

Reactions of $(\text{Me}_2\text{C})(\text{Me}_2\text{Si})[(\eta^5\text{-C}_5\text{H}_3)\text{Mo}(\text{CO})_3]_2$ with nitrile and subsequent cleavage of the $\text{C}\equiv\text{N}$ bond by cooperation of molybdenum and ruthenium

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Abstract

Reaction of the doubly bridged dinuclear molybdenum complex $(\text{Me}_2\text{C})(\text{Me}_2\text{Si})[(\eta^5\text{-C}_5\text{H}_3)\text{Mo}(\text{CO})_3]_2$ (**1**) with benzonitrile in refluxing xylene afforded complexes $(\text{Me}_2\text{C})(\text{Me}_2\text{Si})[(\eta^5\text{-C}_5\text{H}_3)_2\text{Mo}_2(\text{CO})_4(\mu\text{-}\eta^2\text{-}\eta^2(\perp)\text{-N}\equiv\text{CPh})]$ (**2**) (50%) and $(\text{Me}_2\text{C})(\text{Me}_2\text{Si})[(\eta^5\text{-C}_5\text{H}_3)_2\text{Mo}_2(\text{CO})_4(\mu\text{-}\eta^1\text{-}\eta^2\text{-N}\equiv\text{CPh})]$ (**3**) (6%) with different coordination of nitrile. The corresponding $\mu\text{-}\eta^2\text{-}\eta^2$ acetonitrile and propionitrile complexes **4** and **5** could be obtained from the reactions of $(\text{Me}_2\text{C})(\text{Me}_2\text{Si})(\text{C}_5\text{H}_4)_2$ with $(\text{RCN})_3\text{Mo}(\text{CO})_3$ ($\text{R} = \text{Me}, \text{Et}$) in refluxing xylene. Reactions of **1** with isonitriles generated $\mu\text{-}\eta^1\text{-}\eta^2\text{-C}\equiv\text{NR}$ ($\text{R} = \text{tBu}, \text{Ph}, \text{C}_6\text{H}_{11}$) bridged complexes **6–8** in 53–63% yields. Subsequent reaction of **4** with $\text{Ru}_3(\text{CO})_{12}$ yielded two $\text{C}\equiv\text{N}$ bond cleaved MoRu clusters $(\text{Me}_2\text{C})(\text{Me}_2\text{Si})(\eta^5\text{-C}_5\text{H}_3)_2\text{Mo}_2\text{Ru}_3(\text{CO})_{10}(\mu\text{-CO})(\mu_3\text{-CMe})(\mu_4\text{-N})$ (**9**) (7%) and $[(\text{Me}_2\text{C})(\text{Me}_2\text{Si})(\eta^5\text{-C}_5\text{H}_3)_2]_2\text{Mo}_4\text{Ru}_6(\text{CO})_{16}(\mu\text{-CO})(\mu_4\text{-CO})_2(\mu_3\text{-}\eta^1\text{-}\eta^2\text{-}\eta^2\text{-N}\equiv\text{CMe})(\mu_3\text{-CMe})(\mu_5\text{-N})$ (**10**) (8%). All the new complexes have been fully characterized. The molecular structures of **2**, **4**, **6**, **9**, and **10** have been determined by X-ray diffraction analysis.

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1. Introduction

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 maintaining 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 [1]. The Me_2C and Me_2Si doubly bridged bis(cyclopentadienyl) dinuclear molybdenum carbonyl complex $(\text{Me}_2\text{C})(\text{Me}_2\text{Si})[(\eta^5\text{-C}_5\text{H}_3)\text{Mo}(\text{CO})_3]_2$ (**1**) exhibited unusually long Mo–Mo bond distances due to the rigidity of the ligand [2]. We were, therefore, interested in the different reactivity

of the superlong Mo–Mo bond of **1**, especially for the activation of unreactive bonds.

Nitrile is an important functional group in organic synthesis, for it can be readily converted into many other organic functional groups such as amine or amide. It is important to prove the reactivity of a nitrile ligand with organometallic complexes so as to elucidate the mechanism of the reaction performed on a metal surface. Examples of η^2 -coordinated nitrile for monometallic complexes are well established (**A**, Chart 1) [3], but for bimetallic complexes are very limited (**B**) [4,5], and there are only a few examples of bimetallic complexes with $\mu\text{-}\eta^2\text{-}\eta^2(\perp)\text{-C}\equiv\text{N}$ coordination (**C**) [5]. On the other hand, the cleavage of the $\text{C}\equiv\text{N}$ bond of nitrile is usually regarded as an analogue of $\text{N}\equiv\text{N}$ bond activation of dinitrogen since the nitrile group contains an sp hybridized nitrogen atom as well as dinitrogen [6]. In contrast to the numerous examples of carbon–nitrogen triple bond cleavage of nitrile by way of hydration

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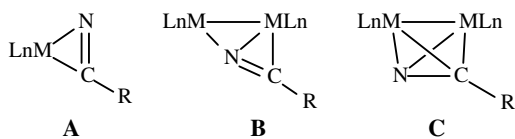


Chart 1.

in organic synthesis [7], as well as its reductive cleavage catalyzed by nitrogenase enzymes [8], examples of organo-transition metal-mediated C≡N bond cleavage of nitrile are limited to Ru [6], Ti [9], Zr [10], Mo [11], and W [12].

The cleavage of the C≡C bonds of alkynes has been observed in metal clusters with both homo- and heterometallic complexes [13], or by cooperation reaction of two different metal complexes [13b,14]. However, there was no report about the C≡N bond cleavage of nitrile involving reaction on a polynuclear cluster with heterometallic framework, nor with cooperation of two different metal complexes. In this contribution, we report the synthesis of the $\mu\text{-}\eta^2\text{-}\eta^2$ -nitrile complexes $(\text{Me}_2\text{C})(\text{Me}_2\text{Si})[(\eta^5\text{-C}_5\text{H}_3)_2\text{Mo}_2(\text{CO})_4(\mu\text{-}\eta^2\text{-}\eta^2(\perp)\text{-N}\equiv\text{CR})]$ (R = Ph, **2**; R = Me, **4**; R = Et, **5**), and the further reaction of **4** with $\text{Ru}_3(\text{CO})_{12}$, which afforded two C≡N bond cleaved MoRu clusters $[(\text{Me}_2\text{C})(\text{Me}_2\text{Si})(\eta^5\text{-C}_5\text{H}_3)_2]\text{Mo}_2\text{Ru}_3(\text{CO})_{10}(\mu\text{-CO})(\mu_3\text{-CMe})(\mu_4\text{-N})$ (**9**) and $[(\text{Me}_2\text{C})(\text{Me}_2\text{Si})(\eta^5\text{-C}_5\text{H}_3)_2]_2\text{Mo}_4\text{Ru}_6(\text{CO})_{16}(\mu\text{-CO})(\mu_4\text{-CO})_2(\mu_3\text{-}\eta^1\text{-}\eta^2\text{-}\eta^2\text{-N}\equiv\text{CMe})(\mu_3\text{-CMe})(\mu_5\text{-N})$ (**10**) in low yield. The reactions of **1** with isocyanides were also studied for comparison.

2. Experimental

2.1. General considerations

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. IR spectra were recorded as KBr disks on a Nicolet 560 ESP FTIR spectrometer. Elemental analyses were performed on a Perkin–Elmer 240C analyzer. Complex **1** [2] and isocyanides RNC (R = *t*Bu [15], Ph [16], C_6H_{11} [17]) were prepared by the literature methods.

2.2. Reaction of **1** with PhCN and synthesis of $(\text{Me}_2\text{C})(\text{Me}_2\text{Si})[(\eta^5\text{-C}_5\text{H}_3)_2\text{Mo}_2(\text{CO})_4(\mu\text{-}\eta^2\text{-}\eta^2(\perp)\text{-N}\equiv\text{CPh})]$ (**2**) and $(\text{Me}_2\text{C})(\text{Me}_2\text{Si})[(\eta^5\text{-C}_5\text{H}_3)_2\text{Mo}_2(\text{CO})_4(\mu\text{-}\eta^1\text{-}\eta^2\text{-}\eta^2\text{-N}\equiv\text{CPh})]$ (**3**)

A solution of **1** (117 mg, 0.20 mmol) and PhCN (620 mg, 6.0 mmol) in xylene (30 mL) was refluxed overnight. After removal of solvent the residue was chromatographed on an alumina column. Elution with petroleum ether– CH_2Cl_2 gave a brown-red band, which afforded **2** (64 mg, 50% yield) as brown-red crystals. Elution with CH_2Cl_2 developed a brown band, which afforded **3** (8 mg, 6% yield) as brown crystals.

