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Low-Oxidation-State Molybdenum and Tungsten Complexes with Bis(η^5-cyclopentadienyl) Bridges

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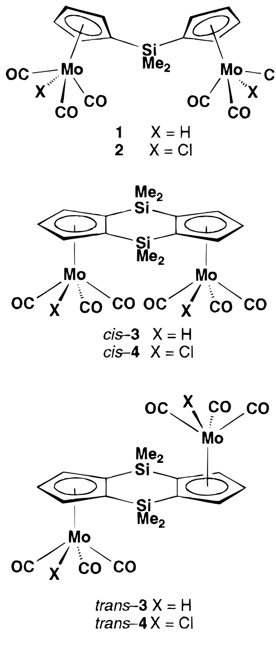
The paper describes the preparation of new dinuclear Mo and W complexes bridged by Cp^{1}Cp[Cp^{1}Cp = $(C_5H_4)_2(SiMe_2)$] or Cp^{2}Cp [Cp^{2}Cp = $(C_5H_3)_2(SiMe_2)_2$] ligands. [{W(CO)$_3$H}$_2$(μ-η^5:η^5-Cp^{2}Cp)] (**5**) or K$_2$[{W(CO)$_3$}$_2$(μ-η^5:η^5-Cp^{2}Cp)] (**6**) are obtained by reaction of [W(CO)$_3$(NCMe)$_3$] with HCp^{2}CpH or K$_2$(Cp^{2}Cp), respectively, as a *cis*−*trans* mixture of isomers which differ in the stereodisposition of the two metals with respect to the Cp^{2}Cp system. *cis*- and *trans*-**5** have been separated and reacted with CCl$_4$ to give [{W(CO)$_3$Cl}$_2$(μ-η^5:η^5-Cp^{2}Cp)] (*cis*- or *trans*-**7**). Reaction of [{Mo(CO)$_3$X}$_2$(μ-η^5:η^5-Cp^{n}Cp)] ($n = 1$, X = H (**1**), Cl (**3**); $n = 2$, X = H (**2**), Cl (**4**)) with CN^{t}Bu gives [{Mo(CO)$_2$(CN^{t}Bu)X}$_2$(μ-η^5:η^5-Cp^{n}Cp)] (**8**−**11**). Reaction of **9** with KH gives K$_2$[{Mo(CO)$_2$(CN^{t}Bu)}$_2$(μ-η^5:η^5-Cp^{2}Cp)] (**12**). The *cis* isomers of the chloro derivatives **4**, **7**, or **11** are reduced to the dinuclear metal−metal-bonded complexes [{M(CO)$_2$L}$_2$(μ-η^5:η^5-Cp^{2}Cp)](*M*−*M*) (L = CO, M = Mo (**13**), W (**15**), L = CN^{t}Bu, M = Mo (**16**)) by reaction with MeMgCl, whereas the *trans* isomer of **4** affords the polymer [{Mo(CO)$_3$}$_2$(μ-η^5:η^5-Cp^{2}Cp)]$_n$(*Mo*−*Mo*) (**17**). *cis*-**2** reacts with H$_2$O$_2$ to give a mixture of **13** and [{Mo(CO)$_3$}$_2${μ-η^5:η^5-(C$_5$H$_3$(SiMe$_2$OH)SiMe$_2$C$_5$H$_4$)}](*Mo*−*Mo*) (**14**).

Introduction

Recently, we reported the synthesis of the dinuclear hydrido- and chlorotricarbonylmolybdenum complexes **1**−**4** (Chart 1) and some of their derivatives.[1−3] The metals of these dinuclear complexes are linked by the bis(cyclopentadienyl) monobridged Cp^{1}Cp [Cp^{1}Cp = $(C_5H_4)_2(SiMe_2)$] or dibridged Cp^{2}Cp [Cp^{2}Cp = $(C_5H_3)_2(SiMe_2)_2$] ligands. The dibridged complexes **3** and **4** can be obtained selectively either as *cis* or as *trans* isomers, depending on the synthetic route employed. The work presented here focuses on two aspects of the chemistry of these complexes: (a) an extension of the preparative methods to the related tungsten compounds and (b) a comparison of their chemical behavior with the chemistry of related low-oxidation-state mononuclear derivatives.

Chart 1



Results and Discussion

Preparative Methods. Reaction of [W(CO)$_3$(NCMe)$_3$] with HCp^{2}CpH [HCp^{2}CpH = $(C_5H_4)_2(SiMe_2)_2$] in THF resulted in the substitution of the three acetonitrile ligands by a single cyclopentadienyl group, a *ca.* 2:1 mixture of *cis*- and *trans*-[{W(CO)$_3$H}$_2$(μ-η^5:η^5-Cp^{2}Cp)] (**5**) (Scheme 1). Reactions of this type have been extensively used in the synthesis or group 6 metal cyclopentadienyl complexes[4] and proceed by cyclopentadiene C−H activation with transfer of H to the metal center. The *cis* and *trans* isomers were readily separated by treatment of the mixture with hexane. *trans*-**5** was isolated from the solution after filtration, and the hexane-insoluble residual solid was characterized as *cis*-**5**. Reaction of [W(CO)$_3$(NCMe)$_3$] with K$_2$[Cp^{2}Cp] affords K$_2$[{W(CO)$_3$}$_2$(μ-η^5:η^5-Cp^{2}Cp)] (**6**) as a mixture of *cis* and *trans* isomers, together with various byproducts (Scheme 1). Although pure complex **6** has not been isolated, the proposed formulation is supported by the formation of

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(1) Gómez-Sal, P.; de Jesús, E.; Pérez, A. I.; Royo, P. *Organometallics* **1993**, *12*, 4633−4639.

(2) Amor, F.; Gómez-Sal, P.; de Jesús, E.; Royo, P.; de Miguel, A. V. *Organometallics* **1994**, *13*, 4322−4327.

