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Dimetallic Imido Complexes of Molybdenum and Tungsten with Bridged Bis(η^5-cyclopentadienyl) Ligands. Molecular Structure of [(MoO)$_2$(μ-N^{t}Bu)$_2${μ-(η^5-C$_5$H$_4$)$_2$SiMe$_2$}]

Francisco Amor, Pilar Gómez-Sal, Ernesto de Jesús, Avelino Martín,
Ana I. Pérez, Pascual Royo,* and Amelio Vázquez de Miguel

Departamento de Química Inorgánica, Universidad de Alcalá de Henares,
Campus Universitario, 28871 Alcalá de Henares, Madrid, Spain

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New imido and oxo dimetallic complexes of Mo and W with the monobridged or dibridged bis(cyclopentadienyl) ligands Cp^{1}Cp or Cp^{2}Cp [Cp^{1}Cp = (η^5-C$_5$H$_4$)$_2$SiMe$_2$, Cp^{2}Cp = (η^5-C$_5$H$_3$)$_2$(SiMe$_2$)$_2$] have been synthesized. The Cp^{2}Cp complexes have been obtained as both *cis* and *trans* isomers which differ in the stereodisposition of the two metal fragments with respect to the Cp^{2}Cp system, the stereochemistry being unchanged in all the reactions described. Addition of H$_2$N^{t}Bu to [(MCl$_4$)$_2$(μ-Cp^{n}Cp)] (M = Mo, $n = 1$, **2a**; $n = 2$, **2b**; M = W, $n = 2$, **2c**) affords the imido M(V) complexes [{M(N^{t}Bu)Cl$_2$}$_2$(μ-Cp^{n}Cp)] (**4a**−**c**). Complexes **4a,c** are oxidized by PCl$_5$ to give [{M(N^{t}Bu)Cl$_3$}$_2$(μ-Cp^{n}Cp)] (**5a,c**). Both **4a** and **5a** afford [{MoCl(μ-N^{t}Bu)}$_2$(μ-Cp^{1}Cp)] (**6**) by reduction with sodium amalgam. The differences found between this reaction and the related reductions of the mononuclear Cp analogues are discussed. Reaction of **6** with HgO affords the oxo complex [{MoO(μ-N^{t}Bu)}$_2$(μ-Cp^{1}Cp)] (**7**). [(MoOCl)$_2$(μ-O)(μ-Cp^{2}Cp)] (**3**) is obtained by reaction of [{Mo(CO)$_3$Cl}$_2$(μ-Cp^{2}Cp)] with CH$_3$NO$_2$ or bubbling air through a THF solution of *cis*-[(MoCl$_4$)$_2$(μ-Cp^{2}Cp)]. The molecular structure of **7** has been determined by a single-crystal X-ray analysis.

Introduction

The chemistry of imido transition metal complexes continues to attract considerable attention, and a substantial number of imido cyclopentadienyl complexes of group 6 metals have been reported.[1] We reported[2−6] previously the isolation of molybdenum and tungsten complexes with the monobridged and dibridged bis(cyclopentadienyl) ligands Cp^{1}Cp and Cp^{2}Cp [Cp^{1}Cp = (η^5-C$_5$H$_4$)$_2$(SiMe$_2$), Cp^{2}Cp = (η^5-C$_5$H$_3$)$_2$(SiMe$_2$)$_2$]. Herein, we report the results of our studies on the isolation of their related dinuclear imido complexes and the significant differences found between the chemical behavior of bridged and unbridged cyclopentadienyl systems. Known Cp complexes (Cp = C$_5$H$_5$ or C$_5$H$_4$Me) related to those here reported include [CpMo(N^{t}Bu)Cl$_2$], obtained by reaction of [CpMoCl$_4$] with NH$_2$^{t}Bu,[1,7] [CpMo(N^{t}Bu)Cl$_3$], prepared by treatment of [CpMo(N^{t}Bu)$_2$Cl] with HCl[8,9] or [CpMo(N^{t}Bu)$_2$Cl] with Cl$_2$,[7] and [CpMo(N^{t}Bu)ClL], prepared by reduction of [CpMo(N^{t}Bu)Cl$_2$] in the presence of free ligands.[1,7]

Results and Discussion

Preparative Methods. Paramagnetic ($\mu_{\mathrm{eff}} \approx 2.0-2.2\ \mu_{\mathrm{B}}$) tetrahalo complexes *cis*- and *trans*-[(MCl$_4$)$_2$(μ-Cp^{2}Cp)] (M = Mo (**2b**), M = W (**2c**)) were prepared by oxidation of [{M(CO)$_3$Cl}$_2$(μ-Cp^{2}Cp)] (**1b,c**) with PCl$_5$ as chlorinating agent,[10] as we have already reported[2] for the preparation of the related monobridged Mo complex **2a** (Scheme 1). Treatment of *cis*-**1b** with CH$_3$NO$_2$ in toluene results in complete decarbonylation and formation of the oxo complex [(MoOCl)$_2$(μ-O)(μ-Cp^{2}Cp)] (**3**) after heating the mixture at 80 °C overnight. Alternatively, complex **3** can be obtained by bubbling air through a THF solution of complex *cis*-**2b** for 1 h. The d^1−d^1 complex **3** is diamagnetic, as are [(CpMoOX)$_2$(μ-O)] (Cp = η-C$_5$H$_5$, C$_5$Me, X = Cl,[11] I[12]).