For compound **2**, mp: 183 °C (dec.). Anal. Calc. for $\text{C}_{26}\text{H}_{23}\text{Mo}_2\text{NO}_4\text{Si}$: C, 49.28; H, 3.66; N, 2.21. Found: C, 49.22; H, 3.70; N, 2.10%. ^1H NMR (CDCl_3) δ 7.64 (d, $J = 6.15$ Hz, 2H, Ph-H), 7.34 (t, 2H, Ph-H), 7.19 (t, 1H, Ph-H), 5.60 (br s, 2H, Cp-H), 5.47 (br s, 2H, Cp-H), 5.21 (t, 2H, Cp-H), 1.65 (s, 3H, CMe), 1.37 (s, 3H, CMe), 0.65 (s, 3H, SiMe), 0.43 (s, 3H, SiMe); IR (ν_{CO} , cm^{-1}): 1981(s), 1954(s), 1914(s), 1902(s).

For compound **3**, mp: 203 °C (dec.). Anal. Calc. for $\text{C}_{26}\text{H}_{23}\text{Mo}_2\text{NO}_4\text{Si}$: C, 49.28; H, 3.66; N, 2.21. Found: C, 49.65; H, 3.96; N, 1.98%. ^1H NMR (CDCl_3) δ 8.28 (m, 2H, Ph-H), 7.62 (m, 2H, Ph-H), 7.50 (m, 1H, Ph-H), 7.11 (m, 1H, Cp-H), 6.27 (m, 1H, Cp-H), 5.75 (m, 1H, Cp-H), 5.49 (m, 1H, Cp-H), 5.15 (m, 1H, Cp-H), 4.25 (m, 1H, Cp-H), 1.19 (s, 6H, CMe), 0.87 (s, 3H, SiMe), -0.34 (s, 3H, SiMe); IR (ν_{CO} , cm^{-1}): 1940(s), 1859(s).

2.3. Synthesis of $(\text{Me}_2\text{C})(\text{Me}_2\text{Si})[(\eta^5\text{-C}_5\text{H}_3)_2\text{Mo}_2(\text{CO})_4(\mu\text{-}\eta^2\text{-}\eta^2(\perp)\text{-N}\equiv\text{CMe})]$ (**4**)

A solution of $(\text{Me}_2\text{C})(\text{Me}_2\text{Si})(\text{C}_5\text{H}_4)_2$ (0.5 g, 2.19 mmol) and $(\text{MeCN})_3\text{Mo}(\text{CO})_3$ [prepared from $\text{Mo}(\text{CO})_6$ (1.00 g, 3.79 mmol) in refluxing acetonitrile (10 mL) over about 6 h] [18] in xylene (50 mL) was refluxed for 15 h. After removal of solvent the residue was chromatographed on an alumina column using petroleum ether– CH_2Cl_2 as eluent. The first band (red) afforded the desilylation product $(\text{Me}_2\text{C})[(\eta^5\text{-C}_5\text{H}_4)\text{Mo}(\text{CO})_3]_2$ [19] (38 mg, 4% yield) as deep red crystals. The second band (green) gave **1** [2] (55 mg, 8% yield) as purple crystals. The third band (brown-red) gave **4** (310 mg, 29% yield) as brown-red crystals. For compound **4**, mp: 172 °C (dec.). Anal. Calc. for $\text{C}_{21}\text{H}_{21}\text{Mo}_2\text{NO}_4\text{Si}$: C, 44.15; H, 3.70; N, 2.45. Found: C, 44.17; H, 3.66; N, 2.44%. ^1H NMR (CDCl_3): δ 5.61 (t, 2H, Cp-H), 5.45 (m, 2H, Cp-H), 5.17 (m, 2H, Cp-H), 2.97 (s, 3H, NCMe), 1.63 (s, 3H, CMe), 1.29 (s, 3H, CMe), 0.61 (s, 3H, SiMe), 0.31 (s, 3H, SiMe); IR (ν_{CO} , cm^{-1}): 1980(s), 1944(s), 1928(s), 1909(s).

Reduction of the reaction time to 6 h afforded 4% of $(\text{Me}_2\text{C})[(\eta^5\text{-C}_5\text{H}_4)\text{Mo}(\text{CO})_3]_2$ and increased the yield of **1** up to about 40% and decreased the yield of **4** to trace amount.

2.4. Synthesis of $(\text{Me}_2\text{C})(\text{Me}_2\text{Si})[(\eta^5\text{-C}_5\text{H}_3)_2\text{Mo}_2(\text{CO})_4(\mu\text{-}\eta^2\text{-}\eta^2(\perp)\text{-N}\equiv\text{CEt})]$ (**5**)

Using a procedure similar to that described above, reaction of $(\text{Me}_2\text{C})(\text{Me}_2\text{Si})(\text{C}_5\text{H}_4)_2$ with $(\text{EtCN})_3\text{Mo}(\text{CO})_3$ gave complex **5** as brown-red crystals in 26% yield. For compound **5**, mp: 156–157 °C. Anal. Calc. for $\text{C}_{22}\text{H}_{23}\text{Mo}_2\text{NO}_4\text{Si}$: C, 45.14; H, 3.96; N, 2.39. Found: C, 45.25; H, 3.88; N, 2.49%. ^1H NMR (CDCl_3) δ 5.74 (m, 2H, Cp-H), 5.55 (m, 2H, Cp-H), 5.15 (m, 2H, Cp-H), 3.33 (s, 2H, Et- CH_2), 1.65 (s, 3H, CMe), 1.43 (m, 3H, Et- CH_3), 1.27 (s, 3H, CMe), 0.64 (s, 3H, SiMe), 0.34 (s, 3H, SiMe). IR (ν_{CO} , cm^{-1}): 1982(s), 1944(s), 1935(s), 1909(s).

2.5. Reaction of **1** with isonitrile RNC ($R = {}^t\text{Bu}, \text{Ph}, \text{C}_6\text{H}_{11}$)

A solution of **1** (117 mg, 0.20 mmol) and ${}^t\text{BuNC}$ (17 mg, 0.20 mmol) in toluene (30 mL) was refluxed for 15 h. After removal of solvent the residue was chromatographed on an alumina column. Elution with petroleum ether– CH_2Cl_2 gave a green band, which afforded **6** (64 mg, 50% yield) as green crystals as a mixture of two isomers in the ratio 7:1. For compound **6**, mp: 196 °C (dec.). Anal. Calc. for $\text{C}_{24}\text{H}_{27}\text{Mo}_2\text{NO}_4\text{Si}$: C, 47.00; H, 4.44; N, 2.28. Found: C, 46.88; H, 4.25; N, 2.19%. ${}^1\text{H}$ NMR (CDCl_3) for the major isomer: δ 6.04 (m, 1H, Cp-H), 5.89 (m, 1H, Cp-H), 5.44 (m, 1H, Cp-H), 5.37 (m, 1H, Cp-H), 5.23 (m, 1H, Cp-H), 4.92 (m, 1H, Cp-H), 1.40 (s, 9H, ${}^t\text{Bu-H}$), 1.29 (s, 3H, CMe), 0.86 (s, 3H, CMe), 0.70 (s, 3H, SiMe), 0.53 (s, 3H, SiMe); for the minor isomer: δ 5.97 (m, 1H, Cp-H), 5.61 (m, 1H, Cp-H), 5.47 (m, 1H, Cp-H), 5.29 (m, 2H, Cp-H), 4.85 (m, 1H, Cp-H), 1.74 (s, 3H, CMe), 1.46 (s, 3H, CMe), 1.34 (s, 9H, ${}^t\text{Bu-H}$), 0.36 (s, 3H, SiMe), 0.21 (s, 3H, SiMe). IR (cm^{-1} , as mixture of isomers): ν_{CO} 1961(s), 1920(s), 1879(s), 1821(s); ν_{CN} 1716(m).