(3) Amor, F.; de Jesús, E.; Royo, P.; de Miguel, A. V. *Inorg. Chem.* **1995**, *34*, in press.

(4) See for example: (a) Brunner, H.; Grassl, R.; Wachter, J.; Nuber, B.; Ziegler, M. L. *J. Organomet. Chem.* **1992**, *431*, 143−150. (b) Bitterwolf, T. E.; Rheingold, A. L. *Organometallics* **1991**, *10*, 3856−3860. (c) Abriel, W.; Heck, J. *J. Organomet. Chem.* **1986**, *302*, 363−370. (d) Heck, J.; Kriebisch, K.-A.; Mellinghoff, H. *Chem. Ber.* **1988**, *121*, 1753−1757.

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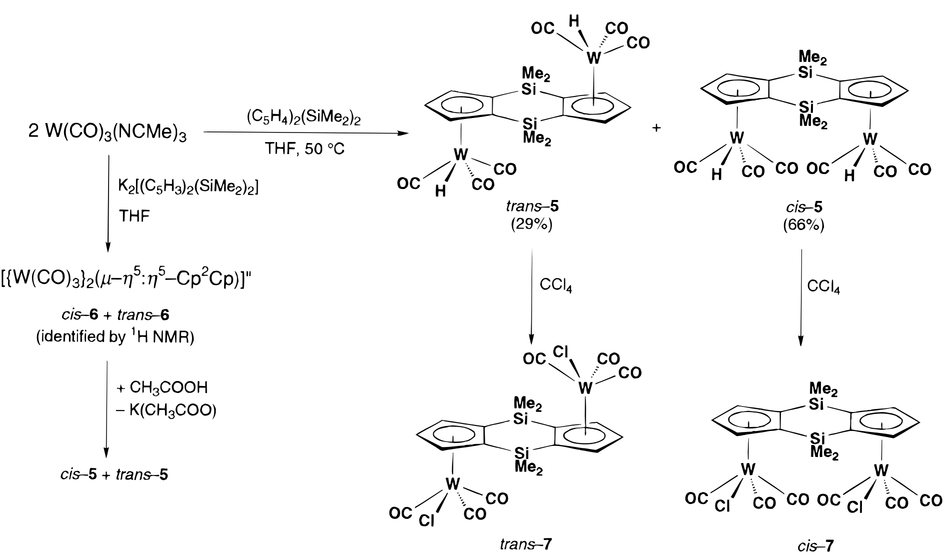
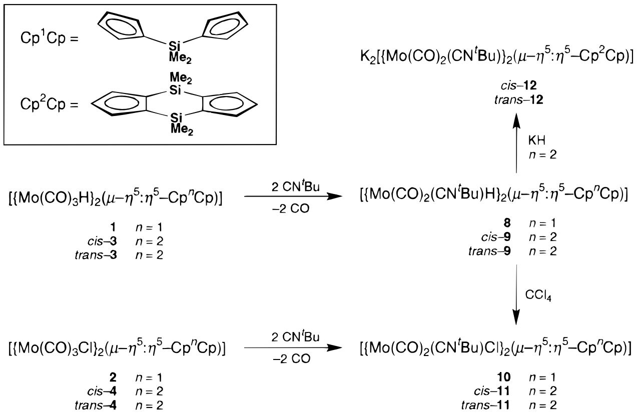
Scheme 1



Scheme 2



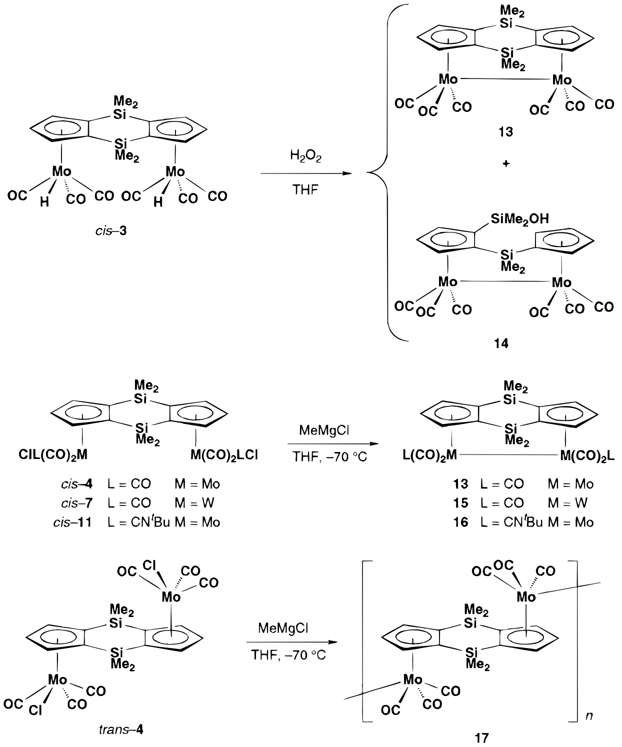
the hydride **5** (*cis* and *trans*) after addition of acetic acid to the crude mixture containing **6**.

These results differ from those reported[2] for the molybdenum derivatives in the following two ways. First, for molybdenum, the lability of the arene ligand in [Mo(CO)$_3$(1,3,5-C$_6$H$_3$Me$_3$)] makes this complex a better starting material than [Mo(CO)$_3$(NCMe)$_3$] whereas [W(CO)$_3$(1,3,5-C$_6$H$_3$Me$_3$)] does not react with HCp^{2}CpH. Second, the reaction of [Mo(CO)$_3$(1,3,5-C$_6$H$_3$Me$_3$)] with either HCp^{2}CpH or K$_2$[Cp^{2}Cp] is selective and affords the *cis* isomer of **3** with the former and the *trans* isomer of K$_2$[{Mo(CO)$_3$}$_2$(μ-η^5:η^5-Cp^{2}Cp)] with the latter; in contrast the tungsten complex always gives mixtures of *cis* and *trans* isomers.