Addition of 6 equiv of N^{t}BuH$_2$ to the halo complexes **2** affords the imido compounds [{M(N^{t}Bu)Cl$_2$}$_2$(μ-Cp^{n}Cp)] (**4a**−**c**), by a reaction similar to that used for the synthesis of the related C$_5$H$_5$ complexes.[7] Compounds **4a,c** could not be isolated, although the resulting brown solids can be used as starting materials for further reactions. Oxidation of complexes **4a,c** with PCl$_5$ gives the M(VI) complexes [{M(N^{t}Bu)Cl$_3$}$_2$(μ-Cp^{n}Cp)] ($n = 1$, M = Mo (**5a**); $n = 2$, M = W (**5c**)). Reaction of **4b** with

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[⊗] Abstract published in *Advance ACS Abstracts,* March 15, 1996.

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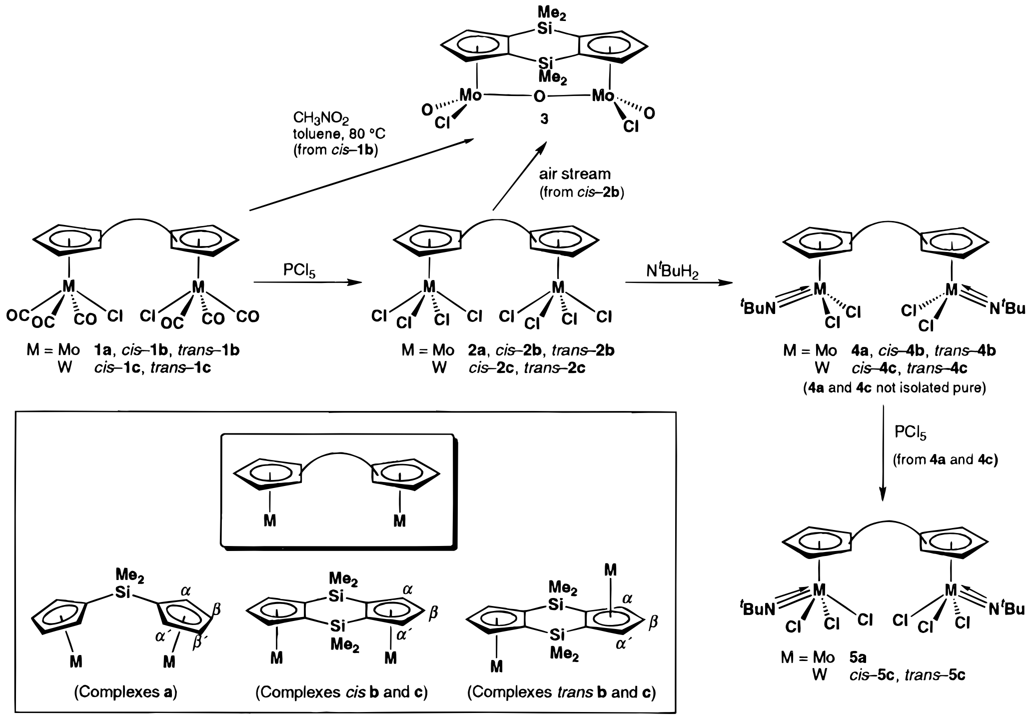
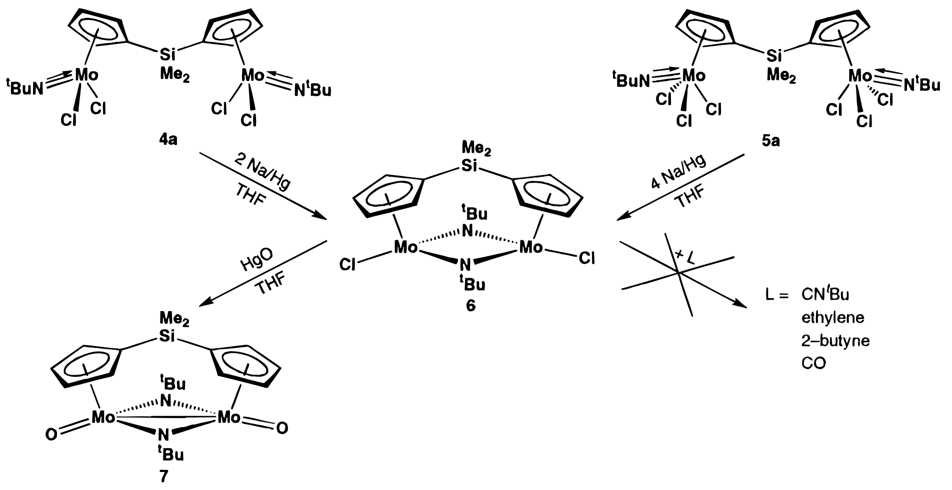
Scheme 1



Scheme 2



PCl$_5$ gives an unresolved mixture of compounds. Reduction of the Mo(V) {[Mo(N^{t}Bu)Cl$_2$}$_2$(μ-Cp^{1}Cp)] (**4a**) or the Mo(VI) [{Mo(N^{t}Bu)Cl$_3$}$_2$(μ-Cp^{1}Cp)] (**5a**) complexes with the appropriate stoichiometric amounts of sodium amalgam affords the Mo(IV) derivative [{MoCl(μ-N^{t}Bu)}$_2$(μ-Cp^{1}Cp)] (**6**) (Scheme 2) in which two imido groups are bridging both metal centers (see Structural Study). Compound **6** does not react either by addition of ligands (CN^{t}Bu, ethylene, 2-butyne, or CO) or by reduction of **4a** or **5a** in the presence of free ligands, and therefore the dimetallic complexes [{Mo(N^{t}Bu)ClL}$_2$(μ-Cp^{1}Cp)] could not be obtained, in contrast with the related Cp complexes.[1,7] This behavior indicates that the bridged Cp^{1}Cp system seems to favor the formation of the more stable chelated Mo(μ-N^{t}Bu)$_2$Mo ring in relation to the unbridged Cp systems. Unfortunately, we were not able to obtain the analogue with the dibridged Cp^{2}Cp ligand to compare the behavior of both types of bridged systems.

