Unexpected reactions of $(Me_2C)(Me_2Si)[(\eta^5\text{-}C_5H_3)Mo(CO)_3]_2$ with diazoalkane and carbon disulfide: Activation and cleavage of the N=N bond and disproportionation of carbon disulfide

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Abstract

The N–N bond cleavage of diazoalkane Ar_2CN_2 following a orthometalation of the aryl occurred in the thermal reactions with $(Me_2C)(Me_2Si)[(\eta^5\text{-}C_5H_3)Mo(CO)_3]_2$ (**1**), which led to $(Me_2C)(Me_2Si)[(\eta^5\text{-}C_5H_3)_2Mo_2(CO)_2(O)\{\mu\text{-}\eta^1{:}\eta^2\text{-}N=C(RC_6H_3)(RC_6H_4)\}]$ [R = H (**2**), *p*-Me (**3**)]. Two products $(Me_2C)(Me_2Si)[(\eta^5\text{-}C_5H_3)_2Mo_2(CO)_4(\mu\text{-}\eta^1{:}\eta^2\text{-}CS)]$ (**4**) and $(Me_2C)(Me_2Si)[(\eta^5\text{-}C_5H_3)_2Mo_2(CO)_4(\mu\text{-}\eta^2{:}\eta^2\text{-}CS_3)]$ (**5**) were isolated in the reaction of complex **1** with CS_2 with the disproportionation of carbon disulfide. The molecular structures of **2–5** have been determined by X-ray diffraction analysis. The proposed mechanism was discussed.
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Keywords: N–N bond cleavage; Disproportionation; Doubly bridged bis(cyclopentadienyl) ligand; Mo–Mo bond

1. Introduction

Several years ago we reported the Me2C and Me2Si doubly bridged bis(cyclopentadienyl) dinuclear molybdenum carbonyl complex $(Me_2C)(Me_2Si)[(\eta^5\text{-}C_5H_3)Mo(CO)_3]_2$ (**1**) contained unusually long Mo–Mo bond distances [1]. In comparison with singly bridged bis(cyclopentadienyl) metal complexes, doubly bridged bis(cyclopentadienyl) ligands are more rigid, locking the two metals on either the same or opposite faces of the ligand, and maintain the two metal centers in close proximity even after the metal–metal bond cleavage, which could result in unique properties in structures, reactivity and catalysis [2]. We were, therefore, interested in complex **1** as a precursor for the synthesis of other new dinuclear molybdenum complexes and have found it enters into a number of interesting but not always predictable reactions. In this contribution we report the reaction of complex **1** with diazoalkane $(RC_6H_4)_2CN_2$ (R = H, *p*-Me) and carbon disulfide, which

generate the N=N bond cleavage and carbon disulfide disproportionation products, respectively.

2. Results and discussion

2.1. Reaction of $(Me_2C)(Me_2Si)[(\eta^5\text{-}C_5H_3)Mo(CO)_3]_2$ (1) with diazoalkane $(RC_6H_4)_2CN_2$ (R = H, p-Me)

Previous studies have shown that the reaction of $[CpMo(CO)_3]_2$ (or $[CpMo(CO)_2]_2$) with different diazoalkanes led to various bonds activation and cleavage to construct many structure-novelty compounds [3–6]. The reaction of $[CpMo(CO)_2]_2$ with $(RC_6H_4)_2CN_2$ (R = H, *p*-Me) afforded diazoalkane adduct $Cp_2Mo_2(CO)_4[N_2C\text{-}(RC_6H_4)_2]$, which was thermally decomposed with loss of nitrogen to afford the μ-diarylmethylene complexes $Cp_2Mo_2(CO)_4[C(RC_6H_4)_2]$ [4b]. The N–N bond cleavage with subsequent rearrangement to yield the terminal isocyanato ligand with azavinylidene ligand was observed in the reaction of $[CpMo(CO)_2]_2$ with Me_2CN_2 [5f]. To compare the reactivity of complex **1** with that of $[CpMo(CO)_3]_2$ (or $[CpMo(CO)_2]_2$), reactions of **1** with diazoalkanes

$(RC_6H_4)_2CN_2$ (R = H, p-Me) were carried out, and the N=N bond cleavage following an orthometalation of aryl products $(Me_2C)(Me_2Si)[(\eta^5-C_5H_3)_2Mo_2(CO)_2(O)\{\mu-\eta^1:\eta^2-N=C(RC_6H_3)(RC_6H_4)\}]$ (R = H, **2**; R = p-Me, **3**) were obtained in 11% and 10% yields, respectively (Scheme 1). The products were characterized on the basis of IR, ^{1}H NMR and X-ray diffraction analysis.

Both **2** and **3** are air stable crystals, but in solution they are somewhat air sensitive. The IR and ^{1}H NMR spectra of **2** and **3** are similar. Except for two stretching vibrations for carbonyl ligands, the absorptions at 923 cm^{−1} (for **2**) and 939 cm^{−1} (for **3**) in their IR spectra can be assigned to $v(Mo=O)$ frequency [7] with the aid of crystallographic results. Their ^{1}H NMR spectra indicate the orthometalation of phenyl rings (several coupled resonances in the range of δ 8.4–6.9 ppm for **2** and δ 8.2–7.0 ppm for **3**, respectively) and the inequivalent of the two Cp ligands (six resonances in the range of δ 6.7–4.1 ppm for **2** and δ 6.6–4.1 ppm for **3**, respectively). The signals for the CMe_2 equatorial methyl protons (δ 0.46 and 0.37 ppm for **2** and **3**, respectively) are approximately 0.7 ppm upfield from the typical one.
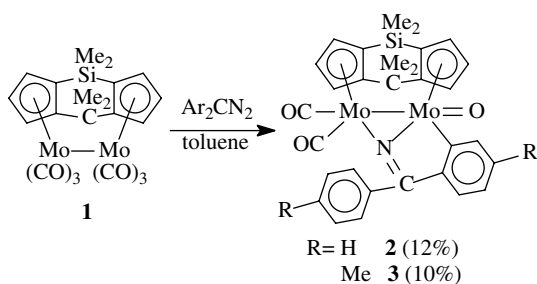
The molecular structures of **2** and **3** were determined by X-ray diffraction (Figs. 1 and 2) and similar structures were found. The Mo–Mo bond in **2** is unsymmetrically spanned by the nitrogen atom of an orthometalated 2,2-diphenyl-1-azavinylidene ligand [N(1)–Mo(1) 2.037(3), N(1)–Mo(2) 2.091(3) Å] [8], which acts as a four-electron donor and inclines to the bridging CMe_2 side. The N(1)–C(18) distance of 1.296(4) Å reveals its double bond character. The metalated phenyl ring and atoms N(1), C(18), Mo(1), and Mo(2) are well settled in one plane, none deviating more than 0.0322 Å from the mean plane, which construct a large conjugated unit (see the right drawing of Fig. 1). The bridging atom C(15) might just locate at the shielding zone of the conjugated system [C(15)–C(18) = 3.907 Å, C(15)–N(1) = 3.529 Å], so the signal for the methyl protons is somewhat upfield. Mo(1) coordinates with two carbonyls, while Mo(2) coordinates with an oxygen ligand [O(3)–Mo(2) 1.690(2) Å]. The Mo–Mo bond length is 2.8933(4) Å, a value approximately midway between the Mo–Mo single in $[CpMo(CO)_3]_2$ (3.235 Å) [9] and triple bond lengths in $[CpMo(CO)_2]_2$ (2.448 Å) [10], indicative of the multiple-bonding character of the Mo–Mo bond. The bridge bonding in the bimetallic complex is best described by the resonance structures **2A** and **2B** considering the Mo–Mo multiple-bonding character, and both resonance structures obey the 18-electron rule (Chart 1).