Metathetical replacement of hydride by chloride is readily achieved when hydride **5** (*cis* or *trans*) is stirred in CCl$_4$, giving *cis*- or *trans*-[{W(CO)$_3$Cl}$_2$(μ-η^5:η^5-Cp^2-Cp)] (**7**).

One CO ligand in each of the hydrides **1** and **3** (Scheme 2) is readily replaced by isocyanide giving [{Mo(CO)$_2$(CN^{t}Bu)H}$_2$(μ-η^5:η^5-Cp^{n}Cp)] ($n = 1$ (**8**) or $n = 2$ (**9**)). A similar substitution takes place when chloride complexes **2** or **4** are reacted with isocyanide, affording [{Mo(CO)$_2$(CN^{t}Bu)Cl}$_2$(μ-η^5:η^5-Cp^{n}Cp)] ($n = 1$ (**10**) or $n = 2$ (**11**)). The chlorides **10** and **11** are also obtained via the reaction of hydrides **8** and **9** with CCl$_4$ (Scheme 2). Deprotonation of **9** (*cis* or *trans*) with KH in THF gives K$_2$[{Mo(CO)$_2$(CN^{t}Bu)}$_2$(μ-η^5:η^5-Cp^{2}Cp)] (**12**).

Scheme 3



We reported[1] that an aqueous solution of H$_2$O$_2$ reacts with [{Mo(CO)$_3$H}$_2$(μ-η^5:η^5-Cp^{1}Cp)] (**1**) affording the metal−metal-bonded complex [{Mo(CO)$_3$}$_2$(μ-η^5:η^5-Cp^1-Cp)](*Mo*—*Mo*). Although O$_2$ was employed as an oxidizing agent in the preparation of [Mo(CO)$_3$Cp] from [Mo(CO)$_3$H],[5] H$_2$O$_2$ was found to be a more efficient oxidizing agent in this case. However, the reaction of *cis*-**3** with H$_2$O$_2$ gives a mixture of products, the expected complex [{Mo(CO)$_3$}$_2$(μ-η^5:η^5-Cp^{2}Cp)](*Mo*—*Mo*) (**13**) and complex **14** (Scheme 3). The formation of the latter complex can be rationalized as the result of the hydrolysis of one of the bridges of the ring system by H$_2$O from the H$_2$O$_2$ solution. This observation supports the reported[3,4d] thermal and hydrolytic fragility of silicon-bridged bis(cyclopentadienyl) systems, which seems to be heightened in Cp^{2}Cp complexes in compari-

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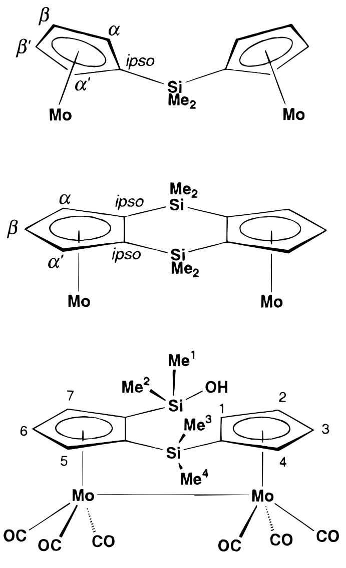
[5] King, R. B.; Stone, F. G. A. *Inorg. Synth.* **1963**, *7*, 99−115. Davis, R.; Kane-Maguire, L. A. P. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, U.K., 1982; Vol. 3, p 1184.

Chart 2



14

son with Cp^{1}Cp systems. A more effective route to **13** is via the reaction of the chloride *cis*-**4** with alkylating agents such as MeMgCl or MeLi. Since the methyl derivatives are stable, a mechanism involving the formation of Me−Mo bonds with the reductive elimination of ethane can be disregarded in the formation of **13**. An alternative route is the transmetalation to form MeCl and coupling of the Mg or Li species with the adjacent chloride. Similar behavior is observed for *cis*-**7** and *cis*-**11** which react with MeMgCl to give [{M(CO)$_2$L}$_2$(μ-η^5:η^5-Cp^{2}Cp)](*M*−*M*) (M = W, L = CO (**15**), M = Mo, L = CN^{t}Bu (**16**)), whereas *trans*-**4** reacts with MeMgCl, giving complex **17**, which is insoluble in all common organic solvents, consistent with its polymeric structure.

Structural Study. Spectroscopic data for all the new complexes are given in the Experimental Section. The ν(CO) frequencies are in the ranges 2051−1882 cm^{-1} for neutral and 1890−1710 cm^{-1} for anionic complexes, as expected for terminal carbonyls. All of the isocyanide complexes show a single ν(CN) absorption in the range 2158−2112 for neutral complexes and 1872−1870 cm^{-1} for anionic complexes. All of the new complexes have been characterized by ^{1}H NMR, and their spectra show typical resonances in the range 6.5−4.2 ppm for the cyclopentadienyl ring and in the range 0.9−0.0 ppm for SiMe$_2$. The ring protons of the dibridged Cp^{2}Cp complexes appear as two groups of resonances assigned to the protons α and β (Chart 2) and corresponding to the A and BB′ parts, respectively, of an ABB′ spin system. Their ^{1}H and ^{13}C NMR spectra show one resonance for the SiMe$_2$ groups of the *trans* isomers and two resonances for the SiMe$_2$ groups of the *cis* isomers.[3,6] The ring protons of the monobridged Cp^{1}Cp complexes comprise two groups of resonances of an AA′BB′ spin system, and their SiMe$_2$ groups appear as a singlet. The spectrum of the complex **14** comprises four resonances for methyl groups and seven resonances for the cyclopentadienyl ring protons, as expected for molecules of low symmetry where each cyclopentadienyl ring is in a different environment. Selective irradiation of the ring proton resonances enabled the assignment shown in Chart 2 (see Experimental Section).