Reaction of **6** with HgO in THF affords the oxo complex [(MoO)$_2$(μ-N^{t}Bu)$_2$(μ-Cp^{1}Cp)] (**7**). This complex shows a *cis* disposition of the cyclopentadienyl rings along the Mo−Mo bond imposed by the Cp^{1}Cp bridge whereas a *trans* arrangement has been proposed for the related Cp complexes [{MoO(μ-NR)(η^5-C$_5$H$_4$Me)}$_2$] (R = ^{t}Bu,[13] Ph[14]). The molecular structure of **7** is discussed below.

Structural Study. Spectroscopic data for all the new complexes are given in the Experimental Section. All the diamagnetic complexes have been characterized by ^{1}H NMR, and their spectra show typical resonances for the cyclopentadienyl ring in the range 5.1−7.4 ppm and for SiMe$_2$ in the range −0.5 to 1.1 ppm. The ring protons appear as two groups of resonances corresponding to the AA′ and BB′ parts of an AA′BB′ spin system, for the monobridged Cp^{1}Cp complexes **5a**, **6**, and **7**, and corresponding to the A and BB′ parts of an ABB′ spin system, for the dibridged Cp^{2}Cp complexes **5c**. The ^{13}C-{^{1}H} NMR data confirm that the four α- and the four/

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two β-carbons and their substituents are chemically equivalent at room temperature in complexes **5**−**7**. This chemical equivalency implies the existence of two planes of symmetry (one defined by the $SiMe_2$ groups, and the other perpendicular to it and passing through the metal centers) in the structure of a rigid molecule or in the average structure of a fluxional molecule. The ^{t}Bu groups of the imido ligands appear as singlets at *ca.* 1.5 ppm for the terminal ligands and at *ca.* 1.7 ppm for the bridging ligands.

The ^{13}C CP-MAS spectrum of [{Mo(N^{t}Bu)Cl$_3$}$_2$(μ-η^5:η^5-Cp^{1}Cp)] (**5a**), slightly soluble in common organic solvents, is in agreement (see Experimental Section) with the lower symmetry expected for the supression in the solid state of some of the dynamic processes occurring in solution. The ^{1}H NMR spectrum of the oxo complex **3** shows four resonances for the $SiMe_2$ groups. The cyclopentadienyl protons appear as two groups of resonances that are centered at 6.37 and 7.18 ppm. The pattern of these resonances is more complicated than expected for an ABB′ spin system, and they are assigned to an ABC spin system in which the B and C parts, corresponding to the α and α′ protons, have a similar chemical shift. The absence of a plane of symmetry passing through the Cp centroids and Mo atoms or of a C_2 axis is confirmed by the ^{13}C{^{1}H} NMR spectrum that shows four resonances for the Me_2Si groups and five resonances for the cyclopentadienyl ring carbons. These data are in agreement with the structure proposed for **3**, characterized by a linear bridging oxygen atom, as found for other d^1−d^1 and d^0−d^0 Mo−O−Mo systems,[11,12,15] and by a *cis* disposition of the Cl and O atoms through the Mo$_2$(μ-N^{t}Bu)$_2$ plane.

Crystal Structure of 7. The molecular structure of **7** based on the X-ray structural analysis is shown in Figure 1 with the numbering scheme employed. Important bond distances and angles are listed in Table 1. Two independent molecules exist in the asymmetric unit of the unit cell of **7**. Molecule A is defined as that containing Mo(1) and Mo(2), and molecule B, as that containing Mo(3) and Mo(4). Molecule B parameters are given in brackets. The molecular parameters for A and B are very similar.

The molecular structure of **7** comprises a dinuclear system with the two Mo atoms bridged by one Cp^{1}Cp and two N^{t}Bu ligands. Each Mo atom has a "three-legged piano stool" geometry, where the legs are formed by two bridging N^{t}Bu groups and one oxygen atom. If the centroid of each Cp ring is taken as a coordination site, the angles around Mo between this point and the legs range from 113 to 126° and between legs range from 94.0 to 94.6° (N−Mo−N angles) and from 104.5 to 105.6° (O−Mo−N angles).

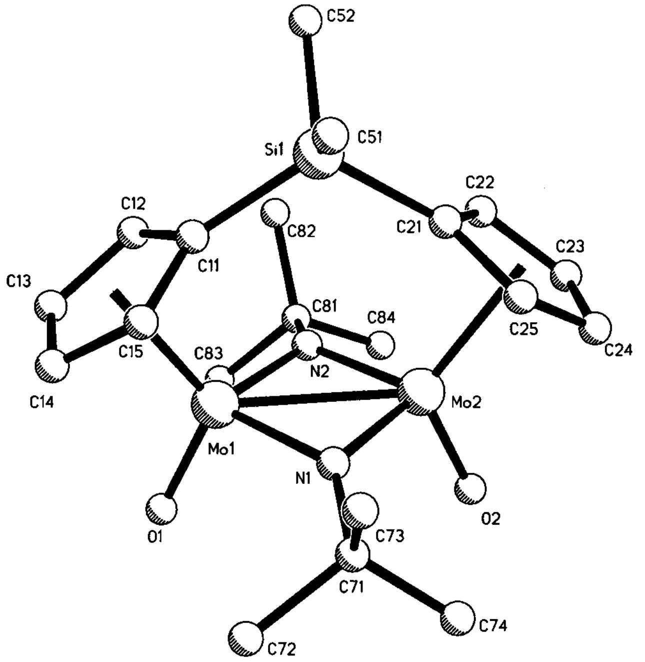

Figure 1. Perspective view of the molecular structure of [{MoO(μ-N^{t}Bu)}$_2$(μ-Cp^{1}Cp)] (**7**) with the atom-numbering scheme.