Using a procedure similar to that described above, reactions of **1** with $\text{C}_6\text{H}_{11}\text{NC}$ and PhNC afforded **7** (two isomers in the ratio 5:1) and **8** (two isomers in the ratio of 3:1) as green crystals in 58% and 63% yield, respectively.

For compound **7**, mp: 208 °C (dec.). Anal. Calc. for $\text{C}_{26}\text{H}_{29}\text{Mo}_2\text{NO}_4\text{Si}$: C, 48.83; H, 4.57; N, 2.19. Found: C, 48.60; H, 4.39; N, 2.23%. ${}^1\text{H}$ NMR (CDCl_3) for the major isomer: δ 6.01 (m, 1H, Cp-H), 5.85 (m, 1H, Cp-H), 5.45 (m, 1H, Cp-H), 5.35 (m, 1H, Cp-H), 5.24 (m, 1H, Cp-H), 4.94 (m, 1H, Cp-H), 3.48 (m, 1H, Cy-CH), 2.24–2.08 (m, 2H, Cy- CH_2), 1.87–1.75 (m, 2H, Cy- CH_2), 1.72–1.63 (m, 2H, Cy- CH_2), 1.44–1.34 (m, 4H, Cy- CH_2), 1.29 (s, 3H, CMe), 0.84 (s, 3H, CMe), 0.69 (s, 3H, SiMe), 0.53 (s, 3H, SiMe); for the minor isomer: δ 5.94 (m, 1H, Cp-H), 5.86 (m, 2H, Cp-H), 5.62 (m, 1H, Cp-H), 5.29 (m, 1H, Cp-H), 4.86 (m, 1H, Cp-H), 3.45 (m, 1H, Cy-CH), 2.24–2.08 (m, 2H, Cy- CH_2), 1.87–1.75 (m, 2H, Cy- CH_2), 1.73 (s, 3H, CMe), 1.72–1.63 (m, 2H, Cy- CH_2), 1.45 (s, 3H, CMe), 1.44–1.34 (m, 4H, Cy- CH_2), 0.35 (s, 3H, SiMe), 0.17 (s, 3H, SiMe). IR (cm^{-1} , mixture of isomers): ν_{CO} 1972(s), 1927(s), 1875(s), 1825(s); ν_{CN} 1729(m).

For compound **8**, mp: 191 °C (dec.). Anal. Calc. for $\text{C}_{26}\text{H}_{23}\text{Mo}_2\text{NO}_4\text{Si}$: C, 49.30; H, 3.66; N, 2.21. Found: C, 49.28; H, 3.68; N, 2.24%. ${}^1\text{H}$ NMR (CDCl_3) for the major isomer: δ 7.48–7.33 (m, 5H, Ph-H), 6.19 (m, 1H, Cp-H), 5.94 (m, 1H, Cp-H), 5.57 (m, 1H, Cp-H), 5.40 (m, 1H, Cp-H), 5.36 (m, 1H, Cp-H), 5.06 (m, 1H, Cp-H), 1.28 (s, 3H, CMe), 0.74 (s, 3H, CMe), 0.65 (s, 3H, SiMe), 0.58 (s, 3H, SiMe); for the minor isomer: δ 7.19–7.14 (m, 5H, Ph-H), 6.02 (m, 2H, Cp-H), 5.81 (m, 1H, Cp-H), 5.53 (m, 1H, Cp-H), 5.41 (m, 1H, Cp-H), 4.98 (m, 1H, Cp-H), 1.79 (s, 3H, CMe), 1.50 (s, 3H, CMe), 0.32 (s, 3H, SiMe), -0.11 (s, 3H, SiMe). IR (cm^{-1} , as mixture of isomers): ν_{CO} 1967(s), 1920(s), 1879(s), 1831(s); ν_{CN} 1680(s).

2.6. Reaction of **4** with $\text{Ru}_3(\text{CO})_{12}$

A solution of **4** (300 mg, 0.52 mmol) and $\text{Ru}_3(\text{CO})_{12}$ (250 mg, 0.39 mmol) in toluene (60 mL) was refluxed for 5 h. After removal of solvent the residue was chromatographed on an alumina column using petroleum ether/ CH_2Cl_2 as eluent. The first band (yellow) gave 68 mg of unreacted $\text{Ru}_3(\text{CO})_{12}$. The second band (green) gave **1** (102 mg, 33% yield) as purple crystals. The third band (deep-gray) afforded **9** (21 mg, 7% yield) as deep-brown crystals. The fourth band (brown) afforded **10** (23 mg, 8% yield) as deep-brown crystals.

For compound **9**, mp: 242 °C (dec.). Anal. Calc. for $\text{C}_{28}\text{H}_{21}\text{Mo}_2\text{NO}_{11}\text{Ru}_3\text{Si}$: C, 31.41; H, 1.98; N, 1.31. Found: C, 31.71; H, 1.80; N, 1.38%. ${}^1\text{H}$ NMR (CDCl_3): δ 5.74 (m, 1H, Cp-H), 5.59 (m, 1H, Cp-H), 5.54 (m, 2H, Cp-H), 5.28 (m, 1H, Cp-H), 4.56 (t, 1H, Cp-H), 4.29 (s, 3H, $\mu_3\text{-CMe}$), 1.96 (s, 3H, CMe), 1.71 (s, 3H, CMe), 0.60 (s, 6H, SiMe); IR (ν_{CO} , cm^{-1}): 2070(s), 2050(s), 2028(s), 2004(m), 1995(m), 1979(s), 1962(s), 1912(s), 1885(s), 1855(s), 1788(s).

For compound **10**. Mp: >300 °C. Anal. Calc. for $\text{C}_{53}\text{H}_{42}\text{Mo}_4\text{N}_2\text{O}_{19}\text{Ru}_6\text{Si}_2$: C, 30.94; H, 2.06; N, 1.36. Found: C, 30.88; H, 1.96; N, 1.26%. ${}^1\text{H}$ NMR (CDCl_3): δ 6.94 (m, 1H, Cp-H), 6.32 (m, 1H, Cp-H), 6.02 (m, 1H, Cp-H), 5.96 (m, 1H, Cp-H), 5.75 (m, 1H, Cp-H), 5.71 (m, 1H, Cp-H), 5.55 (m, 1H, Cp-H), 5.53 (m, 1H, Cp-H), 5.43 (m, 1H, Cp-H), 5.40 (m, 1H, Cp-H), 5.07 (m, 1H, Cp-H), 5.01 (m, 1H, Cp-H), 4.49 (s, 3H, $\mu_3\text{-CMe}$), 3.06 (s, 3H, NCMe), 1.76 (s, 6H, CMe), 1.68 (s, 3H, CMe), 1.15 (s, 3H, CMe), 0.65 (s, 3H, SiMe), 0.33 (s, 6H, SiMe), -0.94 (s, 3H, SiMe); IR (ν_{CO} , cm^{-1}): 2051(s), 2027(s), 1999(br s), 1968(br s), 1938(br s), 1828(m), 1491(m), 1473(m).

2.7. Crystallographic studies

Single crystals of complexes **2**, **4**, **6**, and **9** suitable for X-ray diffraction were obtained from hexane/ CH_2Cl_2 , whereas complex **10** was from hexane/ CHCl_3 solution. Data collection was performed on a Bruker SMART 1000, using graphite-monochromated Mo $\text{K}\alpha$ 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 **10** contained two CHCl_3 of solvation. The crystal data and summary of X-ray data collection are presented in Table 1.

