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Bimetallic Complexes Containing the Bis(tetramethylcyclopentadienyl)ethane Ligand

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Heterobimetallic complexes containing the η^5,η^5-$\mathrm{Me_4C_5CH_2CH_2C_5Me_4}$ ligand ($\mathrm{Cp^2}$) can be prepared in which one ring is bound to tungsten and the other is bound to rhodium or cobalt. $[\mathrm{WCl_4}](\mathrm{Cp^2})[\mathrm{RhCl_2}]$ was prepared by treating the tungstacyclobutadiene complex $\mathrm{W(C_3Me_3)Cl_3}$ (**1**) with 1.5 equiv of $\mathrm{RhCl_2}(\eta^5\text{-}\mathrm{Me_4C_5CH_2CH_2C{\equiv}CMe})$ followed by addition of 1 equiv of $\mathrm{PCl_5}$. Addition of $[\mathrm{W(PMe_3)Cl_4}](\mathrm{Cp^2})[\mathrm{Rh(PMe_3)Cl_2}]$ to excess $\mathrm{LiAlH_4}$ followed by treatment with methanol yields $[\mathrm{W(PMe_3)H_5}](\mathrm{Cp^2})[\mathrm{Rh(PMe_3)H_2}]$, which upon reaction with CO at 1000 psi yields $[\mathrm{W(PMe_3)H_5}](\mathrm{Cp^2})[\mathrm{Rh(CO)(PMe_3)}]$ (**6**). Addition of 1 equiv of MeI to **6** yields $[\mathrm{W(PMe_3)H_5}](\mathrm{Cp^2})[\mathrm{Rh(COMe)I(PMe_3)}]$. Treatment of **6** with 1 equiv of $\mathrm{MeOSO_2CF_3}$ yields $[\mathrm{W(PMe_3)H_5}](\mathrm{Cp^2})\{[\mathrm{RhMe(CO)(PMe_3)}][\mathrm{OTf}]\}$, while treatment with excess MeOTf yields $[\mathrm{WH_3(OTf)_2(PMe_3)}](\mathrm{Cp^2})\{[\mathrm{RhMe(CO)(PMe_3)}][\mathrm{OTf}]\}$ (**8**). Treatment of **8** with 1 equiv of NaI yields $[\mathrm{WH_3(OTf)_2(PMe_3)}](\mathrm{Cp^2})[\mathrm{Rh(COMe)I(PMe_3)}]$. Reaction of **1** with 1.5 equiv of 1-(3-pentynyl)-2,3,4,5-tetramethylcyclopentadiene yields $[\mathrm{WCl_4}](\eta^5\text{-}\mathrm{Me_4C_5CH_2CH_2C_5Me_4H})$ (**11**). Addition of 4 equiv of MeMgCl to **11** yields $[\mathrm{WMe_4}](\eta^5\text{-}\mathrm{Me_4C_5CH_2CH_2C_5Me_4H})$ (**12**) while carbonylation produces $[\mathrm{WMe(CO)_3}](\eta^5\text{-}\mathrm{Me_4C_5CH_2CH_2C_5Me_4H})$ (**13**). Addition of $\mathrm{Co_2(CO)_8}$ to **13** in neat *tert*-butylethylene yields $[\mathrm{WMe(CO)_3}](\mathrm{Cp^2})[\mathrm{Co(CO)_2}]$ (**14**). $[\mathrm{WCl_4}](\mathrm{Cp^2})[\mathrm{WMe(CO)_3}]$ (**17**) is prepared by treating $\mathrm{W(C_3Me_3)Cl_3}$ with 1.5 equiv of $[\mathrm{WMe(CO)_3}](\eta^5\text{-}\mathrm{Me_4C_5CH_2CH_2C{\equiv}CMe})$. Addition of **17** to 4 equiv of MeMgCl yields $[\mathrm{WMe_4}](\mathrm{Cp^2})[\mathrm{WMe(CO)_3}]$, which can be selectively oxidized to $\{[\mathrm{WMe_4}][\mathrm{PF_6}]\}(\mathrm{Cp^2})[\mathrm{WMe(CO)_3}]$.

Introduction

Known homogeneous processes for the catalytic hydrogenation of carbon monoxide all require high temperatures (usually >200 °C) and high pressures of $\mathrm{CO/H_2}$ (100–2500 atm) in order to obtain reasonable conversion rates.[1] One approach to carrying out reduction at lower temperatures and pressures is to employ at least two transition metals, preferably one from the early part of the series and one from later in the series, in order to lower the barrier encountered in what is generally considered to be the first step of homogeneous CO reduction, formation of a formyl ligand. The validity of this approach has been strengthened by many examples of reactions between late- and early-transition-metal complexes that lead to activated carbon monoxide ligands or stable intermediates that one might expect to find in a CO hydrogenation process.[2]

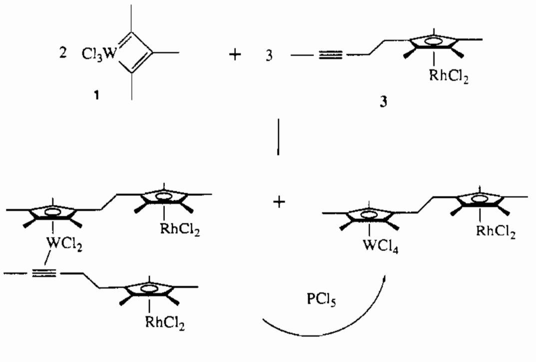
We have previously reported the syntheses of heterobimetallic complexes of a 1-(tetraethylcyclopentadienyl)-2-(tetramethylcyclopentadienyl)ethane ligand.[3] Tethering two different metals to each other via a relatively short flexible linkage might encourage reactions that do not take place in systems containing analogous "unlinked" cyclopentadienyl complexes. Peralkylated cyclopentadienyl ligands bind strongly to most transition metals, and complexes containing such ligands therefore should be able to withstand conditions that may be necessary for CO reduction.

Homobimetallic complexes of ligands having two tetramethylcyclopentadienyl rings linked by a one-atom bridge[4] or a three-atom bridge[5] are known, but preparing a ligand having two tetramethylcyclopentadienyl rings connected by a $-\mathrm{CH_2CH_2}-$ bridge has been challenging. The free ligand has now been prepared in low yield, and a monometallic zirconium complex containing it was prepared.[6] Since the relatively new tungstacyclobutadiene complex $\mathrm{W(C_3Me_3)Cl_3}$ (**1**)[7] reacts with internal acetylenes to yield tungsten cyclopentadienyl complexes, it should be possible to prepare bimetallic complexes of the η^5,η^5-$\mathrm{Me_4C_5CH_2CH_2C_5Me_4}$ ligand by methods analogous to those used to prepare complexes containing the ethyl-substituted linked cyclopentadienyl ligand; the permethylated ligand system should allow NMR studies to be simpler and more straightforward. In this paper, we extend and develop the chemistry of heterobimetallic complexes, and some homobimetallic (tungsten/tungsten) complexes, containing the simpler fully methyl-substituted system, η^5,η^5-$\mathrm{Me_4C_5CH_2CH_2C_5Me_4}$ (abbreviated as $\mathrm{Cp^2}$).

Results

Syntheses of Tungsten/Rhodium Complexes. The (3-pentynyl)cyclopentadienyl complex $\mathrm{Rh}(\eta^5\text{-}\mathrm{Me_4C_5CH_2CH_2C{\equiv}CMe})(\mathrm{CO})_2$ (**2**) was prepared by the route reported for the analogous complex $\mathrm{Rh}(\eta^5\text{-}\mathrm{Me_4C_5CH_2CH_2C{\equiv}CEt})(\mathrm{CO})_2$.[3] The rhodium dicarbonyl center in **2** is apparently incompatible with $\mathrm{W(C_3R_3)Cl_3}$ complexes[3] so it had to be converted into a Rh(III) dichloride by exposing a pentane solution of **2** to 1 equiv of chlorine gas at 0 °C; $\mathrm{Rh}(\eta^5\text{-}\mathrm{Me_4C_5CH_2CH_2C{\equiv}CMe})\mathrm{Cl_2}$ (**3**) was generated in high yield as an orange powder. Precipitation of **3** immediately from the pentane solution as it formed protected the acetylenic unit from any reaction with chlorine. A ^{13}C NMR spectrum of **3** exhibits signals for the inequivalent acetylenic carbon atoms at 77.3 and 77.4 ppm.

As shown in eq 1, treating **1** with 1.5 equiv of **3** generates two tungsten/rhodium complexes, insoluble $[\mathrm{WCl_4}](\mathrm{Cp^2})[\mathrm{RhCl_2}]$ ($\mathrm{Cp^2} = \eta^5,\eta^5$-$\mathrm{Me_4C_5CH_2CH_2C_5Me_4}$) and soluble $[\mathrm{WCl_2}\{\eta^2\text{-}\mathrm{MeC}\equiv$



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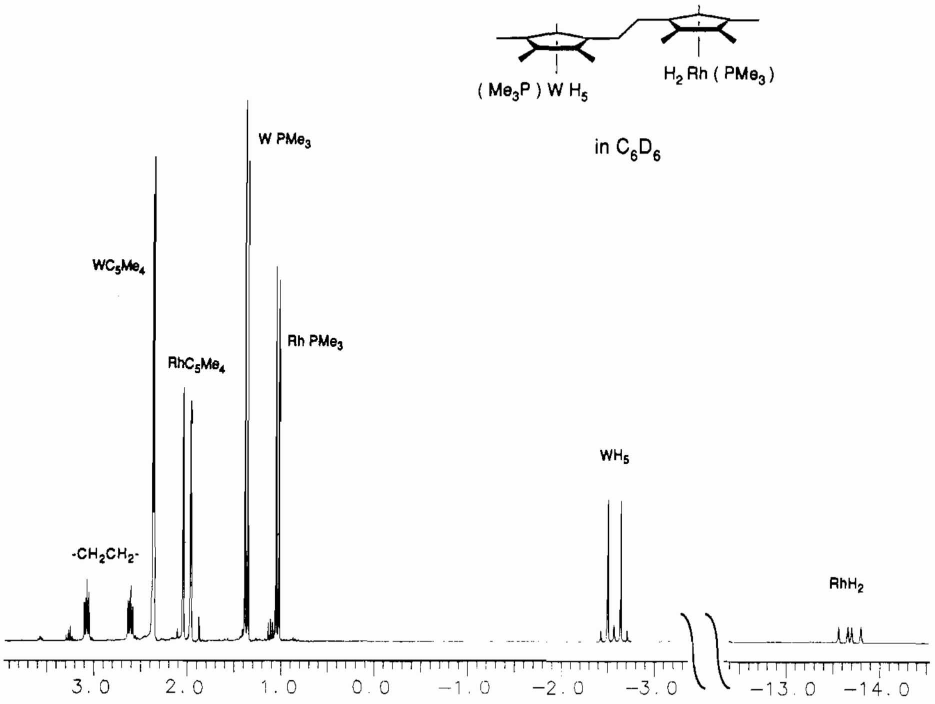


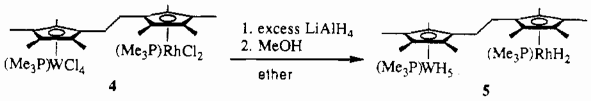
Figure 1. ^{1}H NMR spectrum of [W(PMe$_3$)H$_5$](Cp^2)[Rh(PMe$_3$)H$_2$] (**5**).