Table 1. Selected Bond Distances (Å) and Bond Angles (deg) for 7

molecule A		molecule B	
	Distances		
Mo(1)−Mo(2)	2.634(1)	Mo(3)−Mo(4)	2.630(1)
Mo(1)−O(1)	1.703(6)	Mo(3)−O(3)	1.707(7)
Mo(2)−O(2)	1.696(6)	Mo(4)−O(4)	1.707(6)
Mo(1)−N(1)	1.945(7)	Mo(3)−N(3)	1.930(7)
Mo(1)−N(2)	1.939(7)	Mo(3)−N(4)	1.941(8)
Mo(2)−N(1)	1.938(7)	Mo(4)−N(3)	1.920(7)
Mo(2)−N(2)	1.929(8)	Mo(4)−N(4)	1.957(7)
Mo(1)−cp(1)[a]	2.096	Mo(3)−cp(3)[a]	2.126
Mo(2)−cp(2)[a]	2.115	Mo(4)−cp(4)[a]	2.107
Si(1)−C(11)	1.840(9)	Si(2)−C(31)	1.864(10)
Si(1)−C(21)	1.864(10)	Si(2)−C(41)	1.850(9)
Si(1)−C(51)	1.88(2)	Si(2)−C(61)	1.81(2)
Si(1)−C(52)	1.84(2)	Si(2)−C(62)	1.89(2)
N(1)−C(71)	1.508(12)	N(3)−C(91)	1.486(12)
N(2)−C(81)	1.487(13)	N(4)−C(101)	1.458(13)
	Angles		
cp(1)[a]−Mo(1)−O(1)	119.0	cp(3)[a]−Mo(3)−O(3)	121.1
cp(1)[a]−Mo(1)−Mo(2)	125.6	cp(3)[a]−Mo(3)−Mo(4)	124.6
cp(1)[a]−Mo(1)−N(1)	114.7	cp(3)[a]−Mo(3)−N(3)	115.2
cp(1)[a]−Mo(1)−N(2)	114.7	cp(3)[a]−Mo(3)−N(4)	112.7
cp(2)[a]−Mo(2)−O(2)	120.7	cp(4)[a]−Mo(4)−O(4)	120.4
cp(2)[a]−Mo(2)−Mo(1)	125.0	cp(4)[a]−Mo(4)−Mo(3)	125.5
cp(2)[a]−Mo(2)−N(1)	114.7	cp(4)[a]−Mo(4)−N(3)	115.7
cp(2)[a]−Mo(2)−N(2)	113.7	cp(4)[a]−Mo(4)−N(4)	113.2
O(1)−Mo(1)−Mo(2)	115.4(3)	O(3)−Mo(3)−Mo(4)	114.3(3)
O(2)−Mo(2)−Mo(1)	114.3(3)	O(4)−Mo(4)−Mo(3)	113.9(3)
N(1)−Mo(1)−N(2)	94.0(3)	N(3)−Mo(3)−N(4)	94.5(3)
N(1)−Mo(2)−N(2)	94.6(3)	N(3)−Mo(4)−N(4)	94.3(3)
Mo(1)−N(1)−Mo(2)	85.4(3)	Mo(3)−N(3)−Mo(4)	86.2(3)
Mo(1)−N(2)−Mo(2)	85.8(3)	Mo(3)−N(4)−Mo(4)	84.9(3)
C(11)−Si(1)−C(21)	113.3(4)	C(31)−Si(2)−C(41)	113.2(4)
C(51)−Si(1)−C(52)	112.6(8)	C(61)−Si(2)−C(62)	112.2(8)
C(71)−N(1)−Mo(1)	138.1(6)	C(91)−N(3)−Mo(3)	133.9(6)
C(71)−N(1)−Mo(2)	135.0(6)	C(91)−N(3)−Mo(4)	137.2(6)
C(81)−N(2)−Mo(1)	135.7(7)	C(101)−N(4)−Mo(3)	135.1(6)
C(81)−N(2)−Mo(2)	135.0(6)	C(101)−N(4)−Mo(4)	134.9(6)

[a] cp(1) is the centroid of C(11)−C(15); cp(2) is the centroid of C(21)−C(25); cp(3) is the centroid of C(31)−C(35); cp(4) is the centroid of C(41)−C(45).