The ^{1}H NMR spectra of the hydride complexes show high-field hydride singlets between −5.2 and −7.3 ppm with W satellites resolved for **5**. The chemical shift difference between the hydride resonances of *cis*-**5** and *trans*-**5** (Table 1) is large, 0.74 ppm, and is similar to that of the related Mo complex **2**, 0.67 ppm. These displacements are larger than would be expected from the chemical differences between *cis* and *trans* complexes and may be influenced by the magnetic anisotropy of the cyclopentadienyl rings, since the effect of this anisotropy on δ is dependent on molecular geometry. This argument is supported by the δ values measured for Mo and W cyclopentadienyl hydride complexes; selected data are shown in Table 1, where the difference in δ between *cis* and *trans* isomers is significantly larger than the difference between *trans* isomers and other mononuclear and dinuclear complexes.

The ^{13}C NMR spectrum of hydride **5** recorded at room temperature shows a single broad resonance at 215.6 (*cis*) or 216.9 (*trans*) ppm for the carbonyl carbons. When the temperature is lowered to −50 °C this singlet is resolved into two resonances, one for the CO *trans* to H and the other for the two CO moieties *trans* to each other (224.3 and 214.1 ppm, for *cis*-**5**, or 224.4 and 214.1 ppm, for *trans*-**5**). In contrast, chloro complexes **7** show two resonances even at room temperature. This difference in behavior may be related to the low-energy barriers to hydride motion between piano-stool legs.[8] Complexes **8**−**11** can exist as a variety of isomers, differing on the relative disposition of the CO, CN^{t}Bu, and H or Cl ligands around each metal. The NMR spectra of **8** and **9** show the presence of only one isomer even at −85 °C in toluene-d_8, suggesting either a rapid interconversion of isomers by hydride motion or, more probably, the existence of only one isomer with the H *trans* to the CN^{t}Bu ligand. In contrast, the ^{1}H NMR spectra of chloro complexes **10** and **11** recorded at room temperature show several isomers interconverting slowly in the NMR time scale.

The ^{13}C NMR spectra of the metal−metal-bonded complexes [{M(CO)$_3$}$_2$(μ-η^5:η^5-Cp^{2}Cp)] (**14** or **16**) recorded at room temperature comprised a single resonance for the three CO carbons whereas three resonances appeared in the spectra of the monobridged derivatives [{M(CO)$_3$}$_2$(μ-η^5:η^5-Cp^{1}Cp)].[4b−d] The link between the Cp ligands in these monobridged complexes determines two conformations *gauche* and *syn* (Chart 3), the *gauche* being preferred for steric reasons.[4b−d] The three resonances shown in the spectrum of [{M(CO)$_3$}$_2$(μ-η^5:η^5-Cp^{1}Cp)] indicate that in this conformation the three CO groups are inequivalent. At higher temperatures (360 K for W), coalescence of the signals due to the two CO moities *cis* to the M−M bond is observed. This is a consequence of a rapid equilibrium *gauche* $\rightleftharpoons$ *syn* $\rightleftharpoons$ *gauche* which averages both CO *cis* groups. In **14** and **16**, the rigidity of the dibridged ligand imposes a mainly *syn* conformation with two equivalent *cis* CO groups. The equivalence between the CO groups *cis* and *trans* to the M−M bond observed in **14** and **16**, but not

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(6) Siemeling, U.; Jutzi, P.; Neumann, B.; Stammler, H.-G.; Hursthouse, M. B. *Organometallics* **1992**, *11*, 1328−1333.

(7) (a) Piper, T. S.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1956**, *3*, 104−124. (b) Drage, J. S.; Vollhardt, K. P. C. *Organometallics* **1986**, *5*, 280−297. (c) Tilset, M.; Vollhardt, K. P. C.; Boese, R. *Organometallics* **1994**, *13*, 3146−3169.

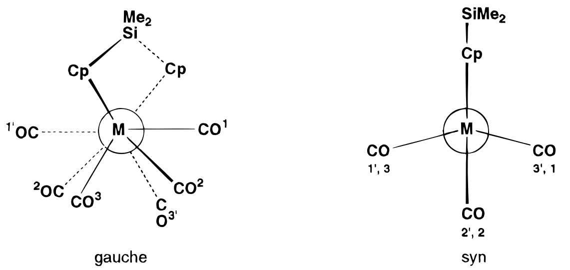
(8) Pince, R.; Poilblanc, R.; Roussel, A. S. *J. Organomet. Chem.* **1970**, *24*, 445.

Table 1. ^{1}H NMR Chemical Shifts in ppm for the Hydride Resonance in [CpM(CO)$_3$H] Complexes in C_6D_6

complex	M = Mo	M = W
$[M(CO)_3H(\eta^5\text{-}C_5H_5)]$	−5.70 (ref 7a)[a]	−7.33
$[\{M(CO)_3H\}_2(\mu\text{-}\eta^5{:}\eta^5\text{-}C_{10}H_8)]$	−5.43 (ref 7b)[b]	−6.98 (ref 7c)[a]
$[\{M(CO)_3H\}_2\{\mu\text{-}\eta^5{:}\eta^5\text{-}(C_5H_4)_2SiMe_2\}]$	−5.63 (**1**)	−7.43 (ref 4d)
cis-$[\{M(CO)_3H\}_2\{\mu\text{-}\eta^5{:}\eta^5\text{-}(C_5H_4)_2SiMe_2\}]$	−4.95 (*cis*-**2**)	−6.53 (*cis*-**5**)
trans-$[\{M(CO)_3H\}_2\{\mu\text{-}\eta^5{:}\eta^5\text{-}(C_5H_4)_2SiMe_2\}]$	−5.61 (*trans*-**2**)	−7.27 (*trans*-**5**)

[a] In toluene-d_8. [b] In THF-d_8.

Chart 3



gauche syn

in the related monobridged complexes, suggests a rapid scrambling of carbonyl groups through the M−M bond. This is not unexpected because interaction of the CO groups in the *cis* isomer with the appropriate orbitals of the neighboring metal atom is easier in a *syn* than in a *gauche* conformation.