CCH$_2$CH$_2$-η^5-C$_5$Me$_4$)RhCl$_2$}](Cp^2)[RhCl$_2$], as a result of formal disproportionation of W(IV) to W(III) and W(V). The exact nature of the disproportionation reaction has never been elucidated.[8] What is presumed to be the soluble tungsten acetylene adduct was not characterized but converted into [WCl$_4$](Cp^2)[RhCl$_2$] by adding PCl$_5$ to the crude reaction mixture. [WCl$_4$](Cp^2)[RhCl$_2$] thereby could be obtained in about 70% yield relative to **1**, but the 0.5 equiv of **3** could not be recovered, and the final yield in terms of rhodium therefore was <50%. [WCl$_4$](Cp^2)[RhCl$_2$] was isolated as an insoluble orange powder, presumanbly polymeric or oligomeric. (The homometallic Cp* analogues [WCp*Cl$_4$]$_2$[8] and [RhCp*Cl$_2$]$_2$[9] are both dimers.) [WCl$_4$](Cp^2)[RhCl$_2$] never could be obtained in crystalline form and probably contains impurities, as elemental analyses were never completely satisfactory.

Addition of excess PMe$_3$ to a dichloromethane suspension of [WCl$_4$](Cp^2)[RhCl$_2$] results in the formation of an impure brown crystalline product, the EPR and ^{1}H NMR spectra of which support the formulation [W(PMe$_3$)Cl$_4$](Cp^2)[Rh(PMe$_3$)Cl$_2$] (**4**). The W(V) center in **4** exhibits an EPR signal (at g = 1.89 and $w_{1/2}$ = 48 G) that is virtually identical with that observed for WCp*(PMe$_3$)Cl$_4$. Unfortunately **4** also could not be freed of impurities by recrystallization, so its formulation must be regarded as tentative, even though it is known that trimethylphosphine reacts with [WCp*Cl$_4$]$_2$ to yield WCp*(PMe$_3$)Cl$_4$[10] and with [RhCp*Cl$_2$]$_2$ to yield RhCp*(PMe$_3$)Cl$_2$.[12] These findings are analogous to those reported for [W(PMe$_3$)Cl$_4$](η^5,η^5-Et$_4$C$_5$CH$_2$CH$_2$C$_5$Me$_4$)[Rh(PMe$_3$)Cl$_2$].[3]

WCp*(PMe$_3$)Cl$_4$ is known to react with excess LiAlH$_4$ (followed by methanol) to give WCp*(PMe$_3$)H$_5$ in 40% yield.[11] Several groups[12] have reported the high-yield preparation of RhCp*(PMe$_3$)H$_2$ by addition of excess Na[(CH$_3$OCH$_2$CH$_2$O)$_2$AlH$_2$] to RhCp*(PMe$_3$)Cl$_2$. We tested the reaction of RhCp*(PMe$_3$)Cl$_2$ with LiAlH$_4$ under the conditions used to prepare WCp*(PMe$_3$)H$_5$, and good yields of RhCp*(PMe$_3$)H$_2$ were obtained. Therefore we felt confident that we could prepare a heterobimetallic polyhydride complex.

Addition of **4** to excess LiAlH$_4$ in ether followed by the addition of methanol yielded [W(PMe$_3$)H$_5$](Cp^2)[Rh(PMe$_3$)H$_2$] (**5**, eq 2) that could be isolated by column chromatography on alumina,

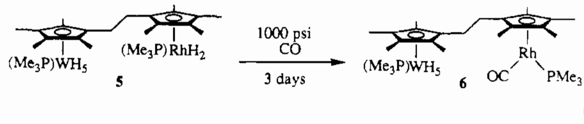


4 **5**

(2)

typically in approximately 30% yield. Compound **5** is very air-sensitive and mildly photosensitive, as is RhCp*(PMe$_3$)H$_2$,[12b] so direct light was avoided whenever possible. Cooling a pentane/ether solution of **5** produced analytically pure white crystals. The ^{1}H NMR spectrum of **5** is shown in Figure 1. Four singlets are observed for the methyl groups of the Cp^2 ligand, in addition to a multiplet for the protons in the –CH$_2$CH$_2$– bridge. The hydride signals and each phosphine signal are virtually identical with those observed in the mononuclear complexes WCp*(PMe$_3$)H$_5$ and RhCp*(PMe$_3$)H$_2$, so we must conclude that the metal centers do not interact. The five-line pattern for the hydride ligands on tungsten at −2.5 ppm results from the near equivalence of J_{HP} and J_{HW}; two of tungsten satellite resonances overlap to give the central resonance of the five-line pattern.

When a toluene solution of **5** was exposed to 1000 psi of carbon monoxide at 25 °C, **6** (eq 3) was formed in 3 days. **6** appeared to be the only diamagnetic product, according to an ^{1}H NMR



5 **6**

(3)

spectrum of the crude product, although on a small scale only ~60% was actually recovered. We presume the hydride ligands in **5** are lost as dihydrogen. The ^{1}H NMR and IR spectra of compound **6** are straightforward, no significant differences from the spectra of the mononuclear Cp* analogues being apparent. Since we have found that the hydrides in WCp*(PMe$_3$)H$_5$ are all equivalent in the ^{1}H NMR spectrum at temperatures as low as −80 °C and have a minimum T_1 value of 650 ms (±10%) at

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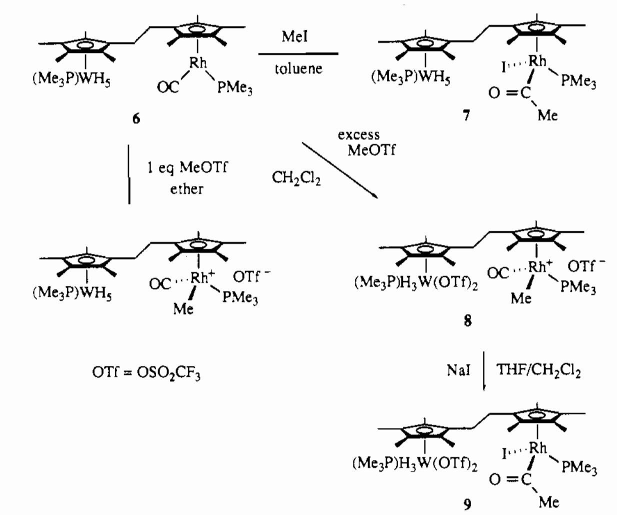
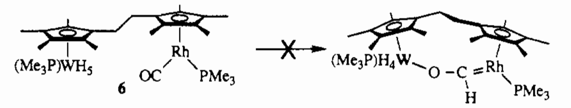
Scheme I



−58 °C, clearly in the range of classical hydrides (vs η^2-H_2 complexes[13a]), we presume that $WCp^*(PMe_3)H_5$ and **6** each contain five "classical" terminal hydride ligands on tungsten. The hydride ligands in a related complex, $ReCp^*H_6$,[13b] were found to have T_1 values of 290 and 618 ms at −70 °C for the axial hydride and the five equatorial hydrides, respectively, consistent with a classical structure. The value for the equatorial hydrides is close to the value obtained for $WCp^*(PMe_3)H_5$, implying the tungsten complex probably has five equatorial halides with the phosphine occupying the axial position.

Isolation of compound such as $[W(PMe_3)H_5](Cp^2)[Rh(CO)(PMe_3)]$, a late-transition-metal carbonyl complex tethered to a high-oxidation-state tungsten hydride complex, was one of the goals of this research. We hoped that the proximity of the two metal centers in **6** would encourage interaction of a hydride(s) with the rhodium carbonyl ligand, *assuming* that the syn configuration (metals on the same side of the bridging ligand system) is readily accessible. Several reactions between the zirconium hydride complexes $ZrCp^*_2H(X)$ (X = H, Cl) and various transition-metal cyclopentadienyl carbonyl complexes have been shown to result in the formation of zirconoxycarbene complexes, i.e., complexes containing a μ-[η^1-C,O]-formyl unit between the metal centers.[2d,e,f] One can envision a similar reaction in **6** as shown in eq 4. Unfortunately, we have seen no evidence for a controlled reaction of this type. Only a small amount of **6** in C_6D_6 in a sealed NMR tube decomposed after 40 h at 82 °C. Decomposition was more rapid at higher temperatures, but no particular product could be identified. The hydrogen ligands of **6** are not expected to be as hydridic as those of $ZrCp^*_2H_2$ or $ZrCp^*_2HCl$, and $WCp^*(PMe_3)H_5$ has proven to be quite inert to reaction with acetone or methanol, so it is perhaps not surprising that the $[W(PMe_3)H_5]$ center in **6** is unreactive toward the rhodium carbonyl. Hydride-transfer reactions between $ZrCp^*_2H(X)$ and metal carbonyl complexes may all involve prior coordination of the carbonyl oxygen to the unsaturated zirconium, and the lack of an open coordination site in the electronically saturated tungsten center probably limits its reactivity.