The N–N bond cleavage of Ph_2CN_2 in the reaction cited in Scheme 1 might follow the same way as mentioned for the N–N bond cleavage of Me_2CN_2 in the reaction with $[CpMo(CO)_2]_2$ [5f]. The proposed mechanism for the formation of complex **2** is outlined in Scheme 2. Due to the high rigidity of the doubly bridged bis(cyclopentadienyl) ligand, complex **1** fails to generate the corresponding
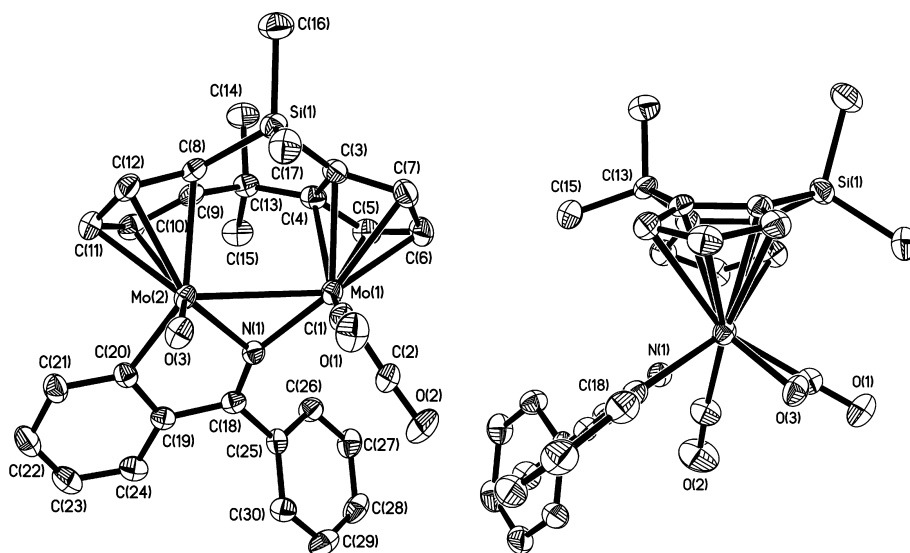

Scheme 1.

Fig. 1. ORTEP diagram of $(Me_2C)(Me_2Si)[(\eta^5-C_5H_3)_2Mo_2(CO)_2(O)\{\mu-\eta^1:\eta^2-N=C(C_6H_4)(C_6H_5)\}]$ (**2**). Thermal ellipsoids are shown at the 30% level. Hydrogen atoms and solvent molecules are omitted for clarity. The left drawing shows the view perpendicular to the Mo–Mo bond. The right drawing depicts the view down the Mo–Mo axis. Selected bond lengths (Å) and angles (°) are as follows: Mo(1)–Mo(2) 2.8933(4), Mo(1)–N(1) 2.037(3), Mo(2)–N(1) 2.091(3), Mo(2)–O(3) 1.690(2), C(18)–N(1) 1.296(4), Mo(2)–C(20) 2.179(4), Mo(2)–N(1)–Mo(1) 88.97(11).
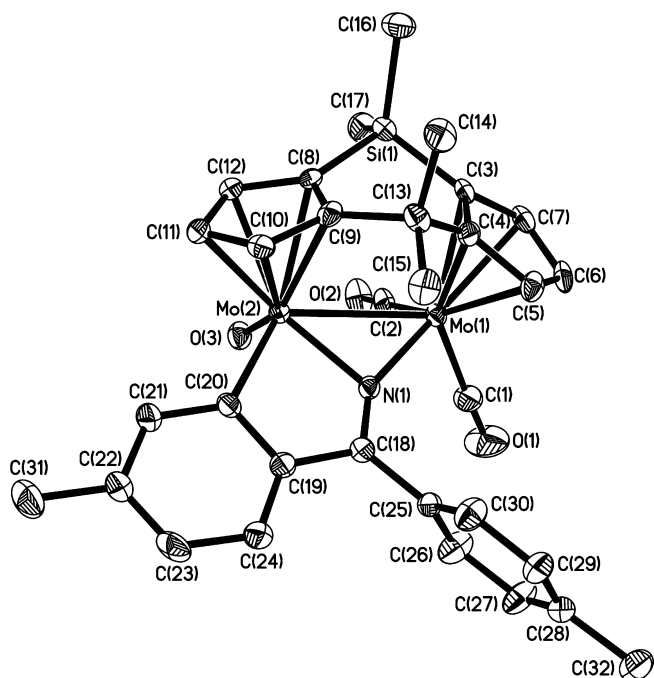
Fig. 2. ORTEP diagram of $(Me_2C)(Me_2Si)[(\eta^5\text{-}C_5H_3)_2Mo_2(CO)_2(O)\{\mu\text{-}\eta^1:\eta^2\text{-}N=C(p\text{-}MeC_6H_3)(p\text{-}MeC_6H_4)\}]$ (**3**). Thermal ellipsoids are shown at the 30% level. Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (°) are as follows: Mo(1)–Mo(2) 2.8933(4), Mo(1)–N(1) 2.037(3), Mo(2)–N(1) 2.091(3), Mo(2)–O(3) 1.690(2), C(18)–N(1) 1.296(4), Mo(2)–C(20) 2.179(4), Mo(2)–N(1)–Mo(1) 88.97(11).
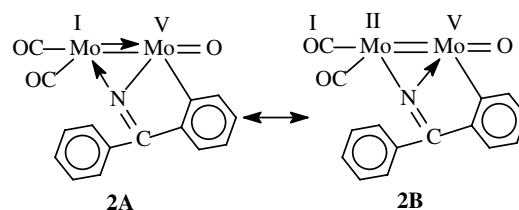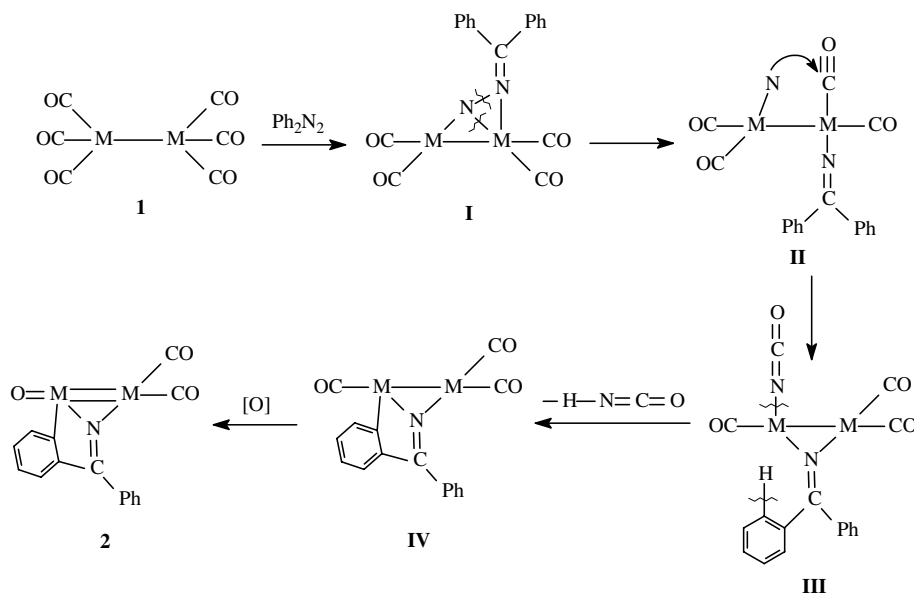