3. Results and discussion

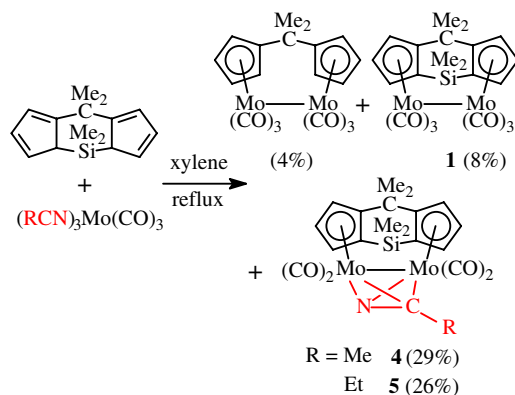
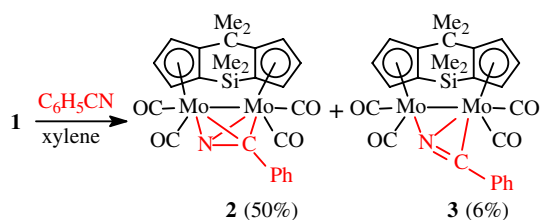
3.1. Reaction of $(\text{Me}_2\text{C})(\text{Me}_2\text{Si})[(\eta^5\text{-C}_5\text{H}_3)\text{Mo}(\text{CO})_3]_2$ (**1**) with nitrile and isonitrile

Reaction of **1** with PhCN in refluxing xylene afforded the perpendicularly coordinated benzonitrile complex

Table 1
Summary of crystallographic data for **2**, **4**, **6**, **9**, and **10** · 2CHCl₃

	2	4	6	9	10 · 2CHCl ₃
Empirical formula	C ₂₆ H ₂₃ Mo ₂ NO ₄ Si	C ₂₁ H ₂₁ Mo ₂ NO ₄ Si	C ₂₄ H ₂₇ Mo ₂ NO ₄ Si	C ₂₈ H ₂₁ Mo ₂ NO ₁₁ Ru ₃ Si	C ₅₅ H ₄₄ Cl ₆ Mo ₄ N ₂ O ₁₉ Ru ₆ Si ₂
Fw	633.42	571.36	613.44	1070.64	2295.98
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Orthorhombic	Monoclinic
Space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2(1)/ <i>c</i>	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	11.1918(19)	10.308(3)	10.694(3)	10.666(3)	15.500(3)
<i>b</i> (Å)	12.724(2)	10.613(3)	13.962(3)	16.159(4)	19.356(3)
<i>c</i> (Å)	17.095(3)	19.737(6)	17.436(4)	18.690(5)	23.100(4)
α (°)	90	90	90	90	90
β (°)	90	96.608(5)	104.099(4)	90	92.952(3)
γ (°)	90	90	90	90	90
<i>V</i> (Å ³)	2434.4(7)	2144.7(11)	2525.0(10)	3221.2(14)	6921(2)
<i>Z</i>	4	4	4	4	4
<i>D</i> _{calc} (g cm ⁻³)	1.728	1.769	1.614	2.208	2.203
μ (mm ⁻¹)	1.113	1.252	1.070	2.228	2.303
<i>F</i> (000)	1264	1136	1232	2056	4408
Crystal size (mm)	0.24 × 0.20 × 0.18	0.30 × 0.20 × 0.06	0.28 × 0.22 × 0.18	0.34 × 0.32 × 0.28	0.24 × 0.20 × 0.16
Maximum 2 θ (°)	52.72	52.84	52.94	54.34	50.02
No. of reflections collected	14149	12115	13937	18299	34959
No. of independent reflections/ <i>R</i> _{int}	4963/0.0245	4380/0.0305	5186/0.0466	7067/0.0268	12204/0.0797
No. of parameters	311	267	296	420	857
Goodness-of-fit on <i>F</i> ²	1.033	1.048	1.004	1.093	1.017
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.0209, 0.0465	0.0259, 0.0565	0.0330, 0.0572	0.0256, 0.0472	0.0461, 0.0990
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0252, 0.0483	0.0407, 0.0628	0.0745, 0.0688	0.0359, 0.0506	0.0944, 0.1197
Largest difference in peak and hole (e Å ⁻³)	0.450 and -0.196	0.584 and -0.281	0.524 and -0.522	0.535 and -0.562	2.222 and -0.971

(Me₂C)(Me₂Si)[(η⁵-C₅H₃)₂Mo₂(CO)₄(μ-η²-η²(⊥)-N≡CPh)] (**2**) and the σ + π coordinated benzonitrile complex (Me₂C)(Me₂Si)[(η⁵-C₅H₃)₂Mo₂(CO)₄(μ-η¹-η²-N≡CPh)] (**3**) (Scheme 1). The interconversion of the isomeric complexes **2** and **3** was not detected by heating **2** or **3** in refluxing xylene separately. The reaction of **1** with CH₃CN in refluxing xylene only afforded the corresponding acetonitrile complex **4** in very poor yield. However, complex **4** was isolated in 29% yield together with the desilylation product (Me₂C)[(η⁵-C₅H₄)Mo(CO)₃]₂ (4%) [19] and **1** (8%) [2] from the reaction of the doubly bridged ligand (Me₂C)(Me₂Si)(C₅H₄)₂ with (MeCN)₃Mo(CO)₃ in refluxing xylene for 15h (Scheme 2). Reduction of the reaction time to 6 h increased the yield of **1** up to about 40% but decreased the yield of **4** to trace amount. The propionitrile complex **5** was synthesized using similar procedure. It is not clear why nitriles with lower boiling points such as acetonitrile and propionitrile react with **1** only produce trace **4** and **5**. It should also note that other nitriles such as PhCH₂CN and EtO₂CCH₂CN do not react with complex **1**. The reason is still not clear, either. The ¹H NMR spectra of **2**, **4**,



and **5** show resonances which can be assigned to equivalent Cp rings, the bridging CMe₂ and SiMe₂ groups and the R groups of the nitrile ligands.

The molecular structure of **2** was determined by single crystal X-ray diffraction analysis (Fig. 1). An important feature of **2** is the μ-η²-η²-N≡CPh bridging ligand, which is perpendicular to the Mo–Mo bond. This is in contrast to the result of the reaction of the non-bridged dimolybdenum complex Cp₂Mo₂(CO)₆ with cyanamide R₂NCN (R = H, Me), which only produced the μ-η¹-η²-C≡N adduct [4a]. This is probably due to the rigidity of the doubly bridged bis(cyclopentadienyl) ligand, which might be in favor of the crosswise-bridging μ-η²-η²(⊥)-C≡N coordination. The crosswise coordination significantly increases the C–N bond distance to 1.299(3) Å and decreases the N–C–Me

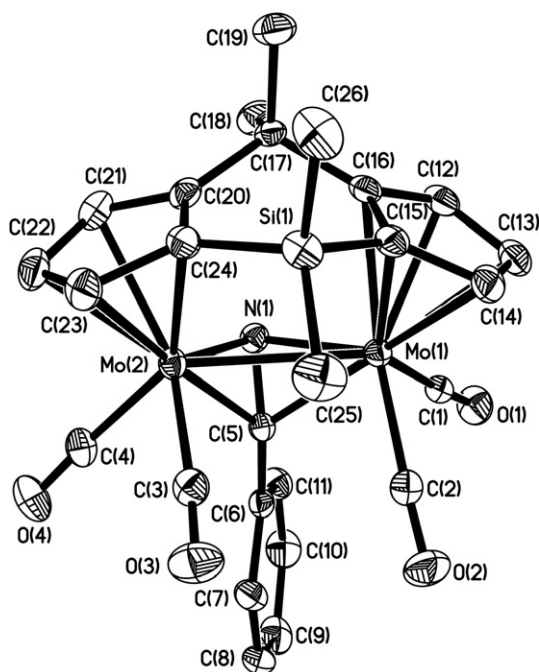


Fig. 1. ORTEP diagram of complex $(\text{Me}_2\text{C})(\text{Me}_2\text{Si})[(\eta^5\text{-C}_5\text{H}_3)_2\text{Mo}_2(\text{CO})_4(\mu\text{-}\eta^2\text{-}\eta^2(\perp)\text{-N}\equiv\text{CPh})]$ (**2**). Thermal ellipsoids are shown at the 30% level. Selected bond lengths [Å] and angles [°] are Mo(1)–Mo(2) 2.8993(5), Mo(1)–N(1) 2.151(2), Mo(2)–N(1) 2.138(3), Mo(1)–C(5) 2.196(3), Mo(2)–C(5) 2.190(3), C(5)–N(1) 1.299(3), Mo(1)–N(1)–Mo(2) 85.06(8), Mo(1)–C(5)–Mo(2) 82.76(9), N(1)–C(5)–C(6) 131.7(3), Cp–Cp fold angle 134.4, Cp(centroid)–Mo(1)–Mo(2)–Cp(centroid) 8.2.