Complex **17** is obtained as a mixture of two isomers in *ca.* 4:1 ratio. ^{1}H and ^{13}C NMR data (i.e. the AA′BB′ system for the ring protons) show that the main isomer has a plane of symmetry that comprises the two Mo and the Si atoms, requiring the isonitrile ligands to be *trans* to the M−M bond. Some of the resonances of the minor isomer are masked by those of the main isomer. The assignment made in the Experimental Section is only tentative, and consequently, we can not draw a definitive structure for it.

Experimental Section

Reagents and General Techniques. All reactions were carried out in dried Schlenk tubes under argon or nitrogen, and the manipulations were carried out using either 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; CCl_4 over $CaCl_2$. 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, in 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. Mass spectra were recorded in a Hewlett-Packard 5988A spectrometer.

Syntheses. Complexes **1** and **2**,[1] **3** and **4**,[2] $[W(CO)_3(NCMe)_3]$,[9] and $(C_5H_4)_2(SiMe_2)_2$[10] were prepared by known procedures.

Preparation of *cis*- and *trans*-$[\{W(CO)_3H\}_2\{\mu\text{-}\eta^5{:}\eta^5\text{-}(C_5H_3)_2(SiMe_2)_2\}]$ (*cis*- and *trans*-5). A solution of $(C_5H_4)_2(SiMe_2)_2$ (0.33 g, 1.35 mmol) and $[W(CO)_3(NCMe)_3]$ (1.06 g, 2.71 mmol) in THF (50 mL) was stirred for 4 h at 50 °C. After solvent evaporation, the residue was washed with *ca.* 4 × 50 mL of hexane and dried *in vacuo* affording *cis*-**5** (0.70 g, 66%) as a white solid. The hexane solution was concentrated to *ca.* 25 mL, and *trans*-**5** crystallized overnight at −40 °C as a yellow solid (0.31 g, 29%). Data for *cis*-**5** are as follows. Anal. Calcd for $C_{20}H_{20}O_6Si_2W_2$: C, 30.8; H, 2.6. Found: C, 30.4; H, 2.5. IR (THF): ν(CO) 2019 s, 1924 vs. ^{1}H NMR (C_6D_6): δ 4.93, 4.71 (A and BB′ parts of an ABB′ spin system, 3 H, C_5H_3), 0.51 (s, 3 H, $SiMe_2$), 0.01 (s, 3 H, $SiMe_2$), −6.53 (s with W satellites, 1 H, W−*H*, ^1J(WH) = 36). $^{13}C\{^1H\}$ NMR ($CDCl_3$, −50 °C): δ 224.3 (s, *C*O *trans* to H), 214.1 (s, *C*O *cis* to H), 101.3 (s, C_5H_3 β), 96.9 (s, C_5H_3 *ipso*), 95.2 (s, C_5H_3 α), 3.8 (s, $SiMe_2$), 3.2 (s, $SiMe_2$). Data *trans*-**5** are as follows. Anal. Calcd for $C_{20}H_{20}O_6Si_2SW_2$: C, 30.8; H, 2.6. Found: C, 31.0; H, 2.6. IR (THF): ν(CO) 2019 s, 1924 vs. ^{1}H NMR (C_6D_6): δ 4.97, 4.90 (A and BB′ parts of an ABB′ spin system, 3 H, C_5H_3), 0.27 (s, 6 H, $SiMe_2$), −7.27 (s with W satellites, 1 H, W−*H*, ^1J(WH) = 37). $^{13}C\{^1H\}$ NMR ($CDCl_3$, −50 °C): δ 224.4 (s, *C*O *trans* to H), 214.1 (s, *C*O *cis* to H), 100.8 (s, C_5H_3 *ipso*), 97.5 (s, C_5H_3 α), 97.1 (s, C_5H_3 β), 3.1 (s, $SiMe_2$).

Reaction of $W(CO)_3(NCMe)_3$ with $K_2[(C_5H_3)_2(SiMe_2)_2]$. A mixture of $K_2[(C_5H_3)_2(SiMe_2)_2]$ (0.52 g, 1.62 mmol) and $[W(CO)_3(NCMe)_3]$ (1.26 g, 3.24 mmol) was stirred for 7 h in THF (50 mL). After filtration, the precipitate gave the spectroscopic data assigned below to *cis*-**6**. This solid was not analytically pure, but its formulation could be supported by its reaction with acetic acid to give *cis*-**5** (^{1}H NMR evidence). The reaction of the THF solution with excess acetic acid give *trans*-**5**. Spectroscopic data for *cis*-**6**: IR (THF) ν(CO) 1890 s, 1784 vs, 1747 vs; ^{1}H NMR (acetone-d_6) δ 5.18 (m, 3 H, C_5H_3), 0.56 (s, 3 H, $SiMe_2$), 0.23 (s, 3 H, $SiMe_2$).

Preparation of *cis*-$[\{W(CO)_3Cl\}_2\{\mu\text{-}\eta^5{:}\eta^5\text{-}(C_5H_3)_2(SiMe_2)_2\}]$ (*cis*-7). A solution of *cis*-**5** (1.52 g, 1.95 mmol) in CCl_4 (*ca.* 50 mL) was stirred overnight at 50 °C. After filtration, the orange solid (1.60 g, 97%) was dried *in vacuo*. Anal. Calcd for $C_{20}H_{18}O_6Si_2Cl_2W_2$: C, 28.3; H, 2.1. Found: C, 27.9; H, 2.1. IR (THF): ν(CO) 2043 s, 1950 vs ^{1}H NMR (CD_2Cl_2): δ 6.44, 5.53 (A and BB′ parts of an ABB′ spin system, 3 H, C_5H_3), 0.81 (s, 3 H, $SiMe_2$), 0.46 (s, 3 H, $SiMe_2$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 231.9 (s, *C*O *trans* to Cl), 215.8 (s, *C*O *cis* to Cl), 109.5 (s, C_5H_3 β), 102.2 (s, C_5H_3 *ipso*), 99.0 (s, C_5H_3 α), 4.4 (s, $SiMe_2$), −0.1 (s, $SiMe_2$).