Chart 1.

ate nitrido(carbonyl)metal species (**II**) to yield **III** with a terminal isocyanato ligand in refluxing toluene condition [5f]. Orthometalation of one phenyl of **III** generates **IV** by releasing one HN=C=O molecule. Further decarbonylation and oxidation of one of the Mo center affords complex **2**. The source of oxygen is not yet clear. The result of monitoring by TLC indicated that complex **2** is not from the oxidation during chromatograph. But it cannot be excluded that the oxygen source comes from the reaction itself. Although the intermediates **I**, **II**, **III**, and **IV** were not isolated in our reaction, the dimethyldiazomethane analogues to **I** and **III**, $Cp_2Mo_2(CO)_4(\mu\text{-}\eta^1:\eta^2\text{-}N_2CMe_2)$ [5d] and $Cp_2Mo_2(CO)_3(NCO)(\mu\text{-}NCMe_2)$ [5f], have been isolated and structurally characterized by X-ray crystallography before.

2.2. Reaction of $(Me_2C)(Me_2Si)[(\eta^5\text{-}C_5H_3)Mo(CO)_3]_2$ (**1**) with CS_2

In 1981, Wachter and coworkers demonstrated that reaction of complex $[CpMo(CO)_3]_2$ with boiling CS_2 gave a dinuclear $\eta^2\text{-}CS_2$ complex in which CS_2 acted as a non-bridging, terminal ligand [11]. Later, the reaction of $[CpMo(CO)_2]_2$ with CS_2 at 120 °C to synthesize a dinuclear $\eta^1:\eta^2\text{-}CS_2$ bridged Mo complex was demonstrated

Mo≡Mo bond complex by decarbonylation upon heating in boiling toluene or higher temperature. Also it did not react with Ph_2CN_2 at room temperature. The diphenyldiazomethane adduct **I** is not isolated since such coordinated diazoalkane tends to undergo an irreversible N–N bond cleavage with subsequent rearrangement of the intermedi-

Scheme 2.

by Schwarzhans and coworkers, with one $CpMo(CO)_2$ group bonded side-on to a C=S bond of CS_2 moiety and the other $CpMo(CO)_3$ attached end-on to the second sulfur of the bridging CS_2 [12]. The reaction of 1 with CS_2 was carried out in toluene under reflux for comparison. Two products $(Me_2C)(Me_2Si)[(\eta^5-C_5H_3)_2Mo_2(CO)_4(\mu-\eta^1:\eta^2-CS)]$ (4) and $(Me_2C)(Me_2Si)[(\eta^5-C_5H_3)_2Mo_2(CO)_4(\mu-\eta^2:\eta^2-CS_3)]$ (5) were isolated in 9% and 11% yields, respectively (Scheme 3). However, reacting 1 in refluxing CS_2 afforded nothing. In addition, Complex 4 could also be obtained in 61% yield from 1 and $S_2CPPr^i_3$ in refluxing toluene with addition a large excess of CS_2 (Scheme 4). This reaction gives rise to the first example for disproportionation of CS_2, although disproportionation of CO_2 with the aid of metal complex has been known for some time [13]. In the ^1H NMR spectrum, 4 shows six resonances for the Cp protons, indicating the unsymmetrical structure, while 5 shows three peaks for the equivalent Cp rings as expected for a symmetrical structure. Both the ^1H NMR spectra of 4 and 5 contain another minor isomer (see Section 3 for details). Due to the difference of the two bridging atoms, the two isomers can be assumed as the structures with exchanging the location of CMe_2 and $SiMe_2$ group in the doubly bridged ligand. The two isomers could not be separated by column chromatograph, or by recrystallization. Such a phenomenon was also observed in complexes obtained from the reaction of 1 and allene or isonitrile [14].