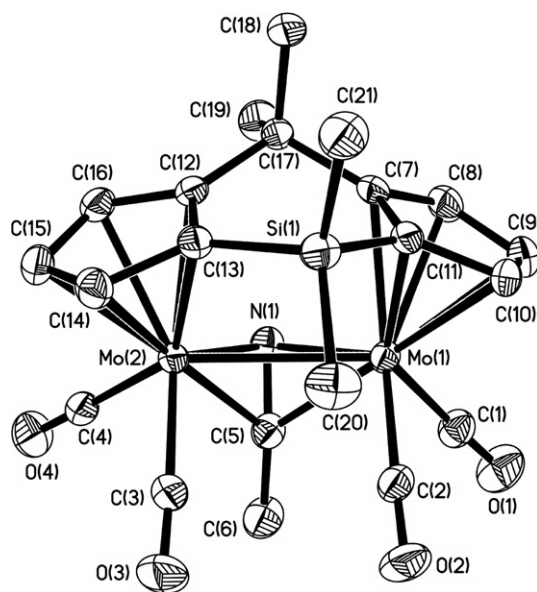


Fig. 2. ORTEP diagram of complex $(\text{Me}_2\text{C})(\text{Me}_2\text{Si})[(\eta^5\text{-C}_5\text{H}_3)_2\text{Mo}_2(\text{CO})_4(\mu\text{-}\eta^2\text{-}\eta^2(\perp)\text{-N}\equiv\text{CMe})]$ (**4**). Thermal ellipsoids are shown at the 30% level. Selected bond lengths [Å] and angles [°] are Mo(1)–Mo(2) 2.9180(9), Mo(1)–N(1) 2.147(2), Mo(2)–N(1) 2.175(3), Mo(1)–C(5) 2.199(3), Mo(2)–C(5) 2.184(3), C(5)–N(1) 1.284(4), Mo(1)–N(1)–Mo(2) 84.93(9), Mo(1)–C(5)–Mo(2) 83.47(10), N(1)–C(5)–C(6) 134.6(3), Cp–Cp fold angle 136.3, Cp(centroid)–Mo(1)–Mo(2)–Cp(centroid) 5.9.

angle to 131.7(3)°, consistent with the absence of $\text{C}\equiv\text{N}$ stretching absorption. Complex **4** has similar structure and its molecular structure is depicted in Fig. 2. In Table 2 the dimensions of core $(\mu\text{-}\eta^2\text{-}\eta^2\text{-RCN})\text{Mo}_2$ units in complexes **2**, **4**, $[\text{Mo}_2(\mu\text{-}\eta^2\text{-NCCH}_3)(\mu\text{-NC}(\text{CH}_3)\text{PPh}_2\text{CH}_2\text{CH}_2\text{PPh}_2)(\text{NCCH}_3)_7](\text{BF}_4)_4$ (**I**) [5a], $[\text{Mo}_2(\mu\text{-}\eta^2\text{-NCCH}_3)(\mu\text{-PPh}_2\text{NHPPH}_2)(\mu\text{-NC}(\text{CH}_3)\text{PPh}_2)\text{NPPH}_2(\text{NCCH}_3)_5](\text{BF}_4)_3$ (**II**) [5b], $[\text{Mo}_2(\mu\text{-}\eta^2\text{-NCCH}_3)(\mu\text{-O})(\mu\text{-PPh}_2\text{NHPPH}_2)(\text{NCCH}_3)_4](\text{BF}_4)_2$ (**III**) [5b], and the corresponding $(\mu\text{-}\eta^2\text{-}\eta^2\text{-CH}_3\text{CN})\text{W}_2$ unit in $\text{W}_2\text{Cl}_4(\mu\text{-PPh}_2\text{CH}_2\text{PPh}_2)_2(\mu\text{-}\eta^2\text{-NCCH}_3)$ (**IV**) [5c] are collected for comparison. All the bridging nitrile ligands are no longer linear and greatly bended. The N–C–C(R) angles in **III** and **IV** [117.7(5)°, 116.7(3)°] are close to the ideal value for sp^2 -hybridized atoms, while those in the former four compounds are significantly large (131–136°). Although the isostructural and isoelectronic alkyne complexes are well studied [20], the nitrile complexes of this kind are still uncommon [5].

Complex **3** is stable in solid state but somewhat air sensitive in solution, which were initially characterized spectroscopically. The IR bands at 1940 and 1859 cm^{-1} are assigned to the carbonyl ligands; the bridging $\eta^1\text{-}\eta^2\text{-N}\equiv\text{CPh}$ stretching vibration is at 1639 cm^{-1} , similar to that of $\text{Cp}_2\text{Mo}_2(\text{CO})_4(\mu\text{-}\eta^1\text{-}\eta^2\text{-N}\equiv\text{CPh})$ [4a]. Its ^1H NMR spectrum exhibits inequivalent resonances for the Cp protons, suggesting the unsymmetrical bonding of benzonitrile to the dimolybdenum moiety. The signals for one

Cp proton at δ 7.11 ppm and for a Si–Me protons at δ –0.34 ppm are significantly downfield or upfield from the typical Cp (δ 4–6 ppm) and Si–Me (δ 0–1 ppm) proton region, respectively, due to the deshielding or shielding effect of the bridging $\text{N}\equiv\text{CPh}$ ligand.

Since the reactions of **1** with nitriles do not parallel with those of non-bridged complex $\text{Cp}_2\text{Mo}_2(\text{CO})_6$, we then choose isonitriles, which also have $\text{C}\equiv\text{N}$ bonds, as substrates to react with **1**. When **1** reacted with equimolar of isonitriles in refluxing toluene, complexes $(\text{Me}_2\text{C})(\text{Me}_2\text{Si})[(\eta^5\text{-C}_5\text{H}_3)_2\text{Mo}_2(\text{CO})_4(\mu\text{-}\eta^1\text{-}\eta^2\text{-C}\equiv\text{NR})]$ (R = 'Bu, **6**; R = Ph, **7**; R = C_6H_{11} , **8**) were obtained in good yield (Scheme 3). This is consistent with the result of the reaction of $\text{Cp}_2\text{Mo}_2(\text{CO})_6$ with isonitriles [21]. The ^1H NMR spectra of **6–8** exhibit inequivalent resonances for the protons of Cp rings, the R group of isonitriles, and the CMe_2 and SiMe_2 groups. The ^1H NMR spectra also show the existence of another minor isomer (see Section 2). In the major isomers, one of the signal (δ = 0.86, 0.74, and 0.84 ppm for **6**, **7**, and **8**, respectively) is approximately 0.4 ppm upfield from the typical CMe_2 region due to the shielding effect of the bridging isonitrile ligand. Their IR spectra display four strong terminal carbonyl absorptions and a low-energy absorption for the $\mu\text{-}\eta^1\text{-}\eta^2\text{-C}\equiv\text{N}^i\text{Bu}$ ligand at 1716, 1680, and 1729 cm^{-1} for **6**, **7**, and **8**, respectively.

Details of the molecular structure of one isomer of **6** were established by an X-ray crystallographic analysis (Fig. 3). The dimension of $\text{Mo}_2(\text{CO})_4(\mu\text{-}\eta^1\text{-}\eta^2\text{-C}\equiv\text{N}^i\text{Bu})$ core structure in **6** is similar to that of the analogues $\text{Cp}_2\text{Mo}_2(\text{CO})_4(\mu\text{-}\eta^1\text{-}\eta^2\text{-C}\equiv\text{NR})$ (R = Me [21a], 'Bu

Table 2
Comparison of selected bond distances (Å) and angles (°) of **2**, **4**, **I**, **II**, **III**, and **IV**^a

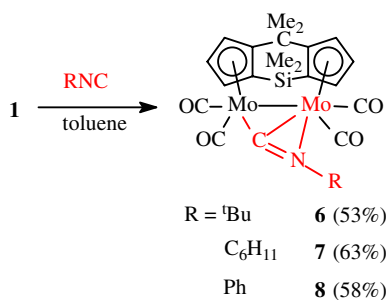
	2	4	I	II	III	IV
N–C	1.299(3)	1.284(4)	1.269(8)	1.27(1)	1.34(1)	1.303(8)
C–C(R)	1.466(4)	1.504(4)	1.514(9)	1.49(2)	1.47(1)	1.617(11)
N–C–C(R)	131.7(3)	134.6(3)	136.2(6)	134.6(10)	117.7(5)	116.7(3)
M–N–M	85.06(8)	84.93(9)	72.0(2)	70.7(2)	69.7(2)	72.9(2)
M–C–M	82.76(9)	83.47(10)	72.8(2)	72.4(3)	69.7(2)	72.8(2)

^a**I**: Mo₂(μ-η²-NCCH₃)(μ-NC(CH₃)PPh₂CH₂CH₂PPh₂)(NCCH₃)₇(BF₄)₄ [5a].