Preparation of *trans*-7. This complex was obtained as an orange solid (0.25 g, 70%) from *trans*-**5** (0.33 g, 0.42 mmol) by the same procedure described for *cis*-**7**. Anal. Calcd for $C_{20}H_{18}O_6Si_2Cl_2W_2$: C, 28.3; H, 2.1. Found: C, 28.5; H, 2.1. IR (THF): ν(CO) 2042 s, 1956 vs. ^{1}H NMR ($CDCl_3$): δ 6.54, 5.63 (A and BB′ parts of an ABB′ spin system, 3 H, C_5H_3), 0.55 (s, 6 H, $SiMe_2$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 231.9 (s, *C*O *trans* to Cl), 214.7 (s, *C*O *cis* to Cl), 107.6 (s, C_5H_3 α), 102.2 (s, C_5H_3 β), 100.0 (s, C_5H_3 *ipso*), 1.6 (s, $SiMe_2$).

Preparation of $[\{Mo(CO)_2(CN^tBu)H\}_2\{\mu\text{-}\eta^5{:}\eta^5\text{-}(C_5H_4)_2(SiMe_2)\}]$ (8). CN^tBu (0.19 mL, 1.7 mmol) was added at room temperature to a solution of **1** (0.83 mmol) in pentane (30 mL). The solution was stirred for 2 h, concentrated up to *ca.* 5 mL, and stored at −40 °C overnight. An orange oil separated and was characterized by IR and ^{1}H and ^{13}C NMR as **8**. IR (pentane): ν(CN) 2112 s; ν(CO) 1956 s, 1895 vs. ^{1}H NMR ($CDCl_3$): δ 5.30, 5.17 (AA′ and BB′ parts of an AA′BB′ spin system, 4 H, C_5H_4), 1.46 (s, 9 H, CN^tBu), 0.39 (s, 3 H, $SiMe_2$), −5.75 (s, 1 H, Mo−*H*). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 231.8 (s, *C*O), 172.0 (s, *C*N^{t}Bu), 95.8 (s, C_5H_4), 94.3 (s, C_5H_4), 91.8 (s, C_5H_4), 58.0 (s, $CNCMe_3$), 30.4 (s, $CNCMe_3$), 0.4 (s, $SiMe_2$).

Preparation of *cis*-$[\{Mo(CO)_2(CN^tBu)H\}_2\{\mu\text{-}\eta^5{:}\eta^5\text{-}(C_5H_3)_2(SiMe_2)_2\}]$ (*cis*-9). This complex was obtained as a white solid

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(0.66 g, 72%) from CN^{t}Bu (0.30 mL, 2.61 mmol) and *cis*-**2** (0.78 g, 1.30 mmol) by the procedure described for **8**. Anal. Calcd for $C_{28}H_{38}N_2O_4Si_2Mo_2$: C, 47.1; N, 3.9; H, 5.4. Found: C, 47.1; N, 4.0; H, 5.6. IR (THF): ν(CN) 2119 s; ν(CO) 1944 s, 1882 s. ^{1}H NMR (C_6D_6): δ 5.27, 5.22 (A and BB′ parts of an ABB′ spin system, 3 H, C_5H_3), 0.94 (s, 9 H, CN^{t}Bu), 0.91 (s, 3 H, $SiMe_2$), 0.56 (s, 3 H, $SiMe_2$), −5.20 (s, 1 H, Mo−*H*). ^{13}C{^{1}H} NMR (C_6D_6): δ 221.1 (s, *C*O), 155.9 (s, *C*NC^{t}Bu), 99.0 (s, C_5H_3 *ipso*), 97.5 (s, C_5H_3 α), 95.2 (s, C_5H_3 β), 56.4 (s, CN*C*Me$_3$), 30.4 (s, CNC*Me*$_3$), 4.4 (s, $SiMe_2$), 3.7 (s, $SiMe_2$).

Preparation of *trans*-9. A solution of *trans*-**2** (0.49 g, 0.82 mmol) and CN^{t}Bu (0.18 mL, 1.64 mmol) in THF (50 mL) was stirred for 2 h and then evaporated *in vacuo* to dryness. A white solid was obtained (0.30 g, 52%) after washing with hexane (10 mL). Anal. Calcd for $C_{28}H_{38}N_2O_4Si_2Mo_2$: C, 47.1; N, 3.9; H, 5.4. Found: C, 47.1; N, 4.0; H, 5.5. IR (THF): ν(CN) 2121 s; ν(CO) 1949 s, 1884 s. ^{1}H NMR (C_6D_6): δ 5.27, 5.22 (A and BB′ parts of an ABB′ spin system, 3 H, C_5H_3), 0.91 (s, 9 H, CN^t*Bu*), 0.56 (s, 6 H, $SiMe_2$), −5.21 (s, 1 H, Mo−*H*). ^{13}C{^{1}H} NMR (C_6D_6): δ 231.5 (s, *C*O), 172.5 (s, *C*N^{t}Bu), 100.4 (s, C_5H_3 *ipso*), 97.5 (s, C_5H_3 α), 95.7 (s, C_5H_3 β), 57.8 (s, CN*C*Me$_3$), 30.3 (s, CNC*Me*$_3$), 4.4 (s, $SiMe_2$).

Preparation of [{Mo(CO)$_2$(CN^{t}Bu)Cl}$_2${μ-η^5:η^5-(C_5H_4)$_2$(SiMe$_2$)}] (10). Method 1. The oil obtained in the preparation of **8** and CCl_4 (10 mL) was stirred for 1 h. The orange solid obtained after solvent evaporation was washed with diethyl ether/hexane (1:3) and dried *in vacuo* (0.40 g, 78%).