The molecular structures of 4 and 5 were finally determined by single crystal X-ray diffraction analysis (Figs. 3 and 5). In complex 4, the Mo–Mo bond is bridged by $\mu-\eta^1:\eta^2$-CS ligand (side-on bonding) in $\sigma + \pi$ fashion, which acts as a four-electron donor to counteract the loss of two carbonyl ligands. It decreases the Mo–Mo bond distance to 3.1861(4) Å. The C(5)–S(1) bond distance of 1.632(3) Å is longer than that of normal C=S double bond (1.60 Å) [15] and CS_2 (1.554 Å) [16]. The long bond length suggests the weak C–S bond, and it is supported by the low absorption of the C–S group at 1113 cm^{-1} in its IR spectrum. Both observations further support the notion that polynuclear coordination will significantly reduce bond
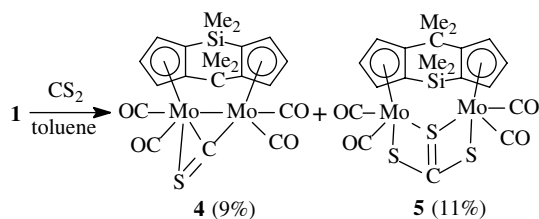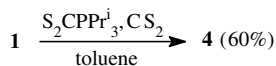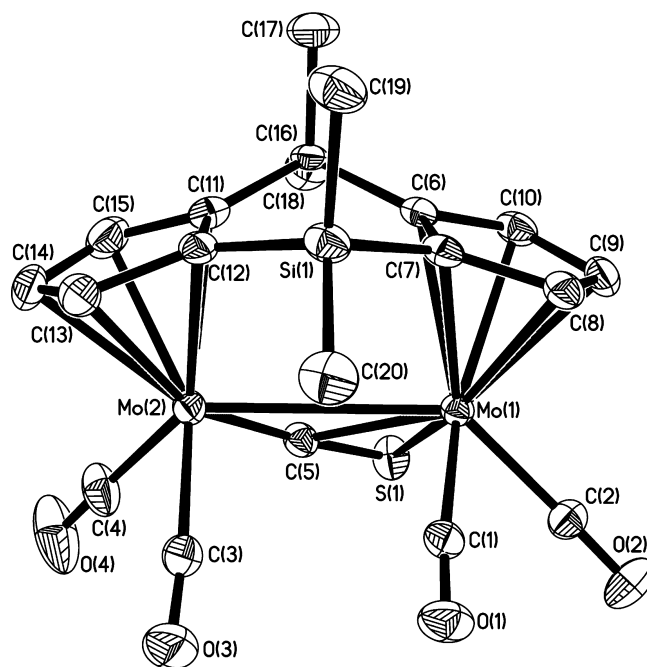

Fig. 3. ORTEP diagram of $(Me_2C)(Me_2Si)[(\eta^5-C_5H_3)_2Mo_2(CO)_4(\mu-\eta^1:\eta^2-CS)]$ (4). Thermal ellipsoids are shown at the 30% level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°) are as follows: Mo(1)–Mo(2) 3.1861(4), Mo(1)–C(5) 2.270(3), Mo(2)–C(5) 1.899(3), Mo(1)–S(1) 2.5396(8), S(1)–C(5) 1.632(3), Mo(2)–C(5)–S(1) 176.28(18), Mo(1)–C(5)–Mo(2) 99.29(12).

order in unsaturated ligands [17]. The $\sigma + \pi$ unit is very close to linear [$\angle Mo(2)–C(5)–S(1) = 176.28(18)°$]. The Mo(2)–C(5) σ bond [1.899(3) Å] is much shorter than that of Mo(1)–C(5) π bond [2.270(3) Å]. Example of side-on bonding CX (X = O [18], N [19]) ligand are well documented, but to our knowledge, a Mo–W complex reported by Angelici and co-workers is the only known example of a side-on bridging thiocarbonyl [20]. The dimensions of the $M_2(\mu-\eta^1:\eta^2-CS)$ unit in the Mo–W complex are comparable to those found for 4 (see Fig. 4 for details).

The molecular structure of 5 has an approximately mirror plane passing through atoms C(16), Si(1), S(1), and C(5). The most striking feature in this structure is the presence of the $\mu-\eta^2:\eta^2$-trithiocarbonate bridging ligand, which is also supported by the strong absorption at

Scheme 3.

Scheme 4.
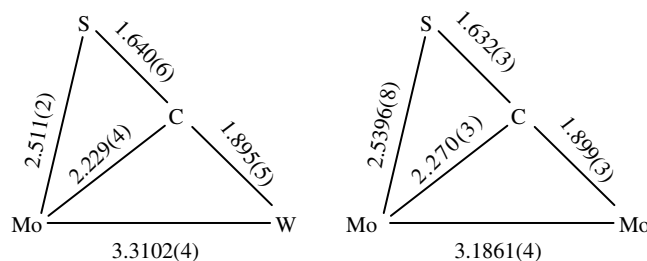
Fig. 4. Comparison of bond distances (Å) and angles (°) in the side-on bonded CS in $[HB(pz)_3](CO)_2W(\mu-CS)Mo(CO)_2(\eta^5-C_9H_7)$ (left) and 4 (right). Selected bond angles are as follows: W–C–S 170.8(3), C–W–Mo 40.2(1), Mo'–C–S 176.28(18), C–Mo'–Mo 44.69(8).
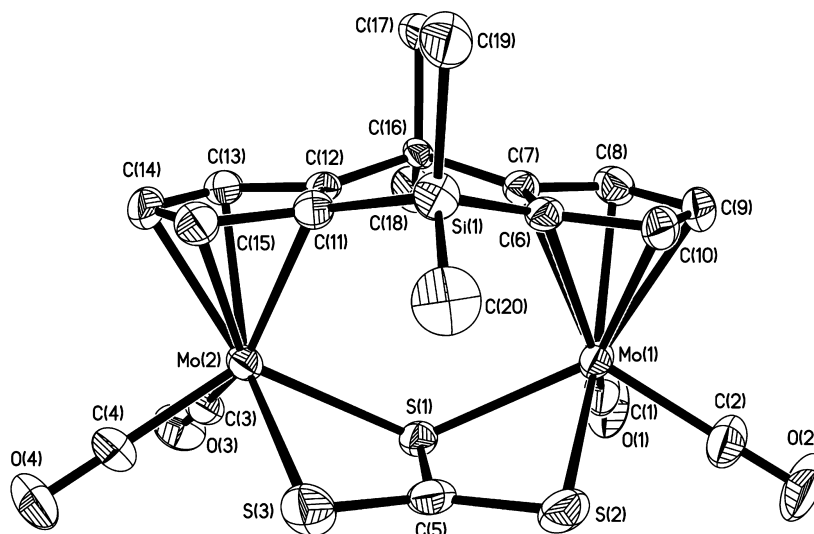
Fig. 5. ORTEP diagram of $(Me_2C)(Me_2Si)[(\eta^5-C_5H_3)_2Mo_2(CO)_4(\mu-\eta^2:\eta^2-CS_3)]$ (**5**). Thermal ellipsoids are shown at the 30% level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°) are as follows: Mo(1)–Mo(2) 4.516, Mo(1)–S(1) 2.5390(10), Mo(1)–S(2) 2.5216(13), Mo(2)–S(1) 2.5409(9), Mo(2)–S(3) 2.5172(12), S(1)–C(5) 1.713(4), S(2)–C(5) 1.690(4), S(3)–C(5) 1.696(4), Mo(1)–S(1)–Mo(2) 125.48(4), S(1)–C(5)–S(2) 114.4(2), S(1)–C(5)–S(3) 113.3(2), S(2)–C(5)–S(3) 131.1(3).