II: Mo₂(μ-η²-NCCH₃)(μ-PPH₂NHPPH₂)(μ-NC(CH₃)PPh₂)NPPH₂(NCCH₃)₅(BF₄)₃ [5b].

III: [Mo₂(μ-η²-NCCH₃)(μ-O)(μ-PPH₂NHPPH₂)(NCCH₃)₄](BF₄)₂ [5b].

IV: W₂Cl₄(μ-PPH₂CH₂PPh₂)₂(μ-η²-NCCH₃) [5c].



[21c]). The bimetallic system is bridged by the CN^tBu ligand coordinated in a σ + π fashion: with isocyano carbon C(5) σ bonded to Mo(1) [Mo(1)–C(5) = 1.946(4) Å], while C–N function π bonded to Mo(2) [Mo(2)–C(5) = 2.282(3) Å, Mo(2)–N(1) = 2.224(3) Å]. The introduction of the isonitrile bridging ligand decreases the Mo–Mo bond distance to 3.2109(6) Å, compared to that of **1** (3.4328(12) Å). The long C(5)–N(1) bond length of 1.226(4) Å agrees with the low-energy absorption in its IR spectrum. The major and minor isomers of the product are obtained as unseparable mixtures and they are not interconvertible in solutions. The amount of the single crystal is not enough to verify that the X-ray analysis for **6** has been done is for the major or minor isomer. Due to the difference of the two bridging atoms, the two isomers can be assumed as the structures with exchanging the location of CMe₂ and SiMe₂ group in the doubly bridged ligand.

3.2. Reaction of **4** with Ru₃(CO)₁₂

Morris and co-workers demonstrated that the thermal reactions of the dimolybdenum alkyne complexes Cp₂Mo₂(CO)₄(μ-η²-η²-R¹C≡CR²) with Ru₃(CO)₁₂ led to the C≡C bond cleavage of alkynes [22]. So the reaction of **4** with Ru₃(CO)₁₂ in refluxing toluene was done, and two nitrido clusters [(Me₂C)(Me₂Si)(η⁵-C₅H₃)₂]Mo₂Ru₃(CO)₁₀(μ-CO)(μ₃-CMe)(μ₄-N) (**9**) and [(Me₂C)(Me₂Si)(η⁵-C₅H₃)₂]Mo₄Ru₆(CO)₁₆(μ-CO)(μ₄-CO)₂(μ₃-η¹-η²-η²-N≡CMe)(μ₃-CMe)(μ₅-N) (**10**) were isolated in low yields

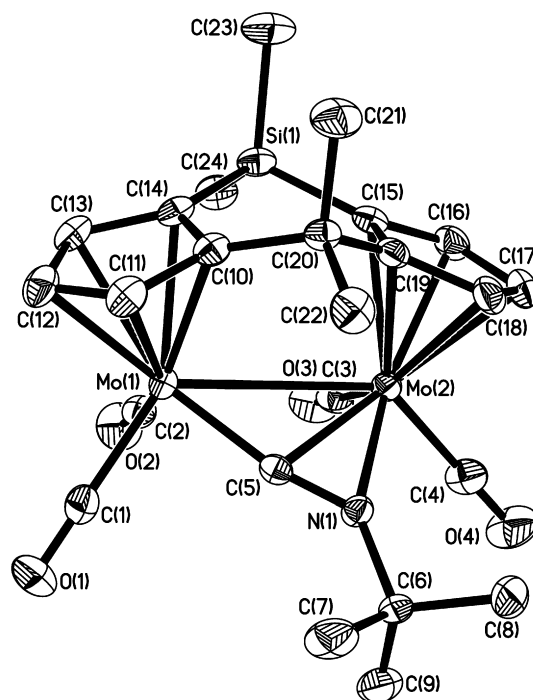
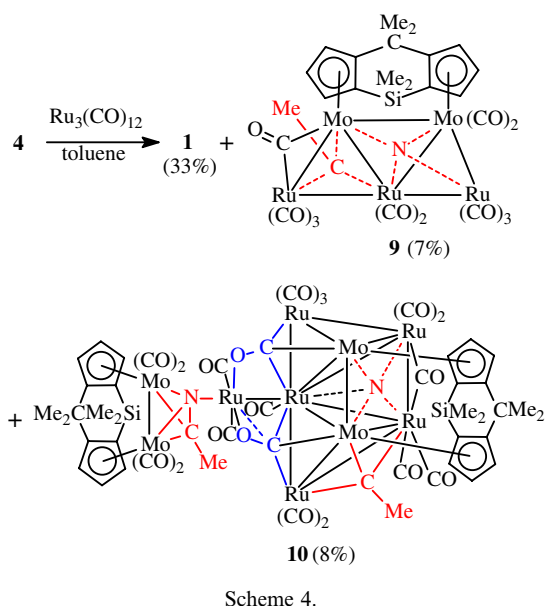


Fig. 3. ORTEP diagram of complex (Me₂C)(Me₂Si)[(η⁵-C₅H₃)₂Mo₂(CO)₄(μ-η¹-η²-N≡C^tBu)] (**6**). Thermal ellipsoids are shown at the 30% level. Selected bond lengths [Å] and angles [°] are Mo(1)–Mo(2) 3.2109(6), Mo(1)–C(5) 1.946(4), Mo(2)–C(5) 2.282(3), Mo(2)–N(1) 2.224(3), Mo(1)–C(5)–N(1) 169.4(3), C(5)–N(1)–C(6) 135.8(3), Mo(1)–C(5)–Mo(2) 98.54(15), Cp–Cp fold angle 143.4, Cp(centroid)–Mo(1)–Mo(2)–Cp(centroid) 0.1.

(7% and 8%, respectively) along with **1** (33%) (Scheme 4). It is evident that the formation of the μ₄- and μ₅-nitrido and μ₃-CMe ligands in complexes **9** and **10** must result from the C≡N bond rupture of acetonitrile. Further reaction of **9** with **4** and Ru₃(CO)₁₂ did not generate **10**. A number of metal clusters containing μ₄-N and μ₅-N ligands have been studied by X-ray diffraction [23–26]. But none of the μ₄- and μ₅-nitrido atoms in these complexes derived from C≡N bond cleavage of nitrile. In contrast to a few illustrations of C≡N bond cleavage to form metal nitride [6,11,12], this is, to the best of our knowledge, the first example that C≡N bond ruptured to construct the μ₄-nitrido and μ₅-nitrido ligands in a heterometallic system.



Both **9** and **10** are air stable crystals, but in solution they are somewhat air sensitive. The ^1H NMR spectrum of **9** shows five groups of peaks for the Cp protons, three groups of peaks for the bridging CMe_2 and SiMe_2 protons, and a singlet at δ 4.29 ppm for the ethylidyne ligand. The signal of the ethylidyne is similar to that for $\text{Cp}_2\text{Mo}_2\text{Ru}_4(\text{CO})_{12}(\mu_3\text{-CMe})$ [**22a**], but significantly downfield relative to the signal of the $\eta^2\text{-}\eta^2\text{-N}\equiv\text{CMe}$ in **4**. The ^1H NMR spectrum of **10** is composed of twelve groups of peaks for the Cp protons, two singlets at δ 4.49 and 3.06 ppm for the $\mu_3\text{-CMe}$ and $\eta^2\text{-}\eta^2\text{-N}\equiv\text{CMe}$ protons, respectively, and six groups of peaks for the bridging CMe_2 and SiMe_2 protons with one of the SiMe_2 protons significantly upfield to -0.94 ppm. This reveals that two molecules of **4** are incorporated in **10**. In IR spectra **9** displays eleven absorptions for both terminal and bridging carbonyls, whereas **10** exhibits eight absorptions for terminal, bridging carbonyls and the quadruply bridging (μ_4) carbonyl ligands.