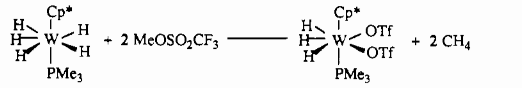


(4)

Preparation of Acyl, Iodo, and Triflate Derivatives. Addition of 1 equiv of methyl iodide to **6** results in the quantitative formation of the rhodium acyl complex $[W(PMe_3)H_5](Cp^2)[Rh(COMe)I(PMe_3)]$ (**7**; Scheme I). A similar reaction is known for $RhCp^*(CO)(PMe_3)$.[14] The asymmetry of **7** causes all methyl groups in the cyclopentadienyl ligand on rhodium to be inequivalent. The ^1H NMR resonance for the hydride ligands is unchanged from what it is in spectra of **5** and **6**. The chemical shift of the acyl carbon atom in **7** is identical with that in $RhCp^*(COMe)I(PMe_3)$, and the IR stretching frequency of the acyl (1638 cm^{-1}) in **7** also matches that in $RhCp^*(COMe)I(PMe_3)$.[14]

Addition of 1 equiv of methyl triflate to an ether solution of **6** resulted in the immediate formation of a white precipitate. An ^1H NMR spectrum of this precipitate in acetonitrile indicated that the rhodium center had been methylated to yield $[W(PMe_3)H_5](Cp^2)\{[RhMe(CO)(PMe_3)]^+[O_3SCF_3]^-\}$ (Scheme I). An IR spectrum of this product in dichloromethane showed a terminal carbonyl stretch at 2051 cm^{-1}, identical with that found in $[RhCp^*Me(CO)(PMe_3)][O_3SCF_3]$ (prepared straightforwardly by adding methyl triflate to $RhCp^*(CO)(PMe_3)$) and very similar to that of the known $[RhCp^*Me(CO)(PMe_3)][PF_6]$.[14] The hydride resonance is at −3.18, similar to that for other compounds of this general type, consistent with virtually no change at the tungsten end of the bimetallic complex.

Addition of excess methyl triflate to a toluene solution of $WCp^*(PMe_3)H_5$ gave $WCp^*(PMe_3)H_3(OSO_2CF_3)_2$ in high yield (eq 5). Evolution of gas, presumably methane, was noted during the reaction. Further reaction to give a tris(triflate) complex was not observed, even after several hours in a toluene solution containing approximately 10% (by volume) of methyl triflate. $WCp^*(PMe_3)H_3(OSO_2CF_3)_2$ is quite soluble in toluene, consistent with, but not demanding, a nonionic structure in which the triflates are bound to tungsten. A hydride resonance of area 2 is found at 3.70 ppm (J_{HH} = 2.9 Hz, J_{HW} = 28 Hz, and J_{HP} = 36 Hz) and one of area 1 at 2.10 ppm ($J_{HW} \approx 20$ Hz, and J_{HP} = 48 Hz), consistent with the tungsten center being more electrophilic. Since the values for J_{HW} and J_{HP} are similar for the two types of hydrides, we assume that they are both classical types. Only one type of triflate is observed by ^{19}F NMR. If this complex has a classical hydride structure, then a structure that is consistent with all the data is that shown in eq 5, an approximate pentagonal bipyramid containing trans Cp* and PMe_3 ligands.



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The reaction between **6** and *excess* (15 equiv) methyl triflate in cold dichloromethane produces $[WH_3(OSO_2CF_3)_2(PMe_3)](Cp^2)\{[RhMe(CO)(PMe_3)][OSO_2CF_3]\}$ (**8**; Scheme I). Off-white microcrystals form upon slowly adding pentane to the reaction solution. The ^{19}F NMR spectrum of **8** consists of two singlets in approximately a 2:1 ratio, with chemical shifts matching those found in $WCp^*(PMe_3)H_3(OSO_2CF_3)_2$ and $[RhCp^*Me(CO)(PMe_3)][OSO_2CF_3]$, respectively. The ν(CO) peak in the IR spectrum of **8** is found at 2053 cm^{-1} and the hydride resonances at 3.78 and 2.49 ppm are very similar to those found in $WCp^*(PMe_3)H_3(OSO_2CF_3)_2$. Again there is no evidence that the two metal centers are cooperating through some bridging ligand system.

Werner[14] reported that the addition of sodium iodide to a nitromethane solution of $[RhCp^*Me(CO)(PMe_3)][PF_6]$ yields the acyl complex $RhCp^*(COMe)I(PMe_3)$. By addition of slightly more than 1 equiv of NaI to a dichloromethane/THF solution of **8**, selective reaction at the rhodium end was achieved in 5 min to yield $[WH_3(OSO_2CF_3)_2(PMe_3)](Cp^2)[Rh(COMe)I(PMe_3)]$ (**9**; Scheme I). (Addition of more than 1 equiv of NaI is believed to result in substitution of the triflate ligands on tungsten by iodides.) **9** could be isolated by extraction of the reaction mixture with toluene, any unreacted starting material being insoluble. The ^1H NMR spectrum of **9** is shown in Figure 2. The doublet of doublets at +3.8 ppm represents two equivalent hydrides and is identical with that observed in the spectrum of $WCp^*(PMe_3)H_3(OSO_2CF_3)_2$. The signal for the unique hydride at ~2.1 ppm overlaps with that for the protons in one of the methylene

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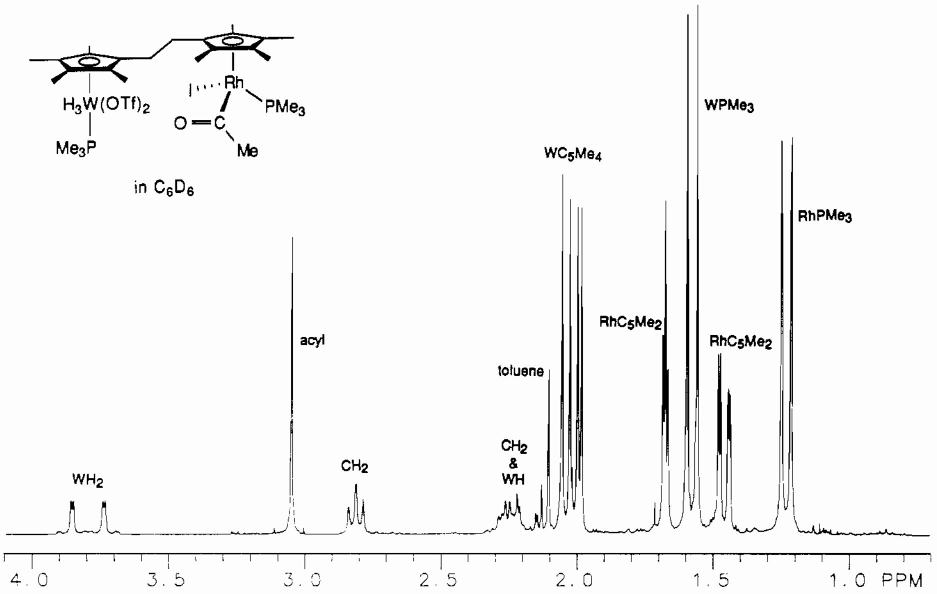
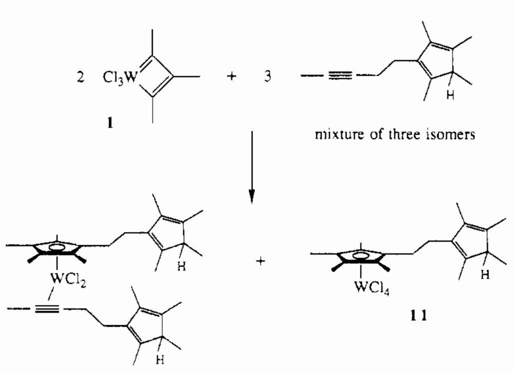


Figure 2. ^{1}H NMR spectrum of [WH$_3$(OSO$_2$CF$_3$)$_2$(PMe$_3$)](Cp^2)[Rh(COMe)I(PMe$_3$)] (**9**).

groups. We had hoped that the electron-rich acyl oxygen in **9** could displace a triflate from tungsten to form a bridging acyl complex. However, the IR spectrum of **9** exhibits a peak for the acyl ligand at 1625 cm^{-1}, virtually identical with what is found in RhCp*(COMe)I(PMe$_3$) (1635 cm^{-1}).[14] A C$_6$D$_6$ solution of **9** in a sealed NMR tube was virtually unchanged after 12 h at 45 °C. After 3 days at 45 °C, a substantial amount of **9** had decomposed to unidentifiable products.

A toluene solution of a small sample of **6** was placed under 1250 psi of CO and heated to 112 °C for 19 h. An ^{1}H NMR spectrum showed the presence of **6** and a closely related compound (**10**) in a 3:2 ratio. The compounds were separated by column chromatography. The ^{1}H NMR spectrum of pure **10** is similar to that of **6**, except that it lacks the methyl resonance for the phosphine ligand bound to rhodium and the IR spectrum exhibits ν(CO) peaks matching those found in RhCp*(CO)$_2$.[15] Therefore we assume **10** to be [W(PMe$_3$)H$_5$](Cp^2)[Rh(CO)$_2$]. (The small scale of the reaction precluded obtaining **10** in pure recrystallized form suitable for elemental analysis.) There was no evidence for formation of any other product in this reaction.

An Alternative Route to Heterobimetallic Complexes: Preparation of Tungsten/Cobalt Complexes. The reaction of the metallacycle W(C$_3$Me$_3$)Cl$_3$ with 1.5 equiv of 1-(3-pentynyl)-2,3,4,5-tetramethylcyclopentadiene is assumed to proceed as shown in eq 6 on the basis of the fact that extraction of the crude product with pentane left pentane-insoluble **11** as a brown powder in 40–45% yield (based on **1**). The acetylene adduct that we presume also is formed was not isolated or characterized. **11** exhibits a single EPR signal at g = 1.92 with $w_{1/2}$ = 59 G, values that are virtually identical with those reported for [WCp*Cl$_4$]$_2$.[8] Therefore, we assume that **11** is also a dimer with μ-Cl ligands. The cyclopentadiene ring is expected to exist in three isomers; with two such rings per dimer, six isomers of **11** are possible. **11** could not be obtained in crystalline form or purified adequately for elemental analysis.