1014 cm^{-1} in its IR spectrum [21]. The four atoms of the CS$_3$ ligand are coplanar, in which the atoms have a mean deviation of 0.0411 Å. The trithiocarbonate moiety itself is distorted from the possible D_{3h} symmetry, probably due to the chelate interactions with the separate Mo centers. Coordination of S(1) to two molybdenum centers is reflected in an increased S(1)–C(5) distance of 1.713(4) Å relative to the S(2)–C(5) and S(3)–C(5) distances of 1.690(4) and 1.696(4) Å, respectively. It is observed that, when bound as a bidentate ligand, the four member ring formation causes the angles ∠S(1)–C(5)–S(2) and ∠S(1)–C(5)–S(3) to decrease from 120° to average 113.8°. The $(Me_2C)(Me_2Si)(\eta^5-C_5H_3)_2$ ligand is almost in a flat conformation (∠Cp–Cp = 170.7°) in consist with the long Mo–Mo non-bonding distance (4.516 Å). So the CS$_3$ ligand acts as a six-electron donor to counteract of the rupture of Mo–Mo bond and loss of two carbonyl ligands and makes

the two Mo atoms satisfy 18 valence electrons. Indeed, complex **5** offers the first example with "$\mu-\eta^2:\eta^2$-" coordination mode of the trithiocarbonate ligand, although a few complexes with such coordinated carbonate ligand are present [22]. It is noteworthy that the angles at the bridging atom O of the carbonate ligand, ∠M–O–M, are almost close to 180°, but the angle ∠Mo(1)–S(1)–Mo(2) in complex **5** is very bended, which is only 125.48(4)°.

The proposed mechanism of the formation of complexes **4** and **5** is shown in Scheme 5. According to Schwarzhans and co-workers' report, $[CpMo(CO)_2]_2$ reacts with CS$_2$ at 120 °C to generate a dinuclear $\eta^1:\eta^2$-CS$_2$ bridged Mo complex without Mo–Mo bond. Due to the restriction of doubly bridged ligand, the distance between the two Mo centers in complex **1** can not accommodate the $\eta^1:\eta^2$-CS$_2$ ligand. Thus, the intermolecular $\eta^1:\eta^2$-CS$_2$ intermediate **V** could be generated from two molecules of **1** and CS$_2$
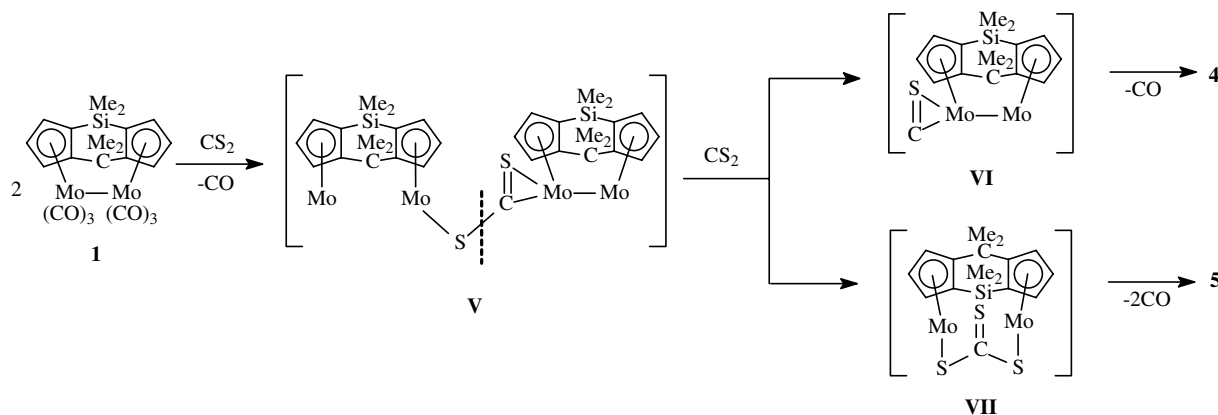
Scheme 5.

in refluxing toluene. Then intermediate **V** reacts with another CS_2 with the cleavage of the C–S bond of the η^1:η^2-CS_2 ligand to afford intermediates **VI** and **VII**. Complex **4** can be easily obtained by decarbonylation with the η^2-CS ligand coordinating with the other Mo center of intermediate **VI**. The coordinate mode of μ–η^1:η^1-CO_3 ligand, which is similar to that of intermediate **VII**, was reported before, such as complexes $KAgCO_3$ [23] and $Cs_4[Rh_2(CO)_4(H_2O)_2] \cdot 6H_2O$ [24]. After cleavage of two carbonyls in company with buildup of two S–Mo bonds, complex **5** is formed.

In summary, we report the reaction of the Me_2C and Me_2Si doubly bridged bis(cyclopentadienyl) dinuclear molybdenum carbonyl complex with unsaturated small organic molecules diazoalkane $(RC_6H_4)_2CN_2$ (R = H, p-Me) and carbon disulfide. The N–N bond cleavage of diazoalkane Ar_2CN_2 following an orthometalation of the aryl and disproportionation of CS_2 were observed in the thermal reactions with $(Me_2C)(Me_2Si)[(\eta^5-C_5H_3)Mo(CO)_3]_2$ (**1**), respectively.

3. Experimental

3.1. General procedures

Schlenk and vacuum line techniques were employed for all manipulations. All solvents were distilled from appropriate drying agents under argon prior to use. ^1H NMR spectra were recorded on a Bruker AV300 instrument. $^{13}C\{^1H\}$ NMR experiments were carried out on a Varian Mercury VX300 instrument at 75.5 MHz. IR spectra were recorded as KBr disks on a Nicolet 560 ESP FTIR spectrometer. Elemental analyses were performed on a Perkin–Elmer 240C analyzer. $(Me_2C)(Me_2Si)[(\eta^5-C_5H_3)Mo(CO)_3]_2$ [1] (**1**), $(RC_6H_4)_2CN_2$ (R = H, p-Me) [25] and $S_2CPPr^i_3$ [26] were prepared by the literature methods.

3.2. Reaction of **1** with $(RC_6H_4)_2CN_2$ (R = H, p-Me) and syntheses of $(Me_2C)(Me_2Si)[(\eta^5-C_5H_3)_2Mo_2(CO)_2(O)-\{\mu$–$\eta^1$:$\eta^2$-N=$C(RC_6H_3)(RC_6H_4)\}]$ (R = H, **2**; R = p-Me, **3**)

A solution of **1** (117 mg, 0.20 mmol) and Ph_2CN_2 (80 mg, 0.41 mmol) in toluene (30 mL) was refluxed for 4 h. After removal of solvent the residue was chromatographed on an alumina column using petroleum ether/CH_2Cl_2 as eluent. The first green band gave 8 mg of unreacted **1**. The second green band afforded **2** (15 mg, 11% yield) as green crystals. **2**: m.p.: 175 °C (dec.). Anal. Calc. for $C_{30}H_{27}Mo_2O_3SiN$: C, 53.82; H, 4.06; N, 2.09. Found: C, 54.12; H, 4.16; N, 2.21%. ^1H NMR (CDCl$_3$) δ 8.40 (d, 1H, J = 6.8 Hz, Ph–H), 7.52 (m, 5H, Ph–H), 7.20 (m, 2H, Ph–H), 6.96 (m, 1H, Ph–H), 6.64 (m, 1H, Cp–H), 5.99 (m, 1H, Cp–H), 5.63 (m, 1H, Cp–H), 5.56 (m, 1H, Cp–H), 5.35 (m, 1H, Cp–H), 4.12 (m, 1H, Cp–H), 1.48 (s, 3H, CMe), 0.89 (s, 3H, SiMe), 0.83 (s, 3H, SiMe), 0.46 (s, 3H, CMe); IR (cm^{-1}): v_{CO} 1936 (s), 1827 (s); $v_{Mo=O}$ 932 (m).