Method 2. A mixture of **3** (0.50 g, 0.81 mmol) and CN^{t}Bu (0.18 mL, 1.62 mmol) in THF (30 mL) was stirred overnight. The orange solid obtained after solvent evaporation was washed with diethyl ether/hexane (1:3) and dried *in vacuo* (0.46 g, 92%). **10** is a mixture of isomers differing on the relative disposition of CO, CN^{t}Bu, and Cl. Anal. Calcd for $C_{18}H_{14}O_6SiCl_2Mo_2$: C, 43.4; H, 4.4; N, 3,3. Found: C, 43.1; H, 4.4; N, 3.4. IR (CCl_4): ν(CN) 2153 s; ν(CO) 1982 s, 1915 vs ^{1}H NMR ($CDCl_3$): δ 5.7−5.0 (4 H, C_5H_4), 1.57, 1.51 (9 H, CN^t*Bu*), 0.57−0.46 (3 H, $SiMe_2$).

Preparation of *cis*-[{Mo(CO)$_2$(CN^{t}Bu)Cl}$_2${μ-η^5:η^5-(C_5H_3)$_2$(SiMe$_2$)$_2$}] (*cis*-11). This complex was obtained as a red solid (0.43 g, 88%) starting from CN^{t}Bu (0.14 mL, 1.24 mmol) and *cis*-**4** (0.42 g, 0.62 mmol), as described for **10**. *cis*-**11** is a mixture of isomers differing on the relative disposition of CO, CN^{t}Bu, and Cl. Anal. Calcd for $C_{28}H_{36}N_2O_4Si_2Cl_2Mo_2$: C, 42.9; N, 3.6; H, 4.6. Found: C, 42.6; N, 3.6; H, 4.8. IR (THF): ν(CN) 2157 s; ν(CO) 1971 s, 1900 s. ^{1}H NMR ($CDCl_3$): δ 6.0−5.0 (3 H, C_5H_3), 1.54 (9 H, CN^t*Bu*), 0.84−0.33 (6 H, $SiMe_2$).

Preparation of *trans*-11. This complex was obtained as an orange-red solid (0.68 g, 88%; 0.28 g, 59%) starting from CN^{t}Bu (0.22 mL, 1.96 mmol) and *trans*-**4** (0.66 g, 0.98 mmol) or from *trans*-**9** (0.43 g, 0.60 mmol) as described for **10**. *trans*-**11** is a mixture of isomers differing on the relative disposition of CO, CN^{t}Bu, and Cl. Anal. Calcd for $C_{28}H_{36}N_2O_4Si_2Cl_2Mo_2$: C, 42.9; N, 3.6; H, 4.6. Found: C, 42.9; N, 3.2; H, 4.7. IR (THF): ν(CN) 2158 s; ν(CO) 1974 s, 1906 s. ^{1}H NMR ($CDCl_3$): δ 6.1−4.9 (3 H, C_5H_3), 1.53 (9 H, CN^t*Bu*), 0.56−0.35 (6 H, $SiMe_2$).

Preparation of *cis*-K$_2$[{Mo(CO)$_2$(CN^{t}Bu)}$_2${μ-η^5:η^5-(C_5H_3)$_2$(SiMe$_2$)$_2$}] (*cis*-12). A solution of *cis*-**9** (0.93 g, 1.3 mmol) in THF (50 mL) was added to KH (0.10 g, 2.6 mmol) and stirred overnight. After filtration, the solvent was evaporated and the residue was washed with hexane (3 × 25 mL) to afford *cis*-**12** (0.92 g, 89%) as a yellow solid. Anal. Calcd for $C_{28}H_{36}N_2O_4K_2Si_2Mo_2$: C, 42.5; N, 3.5; H, 4.6. Found: C, 43.0; N, 3.8; H, 4.9. IR (THF): ν(CN) 1872 s; ν(CO) 1762 s, 1710 s.

Preparation of *trans*-12. This complex was obtained as a yellow solid (0.32 g, 97%) from *trans*-**9** (0.30 g, 0.42 mmol) and KH (0.06 g, 1.5 mmol) in THF (50 mL) by the same procedure described for *cis*-**12**. Anal. Calcd for $C_{28}H_{36}N_2O_4K_2Si_2Mo_2$: C, 42.5; N, 3.5; H, 4.6. Found: C, 42.6; N, 3.3; H, 5.1. IR (THF): ν(CN) 1870 s; ν(CO) 1762 s, 1706 s.

Preparation of [{Mo(CO)$_3$}$_2${μ-η^5:η^5-(C_5H_3)$_2$(SiMe$_2$)$_2$}](*Mo*−*Mo*) (13). A 3.0 M solution of MeMgCl (0.15 mL, 0.45 mmol) in toluene was added dropwise to a solution of *cis*-**4** (0.15 g, 0.22 mmol) in toluene (70 mL). The solution was stirred for 2 h and then evaporated to dryness, and the residue was extracted with hexane (2 × 50 mL). Evaporation of the solvent afforded complex **13** as a red solid (0.06 g, 45%). Anal. Calcd for $C_{20}H_{18}O_6Si_2Mo_2$: C, 39.9; H, 3.0. Found: C, 39.8; H, 3.0. IR (THF): ν(CO) 2012 s, 1957 vs, 1927 br. ^{1}H NMR (C_6D_6): δ 4.84, 4.61 (A and BB′ parts of an ABB′ spin system, 3 H, C_5H_3), 0.24 (s, 3 H, $SiMe_2$), 0.10 (s, 3 H, $SiMe_2$). ^{13}C{^{1}H} NMR (C_6D_6): δ 229.5 (s, *C*O), 106.0 (s, C_5H_3 *ipso*), 96.0 (s, C_5H_3 α), 93.6 (s, C_5H_3 β), 5.6 (s, $SiMe_2$), −2.6 (s, $SiMe_2$).