Since neither the NMR nor the IR spectra on **9** and **10** were structurally definitive, the single crystal X-ray diffraction studies were carried out which revealed the structures shown in Figs. 4 and 5, respectively. The metal framework of **9** consists of a Mo_2Ru_2 butterfly fragment with an additional Ru(3) atom spanning one of the Mo–Ru bonds. The nitrido ligand is semi-encapsulated within the Mo_2Ru_2 butterfly moiety and the ethylidyne ligand caps the MoRu_2 triangular face. This metal framework geometry bears a striking resemblance to that of $\text{Cp}_3^*\text{Mo}_3\text{Co}_2(\text{CO})_8(\mu_3\text{-NH})(\mu_4\text{-N})$ except the difference of the butterfly hinge position [**24d**]. The Mo–Ru and Ru–Ru bond distances of cluster **9** are comparable to or a little shorter than those found in other Mo–Ru clusters [**22,27**]. The N–Mo [**24d**] and N–Ru [**24b,24c–26**] bond lengths are similar to those found for $\mu_4\text{-N}$ clusters. The μ_3 -alkylidyne carbon C(12), caps the triangle somewhat unsymmetrically [Mo(2)–C(12) = 1.995(4) Å, Ru(2)–C(12) = 2.162(5) Å, Ru(3)–

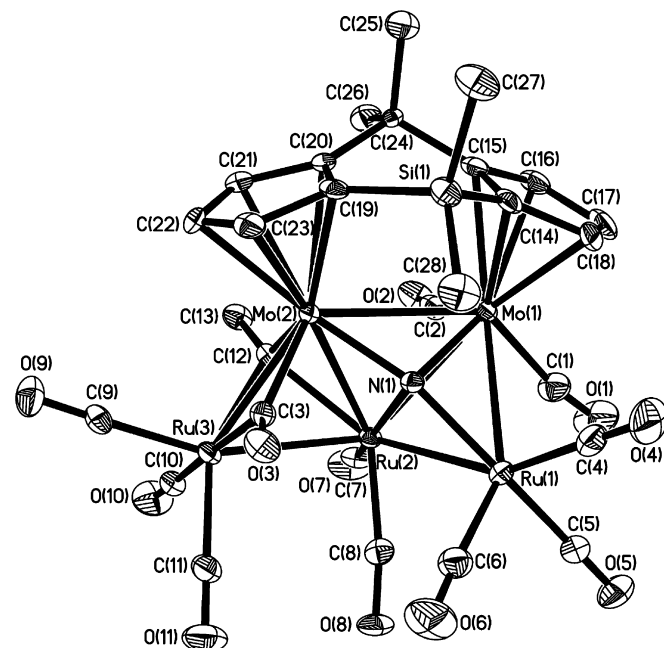


Fig. 4. ORTEP diagram of complex $[(\text{Me}_2\text{C}(\text{Me}_2\text{Si})(\eta^5\text{-C}_5\text{H}_3)_2)]\text{Mo}_2\text{Ru}_3(\text{CO})_{10}(\mu\text{-CO})(\mu_3\text{-CMe})(\mu_4\text{-N})$ (**9**). Thermal ellipsoids are shown at the 30% level. Selected bond lengths [Å] and angles [°] are Mo(1)–Mo(2) 3.0014(8), Mo(1)–Ru(1) 2.8505(7), Mo(1)–Ru(2) 2.8203(8), Mo(2)–Ru(2) 2.7242(7), Mo(2)–Ru(3) 2.7943(8), Ru(1)–Ru(2) 2.7803(8), Ru(2)–Ru(3) 2.7426(7), Mo(1)–N(1) 2.073(3), Mo(2)–N(1) 1.934(3), Ru(1)–N(1) 1.961(3), Ru(2)–N(1) 2.117(3), Mo(2)–C(12) 1.995(4), Ru(2)–C(12) 2.162(5), Ru(3)–C(12) 2.107(4), Mo(2)–N(1)–Ru(2) 84.41(13), Ru(1)–N(1)–Ru(2) 85.87(13), Mo(1)–N(1)–Ru(2) 84.61(13), Mo(1)–N(1)–Mo(2) 96.96(14), Ru(1)–N(1)–Mo(1) 89.86(13), Mo(2)–N(1)–Ru(1) 167.54(19), Mo(2)–C(12)–Ru(3) 85.82(16), Mo(2)–C(12)–Ru(2) 81.77(16), Ru(2)–C(12)–Ru(3) 79.92(15), Cp–Cp fold angle 138.0, Cp(centroid)–Mo(1)–Mo(2)–Cp(centroid) 13.7.

C(12) = 2.107(4) Å], and their lengths are comparable to those found for $\text{Cp}_2\text{Mo}_2\text{Ru}_4(\text{CO})_{12}(\mu_3\text{-CMe})_2$ [**22a**]. One of the eleven carbonyl groups, C(3)–O(3), bridges Mo(2)–Ru(3) bond. The others are all linear terminal carbonyl ligands except C(2)–O(2) and C(8)–O(8), which adopts a weak semi-bridging coordination to the Mo(1)–Mo(2) and Ru(2)–Ru(1) bonds, respectively [$\angle\text{Mo(1)–C(2)–C(2)}$ 166.7(4)°, $\angle\text{Ru(2)–C(8)–C(8)}$ 169.5(4)°] [**28**]. All the arrangements of carbonyl ligands are in good agreement with its IR spectrum. In the case that $\mu_4\text{-N}$ ligand is a five electron donor, **9** has a total 76 cluster valence electrons. So the cluster obeys both the Wade–Mingos rules [**29**] and the 18-electron rule.

Cluster **10** has a tetrahedral Mo_2 -nitrile [Mo(1)–Mo(2)] structure unit, namely, one molecule of **4** linked to a $\text{Mo}_2\text{Ru}_6\text{-}\mu_5$ -nitrido [Mo(3)–Mo(4)] moiety via N(1)–Ru(1) dative bond. Since the $\eta^2\text{-}\eta^2(\text{L})$ -nitrile ligand of **4** acts as a four-electron donor to the dimolybdenum centers, it can still coordinate to Ru(1) atom with its lone-pair electron in a $k\text{-N}$ fashion [**30**]. The unique geometry of $\text{Mo}_2\text{Ru}_6\text{-}\mu_5$ -nitrido moiety can be described as a distorted bicapped [Ru(3) and Ru(6)] square pyramid [μ_5 -nitrido- Mo_2Ru_3] with a “spiked” atom Ru(1) attached to the apical ruthenium atom