We have reported previously[2] that the angles θ_1 and θ_2 between the cp(1)−Si−cp(2) plane and the cp(1)−Mo(1) and cp(2)−Mo(2) axis, respectively (Chart 1; cp = centroid of the cyclopentadienyl ring) can be used to rationalize the arrangement of the metal centers in the structures of bimetallic Cp^{1}Cp complexes. In complex **1a**, where metal−metal bond and ligand bridges (other than the Cp^{1}Cp bridge) are absent, the values of the θ angles are close to 180°, moving the two metal centers apart.[2] In complexes with metal−metal bonds or ligand

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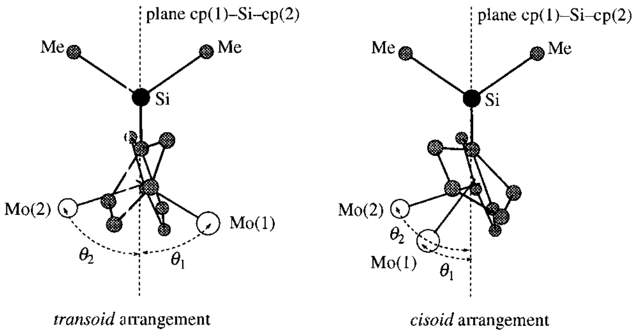
Chart 1



bridges, the θ angles are decreased to accommodate the metal–metal distance. Thus, in **7** these angles are close to 0°, being 0.8 and −1.4° [4.6 and −4.7°], as expected[2] for a Mo–Mo distance as short as 2.63 Å. The distance between metals does not completely determine the stereodisposition of the Mo(Cp^{1}Cp)Mo system because a given distance can be achieved in both a *cisoid* or *transoid* arrangement. Complex **7** shows a *cisoid* arrangement imposed by the double imido bridge, resulting in a very symmetrical structure. Thus, Si(1), Mo(1), Mo(2), C(11), and C(21) [Si(2), Mo(3), Mo(4), C(31), and C(41)] define a vertical plane that also contains the oxygen atoms, with a maximum deviation of 0.053(9) Å for O(3).

The Mo–Mo distance of 2.634(1) [2.630(1)] Å is slightly shorter than those reported for $[\{(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{Mo(NPh)}\}_2(\mu\text{-NPh})_2]$ [2.717(1) Å],[14] $[\{(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{MoO}\}_2(\mu\text{-O})(\mu\text{-NPh})]$ [2.662(1) Å],[16] $[\{(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{MoO}\}_2(\mu\text{-NPh})_2]$ [2.691(1) Å]),[16] and $[\{(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{MoO}\}_2(\mu\text{-N(C}_6\text{F}_5))_2]$ [2.686(1) Å].[17] The Mo–N(bridge) and Mo–O distances are typical for these complexes (1.92–1.94 and 1.70–1.71 Å, respectively). It has been observed that complexes of the form $[(\text{CpMoX})_2(\mu\text{-Y})_2]$ (X, Y = O and NPh) have planar $\text{Mo}_2(\mu\text{-Y})_2$ cores when the Cp ligands are *trans* and puckered $\text{Mo}_2(\mu\text{-Y})_2$ cores with the μ-Y ligands folded toward the rings when the Cp ligands are *cis*.[14,16–18] The coordination around the μ-N atoms is always planar in these complexes. In contrast, the $\text{Mo}(\mu\text{-N})_2\text{Mo}$ core is planar in the *cis* complex **7**, the maximum deviation from planarity being −0.04 Å with a dihedral angle between the two $\text{Mo}_2(\mu\text{-N})$ planes of 176.2(3)° [176.5(3)°] and with the N atoms slightly folded away from the Cp^{1}Cp system. The coordination around the μ-N atoms in **7** is slightly pyramidalized, the distances from the C(bonded to N) to the Mo_2N_2 plane being in the range 0.336(7)–0.50(1) Å. These differences between **7** and other $[(\text{CpMoX})_2(\mu\text{-Y})_2]$ systems may be due to the greater steric hindrance created by the ^{t}Bu and the bridged Cp^{1}Cp compared with the Ph and unbridged Cp that moves the N atoms and the ^{t}Bu groups away from the Cp^{1}Cp system.

Experimental Section

Reagents and General Techniques. All reactions were carried out in dried Schlenk tubes under an atmosphere of argon or nitrogen, and manipulations were carried out using syringes or cannulae through Subaseals. Solvents were dried and distilled under nitrogen: CH_2Cl_2 over P_4O_{10}; diethyl ether and tetrahydrofuran from sodium benzophenone ketyl; hexane, pentane, and toluene from sodium. Unless otherwise stated, reagents were obtained from commercial sources and used as received. IR spectra were recorded in Nujol mulls for solids or in CaF_2 cells for solutions, over the range 4000–200 cm^{-1} on a Perkin-Elmer 583 spectrophotometer. IR data are given in cm^{-1}. The ^{1}H and ^{13}C NMR spectra were recorded at 299.95 and 75.43 MHz, respectively, on a Varian Unity 300 spectrometer; chemical shifts, in ppm, are positive downfield relative to external SiMe_4; coupling constants are in Hz. C, H, and N analyses were performed with a Perkin-Elmer 240-B instrument. The chloride analyses were performed according to ref 19. ESR spectra were recorded on a Varian Unity E-12 spectrometer. Magnetic susceptibilities were measured in a Bruker B-E15 magnetic balance. Mass spectra were recorded in a Hewlett-Packard 5988A spectrometer.

Starting Materials. Complexes **1b**,[3] **1c**,[6] and **2a**[2] were prepared according to reported methods.

Preparation of *cis*-$[(\text{MoCl}_4)_2\{\mu\text{-}(\eta^5\text{-C}_5\text{H}_3)_2(\text{SiMe}_2)_2\}]$ (*cis*-2b). *cis*-**1b** (1.88 g, 2.79 mmol) and PCl_5 (2.33 g, 11.2 mmol) were suspended in toluene (50 mL) and stirred overnight at 80 °C. The mixture was filtered and the residue washed with cold CH_2Cl_2. Complex *cis*-**2b** was obtained as a purple solid (1.80 g, 90%). Anal. Calcd for $\text{C}_{14}\text{H}_{18}\text{Si}_2\text{Cl}_8\text{Mo}_2$: C, 23.4; H, 2.5. Found: C, 24.0; H, 3.0. ESR (THF): $g = 1.92$.