Using a procedure similar to that described above, reaction of **1** with $(p$-$MeC_6H_4)_2CN_2$ gave **3** in 10% yield as green crystals. **3**: m.p.: 232 °C (dec.). Anal. Calc. for $C_{32}H_{31}Mo_2O_3SiN$: C, 55.10; H, 4.48; N, 2.01. Found: C, 54.99; H, 4.65; N, 2.11%. ^1H NMR (CDCl$_3$) δ 8.24 (m, 1H, p-MeC_6H_4), 7.42 (m, 2H, p-MeC_6H_4), 7.33 (m, 3H, p-MeC_6H_4), 6.99 (m, 1H, p-MeC_6H_4), 6.63 (m, 1H, Cp–H), 5.97 (m, 1H, Cp–H), 5.59 (m, 2H, Cp–H), 5.33 (m, 1H, Cp–H), 4.11 (m, 1H, Cp–H), 2.46 (s, 6H, p-$CH_3C_6H_4$), 1.48 (s, 3H, CMe), 0.89 (s, 3H, SiMe), 0.83 (s, 3H, SiMe), 0.43 (s, 3H, CMe); IR (cm^{-1}): v_{CO} 1925 (s), 1843 (s); $v_{Mo=O}$ 939 (m).

3.3. Reaction of **1** with CS_2 and syntheses of $(Me_2C)(Me_2Si)[(\eta^5-C_5H_3)_2Mo_2(CO)_4(\mu$–$\eta^1$:$\eta^2$-CS)]$ (**4**) and $(Me_2C)(Me_2Si)[(\eta^5-C_5H_3)_2Mo_2(CO)_4(\mu$–$\eta^2$:$\eta^2$-$CS_3$)]$ (**5**)

A solution of **1** (100 mg, 0.17 mmol) and excess CS_2 (10 mL) in toluene (30 mL) was refluxed for 24 h. After removal of solvent the residue was chromatographed on an alumina column using petroleum ether/CH_2Cl_2 as eluent. The first band (brown) gave **4** (9 mg, 9% yield) as deep-brown crystals as a mixture of two isomers in the ratio 4:1. The second band (purple) gave **5** (12 mg, 11% yield) as purple crystals as a mixture of two isomers in the ratio 6:1.

For complex **4**: m.p.: 173 °C (dec.). Anal. Calc. for $C_{20}H_{18}Mo_2O_4SSi$: C, 41.82; H, 3.16. Found: C, 41.59; H, 3.18%. ^1H NMR (CDCl$_3$) of major isomer: δ 5.99 (m, 1H, Cp–H), 5.85 (m, 1H, Cp–H), 5.50 (m, 1H, Cp–H), 5.39 (m, 1H, Cp–H), 5.27 (m, 1H, Cp–H), 4.98 (m, 1H, Cp–H), 1.32 (s, 3H, CMe), 0.76 (s, 3H, CMe), 0.66 (s, 3H, SiMe), 0.63 (s, 3H, SiMe); minor isomer: δ 5.94 (m, 1H, Cp–H), 5.89 (m, 1H, Cp–H), 5.60 (m, 1H, Cp–H), 5.41 (m, 1H, Cp–H), 5.24 (m, 2H, Cp–H), 1.86 (s, 3H, CMe), 1.57 (s, 3H, CMe), 0.34 (s, 3H, SiMe), 0.05 (s, 3H, SiMe); $^{13}C\{^1H\}$ NMR (CDCl$_3$) of major isomer: 297.45 (CS), 240.44, 240.34, 228.91, 224.75 (CO), 135.79, 127.72, 103.70, 101.71 (d, J = 14.4 Hz), 98.96, 90.29, 89.35 (d, J = 7.2 Hz), 88.46 (d, J = 12.6 Hz), 87.01 (d, J = 9.0 Hz), 86.50 (Cp), 37.84 (CMe$_2$), 36.17 (CMe$_2$), 24.41 (CMe$_2$), 6.19, −0.03 (SiMe$_2$); IR (v_{CO}, cm^{-1}, mixture of isomer): 1998 (s), 1951 (s), 1922 (s), 1847 (m).

For complex **5**: m.p.: 189 °C (dec.). Anal. Calc. for $C_{20}H_{18}Mo_2O_4S_3Si$: C, 37.62; H, 2.84. Found: C, 37.40; H, 3.29%. H NMR (CDCl$_3$) of major isomer: δ 5.72 (m, 2H, Cp–H), 5.44 (m, 2H, Cp–H), 5.04 (m, 2H, Cp–H), 1.85 (s, 3H, CMe), 1.36 (s, 3H, CMe), 0.72 (s, 3H, SiMe), 0.30 (s, 3H, SiMe); minor isomer: δ 6.29 (m, 2H, Cp–H), 5.20 (m, 2H, Cp–H), 4.97 (m, 2H, Cp–H), 1.70 (s, 3H, CMe), 1.50 (s, 3H, CMe), 0.49 (s, 3H, SiMe), 0.39 (s, 3H, SiMe); $^{13}C\{^1H\}$ NMR (CDCl$_3$) of major isomer: 251.34, 248.42 (CO), 223.2 (CS$_3$), 142.53, 100.29, 99.70, 98.82, 98.47, 90.39, 88.85 (Cp), 35.22 (CMe$_2$), 34.04 (CMe$_2$), 30.46 (CMe$_2$), 4.93, −4.69 (SiMe$_2$); IR (v_{CO}, cm^{-1}, mixture of isomer): 1973 (s), 1950 (s), 1891 (s), 1876 (s), 1867 (s).