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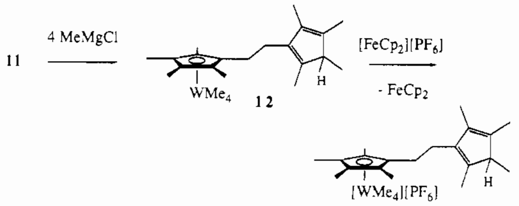
Compound **11** could be alkylated by 4 equiv of MeMgCl in THF to yield [WMe$_4$](η^5-Me$_4$C$_5$CH$_2$CH$_2$C$_5$(H)Me$_4$) (**12**; eq 7). **12** was isolated by column chromatography and recrystallized from pentane. Its EPR spectrum is identical with that of WCp*Me$_4$.[10]



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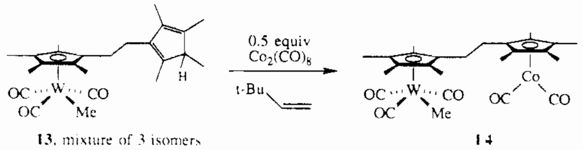
It is known that WCp*Me$_4$ is cleanly oxidized by [FeCp$_2$][PF$_6$] to the diamagnetic d^0 complex [WCp*Me$_4$][PF$_6$].[10] Although we have observed that pentamethylcyclopentadiene itself is decomposed by the ferrocenium cation, addition of 0.9 equiv of [FeCp$_2$][PF$_6$] to a dichloromethane solution of **12** resulted in oxidation of the tungsten center to yield {[WMe$_4$][PF$_6$]}(η^5-Me$_4$C$_5$CH$_2$CH$_2$C$_5$(H)Me$_4$), isolated as an analytically pure yellow-green powder. The ^{1}H NMR spectrum shows broad methyl resonances consistent with the presence of three isomers of the free cyclopentadienyl ring.

Compound **12** was cleanly carbonylated to [WMe(CO)$_3$](η^5-Me$_4$C$_5$CH$_2$CH$_2$C$_5$(H)Me$_4$) (**13**) at 850 psi of CO. Compound **13** can be recrystallized from pentane as a yellow solid. Its ^{1}H NMR spectrum contains many signals for methyl groups of the cyclopentadienyl and cyclopentadiene rings, consistent with cyclopentadiene ring isomers being present. The three singlets at 0.40, 0.39, and 0.34 ppm are each assigned to a single methyl ligand on tungsten in one of the three possible isomers.

Compound **13** reacted with 0.5 equiv of Co$_2$(CO)$_8$ to yield the heterobimetallic complex [WMe(CO)$_3$](η^5,η^5-Me$_4$C$_5$CH$_2$CH$_2$C$_5$Me$_4$)[Co(CO)$_2$] (**14**; eq 8). *tert*-Butylethylene serves as a hydrogen sponge,[16] thereby avoiding hydrogenation



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[15] Rerek, M. E.; Basolo, F. *Organometallics* **1983**, *2*, 372.

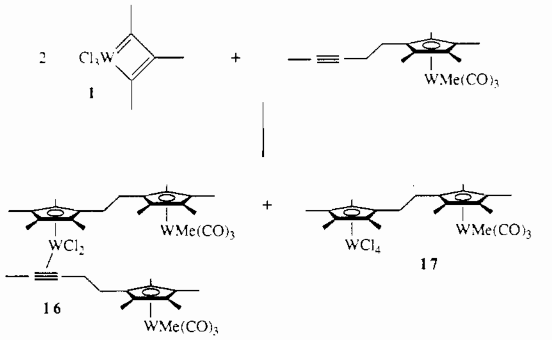
of a cyclopentadiene ring in the remaining reaction pool of **13**. This approach is analogous to that employed previously to prepare heterobimetallic complexes of this type.[3] The ^1H NMR spectrum of **14** is a simple set of six singlets, the four protons of the two-carbon linking unit being accidentally equivalent. The carbonyl region of the IR spectrum of **14** is virtually a composite of the IR spectra of $WCp^*Me(CO)_3$[17] and $CoCp^*(CO)_2$.[18]

Although the tungsten center in **14** is not expected to be very oxophilic, heterobimetallic μ-[η^1-C,O]-acyl complexes are known in which the acyl oxygen is bound to a low-oxidation-state transition-metal center, such as Mo(II)[19] or Mn(I).[20] We placed a toluene solution of the tungsten/cobalt complex **14** under a 1:2 CO/H_2 mixture at elevated temperatures. After 13 h under 1400 psi at 156 °C, an ^1H NMR spectrum of the sample showed a 3:1 mixture of starting material and a compound later confirmed to be $[WH(CO)_3](Cp^2)[Co(CO)_2]$ (**15**). Gas chromatographic and NMR analysis of the volatile components from the reaction mixture showed only toluene. The reaction was repeated with a toluene-d_8 solution of **14** (1240 psi of 1:2 CO/H_2 at 155 °C for 7 h). An ^1H NMR spectrum of the reaction solution showed an approximate 2:1 mixture of starting material and **15** in a total yield of 80% vs an internal mesitylene standard. An IR spectrum showed a small peak that was assigned to $W(CO)_6$.

The reactions of **14** under syngas were modeled by similar reactions of the mononuclear tungsten and cobalt analogues. A toluene solution of $WCp^*Me(CO)_3$ was placed under 1400 psi of CO/H_2 (1:2) at 170 °C for 11 h. An ^1H NMR spectrum of the nonvolatile components of the reaction mixture showed starting material and the known hydride complex $WCp^*H(CO)_3$[21] in approximately a 1:1 ratio. The carbonyl region of the IR spectrum of a pentane solution of the residue consisted of two peaks assigned to $WCp^*Me(CO)_3$ and $WCp^*H(CO)_3$, as well as a peak of approximately equal intensity at 1979 cm^{-1} assigned to $W(CO)_6$. At the high temperatures and pressures of this reaction, a process involving ring displacement in $WCp^*Me(CO)_3$ could produce HC_5Me_5 and $W(CO)_6$, which could then recombine to form $WCp^*H(CO)_3$. However, when equimolar amounts of $W(CO)_6$ and HC_5Me_5 in toluene were placed under 1000 psi of a 1:2 CO/H_2 gas mixture at 165 °C for 6 h, no Cp* complexes formed, and gas chromatography showed only recovered HC_5Me_5. Likewise, a toluene solution of $CoCp^*(CO)_2$ and 1.9 equiv of HC_5Me_4Et that had been exposed to 1250 psi of 1:2 CO/H_2 at 155 °C for 6 was shown by ^1H NMR to contain only $CoCp^*(CO)_2$ and no $Co(\eta^5$-$C_5Me_4Et)(CO)_2$. On the basis of these findings, we conclude that **15** forms directly from **14** by hydrogenolysis of the W–Me bond in a reaction that is independent of the presence of both metals in the bimetallic complex.

Synthesis of Mixed-Oxidation-State Ditungsten Complexes. The approach to bimetallic species described in the above section should make it possible to prepare ditungsten complexes of the Cp^2 ligand in which the tungsten centers are in different oxidation states. In the numerous examples of homobimetallic complexes of various linked-cyclopentadienyl ligands the metal centers are in the same oxidation state.[4,5,22] To our knowledge, the only reported example of a complex of a bis(cyclopentadienyl) ligand containing the same metal in different oxidation states is the zwitterionic fulvalene complex $[Mo(CO)_2(PMe_3)_2]^+(\eta^5,\eta^5$-fulvalene$)[Mo(CO)_3]^-$.[23]

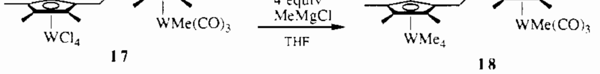
The reaction between $W(C_3Me_3)Cl_3$ and 1.5 equiv of $WMe(CO)_3(\eta^5$-$Me_4C_5CH_2CH_2C{\equiv}CMe)$ yielded **17** (eq 9).



(9)

$[WCl_4](Cp^2)[WMe(CO)_3]$ was isolated as an orange precipitate in 41% yield based on **1**. It is assumed to have a dimeric structure analogous to that of $[WCp^*Cl_4]_2$.[10] An IR spectrum of **17** shows ν(CO) peaks matching those found for $WCp^*Me(CO)_3$.[17] Good evidence for the formulation of **17** is its reaction with PMe_3 to give a dichloromethane-soluble product whose ^1H NMR, EPR, and IR spectra are totally consistent with the formulation $[WCl_4(PMe_3)](Cp^2)[WMe(CO)_3]$. It was not characterized. The other product, **16**, was not isolated, but converted into $[WCl_4]_2(Cp^2)$ by treating it with PCl_5.

The reaction between **17** and 4 equiv of MeMgCl in THF yielded $[WMe_4](Cp^2)[WMe(CO)_3]$ (**18**; eq 10). The surprisingly low solubility of **18** in THF required that it be extracted from the precipitate formed in the reaction. Cooling the dichloromethane extract to –30 °C afforded **18** as analytically pure yellow needles. IR and EPR spectra are entirely as expected if there were no interaction between the tungsten centers. The partial ^1H NMR spectrum of **18** is shown in Figure 3. Resonances for the methyl substituents on the cyclopentadienyl ring attached to the $[WMe(CO)_3]$ center are labeled as Me^{α}_2 and Me^{β}_2, where Me^{α}_2 represents the methyl groups nearest to the C_2H_4 bridge and therefore closer to the paramagnetic W(V) center on average. The broad lump centered at 4.0 ppm is assigned to the methylene group of the C_2H_4 bridge that is furthest from the paramagnetic center. Not shown in Figure 3 are the very broad resonances at +36 and +17 ppm, which are assigned to the methyl groups on the cyclopentadienyl ring attached to the tetramethyl tungsten center and the methylene unit attached to this same ring, respectively. These latter assignments were made by comparison



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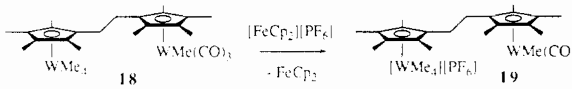
of these data with those for WCp^*Me_4[10] and $W(\eta^5\text{-}C_5Et_5)Me_4$.[3]

Addition of 1 equiv of $[FeCp_2][PF_6]$ to a dichloromethane solution of **18** resulted in selective oxidation of the W(V) center to yield $\{[WMe_4][PF_6]\}(Cp^2)[WMe(CO)_3]$ (**19**; eq 11). We did not expect the d^4 W(II) center to be oxidized since $WCp^*Me(CO)_3$ does not react with $[FeCp_2][PF_6]$. Compound **19** was recrystallized from a mixture of dichloromethane and ether as tan microcrystals. Again there was no evidence for any interaction between a carbonyl ligand and the cationic 14 electron metal center in **19**.