Preparation of *trans*-2b. This complex was obtained as a purple solid (1.93 g, 85%) from *trans*-**1b** (2.14 g, 3.18 mmol) and PCl_5 (3.0 g, 14.4 mmol) in toluene (60 mL) by the procedure described for *cis*-**2b**. Anal. Calcd for $\text{C}_{14}\text{H}_{18}\text{Si}_2\text{Cl}_8\text{Mo}_2$: C, 23.4; H, 2.5. Found: C, 23.0; H, 2.5. ESR (THF): $g = 1.92$.

Preparation of *cis*-$[(\text{WCl}_4)_2\{\mu\text{-}(\eta^5\text{-C}_5\text{H}_3)_2(\text{SiMe}_2)_2\}]$ (*cis*-2c). This complex was obtained as a brown solid (1.23 g, 73%) from *cis*-**1c** (1.60 g, 1.88 mmol) and PCl_5 (1.57 g, 7.54 mmol) in CH_2Cl_2 (70 mL) by the procedure described for *cis*-**2b**. Anal. Calcd for $\text{C}_{14}\text{H}_{18}\text{Si}_2\text{Cl}_8\text{W}_2$: C, 18.8; H, 2.0. Found: C, 18.8; H, 2.1. ESR (THF): $g = 1.92$.

Preparation of *trans*-2c. The complex was obtained as a brown solid (0.24 g, 42%) from *trans*-**1c** (0.54 g, 0.64 mmol) and PCl_5 (0.53 g, 2.5 mmol) in CH_2Cl_2 (50 mL) by the procedure described for *cis*-**2b**. Anal. Calcd for $\text{C}_{14}\text{H}_{18}\text{Si}_2\text{Cl}_8\text{W}_2$: C, 18.8; H, 2.0. Found: C, 19.2; H, 2.0. ESR (THF): $g = 1.92$.

Preparation of $[(\text{MoOCl})_2(\mu\text{-O})\{\mu\text{-}(\eta^5\text{-C}_5\text{H}_3)_2(\text{SiMe}_2)_2\}]$ (3). From *cis*-1b. A mixture of *cis*-**1b** (0.59 g, 0.88 mmol) and CH_3NO_2 (0.10 mL, 1.8 mmol) was heated overnight in toluene (50 mL) at 80 °C. The solution changed from red to purple. After filtration, the solvent was completely removed *in vacuo* and the residue dissolved in CH_2Cl_2 (5 mL). Complex **3** (0.28 g, 58%) was precipitated with pentane (50 mL) as a purple solid.

From *cis*-2b. An air stream was bubbled through a solution of *cis*-**2b** (0.40 g, 0.56 mmol) in THF (100 mL) for 1 h. After evaporation, the residue was dissolved in CH_2Cl_2 (25 mL) and dried over Na_2SO_4. The solvent was partially evaporated (up to *ca.* 15 mL), and complex **3** (0.15 g, 48%) was precipitated by addition of pentane (50 mL). Anal. Calcd for $\text{C}_{14}\text{H}_{18}\text{O}_3\text{Si}_2\text{Cl}_2\text{Mo}_2$: C, 30.4; H, 3.3; Cl, 12.8. Found: C, 30.8; H, 3.7, Cl, 12.0. MS: m/e 556 (M$^+$). IR (Nujol): ν(Mo=O) 937 s; ν(Mo–O–Mo) 786 s. ^{1}H NMR (CDCl_3): δ 7.18, 6.37 (A and BC parts of an ABC spin system, 6 H, C_5H_3), 0.75 (s, 3 H, SiMe_2), 0.64 (s, 3 H, SiMe_2), 0.44 (s, 3 H, SiMe_2), 0.42 (s, 3 H, SiMe_2). ^{13}C{^{1}H} NMR (CDCl_3): δ 130.8 (s, $C_5\text{H}_3$ β, from ^{13}C NMR: ^1J(CH) = 180), 124.8 (s, $C_5\text{H}_3$ *ipso*), 122.1 (s, $C_5\text{H}_3$ α, from ^{13}C NMR: ^1J(CH) = 178), 117.0 (s, $C_5\text{H}_3$ *ipso*), 105.7 (s, $C_5\text{H}_3$ α), 1.0 (s, SiMe_2), −3.4 (s, SiMe_2), −4.5 (s, SiMe_2), −5.4 (s, SiMe_2).

Preparation of *cis*-$[\{\text{Mo(N}^t\text{Bu)Cl}_2\}_2\{\mu\text{-}(\eta^5\text{-C}_5\text{H}_3)_2(\text{SiMe}_2)_2\}]$ (*cis*-4b). N^tBuH_2 (0.44 mL, 4.17 mmol) was added over a suspension of *cis*-**2b** (0.50 g, 0.69 mmol) in toluene (50 mL). The solution changed from purple to yellow-brown. The mixture was stirred for 7 h and then was filtered. The solvent

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was completely removed *in vacuo*. The brown solid obtained was extracted into toluene (30 mL), and the solvent was completely removed *in vacuo* to give a brown solid (0.38 g, 76%). Anal. Calcd for $C_{22}H_{36}N_2Si_2Cl_4Mo_2$: C, 36.8; N, 3.9; H, 5.0. Found: C, 37.2; N, 3.8; H, 4.9. ESR (toluene): $g = 1.98$.