Table 1
Crystal data and summary of X-ray data collection for **2**–**5**

	2 · CH₂Cl₂	3	4	5
Empirical formula	$C_{31}H_{29}Cl_2Mo_2NO_3Si$	$C_{32}H_{31}Mo_2NO_3Si$	$C_{20}H_{18}Mo_2O_4SSi$	$C_{20}H_{18}Mo_2O_4S_3Si$
Formula weight	754.42	697.55	574.37	638.49
Crystal system	Monoclinic	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/n$	$P2_12_12_1$
a (Å)	13.9179(13)	10.1160(17)	8.8676(9)	9.8808(11)
b (Å)	11.4811(11)	11.311(2)	15.0950(15)	11.4936(12)
c (Å)	19.0049(19)	25.282(4)	15.9898(16)	20.670(2)
α (°)	90	90	90	90
β (°)	91.153(2)	93.162(3)	95.664(2)	90
γ (°)	90	90	90	90
V (Å³)	3036.2(5)	2888.5(9)	2129.9(4)	2347.4(4)
Z	4	4	4	4
$D_{calc.}$ (g cm⁻³)	1.650	1.604	1.791	1.807
μ (mm⁻¹)	1.075	0.944	1.355	1.410
$F(000)$	1512	1408	1136	1264
Crystal size (mm)	0.24 × 0.22 × 0.20	0.32 × 0.24 × 0.10	0.24 × 0.16 × 0.14	0.22 × 0.20 × 0.18
Maximum 2θ (°)	52.72	52.78	52.72	52.78
Number of reflections collected	16,769	15,713	11,794	13,264
Number of independent reflections/R_{int}	6194/0.0298	5879/0.0475	4330/0.0237	4792/0.0287
Number of parameters	390	352	257	275
Goodness-of-fit on F^2	1.040	1.127	1.040	1.049
R_1, wR_2 [$I > 2\sigma(I)$]	0.0331, 0.0773	0.0592, 0.1233	0.0246, 0.0582	0.0268, 0.0497
R_1, wR_2 (all data)	0.0517, 0.0871	0.0898, 0.1338	0.0352, 0.0629	0.0367, 0.0527
Largest peak in final difference map (e/Å³)	0.733	0.901	0.515	0.324

3.4. Reaction of **1** with $S_2CPPr_3^i$ and CS_2 and synthesis of $(Me_2C)(Me_2Si)[(\eta^5-C_5H_3)_2Mo_2(CO)_4(\mu-\eta^1:\eta^2-CS)]$ (**4**)

A solution of **1** (100 mg, 0.17 mmol) and $S_2CPPr_3^i$ (60 mg, 0.25 mmol) in toluene (30 mL) with addition CS_2 (1 mL) was refluxed for 12 h. After removal of solvent the residue was chromatographed on an alumina column. Elution with petroleum ether–CH_2Cl_2 developed a brown band, which afforded **4** (60 mg, 61% yield) as brown crystals.

3.5. Crystallographic studies

Single crystals of complexes **2**–**5** suitable for X-ray diffraction were obtained from hexane/CH_2Cl_2. Data collection was performed on a Bruker SMART 1000, using graphite-monochromated Mo Kα radiation (ω–2θ scans, $\lambda = 0.71073$ Å). Semiempirical absorption corrections were applied for all complexes. The structures were solved by direct methods and refined by full-matrix least-squares. All calculations were using the SHELXTL-97 program system. The molecular structures of **2** contained a CH_2Cl_2 of solvation. The crystal data and summary of X-ray data collection are presented in Table 1.

Appendix A. Supplementary material

CCDC 636555, 636556, 636557, and 636558 contain the supplementary crystallographic data for **2**, **3**, **4**, and **5**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam. ac.uk/data_request/cif.

References

[1] B. Wang, B. Zhu, S. Xu, X. Zhou, Organometallics 22 (2003) 4842.
[2] See, for examples: (a) U. Siemeling, P. Jutzi, B. Neumann, H.G. Stammler, M.B. Hursthouse, Organometallics 11 (1992) 1328;
(b) F. Amor, E. de Jesus, A.I. Perez, P. Royo, A.V. de Miguel, Organometallics 15 (1996) 365;
(c) M.V. Ovchinnikov, R.J. Angelici, J. Am. Chem. Soc. 122 (2000) 6130;
(d) M.V. Ovchinnikov, I.A. Guzei, R.J. Angelici, Organometallics 20 (2001) 691;
(e) M.V. Ovchinnikov, A.M. Ellern, I.A. Guzei, R.J. Angelici, Inorg. Chem. 40 (2001) 7014;
(f) M.V. Ovchinnikov, E. LeBlanc, I.A. Guzei, R.J. Angelici, J. Am. Chem. Soc. 123 (2001) 11494;
(g) M.V. Ovchinnikov, D.P. Klein, I.A. Guzei, M.-G. Choi, R.J. Angelici, Organometallics 21 (2002) 617;
(h) S.G. McKinley, R.J. Angelici, Organometallics 21 (2002) 1235;
(i) M.V. Ovchinnikov, X. Wang, A.J. Schultz, I.A. Guzei, R.J. Angelici, Organometallics 21 (2002) 3292;
(j) B. Zhu, B. Wang, S. Xu, X. Zhou, Chinese J. Org. Chem. 23 (2003) 1049.
[3] For reviews, see: (a) M. Dartiguenave, M.J. Menu, E. Deydier, Y. Dartiguenave, H. Siebald, Coord. Chem. Rev. 178–180 (1998) 623;

(b) Y. Mizobe, Y. Ishii, M. Hidai, Coord. Chem. Rev. 139 (1995) 281;

(c) D. Sutton, Chem. Rev. 93 (1993) 995;

(d) H. Kisch, P. Holzmeier, Adv. Organomet. Chem. 34 (1992) 67;

(e) W.A. Herrmann, Adv. Organomet. Chem. 20 (1982) 159;

(f) W.A. Herrmann, Angew. Chem., Int. Ed. Engl. 17 (1978) 800.

[4] (a) L. Messerle, M.D. Curtis, J. Am. Chem. Soc. 102 (1980) 7789;

(b) L. Messerle, M.D. Curtis, J. Am. Chem. Soc. 104 (1982) 889;

(c) J.J. D'Errico, L. Messerle, M.D. Curtis, Inorg. Chem. 22 (1983) 849;

(d) J.J. D'Errico, M.D. Curtis, J. Am. Chem. Soc. 105 (1983) 4479;

(e) M.D. Curtis, L. Messerle, J.J. D'Errico, W.M. Butler, M.S. Hay, Organometallics 5 (1986) 2283;

(f) M.D. Curtis, L. Messerle, Organometallics 6 (1987) 1713;

(g) M.D. Curtis, L. Messerle, J.J. D'Errico, H.E. Solis, I.D. Barcelo, W.M. Butler, J. Am. Chem. Soc. 109 (1987) 3603.