(11)

Discussion

Although the synthetic methods presented here are nontrivial, they at least allowed us to prepare workable quantities of some unusual bimetallic complexes. In the case of heterobimetallic complexes, this approach offers at least one advantage over those employing the free ligand, namely that the metals may be attached step-wise.

Although we have been able to prepare a variety of complexes containing the Cp^2 ligand, our most basic goal—observation of a definitive difference in the reactivity of a heterobimetallic complex of a linked-cyclopentadienyl ligand versus the reactivity of the analogous unlinked cyclopentadienyl complexes—has eluded us. The basic premise—that tethering two different cyclopentadienyl complexes through a flexible linkage should encourage cooperative interactions and reactions between two proximal metal centers—appears to be faulty. The failure to observe cooperative reactions might be blamed in part on the generally bulky nature of the bridging cyclopentadienyl ligand system and the likelihood that a significant amount of energy will be required to orient the two ends of the system in a configuration conducive to cooperative reactions. This conclusion runs counter to our initial hypothesis that some flexibility in the bridging ligand system would be beneficial. Since we are not justified in stretching these conclusions to include other linked-metal systems, cooperative reactions between metals must still be regarded as a sound goal.

Experimental Section

General Details. All experiments were performed under a nitrogen atmosphere in a Vacuum Atmospheres drybox or by using standard Schlenk techniques. Reagent grade ether, tetrahydrofuran, and toluene were distilled from sodium benzophenone ketyl under nitrogen. Pentane was washed with 5% nitric acid in sulfuric acid, stored over calcium chloride, and then distilled from sodium benzophenone ketyl under nitrogen. Methylene chloride was distilled from calcium hydride under nitrogen. 3,3-Dimethyl-1-butene was refluxed over phosphorus pentoxide and distilled under nitrogen. Methanol was distilled from magnesium methoxide and stored over 3A sieves. Deuteriated NMR solvents were passed through a column of activated alumina or stored over 4A molecular sieves. Alumina (ICN-brand) for chromatography was kept under vacuum overnight and deactivated by adding 7% water. 2,3,4,5-Tetramethyl-2-cyclopentenone was purchased from Aldrich. High-purity CO and the high-purity CO/H_2 gas mixture (1:2) were obtained from Matheson. High-pressure reactions were performed in a Parr bomb with 30-mL capacity. $W(C_3Me_3)Cl_3$ was prepared as described in the literature.[7]

NMR data are listed in parts per million relative to Me_4Si for ^1H and ^{13}C, relative to $CFCl_3$ for ^{19}F, and relative to H_3PO_4 for ^{31}P. Coupling constants are quoted in hertz. Ordinary aliphatic coupling constants (those in the range 125–130 Hz) are not noted specifically. Spectra were obtained in C_6D_6 at 25 °C unless otherwise noted. EPR spectra were recorded as the first-derivative curves. All samples were studied at room temperature, and no hyperfine coupling was observed in any spectra. $w_{1/2}$ (width at half-height) values given are the average of the $w_{1/2}$ values for each of the two peaks of the signal.

Preparation of Compounds. $HC_5Me_4(CH_2CH_2C{\equiv}CMe)$. The compound was prepared by a reaction analogous to that used to prepare $HC_5Me_4(CH_2CH_2C{\equiv}CEt)$,[3] using 1-iodo-3-pentyne[24] instead of 1-iodo-3-hexyne. The crude product was distilled through a Vigreux column (20 cm) at 64–68 °C and 0.1 Torr to afford a yellow oil. The reaction can be scaled up to yield approximately 50 g with typical yields being 60–70%. The product is a mixture of the three possible isomers of the cyclopentadiene ring. ^1H NMR (mixture of 3 isomers): δ 2.64–2.40 (m, ring proton), 2.28–2.20 and 2.02–1.96 (m, CH_2CH_2), 1.79, 1.75, 1.73, 1.71, 1.70, 1.69, and 1.66 (s, olefinic methyl groups), 1.56 (m, $C{\equiv}CMe$), 0.94 and 0.93 (d, aliphatic ring methyl group).

$LiC_5Me_4(CH_2CH_2C{\equiv}CMe)$. A solution of $HC_5Me_4(CH_2CH_2C{\equiv}CMe)$ (3.68 g, 19.5 mmol) in ether (50 mL) was cooled to −30 °C. *n*-Butyllithium (8.5 mL of a 2.3 M solution in hexane, 19.5 mmol) was added with stirring, and the mixture was allowed to warm to room temperature. After 15 min, the pale yellow precipitate was collected by filtration and dried in vacuo (yield, 3.49 g, 92%). This material is only sparingly soluble in THF and thus could not be characterized by ^1H NMR. A similar compound, $LiC_5Me_4(CH_2CH_2C{\equiv}CEt)$,[3] is more soluble in THF and has been characterized by ^1H and ^{13}C NMR.

$Rh(\eta^5\text{-}Me_4C_5CH_2CH_2C{\equiv}CMe)(CO)_2$ (2). $LiC_5Me_4(CH_2CH_2C{\equiv}CMe)$ (1.09 g, 5.6 mmol) was suspended in THF (35 mL), and the solution was cooled to −30 °C. $[Rh(CO)_2Cl]_2$ (1.09 g, 2.8 mmol) was added with stirring. The resulting dark brown solution was allowed to warm to room temperature, and after 20 min the THF was removed in vacuo. The residue was extracted with pentane (15 mL), and the extract was filtered through Celite. The filtrate was concentrated and placed on a column of deactivated alumina (12 × 2.5 cm) made up in pentane. A broad orange band was easily eluted with pentane. The solvent was evaporated to leave an orange oil (1.40 g, 72%) that was pure by ^1H NMR. An analytically pure sample was obtained by allowing a concentrated pentane solution to stand at −30 °C to give large orange crystals, which melted at ~20 °C. ^1H NMR: δ 2.47 (t, 2, $C{\equiv}CCH_2CH_2$), 2.15 (tq, 2, $^5J_{HH}$ = 2.8, $C{\equiv}CH_2CH_2$), 1.73 and 1.71 (s, 6 each, C_5Me_4), 1.52 (t, 3, $^5J_{HH}$ = 2.8, $C{\equiv}CMe$). $^{13}C\{^1H\}$ NMR: δ 195.0 (d, J_{CRh} = 85, $Rh(CO)_2$), 105.7, 101.4, and 100.4 (d, J_{CRh} = ~4, ring carbon atoms), 78.8 and 76.1 ($C{\equiv}C$), 25.2 and 22.9 (CH_2CH_2), 10.6 (C_5Me_4), 3.3 ($C{\equiv}CMe$). IR (pentane), cm^{-1}: 2027 s, 1962 s [ν(CO)]. Anal. Calcd for $RhC_{16}H_{19}O_2$: C, 55.51; H, 5.53. Found: C, 55.91; H, 5.57.

$Rh(\eta^5\text{-}Me_4C_5CH_2CH_2C{\equiv}CMe)Cl_2$ (3). A 1-L Schlenk flask containing a solution of $Rh(\eta^5\text{-}Me_4C_5CH_2CH_2C{\equiv}CMe)(CO)_2$ (1.47 g, 4.2 mmol) in pentane (40 mL) and equipped with a septum was placed in an ice bath. The system was closed off at 0 °C, and the solution was stirred as chlorine gas (97 mL at 25 °C and 1 atm, 4.0 mmol) was injected through the septum via a gastight syringe. An orange precipitate formed immediately. After 60 min at 0 °C, the system was opened to a Nujol bubbler, and the mixture was allowed to warm to room temperature. Most of the solids were isolated by filtration. The solids remaining in the flask were washed with pentane, dissolved in dichloromethane (12 mL), and placed in a 100-mL flask. Evaporation of dichloromethane left an orange residue, which was transferred to the frit containing the other isolated solids. The combined solids were washed with ether (3 × 5 mL) and dried in vacuo to yield a dull orange powder (1.26 g, 82% in Rh). ^1H NMR (CD_2Cl_2): δ 2.41 (t, 2, $C{\equiv}CCH_2CH_2$), 2.30 (m, 2, $C{\equiv}CCH_2$), 1.68 (t, 3, $^5J_{HH}$ = 2.7, $C{\equiv}CMe$), 1.61 and 1.57 (s, 6 each, C_5Me_4). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 95.2, 95.1, and 94.4 (d, J_{CRh} = 9.2, ring carbon atoms), 77.4 and 77.3 ($C{\equiv}C$), 24.2 and 16.7 (CH_2CH_2), 9.7 and 9.5 (C_5Me_4), 3.4 ($C{\equiv}CMe$). No ν(CO) peak was found in the IR spectrum.