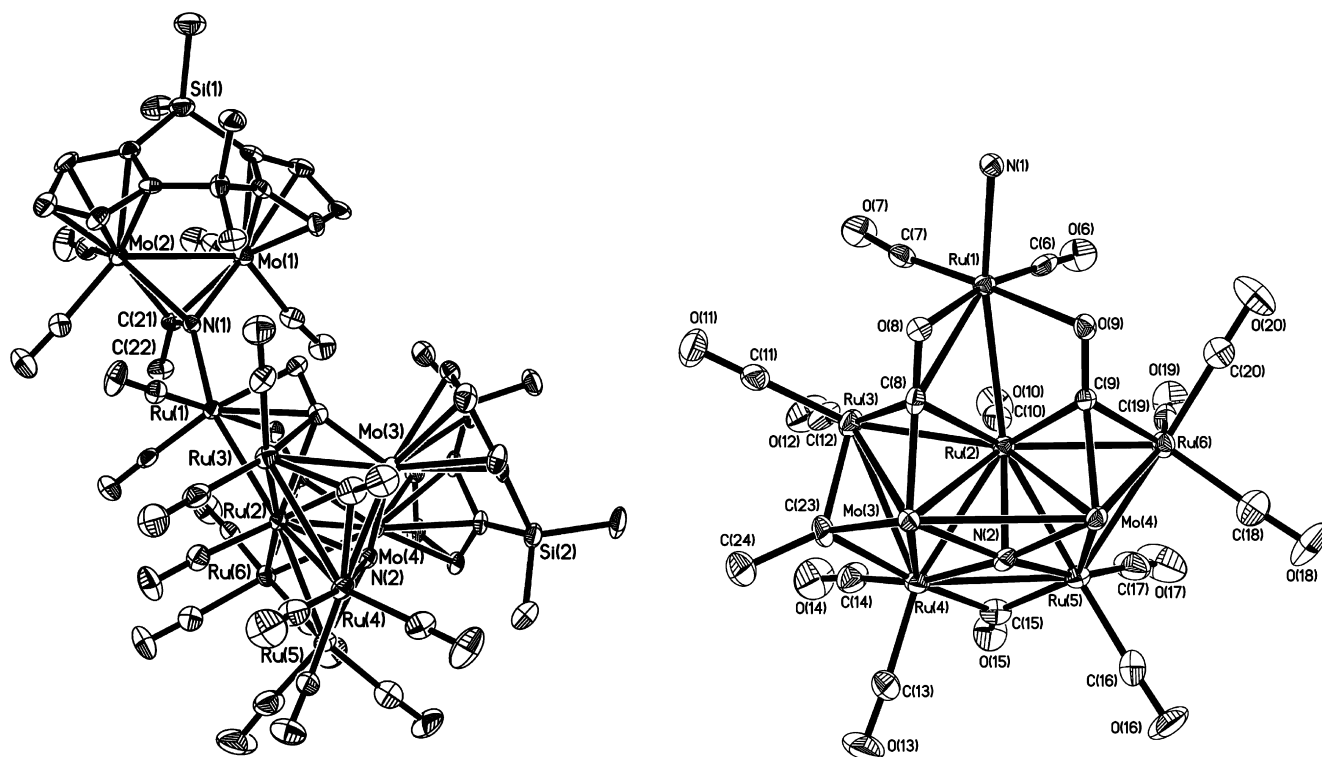


Fig. 5. Molecular structure of $[(\text{Me}_2\text{C})(\text{Me}_2\text{Si})(\eta^5\text{-C}_5\text{H}_3)_2\text{Mo}_4\text{Ru}_6(\text{CO})_{16}(\mu\text{-CO})(\mu_4\text{-CO})_2(\mu_3\text{-}\eta^1\text{-}\eta^2\text{-N}\equiv\text{CMe})(\mu_3\text{-CMe})(\mu_5\text{-N})]$ (**10**). The left drawing shows the whole molecular structure. The right drawing depicts the architecture of the $\text{Mo}_2\text{Ru}_6(\text{CO})_{13}(\mu\text{-CO})(\mu_4\text{-CO})_2(\mu_3\text{-CMe})(\text{N})(\mu_5\text{-N})$ core. Selected bond lengths [\AA] and angles [$^\circ$] are Mo(1)–Mo(2) 2.8695(11), Mo(3)–Mo(4) 3.0250(10), Ru(1)–Ru(2) 2.8214(10), Ru(2)–Ru(3) 2.6561(9), Ru(2)–Ru(4) 2.8753(10), Ru(2)–Ru(5) 2.7677(10), Ru(2)–Ru(6) 2.7683(10), Ru(2)–Mo(3) 2.7993(11), Ru(2)–Mo(4) 2.6627(10), Ru(3)–Ru(4) 3.0457(11), Ru(3)–Mo(3) 2.7988(11), Ru(4)–Ru(5) 2.8244(10), Ru(4)–Mo(3) 2.8364(12), Ru(5)–Ru(6) 2.8070(11), Ru(5)–Mo(4) 2.9305(12), Ru(6)–Mo(4) 2.7545(11), C(21)–N(1) 1.319(9), Ru(1)–N(1) 2.178(6), Ru(1)–O(8) 2.129(6), Ru(1)–C(8) 2.550(8), Ru(1)–O(9) 2.153(5), Ru(2)–C(8) 2.448(8), Ru(2)–C(9) 2.129(7), Ru(3)–C(8) 2.223(8), Ru(3)–C(23) 2.124(9), Ru(4)–C(23) 2.124(9), Ru(6)–C(9) 2.357(8), Mo(3)–C(23) 2.115(8), Mo(3)–C(8) 1.949(9), Mo(4)–C(9) 1.988(8), C(8)–O(8) 1.233(9), C(9)–O(9) 1.226(9), N(2)–Ru(2) 2.048(6), N(2)–Ru(4) 2.082(6), N(2)–Ru(5) 2.081(7), N(2)–Mo(4) 1.980(6), N(2)–Mo(3) 2.112(7), Mo(1)–N(1)–Mo(2) 83.0(2), Mo(1)–C(21)–Mo(2) 83.7(3), N(1)–C(21)–C(22) 131.1(8), C(21)–N(1)–Ru(1) 125.0(5), Ru(2)–N(2)–Ru(4) 88.2(2), Ru(2)–N(2)–Ru(5) 84.2(2), Ru(2)–N(2)–Mo(3) 84.6(2), Ru(2)–N(2)–Mo(4) 82.7(2), Ru(4)–N(2)–Mo(3) 85.1(2), Ru(5)–N(2)–Mo(4) 92.3(3), Mo(3)–N(2)–Mo(4) 95.3(3), Ru(4)–N(2)–Ru(5) 85.4(3), Cp1–Cp2 fold angle 136.7, Cp3–Cp4 fold angle 139.0, Cp(centroid)–Mo(1)–Mo(2)–Cp(centroid) 3.4, Cp(centroid)–Mo(3)–Mo(4)–Cp(centroid) 3.1.

Ru(2). The μ_5 -nitride nitrogen N(2) lies 0.1866 \AA below the basal Mo_2Ru_2 plane of the square pyramid. The ethylidyne ligand $\mu_3\text{-MeC}(23)$ caps a MoRu_2 triangular face [$\text{Mo}(3)\text{Ru}(3)\text{Ru}(4)$], which is analogous to that of **9**. The N–M bond lengths are also comparable to those of **9** and other $\mu_5\text{-N}$ complex [24d,24i,26b]. Both the Mo–Ru and Ru–Ru bond distances span a wide range, which are 2.6627(10)–2.9305(12) and 2.6561(9)–3.0457(11) \AA , respectively. Another feature of **10** is the two μ_4 -carbonyl ligands C(8)–O(8) and C(9)–O(9) [31]. The C–O bond lengths are considerably longer than the terminal C–O bonds [1.233(9) and 1.226(9) \AA vs. av. 1.136 \AA], indicating a significant reduction in CO bond order. This is also supported by its very low IR absorptions at 1491 and 1473 cm^{-1} . Besides C(15)–O(15) is a bridging carbonyl, the others are all terminal in the remaining 17 carbonyl ligands. Assuming that bridging nitrile and μ_5 -nitride ligands act as 6e and 5e donors, respectively, **10** contains 148 cluster valence electrons. Sixteen metal–metal bonds in **10** would be expected by the 18-electron rule, and this is observed.

In conclusion, reactions of the doubly bridged bis(cyclopentadienyl) dinuclear molybdenum complex $(\text{Me}_2\text{C})(\text{Me}_2\text{Si})[(\eta^5\text{-C}_5\text{H}_3)\text{Mo}(\text{CO})_3]_2$ (**1**) with nitrile mainly gave the perpendicularly coordinated nitrile complex $(\text{Me}_2\text{C})(\text{Me}_2\text{Si})[(\eta^5\text{-C}_5\text{H}_3)_2\text{Mo}_2(\text{CO})_4(\mu\text{-}\eta^2\text{-}\eta^2(\perp)\text{-N}\equiv\text{CR})]$. This is in contrast to the reaction of the non-bridged dimolybdenum complex $\text{Cp}_2\text{Mo}_2(\text{CO})_6$ with cyanamide R_2NCN , which only produced the $\mu\text{-}\eta^1\text{-}\eta^2\text{-C}\equiv\text{N}$ adduct. This indicated that the rigidity of the doubly bridged bis(cyclopentadienyl) ligand might be in favor of the crosswise $\mu\text{-}\eta^2\text{-}\eta^2(\perp)\text{-C}\equiv\text{N}$ coordination. Two MoRu clusters containing a μ_4 and a $\mu_5\text{-N}$ ligand, respectively, were obtained via the $\text{C}\equiv\text{N}$ bond cleavage of acetonitrile by cooperation of the dimolybdenum complex and $\text{Ru}_3(\text{CO})_{12}$.

4. Supplementary material

CCDC 636559, 636560, 636561, 636562 and 660007 contain the supplementary crystallographic data for **2**, **4**, **9**, **10**, and **6**. These data can be obtained free of charge from The

Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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