the methylene carbons give three resonances at 32.2, 23.3 and 14.6 ppm. This indicates that the cyclopentadienyl and cyclobutadiene ligands are fluxional with facile ring rotation in solution.

Acknowledgements

We are grateful to the National Science Council of Taiwan for supporting this work.

References

[1] (a) F.L. Bowden, A.B.P. Lever, Organomet. Chem. Rev. 3 (1968) 227. (b) E. Sappa, A. Tiripicchio, P. Braunstein, Chem. Rev. 83 (1983) 203. (c) D.B. Grotjahn, in: Comprehensive

Organometallic Chemistry II, vol. 12, Pergamon, Oxford, 1995, p. 741.

[2] (a) M. Nakagawa, in: Topics in Nonbenzenoid Aromatic Chemistry, vol. 1, Hirokawa, Tokyo, 1973. (b) F. Sondheimer, Acc. Chem. Res. 5 (1972) 81. (c) R. Gleiter, Angew. Chem., Int. Ed. Engl. 31 (1992) 27. (d) R. Gleiter, W. Schäfer, Acc. Chem. Res. 23 (1990) 369.

[3] (a) F. Vögtle, Cyclophane Chemistry: Synthesis, Structures and Reactivity, Wiley, Chichester, 1993. (b) D.J. Cram, J.M. Cram, Container Molecules and Their Guests, Royal Society of Chemistry, London, 1994. (c) R. Gleiter, M. Merger, Angew. Chem., Int. Ed. Engl. 36 (1997) 2426. (d) E. Kloster-Jensen, J. Wirz, Angew. Chem., Int. Ed. Engl. 12 (1973) 671. (e) J.A. Gladysz, J.G. Fulcher, S.J. Lee, A.B. Bocarsley, Tetrahedron Lett. (1977) 3421. (f) R.B. King, A. Efraty, J. Am. Chem. Soc. 92 (1970) 6071; 94 (1972) 3021. (g) R.B. King, M.N. Ackermann, J. Organomet. Chem. 67 (1974) 431. (h) G. Mehta, B. Viswanath, N. Sastry, E.D. Jemmis, D. Sivakumar, K. Reddy, A.C. Kunwar, Angew. Chem., Int. Ed. Engl. 31 (1992) 1488. (h) C.M. Adams, E.M. Holt, Organometallics 9 (1990) 980.

[4] (a) R. Gleiter, H. Stahr, B. Nuber, Organometallics 16 (1997) 646. (b) R. Gleiter, M. Merger, T. Oeser, H. Irngartinger, Tetrahedron Lett. 36 (1995) 4625. (c) R. Gleiter, H. Langer, V. Schehlmann, B. Nuber, Organometallics 14 (1995) 975. (d) R. Gleiter, H. Langer, B. Nuber, Angew. Chem., Int. Ed. Engl. 33 (1994) 1272. (e) R. Gleiter, G. Pflästerer, B. Nuber, J. Chem. Soc., Chem. Commun. (1993) 454. (f) R. Gleiter, G. Pflästerer, Organometallics 12 (1993) 1886. (g) R. Gleiter, V. Schehlmann, Angew. Chem., Int. Ed. Engl. 29 (1990) 1426.

[5] W.-Y. Yeh, M.-A. Hsu, S.-M. Peng, G.-H. Lee, Organometallics 18 (1999) 880.

[6] D.F. Shriver, M.A. Drezdzon, The Manipulation of Air-Sensitive Compounds, Wiley, New York, 1986.

[7] R. Gleiter, R. Merger, B. Treptow, W. Wittwer, G. Pflästerer, Synthesis (1993) 558.

[8] (a) M.D. Curtis, R.J. Klingler, J. Organomet. Chem. 161 (1978) 23. (b) A.R. Manning, P. Hackett, R. Birdwhistell, P. Soye, Inorg. Synth. 28 (1990) 148.

[9] (a) R.J. Klingler, W. Bulter, M.D. Curtis, J. Am. Chem. Soc. 97 (1975) 3535. (b) M.D. Curtis, M.S. Hay, Inorg. Synth. 28 (1990) 150.

[10] (a) M. Dub, Organometallic Compounds, vol. 1, Springer, Berlin, 1966. (b) A.J. Hart-Davis, C. White, R.J. Mawby, Inorg. Chim. Acta 4 (1970) 431. (c) R.B. King, M.Z. Iqbal, A.D. King, J. Organomet. Chem. 171 (1979) 53.

[11] D.D. Perrin, W.L. Armarego, D.R. Perrin, Purification of Laboratory Chemicals, Pergamon, Oxford, 1966.

[12] R.H. Blessing, Acta Crystallogr., Sect. A 51 (1995) 33.

[13] (a) S.A.R. Knox, R.F.D. Stansfield, F.G.A. Stone, M.J. Winter, P. Woodward, J. Chem. Soc., Dalton Trans. (1982) 173. (b) J.A. Beck, S.A.R. Knox, R.F.D. Stansfield, F.G.A. Stone, M.J. Winter, P. Woodward, J. Chem. Soc., Dalton Trans. (1982) 195. (c) W.I. Bailey, M.H. Chisholm, F.A. Cotton, L.A. Rankel, J. Am. Chem. Soc. 100 (1978) 5764. (d) D.S. Ginley, C.R. Bock, M.S. Wrighton, Inorg. Chim. Acta 23 (1977) 85.

[14] J.P. Collman, L.S. Hegedus, J.R. Norton, R.G. Finke, Principles and Applications of Organotransition Metal Chemistry, University Science Books, Milley Valley, CA, 1987.

[15] P. Leoni, F. Marchetti, M. Pasquali, P. Zanello, J. Chem. Soc., Dalton Trans. (1988) 635.

[16] (a) M. Green, N.C. Norman, A.G. Orpen, J. Am. Chem. Soc. 103 (1981) 1269. (b) M. Green, Polyhedron 5 (1986) 427 and Refs. cited therein. (c) L. Brammer, M. Green, A.G. Orpen, K.E. Paddick, D.R. Saunders, J. Chem. Soc., Dalton Trans. (1986) 657. (d) M. Green, N.K. Jetha, R.J. Mercer, N.C. Norman, A.G. Orpen, J. Chem. Soc., Dalton Trans. (1988) 1843.

[17] S.R. Allen, P.K. Baker, S.G. Barnes, M. Green, L. Trollope, L.M. Muir, K.W. Muir, J. Chem. Soc., Dalton Trans. (1981) 873.

[18] J.L. Templeton, P.B. Winston, B.C. Ward, J. Am. Chem. Soc. 103 (1981) 7713.