Preparation of *trans*-4b. This complex was obtained as a brown solid (0.16 g, 70%) from *trans*-**2b** (0.23 g, 0.32 mmol) and N^{t}BuH$_2$ (0.20 mL, 1.92 mmol) by the procedure described for the *cis* isomer. Anal. Calcd for $C_{22}H_{36}N_2Si_2Cl_4Mo_2$: C, 36.8; N, 3.9; H, 5.0. Found: C, 36.9; N, 3.9; H, 5.2 ESR (toluene): $g = 1.98$.

Preparation of [{Mo(N^{t}Bu)Cl$_3$}$_2${*μ*-(*η*^{5}-C$_5$H$_4$)$_2$SiMe$_2$}] (5a). Solid PCl$_5$ (1.20 g, 5.77 mmol) was added to a solution of **4a** (2.50 g, 3.77 mmol) in toluene (40 mL). The mixture was stirred for 14 h at room temperature. The yellow precipitate was isolated by filtration, washed with CH$_2$Cl$_2$/pentane (1:3), and dried *in vacuo* (2.53 g, 92%). Anal. Calcd for $C_{20}H_{32}N_2SiCl_6Mo_2$: C, 32.8; H, 4.4; N, 3.8. Found: C, 32.9; H, 4.35; N, 3.4. ^{1}H NMR (acetone-*d*$_6$): *δ* 7.40, 6.86 (AA′ and BB′ parts of an AA′BB′ spin system, 4 H, C$_5$*H*$_4$), 1.54 (s, 9 H, N^t*Bu*), 0.81 (s, 3 H, Si*Me*$_2$). ^{13}C CP-MAS: *δ* 153.6 (s, *C*$_5$H$_4$), 149.2 (s, *C*$_5$H$_4$), 141.7 (s, *C*$_5$H$_4$), 128.7 (s, *C*$_5$H$_4$), 117.7 (s, *C*$_5$H$_4$), 106.3 (s, *C*$_5$H$_4$), 102.8 (s, *C*$_5$H$_4$), 85.7 (s, N*C*Me$_3$), 28.8 (S, NC*Me*$_3$), 26.1 (s, NC*Me*$_3$), −2.7 (s, Si*Me*$_2$), −4.1 (s, Si*Me*$_2$).

Preparation of *cis*-[{W(N^{t}Bu)Cl$_3$}$_2${*μ*-(*η*^{5}-C$_5$H$_3$)$_2$(SiMe$_2$)$_2$}] (*cis*-5c). N^{t}BuH$_2$ (0.30 mL, 2.3 mmol) was added to a suspension of *cis*-**2c** (0.42 g, 0.47 mmol) in toluene (50 mL), and the mixture was stirred for 7 h. Then, PCl$_5$ (0.20 g, 0.94 mmol) was added and stirring was continued overnight. After filtration, the precipitate was extracted with CH$_2$Cl$_2$ (2 × 25 mL), and solvent was completely removed from the yellow solution *in vacuo*. The solid was recrystallized by dissolution in CH$_2$Cl$_2$ (20 mL) and precipitation with hexane (75 mL) at −40 °C to afford *cis*-**5c** (0.26 g, 57%) as a yellow solid. Anal. Calcd for $C_{22}H_{36}N_2Si_2Cl_6W_2$: C, 27.4; N, 2.9; H, 3.8. Found: C, 27.6; N, 3.0; H, 3.9. ^{1}H NMR (CD$_2$Cl$_2$): *δ* 7.05, 6.54 (A and BB′ parts of an ABB′ spin systems, 3 H, C$_5$*H*$_3$), 1.46 (s, 9 H, N^t*Bu*), 1.08 (s, 3 H, Si*Me*$_2$), 0.78 (s, 3 H, Si*Me*$_2$). ^{13}C{^{1}H} NMR (CDCl$_3$): *δ* 145.4 (s, *C*$_5$H$_3$ *β*), 121.8 (s, *C*$_5$H$_3$ α), 108.1 (s, *C*$_5$H$_3$ *ipso*), 77.2 (s, N*C*Me$_3$), 28.7 (s, NC*Me*$_3$), −0.45 (s, Si*Me*$_2$), −1.81 (s, Si*Me*$_2$).

Preparation of *trans*-5c. This complex was obtained (0.14 g, 54%) as *cis*-**5c** from N^{t}BuH$_2$ (0.17 mL, 1.61 mmol), *trans*-**2c** (0.24 g, 0.27 mmol), and PCl$_5$ (0.11 g, 0.54 mmol) by the procedure described for *cis*-**5c**. Anal. Calcd for $C_{22}H_{36}N_2Si_2Cl_6W_2$: C, 27.4; N, 2.9; H, 3.8. Found: C, 27.6; N, 2.9; H, 3.9. ^{1}H NMR (CD$_2$Cl$_2$): *δ* 6.69, 6.64 (A and BB′ parts of an ABB′ spin system, 3 H, C$_5$*H*$_3$), 1.45 (s, 9 H, N^t*Bu*), 0.81 (s, 6 H, Si*Me*$_2$). ^{13}C{^{1}H} NMR (CDCl$_3$): *δ* 141.2 (s, *C*$_5$H$_3$ *ipso*), 121.5 (s, *C*$_5$H$_3$ α) 107.9 (s, *C*$_5$H$_3$ *β*), 77.4 (s, N*C*Me$_3$), 28.7 (s, NC*Me*$_3$), −0.2 (s, Si*Me*$_2$).