$[WCl_4(PMe_3)](\eta^5,\eta^5\text{-}Me_4C_5CH_2CH_2C_5Me_4)[RhCl_2(PMe_3)]$ (4). $RhCl_2(\eta^5\text{-}Me_4C_5CH_2CH_2C{\equiv}CMe)$ (1.40 g, 3.88 mmol) was dissolved in dichloromethane (20 mL) and the solution was cooled to ~0 °C. $W(C_3Me_3)Cl_3$[7] (0.96 g, 2.59 mmol) was added while the solution was stirred, and the solution was allowed to warm to room temperature. After 10 min a precipitate formed. After 2 h the mixture was cooled to −30 °C and PCl_5 (0.56 g, 2.69 mmol) was added while the solution was stirred. The suspensions was allowed to warm to room temperature, and after 2 h the orange precipitate was collected by filtration. The solid was washed well with dichloromethane (3 × 6 mL) and dried in vacuo (yield 1.34 g, 68% vs W for $[WCl_4](\eta^5,\eta^5\text{-}Me_4C_5CH_2CH_2C_5Me_4)[RhCl_2]$). The powder was suspended in dichloromethane (20 mL), and PMe_3 (0.41 mL, 4.0 mmol) was added. A dark brown solution quickly formed. After 30 min, a small amount of insoluble tan material was filtered off, and dichloromethane was evaporated from the filtrate to leave a brown microcrystalline solid (1.47 g, 63% from $W(C_3Me_3)Cl_3$). ^1H NMR (CD_2Cl_2): δ −3.0 (extremely br, WC_5Me_4), −7.6 (extremely br, $WPMe_3$). (The remaining resonances expected for the complex are present between 2.5 and 1.4 ppm, but resonances due to impurities prohibited their as-

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[24] Ansell, M. F.; Emmett, J. C.; Coombs, R. U. *J. Chem. Soc. C* **1968**, 217.

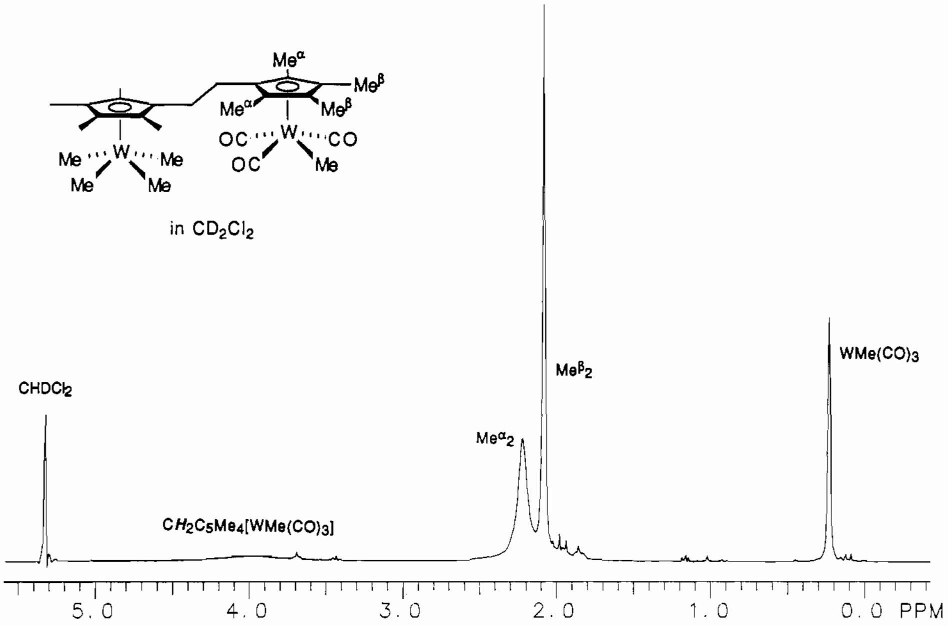

Figure 3. Partial ^1H NMR spectrum of $[WMe_4](Cp^2)[WMe(CO)_3]$ (**18**).

signment.) EPR (CH_2Cl_2): $g = 1.89$; $w_{1/2} = 48$ G.

$[WH_5(PMe_3)](\eta^5,\eta^5$-$Me_4C_5CH_2CH_2C_5Me_4)[RhH_2(PMe_3)]$ (5). $LiAlH_4$ (339 mg, 8.96 mmol) was suspended in ether (50 mL) in a 100-mL flask. **4** (688 mg, 0.75 mmol) was added while the solution was stirred over a period of 5 min. The suspension became a yellow-gray color over a period of 12 h. The mixture was diluted to 75 mL with more ether and cooled to −30 °C. A dropping funnel was attached that contained a solution of methanol (1.26 mL, 31.2 mmol). The methanol was added dropwise over 5 min while the solution was vigorously stirred as it was allowed to warm to room temperature. Gas evolved, and the suspension became thick. After an additional 10 min, the mixture was filtered through Celite, and the filter bed was extracted with ether (2 × 15 mL). Solvent was removed from the filtrate, the brown residue was dissolved in a mixture of pentane and ether (3:1, 10 mL), and the solution was cooled to ~0 °C. The solution was placed on a column of alumina (8 × 2.5 cm), which had been made up in a 4:1 pentane/ether mixture and cooled to ~0 °C. The product was eluted with a mixture of pentane and ether (4:1). (Elution of the compound was judged to be complete when removal of solvent from fractions of the eluant no longer left any residue.) Solvent was evaporated from the combined colorless fractions to leave a white solid (166 mg, 31%). The compound is both thermally sensitive and photosensitive, as is $RhCp^*H_2(PMe_3)$.[12b] It can be recrystallized from a mixture of pentane and ether (3:1, ~6 mL) at −30 °C to afford well-formed white crystals. ^1H NMR (see Figure 1): δ 3.07 and 2.61 (t, 2 each, CH_2CH_2), 2.38 and 2.37 (s, 6 each, WC_5Me_4), 2.05 and 1.97 (s, 6 each, RhC_5Me_4), 1.38 (d, 9, $J_{HP} = 9$, $W(PMe_3)$), 1.04 (d, 9, $J_{HP} = 12$, $Rh(PMe_3)$), −2.56 (d, 5, $J_{HP} = 41$, $J_{HW} = 43$, WH_5), −13.65 (dd, 2, $J_{HP} = 42$, $J_{HRh} = 30$, RhH_2). Anal. Calcd for $WRhC_{26}H_{53}P_2$: C, 43.71; H, 7.48. Found: C, 44.09; H, 7.25.

$[WH_5(PMe_3)](\eta^5,\eta^5$-$Me_4C_5CH_2CH_2C_5Me_4)[Rh(CO)(PMe_3)]$ (6). $[WH_5(PMe_3)](\eta^5,\eta^5$-$Me_4C_5CH_2CH_2C_5Me_4)[RhH_2(PMe_3)]$ (130 mg, 0.182 mmol) was dissolved in toluene (5 mL), placed in a Parr pressure bomb and exposed to 1100 psi of carbon monoxide for 72 h. Shorter reaction times gave incomplete conversion. The pressure was released and the toluene removed in vacuo. The crystalline orange residue was shown to be >95% pure by ^1H NMR (121 mg, 90%). The compound was recrystallized from pentane (~10 mL; −30 °C) to yield small orange needles (85 mg from two crops, 63%). ^1H NMR: δ 3.03 and 2.55 (t, 2 each, CH_2CH_2), 2.36 (s, 12, WC_5Me_4), 1.96 and 1.87 (d, 6 each, $J_{HP} = 1.8$, RhC_5Me_4), 1.37 (d, 9, $J_{HP} = 8.7$, $W(PMe_3)$), 1.04 (dd, 9, $J_{HP} = 9.2$, $J_{HRh} = 2.5$, $Rh(PMe_3)$), −2.58 (d, 5, $J_{HP} = 41$, $J_{HW} = 43$, WH_5). $^{13}C\{^1H\}$ NMR: δ 199.2 (dd, J_{CP}, $J_{CRh} = 87, 25$, CO), 102.8, 102.3, 99.5, 98.9, 98.5, and 97.4 (ring carbon atoms), 30.8 and 29.1 (CH_2CH_2), 29.2 (d, $J_{CP} = 32$, $WPMe_3$), 20.4 (d, $J_{CP} = 31$, $RhPMe_3$), 13.2 ($WC_5\mathit{Me}_4$), 11.3 ($RhC_5\mathit{Me}_4$). ^{31}P NMR: δ −5.7 (d, $J_{PRh} = 202$, $RhPMe_3$), −20.0 (s, $WPMe_3$). IR (pentane), cm^{-1}: 1932 s [ν(CO)] (identical with ν(CO) for $RhCp^*(CO)(PMe_3)$). Anal. Calcd for $WRhC_{27}H_{51}P_2O$: C, 43.80; H, 6.94. Found: C, 44.40; H, 7.15.

T_1 Study of $Cp^*W(PMe_3)H_5$. The T_1 value for the hydride ligands in $WCp^*(PMe_3)H_5$ in toluene-d_8 was determined by using a Varian XL-300 spectrometer and software. A standard 180°–t–90° inversion–recovery pulse sequence was used with the array t = 0.01, 0.05, 0.1, 0.3, 0.5, 0.8, 1.3, 2.0, 4.0, and 10.0 s and a delay of 10 sec between each pulse sequence. The values obtained for the hydride signal are (in s) 2.43 at +23.8 °C, 1.49 at −7.1 °C, 0.78 at −39.0 °C, 0.65 at −58.3 °C, and 0.69 at −73.9 °C.

$[WH_5(PMe_3)](\eta^5,\eta^5$-$Me_4C_5CH_2CH_2C_5Me_4)[Rh(COMe)I(PMe_3)]$ (7). $[WH_5(PMe_3)](\eta^5,\eta^5$-$Me_4C_5CH_2CH_2C_5Me_4)[Rh(CO)(PMe_3)]$ (90 mg, 0.122 mmol) was dissolved in toluene (6 mL) and the solution was cooled to ~0 °C. MeI (9.0 μL, 0.144 mmol) in toluene (2 mL) was added with stirring. The solution went from orange to red as it was allowed to warm to room temperature. After 60 min, toluene and excess MeI were removed in vacuo to leave a red solid (99 mg, 92%). An ^1H NMR spectrum showed the reaction to be quantitative. An analytically pure sample was obtained as red needles from a mixture of pentane and toluene (4:1) at −30 °C. ^1H NMR: δ 3.05 (s, 3, acyl), 2.91 and 2.27 (t, 2 each, CH_2CH_2), 2.31, 2.30, and 2.28 (s, 6, 3, and 3 (respectively), WC_5Me_4), 1.58, 1.56, 1.54, and 1.53 (d, 12 total, $J_{HP} = 2.5$, RhC_5Me_4), 1.36 (d, 9, $J_{HP} = 9.9$, $W(PMe_3)$), 1.21 (d, 9, $J_{HP} = 12$, $Rh(PMe_3)$), −2.58 (d, 5, $J_{HP} = 42$, $J_{HW} = 43$, WH_5). IR (benzene), cm^{-1}: 1638 s [ν(acyl)]. Anal. Calcd for $WRhC_{28}H_{54}IP_2O$: C, 38.12; H, 6.17. Found: C, 37.99; H, 6.03.