Preparation of [{W(CO)$_3$}$_2${μ-η^5:η^5-(C_5H_3)$_2$(SiMe$_2$)$_2$}](*W*−*W*) (15). This complex was obtained as a red solid (0.20 g, 56%) from 3.0 M MeMgCl (0.31 mL, 0.93 mmol) and *cis*-**7** (0.39 g, 0.46 mmol) by the same procedure described for **13**. Anal. Calcd for $C_{20}H_{18}O_6Si_2W_2$: C, 30.9; H, 2.3. Found: C, 31.2; H, 2.1. IR (Nujol): ν(CO) 2010 s, 1954 vs, 1919 br. ^{1}H NMR (C_6D_6): δ 4.72, 4.69 (A and BB′ parts of an ABB′ spin system, 3 H, C_5H_3), 0.28 (s, 3 H, $SiMe_2$), 0.10 (s, 3 H, $SiMe_2$). ^{13}C{^{1}H} NMR (C_6D_6): δ 216.2 (s, *C*O), 104.8 (s, C_5H_3 *ipso*), 95.1 (s, C_5H_3 α), 91.5 (s, C_5H_3 β), 6.8 (s, $SiMe_2$), −2.4 (s, $SiMe_2$).

Reaction of *cis*-2 with H_2O_2. A 9.8 M solution of H_2O_2 in water (0.17 mL, 1.74 mmol) was added to a solution of *cis*-**2** (1.05 g, 1.74 mmol) in THF (50 mL). The mixture was stirred for 10 min, and then Na_2SO_4 was added. After filtration, the solution was evaporated *in vacuo* to dryness. Using chromatography over a 20 × 1 cm column of Silica gel (70−230 mesh, 60 Å), two fractions were separated: the CH_2Cl_2/hexane (1:4) fraction contained **13** (0.52 g, 50%), and evaporation of the CH_2Cl_2 fraction afforded **14** as a red solid (0.32 g, 30%). Data for **14** are as follows. Anal. Calcd for $C_{20}H_{20}O_7Si_2Mo_2$: C, 38.7; H, 3.2. Found: C, 38.2; H, 3.2. MS: *m*/*e* 620 (M^+). IR (THF): ν(CO) 2010 s, 1956 vs, 1912 br. ^{1}H NMR (C_6D_6): δ 6.00 (1 H, cp H^4), 5.61 (1 H, cp H^5), 5.04 (1 H, cp H^6), 4.90 (1 H, cp H^3), 4.81 (1 H, cp H^7), 4.76 (1 H, cp H^2), 4.22 (1 H, cp H^1), 0.33 (s, 3 H, $SiMe_2$), 0.16 (s, 3 H, $SiMe_2$), 0.10 (s, 3 H, $SiMe_2$), 0.02 (s, 3 H, $SiMe_2$).

Preparation of [{Mo(CO)$_2$(CN^{t}Bu)}$_2${μ-η^5:η^5-(C_5H_3)$_2$(SiMe$_2$)$_2$}](*Mo*−*Mo*) (16). This complex was obtained as a green solid (0.27 g, 59%) from 3.0 M MeMgCl (0.43 mL, 1.29 mmol) and *cis*-**11** (0.50 g, 0.64 mmol) by the same procedure described for **13**. **16** was obtained as a *ca.* 1:4 mixture of two isomers differing on the relative disposition of the CN^{t}Bu ligands. Anal. Calcd for $C_{28}H_{36}N_2O_4Si_2Mo_2$: C, 47.2; N, 3.9; H, 5.1. Found: C, 47.1; N, 3.8; H, 5.1. IR (THF): ν(CN) 2108 s; ν(CO) 1945 s, 1884 s. ^{1}H NMR (C_6D_6): δ (main isomer) 5.21, 5.18 (A and BB′ parts of an ABB′ spin system, 3 H, C_5H_3), 1.06 (s, 9 H, CN^t*Bu*), 0.62 (s, 3 H, $SiMe_2$), 0.40 (s, 3 H, $SiMe_2$); δ (second isomer) 5.28, 5.18 (A and BB′ parts of an ABB′ spin system, 3 H, C_5H_3), 1.16 (s, 9 H, CN^t*Bu*), 0.66 (s, 3 H, $SiMe_2$), 0.40 (s, 3 H, $SiMe_2$). ^{13}C{^{1}H} NMR (C_6D_6): δ (main isomer) 232.3 (s, *C*O), 182.8 (s, *C*N^{t}Bu), 104.3 (s, C_5H_3 β), 94.9 (s, C_5H_3 α), 94.2 (s, C_5H_3 *ipso*), 58.4 (s, CN*C*Me$_3$), 30.7 (s, CNC*Me*$_3$), 6.5 (s, $SiMe_2$), −1.9 (s, $SiMe_2$); δ (minor isomer) 231.7 (s, *C*O), 182.8 (s, *C*NC^{t}Bu), 104.3 (s, C_5H_3 β), 93.4 (s, C_5H_3 α), 92.1 (s, C_5H_3 *ipso*), 57.6 (s, CN*C*Me$_3$), 30.6 (s, CNC*Me*$_3$), 6.3 (s, $SiMe_2$), −1.7 (s, $SiMe_2$).

Preparation of [{Mo(CO)$_3$}$_2${μ-η^5:η^5-(C_5H_3)$_2$(SiMe$_2$)$_2$}]$_n$(*Mo*−*Mo*) (17). A 3.0 M solution of MeMgCl (0.30 mL, 0.90 mmol) was added to a solution of *trans*-**4** (0.30 g, 0.45 mmol) in THF (70 mL) at −78 °C. The mixture was allowed to warm up with stirring overnight. The solution was filtered, and the red solid obtained (0.12 g, 44%) was washed several times with THF. Anal. Calcd for $C_{20}H_{18}O_6Si_2Mo_2$: C, 39.9; H, 3.0. Found: C, 39.7; H, 3.1. IR (Nujol): ν(CO) 2051 s, 2015 vs, 1940 br.

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