Preparation of [{MoCl(*μ*-N^{t}Bu)}$_2${*μ*-(*η*^{5}-C$_5$H$_4$)$_2$SiMe$_2$}] (6). A solution of **5a** (0.31 g, 0.42 mmol) in THF (50 mL) was added to a Na amalgam (0.039 g, 1.7 mmol). The solution became green. The mixture was stirred for 1 day and then filtered; solvent was removed *in vacuo*. The oil obtained was extracted into toluene/pentane (80 mL, 1:3) and the solvent removed *in vacuo*. Complex **6** was obtained as a green solid (0.20 g, 80%). Anal. Calcd for $C_{20}H_{32}N_2Cl_2SiMo_2$: C, 40.6; H, 5.5; N, 4.7. Found: C, 40.9; H, 5.5; N, 4.4. ^{1}H NMR (C$_6$D$_6$): *δ* 6.55, 5.11 (AA′ and BB′ parts of an AA′BB′ spin system, 4 H, C$_5$*H*$_4$), 1.69 (s, 9 H, N^t*Bu*), −0.51 (s, 3 H, Si*Me*$_2$). ^{13}C{^{1}H} NMR (C$_6$D$_6$): *δ* 107.5 (s, *C*$_5$H$_4$), 107.4 (s, *C*$_5$H$_4$), 106.8 (s, *C*$_5$H$_4$), 77.0 (s, N*C*Me$_3$), 32.2 (s, NC*Me*$_3$), −3.4 (s, Si*Me*$_2$).

Preparation of [{MoO(*μ*-N^{t}Bu)}$_2${*μ*-(*η*^{5}-C$_5$H$_4$)$_2$SiMe$_2$}](*Mo*−*Mo*) (7). HgO (0.37 g, 1.7 mmol) was added to a solution of **5** (0.40 g, 0.68 mmol) in THF (50 mL). The green solution slowly became orange, and a white-gray precipitate appeared. The mixture was stirred for 1 day and then filtered, and the solvent was removed *in vacuo*. The orange solid was Soxhlet extracted with pentane. Complex **7** was obtained as a yellow microcrystalline solid (0.22 g, 59%). Anal. Calcd for $C_{20}H_{32}N_2O_2SiMo_2$: C, 43.5; H, 5.8; N, 5.1. Found: C, 43.3; H, 5.7; N, 5.0. IR (Nujol): *ν*(Mo═O) 876 s. ^{1}H NMR (C$_6$D$_6$): *δ* 6.50, 5.96 (AA′ and BB′ parts of an AA′BB′ spin system, 4 H, C$_5$*H*$_4$), 1.73 (s, 9 H, N^t*Bu*), −0.22 (s, 3 H, Si*Me*$_2$). ^{13}C{^{1}H} NMR (CDCl$_3$): *δ* 114.1 (s, *C*$_5$H$_4$), 108.2 (s, *C*$_5$H$_4$), 93.8 (s, *C*$_5$H$_4$), 67.8 (s, N*C*Me$_3$), 32.8 (s, NC*Me*$_3$), −3.2 (s, Si*Me*$_2$).

Table 2. Crystallographic Data for 7

formula	$C_{20}H_{32}Mo_2N_2O_2Si$
cryst habit	prismatic
color	yellow
symmetry	monoclinic, *Pn*
unit cell determn	least-squares fit from 25 reflcns
unit cell dimens	
$a-c$, Å	14.989(3), 9.885(2), 15.524(3)
β, deg	94.72(3)
packing	
V, Å^3; Z	2292(1); 4
D_{calcd}, g cm^{-3}	1.601
M_r	552.4
$F(000)$	1120
μ, cm^{-1}	11.63
technique	four-circle diffractometer; bisecting geometry, graphite-oriented monochromator; Mo Kα $\omega-\theta$ scans; θ, 2−25°
no. of rflns	
measd	4295
indep obsd	4219
range of *hkl*	*h*, 0 to 17; *k*, 0 to 11; *l*, −18 to +18
std rflns	2 reflcns every 120 min; no variation
$R_1 = \sum(\lvert F_o\rvert - \lvert F_c\rvert)/\sum\lvert F_o\rvert$	0.038
$wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$	0.104
goodness of fit indicator on F^2	0.966
max peak in final diff map, e/Å^3	0.803
min peak in final diff map, e/Å^3	−0.781

Crystal Structure of 7. A suitable sized orange crystal of **7** was obtained by crystallization from CH$_2$Cl$_2$/hexane. The crystal was mounted in a ENRAF-NONIUS CAD-4 automatic four-circle diffractometer. Crystallographic and experimental details are summarized in Table 2. Data were collected at room temperature. Intensities were corrected for Lorentz and polarization effects in the usual manner. No absorption or extinction corrections were made. The structure was solved by a combination of heavy atom and direct methods and Fourier synthesis.[20] The structure was refined on *F* by full-matrix least-squares calculations. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were introduced from geometrical calculations and refined with fixed thermal parameters ($U = 0.08$ Å^2) using a riding model. Full-matrix least-squares refinement[21] on F^2 for all data and 385 parameters converged to $wR_2 = 0.104$ (all data), conventional $R = 0.038$ (observed data), and GOF = 0.994. The function minimized was $\sum w(F_o^2 - F_c^2)^2$, $w = 1/[\sigma^2(F_o^2) + (0.0786P)^2 + 4.7828P]$, where $P = (F_o^2 + 2F_c^2)/3$ and σ was obtained from counting statistics. Anomalous dispersion corrections and atomic scattering factors were taken from ref 22.

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Supporting Information Available: For **7**, tables of positional parameters and *U* values for non-hydrogen atoms, positional parameters and *U* values for hydrogen atoms, and anisotropic displacement parameters (3 pages). Ordering information is given on any current masthead page.

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