$[WH_5(PMe_3)](\eta^5,\eta^5$-$Me_4C_5CH_2CH_2C_5Me_4)\{[RhMe(CO)(PMe_3)][O_3SCF_3]\}$. $[WH_5(PMe_3)](\eta^5,\eta^5$-$Me_4C_5CH_2CH_2C_5Me_4)[Rh(CO)(PMe_3)]$ (42 mg, 0.057 mmol) was dissolved in ether (4 mL), and the solution was cooled to ~0 °C. A solution of $MeOSO_2CF_3$ (5.0 μL, 0.050 mmol) in either (1 mL) was added with stirring. A white precipitate formed quickly and after 10 min was isolated by filtration, washed with ether (2 × 2 mL), and dried in vacuo to give a pale yellow powder (41 mg, 80%). ^1H NMR (CD_3CN) δ 2.80 and 2.34 (t, 2 each, CH_2CH_2), 2.25 and 2.15 (s, 6 each, WC_5Me_4), 1.84, 1.76, and 1.75 (d, 6, 3, and 3, respectively), $J_{HP} \approx 2.5$, RhC_5Me_4), 1.53 (d, 9, $J_{HP} = 10$, $Rh(PMe_3)$), 1.36 (d, 9, $J_{HP} = 9.7$, $W(PMe_3)$), 0.54 (dd, 3, $J_{HP} = 6.0$, $J_{HRh} = 3.1$, RhMe), −3.18 (d, 5, $J_{HP} = 41$, $J_{HW} = 42$, WH_5). IR (dichloromethane), cm^{-1}: 2051 s [ν(CO)]; 1880 sh, 1835 br [$\nu(WH_5)$]; 1222 s, 1155 s [$\nu(O_3SCF_3)$].

$WCp^*H_3(OSO_2CF_3)_2(PMe_3)$. $MeOSO_2CF_3$ (0.71 g, 4.3 mmol) was added with stirring to a solution of $WCp^*H_5(PMe_3)$ (0.36 g, 0.90 mmol) in toluene (15 mL). Evolution of gas was noted. After standing for 6 h, the solution was light yellow and some colorless crystals had formed. Solvent and excess $MeOSO_2CF_3$ were removed in vacuo. The resulting white solid was recrystallized from a mixture of toluene and pentane (1:1) to yield colorless needles (0.41 g, 65%). ^1H NMR (C_6D_6): δ 3.70 (dd, 2, $J_{HP} = 36.0$, $J_{HH} = 2.9$, $J_{HW} = 28$, WH), 2.10 (dt, 1, $J_{HP} = 48$, $J_{HH} = 2.9$, $J_{HW} \sim 20$, WH), 1.96 (s, 15, C_5Me_5), 1.57 (d, 9, $J_{HP} = 11$, PMe_3). ^1H NMR (CD_2Cl_2): δ 3.76 (dd, 2, $J_{HP} = 35$, $J_{HH} = 2.7$, $J_{HW} = 29$, WH), 2.56 (dt, 1, $J_{HP} = 45$, $J_{HH} = 2.7$, $J_{HW} \sim 19$, WH), 2.35 (s, 15, C_5Me_5); 1.83 (d, 9, $J_{HP} = 11$, PMe_3). ^{19}F NMR (C_6D_6): δ −77.89; (CD_2Cl_2) δ −78.38. IR (CH_2Cl_2), cm^{-1}: 1890 br [ν(WH)]; 1331 vs, 1232 s, 1196, vs [$\nu(OSO_2CF_3)$]. Anal. Calcd for $WC_{15}H_{27}S_2O_6F_6$: C, 25.87; H, 3.91; F, 16.37. Found: C, 26.35; H, 3.88; F, 16.15.

$[WH_3(OSO_2CF_3)_2(PMe_3)](\eta^5,\eta^5$-$Me_4C_5CH_2CH_2C_5Me_4)\{[RhMe(CO)(PMe_3)][O_3SCF_3]\}$ (8). $[WH_5(PMe_3)](\eta^5,\eta^5$-$Me_4C_5CH_2CH_2C_5Me_4)[Rh(CO)(PMe_3)]$ (42 mg, 0.057 mmol) was placed in a vial and cooled to −30 °C and then dissolved in cold dichloromethane (0.5 mL, −30 °C). $MeOSO_2CF_3$ (140 mg, 0.85 mmol) was dissolved in cold dichloromethane (0.5 mL, −30 °C), and this solution was added. The mixture quickly turned from orange to yellow, and gas evolved as the solution was allowed to warm to room temperature. The solution became a light brown color. After 4 h, pentane (2 mL) was added, and off-white microcrystals formed. The solution was removed via pipet, and the crystals were washed with a mixture of dichloromethane and pentane (3:1, 2 × 3 mL) and dried in vacuo (yield 45 mg, 66%). ^{1}H NMR (CD_2Cl_2): δ 3.78 (dd, 2, $J_{HP} = 35$, $J_{HH} = 2.5$, $J_{HW} = 28$, WH), 2.92 and 2.33 (m, 2 each, CH_2CH_2), 2.49 (d of br t, 1, $J_{HP} \approx 48$, WH), 2.37, 2.36, and 2.35 (s, 12 total, WC_5Me_4), 2.00, 1.98, 1.92, and 1.90 (d, 3 each, $J_{HP} = 3$, RhC_5Me_4), 1.82 (d, 9, $J_{HP} = 12$, $W(PMe_3)$), 1.62 (dd, 9, $J_{HP} = 11$, $J_{HRh} = 2.4$, $Rh(PMe_3)$), 0.61 (dd, 3, $J_{HP} = 5.4$, $J_{HRh} = 1.7$, RhMe). ^{19}F NMR (CD_2Cl_2): δ −78.28 (s, $W(OSO_2)CF_3)_2$), −78.72 (s, $[Rh^+][O_3SCF_3^-]$). The ratio of the two signals is approximately 2:1. IR (CH_2Cl_2), cm^{-1}: 2053 s [ν(CO)]; 1333 s, 1198 s [$\nu(W(OSO_2CF_3))$]; 1165 s br [$\nu([Rh^+][O_3SCF_3^-])$].

$[WH_3(OSO_2CF_3)_2(PMe_3)](\eta^5,\eta^5\text{-}Me_4C_5CH_2CH_2C_5Me_4)[Rh(COMe)I(PMe_3)]$ (9). $[WH_5(PMe_3)](\eta^5,\eta^5\text{-}Me_4C_5CH_2CH_2C_5Me_4)[Rh(CO)(PMe_3)]$ (102 mg, 0.138 mmol) was treated with $MeOSO_2CF_3$ (302 mg, 1.84 mmol) as described above. After 3 h, toluene (0.5 mL) was added, and solvent and excess $MeOSO_2CF_3$ were removed in vacuo. The light brown residue was dissolved in a mixture of dichloromethane, and THF (1:1, 4 mL) and NaI (25 mg, 0.17 mmol) were added with stirring. A dark red solution resulted, and after 5 min the solvent was removed in vacuo and the residue was extracted with a mixture of toluene and THF (3:1, 5 mL). The solvent was removed from the extract to leave a red solid, which was recrystallized from toluene at −30 °C (60 mg, 34%) to give red needles. The yield was not optimized. The compound crystallizes with 1.0 equiv of toluene, which is not removed at a vacuum of 0.3 mTorr in 24 h, as evidenced by ^{1}H NMR. ^{1}H NMR (see Figure 2): δ 3.79 (dd, 2, $J_{HP} = 35$, $J_{HH} = 2.7$, $J_{HW} = 28$, WH), 3.05 (s, 3, acyl), 2.81 (t, 2, $WC_5CH_2CH_2$), 2.3–2.15 (m, 3 total, overlap of $RhC_5CH_2CH_2$ and WH)), 2.04, 2.01, 1.98, and 1.97 (s, 3 each, WC_5Me_4), 1.67, 1.66, 1.46, and 1.43 (d, 3 each, $J_{HP} = 2$, RhC_5Me_4), 1.56 (d, 9, $J_{HP} = 11$, $W(PMe_3)$), 1.22 (d, 9, $J_{HP} = 10.3$, $Rh(PMe_3)$). ^{19}F NMR: δ −77.9 (s, CF_3). IR (CH_2Cl_2), cm^{-1}: 1625 s [ν(acyl)]; 1332 s, 1233 m, and 1197 vs [$\nu(OSO_2CF_3)$]. Anal. Calcd for $WRhC_{37}H_{60}C_{37}H_{60}IS_2P_2O_7F_6$ (includes 1.0 toluene of crystallization): C, 34.98; H, 4.76; I, 9.99; F, 8.97. Found: C, 35.44; H, 5.16; I, 10.23; F, 8.50.