[5] (a) W.A. Herrmann, G. Kriechbaum, C. Bauer, E. Guggolz, M.L. Ziegler, Angew. Chem., Int. Ed. Engl. 20 (1981) 815;

(b) W.A. Herrmann, G.W. Kriechbaum, M.L. Ziegler, H. Pfisterer, Angew. Chem., Int. Ed. Engl. 21 (1982) 707;

(c) W.A. Herrmann, L.K. Bell, J. Organomet. Chem. 239 (1982) C4;

(d) L.K. Bell, W.A. Herrmann, G.W. Kriechbaum, H. Pfisterer, M.L. Ziegler, J. Organomet. Chem. 240 (1982) 381;

(e) L.K. Bell, W.A. Herrmann, M.L. Ziegler, H. Pfisterer, Organometallics 1 (1982) 1673;

(f) W.A. Herrmann, L.K. Bell, M.L. Ziegler, H. Pfisterer, C. Pahl, J. Organomet. Chem. 247 (1983) 39.

[6] N.D. Feasey, S.A.R. Knox, A.G. Orpen, J. Chem. Soc., Chem. Commun. (1982) 75.

[7] See, for example: (a) K. Endrich, R. Korswagen, T. Zahn, M.L. Ziegler, Angew. Chem., Int. Ed. 21 (1982) 919;

(b) I. Bernal, M. Draux, H. Brunner, B. Hoffmann, J. Wachter, Organometallics 5 (1986) 655.

[8] Previous examples of orthometalated 2,2-diphenyl-1-azavinylidene ligand, see: J.A. Cabeza, F. Grepioni, M. Moreno, V. Riera, Organometallics 19 (2000) 5424, and references therein.

[9] R.J. Klingler, W.M. Butler, M.D. Curtis, J. Am. Chem. Soc. 100 (1978) 5034.

[10] R.D. Adams, D.M. Collins, F.A. Cotton, Inorg. Chem. 13 (1974) 1086.

[11] H. Brunner, W. Meier, J. Wachter, J. Organomet. Chem. 210 (1981) C23.

[12] W. Deutsch, A. Gieren, C. Ruiz-Perez, K.E. Schwarzhans, J. Organomet. Chem. 355 (1988) 197.

[13] (a) J. Chatt, M. Kubota, G.J. Leigh, F.C. March, R. Mason, D.J. Yarrow, J. Chem. Soc., Chem. Commun. (1974) 1033;

(b) S. Krogsrud, S. Komiya, T. Ito, J.A. Ibers, A. Yamamoto, Inorg. Chem. 15 (1976) 2798;

(c) G.O. Evans, W.F. Walter, D.R. Mills, C.A. Streit, J. Organomet. Chem. 144 (1978) C34;

(d) G. Fachinetti, C. Floriani, A. Chiesi-Villa, C. Guastini, J. Am. Chem. Soc. 101 (1979) 1767;

(e) J.M. Maher, N.J. Cooper, J. Am. Chem. Soc. 102 (1980) 7604;

(f) E. Carmona, F. González, M.L. Poveda, J.M. Marin, J.L. Atwood, R.D. Rogers, J. Am. Chem. Soc. 105 (1983) 3365;

(g) G.R. Lee, J.M. Maher, N.J. Cooper, J. Am. Chem. Soc. 109 (1987) 2956;

(h) K.A. Belmore, R.A. Vanderpool, J.-C. Tsai, M.A. Khan, K.M. Nicholas, J. Am. Chem. Soc. 110 (1988) 2004;

(i) R. Alvarez, J.L. Atwood, E. Carmona, P.J. Pérze, M.L. Poveda, R.D. Rogers, Inorg. Chem. 30 (1991) 1493;

(j) H. Nakajima, Y. Kushi, H. Nagao, K. Tanaka, Organometallics 14 (1995) 5903;

(k) N.W. Davies, A.S.P. Frey, M.G. Gardiner, J. Wang, Chem. Commun. (2006) 4853.

[14] (a) B. Li, S. Xu, H. Song, B. Wang, J. Organomet. Chem. 693 (2008) 87;

(b) B. Li, C. Zhang, S. Xu, H. Song, B. Wang, Eur. J. Inorg. Chem., accepted for publication.

[15] A.G. Orpen, L. Brammer, F.H. Allen, O. Kennard, D.G. Watson, R. Taylor, J. Chem. Soc., Dalton Trans. (1989) S1.

[16] A.H. Guenther, J. Chem. Phys. 31 (1959) 1095.

[17] E.L. Muetterties, J. Stein, Chem. Rev. 79 (1979) 479.

[18] (a) C.P. Horwitz, D.F. Shriver, Adv. Organomet. Chem. 23 (1984) 219;

(b) F.A. Cotton, Prog. Inorg. Chem. 21 (1976) 1.

[19] (a) R.D. Adams, D.A. Katahira, L.-W. Yang, Organometallics 1 (1982) 231;

(b) D. Lentz, I. Brüdgam, H. Hartl, J. Organomet. Chem. 299 (1986) C38;

(c) H. Adams, N.A. Bailey, C. Bannister, M.A. Faers, P. Fedorko, V.A. Osborn, M.J. Winter, J. Chem. Soc., Dalton Trans. (1987) 341.

[20] R.A. Doyle, L.M. Daniels, R.J. Angelici, F.G.A. Stone, J. Am. Chem. Soc. 111 (1989) 4995.

[21] See, for example: W.P. Fehlhammer, A. Mayr, H. Stolzenberg, Angew. Chem., Int. Ed. Engl. 18 (1979) 626.

[22] (a) A.R. Davis, F.W.B. Einstein, N.F. Curtis, J.W.L. Martin, J. Am. Chem. Soc. 100 (1978) 6258;

(b) M.R. Churchill, G. Davies, M.A. El-Sayed, M.F. El-Shazly, J.P. Hutchinson, M.W. Rupich, K.O. Watkins, Inorg. Chem. 18 (1979) 2296;

(c) A.R. Davis, F.W.B. Einstein, Inorg. Chem. 19 (1980) 1203;

(d) N. Kitajima, S. Hikichi, M. Tanaka, Y. Moro-oka, J. Am. Chem. Soc. 115 (1993) 5496;

(e) T.N. Sorrel, W.E. Allen, P. S White, Inorg. Chem. 34 (1995) 352;

(f) M.P. García, M.V. Jiménez, F.J. Lahoz, L.A. Oro, J. Chem. Soc., Dalton Trans. (1995) 917;

(g) M.-H. Hsu, R.-T. Chen, W.-S. Sheu, M. Shieh, Inorg. Chem. 45 (2006) 6740.

[23] G.A. Barclay, B.F. Hoskins, J. Chem. Soc. (1963) 2807.

[24] F.A. Cotton, T.R. Felthouse, Inorg. Chem. 19 (1980) 320.

[25] J. Miller, J. Org. Chem. 24 (1959) 560.

[26] K. Issleib, A. Brack, Z. Anorg. Allg. Chem. 217 (1954) 258.