$[WH_5(PMe_3)](\eta^5,\eta^5\text{-}Me_4C_5CH_2CH_2C_5Me_4)[Rh(CO)_2]$ (10). A toluene solution (5 mL) of $[WH_5(PMe_3)](\eta^5,\eta^5\text{-}Me_4C_5CH_2CH_2C_5Me_4)[Rh(CO)(PMe_3)]$ (50 mg) in a Parr pressure bomb was placed under 1100 psi of CO. The bomb was placed in an oil bath maintained at 112 °C, and the pressure rose to 1250 psi. After 19 h, the bomb was allowed to cool, pressure was released, and volatile components of the reaction solution were quickly removed in vacuo, limiting back-reaction of the product with free PMe_3. An ^{1}H NMR spectrum of the crude reaction mixture consisted of signals for only the starting material and the title compound, in approximately a 3:2 ratio. This mixture was dissolved in pentane and placed on an alumina column (2.5 × 10 cm) made up in pentane. An orange band containing the title compound was separated by elution with an 8:1 pentane/ether mixture, and starting material was subsequently eluted with a 4:1 pentane/ether mixture. The ^{1}H NMR spectrum of the sample of the title compound from the column showed it to be free of impurities. The compound is highly soluble in pentane, and on this small scale a crystalline sample could not be obtained. ^{1}H NMR: δ 2.87 and 2.35 (t, 2 each, CH_2CH_2), 2.33 and 2.25 (s, 6 each, WC_5Me_4), 1.75 and 1.69 (s, 6 each, RhC_5Me_4), 1.35 (d, 9, $J_{HP} = 9.9$, $WPMe_3$), −2.62 (d, 5, $J_{HP} = 41$, $J_{HW} = 42$, WH_5). IR (pentane), cm^{-1}: 2027 s, 1960 s [ν(CO)]; 1840 br [$\nu(WH_5)$].

$[WCl_4](\eta^5\text{-}Me_4C_5CH_2CH_2C_5(H)Me_4)$ (11). $W(C_3Me_3)Cl_3$[7] (0.85 g, 2.29 mmol) was dissolved in cold dichloromethane (10 mL; −30 °C) and $HC_5Me_4(CH_2CH_2C{\equiv}CMe)$ (0.87 g, 4.6 mmol was added with stirring. The solution was allowed to warm to room temperature and after 2 h, solvent was removed in vacuo to leave a dark red tar. This tar was stirred with pentane (30 mL) for 30 min to give a dark red solution and a brown precipitate. The precipitate was isolated by filtration, washed well with pentane (3 × 15 mL), and dried in vacuo to yield a tan powder (0.60 g, 44% yield). EPR (CH_2Cl_2, 25 °C): $g = 1.92$; $w_{1/2} = 59$ G (identical with the EPR data for $[WCp^*Cl_4]_2$[10]).

The pentane was removed from the extract in vacuo to give a dark red oil. The EPR spectrum of this dark red oil (in CH_2Cl_2, 25 °C: $g = 1.94$; $w_{1/2} = 27$ G) was virtually identical with the EPR signal of $WCp^*Cl_2(\eta^2\text{-}C_2Me_2)$[7] in CH_2Cl_2 ($g = 1.94$, $w_{1/2} = 35$ G), consistent with formation of $W(\eta^5\text{-}Me_4C_5CH_2CH_2C_5(H)Me_4)Cl_2(\eta^2\text{-}MeCCCH_2CH_2C_5(H)Me_4)$.

$[WMe_4](\eta^5\text{-}Me_4C_5CH_2CH_2C_5(H)Me_4)$ (12). A 2.8 M solution of MeMgCl (1.50 mL, 4.20 mmol) was diluted to 7 mL with THF and cooled to −30 °C. $[WCl_4](\eta^5\text{-}Me_4C_5CH_2CH_2C_5(H)Me_4)$ (0.60 g, 1.01 mmol) was added with stirring, and the solution became dark green. The solution was allowed to warm to room temperature, and after 1 h THF was removed in vacuo. The residue was extracted with pentane (15 mL) and filtered through Celite. The solution was concentrated and placed on a column of alumina (2.5 × 10 cm) made up in pentane that had been cooled to ~0 °C. A yellow band was easily eluted with cool pentane (~10 °C), and the pentane was removed in vacuo to leave a yellow oil, which solidified upon standing at −30 °C (yield 0.21 g, 41%). Yellow crystals were obtained by allowing concentrated pentane solution to stand at −30 °C. ^{1}H NMR (mixture of three isomers): δ 41 and 38 (v br, WC_5Me_4), 19 (v br, $W(Me_4C_5C\mathit{H}_2)$), 8.0 (br), 4.1 (v br), 3.5 (br), 2.58, 2.41, 1.91, 1.70, 1.63, and 1.09 (br s, $HC_5\mathit{Me}_4$), 0.0 (br, small). EPR (CH_2Cl_2, 25 °C): $g = 2.02$; $w_{1/2} = 130$ G (identical with the EPR data for WCp^*Me_4[10] in CH_2Cl_2: $g = 2.02$; $w_{1/2} = 138$ G). Anal. Calcd for $WC_{24}H_{41}$: C, 56.14; H, 8.05. Found: C, 55.76; H, 7.94.

$\{[WMe_4][PF_6]\}(\eta^5\text{-}Me_4C_5CH_2CH_2C_5(H)Me_4)$. A solution of $[WMe_4](\eta^5\text{-}Me_4C_5CH_2CH_2C_5(H)Me_4)$ (130 mg, 0.253 mmol) in dichloromethane (4 mL) was cooled to −30 °C. $[FeCp_2][PF_6]$ (80 mg, 0.241 mmol) was added with stirring. The mixture became red as it was allowed to warm to room temperature, and after 20 min the solvent was removed in vacuo. Unreacted starting material and $FeCp_2$ were extracted with ether (8 mL), and the insoluble residue was isolated by filtration and dried to give a yellow-green powder (120 mg, 72% in W). The ^{1}H NMR spectrum is complex, but indicative of the presence of three isomers of the cyclopentadiene ring. ^{1}H NMR (CD_2Cl_2): δ 3.4 (br, axial Me of WMe_4), 2.65–2.25 (m, $C_5CH_2CH_2C_5$ and cyclopentadiene ring proton), 2.11, 2.08, 2.07, 2.04, 1.98, 1.95, and 1.91 (s, WC_5Me_4), 1.84, 1.81, 1.78, and 1.73 (s, olefinic Me groups), 1.6 (br, equatorial Me groups of WMe_4), 1.03 and 1.02 (d, aliphatic Me on cyclopentadiene ring). Anal. Calcd for $WC_{24}H_{41}PF_6$: C, 43.78; H, 6.28; F, 17.31. Found: C, 43.83; H, 5.74; F, 16.74.

$[WMe(CO)_3](\eta^5\text{-}Me_4C_5CH_2CH_2C_5(H)Me_4)$ (13). A solution of $[WMe_4](\eta^5\text{-}Me_4C_5CH_2CH_2C_5(H)Me_4)$ (90 mg, 0.175 mmol) in toluene (4 mL) was placed in a Parr pressure bomb. The bomb was cooled to −78 °C and pressurized with carbon monoxide to 850 psi. The bomb was allowed to warm to room temperature, and the pressure was released. Solvent was removed in vacuo, leaving a yellow-orange oil. A concentrated pentane solution was allowed to stand at −30 °C, producing yellow crystals as a mixture of the three possible isomers of the cyclopentadiene ring, as shown by ^{1}H NMR (70 mg in two crops, 72%). ^{1}H NMR (mixture of three isomers): δ 2.48, 2.32–2.08, and 1.86 (m, CH_2CH_2 and cyclopentadiene ring proton), 1.77, 1.74, 1.72, 1.70, 1.67, 1.65, 1.63, 1.59, 1.58, 1.56, 1.55, and 1.53 (s, WC_5Me_4 and olefinic Me groups), 0.92 and 0.90 (aliphatic Me on cyclopentadiene ring), 0.40, 0.39, and 0.34 (s, WMe). IR (pentane), cm^{-1}: 2010 s, 1912 s br [ν(CO)]. Anal. Calcd for $WC_{24}H_{32}O_3$: C, 52.19; H, 5.84. Found: C, 52.18; H, 5.95.

$[WMe(CO)_3](\eta^5,\eta^5\text{-}Me_4C_5CH_2CH_2C_5Me_4)[Co(CO)_2]$ (14). $[WMe(CO)_3](\eta^5\text{-}Me_4C_5CH_2CH_2C_5(H)Me_4)$ (83 mg, 0.150 mmol) was dissolved in 3,3-dimethyl-1-butene (4 mL) and the solution was cooled to ~0 °C. $Co_2(CO)_8$ (27 mg, 0.079 mmol) was added. The red solution was stirred for 2 h, and the vial was periodically opened to release carbon monoxide. A small amount of black precipitate was filtered off, and the solution was allowed to stand at −30 °C. Red needles formed, which were recrystallized from pentane (71 mg, two crops, 71%): ^{1}H NMR: δ 2.13 (s, 4, CH_2CH_2), 1.64, 1.58, 1.56, and 1.49 (s, 6 each, WC_5Me_4 and CoC_5Me_4), 0.36 (s, 3, WMe). IR (pentane), cm^{-1}: 2011 s [$\nu(Co(CO)_2)$ and $\nu(W(CO)_3)$]; 1952 s [$\nu(Co(CO)_2)$]; 1918 s br [$\nu(W(CO)_3)$]. Anal. Calcd for $WCoC_{26}H_{31}O_5$: C, 46.87; H, 4.69. Found: C, 46.97; H, 4.91.

Observation of $[WH(CO)_3](\eta^5,\eta^5\text{-}Me_4C_5CH_2CH_2C_5Me_4)[Co(CO)_2]$ (15). A sample of ~8 mg of $[WMe(CO)_3](\eta^5,\eta^5\text{-}Me_4C_5CH_2CH_2C_5Me_4)[Co(CO)_2]$ was dissolved in toluene (2 mL), and the solution was placed under 1100 psi of a 1:2 CO/H_2 gas mixture in a Parr bomb. The bomb was heated in an oil bath maintained at 173 °C. After 8 h, the bomb was allowed to cool to room temperature. Volatile components of the reaction solution were removed in vacuo. An ^{1}H NMR spectrum of the residue showed mainly the title compound. The mixture was dissolved in pentane and placed on an alumina column (1 × 5 cm). Elution with a 7:1 pentane/ether mixture yielded an orange band containing only the title compound. Recrystallization was not possible on this scale, but IR and NMR spectra showed the sample to be pure. ^{1}H NMR: δ 2.27 and 2.09 (m, 2 each, CH_2CH_2), 1.76, 1.69, 1.61, and 1.45 (s, 6 each, WC_5Me_4 and CoC_5Me_4), −6.55 (s, 1, $J_{HW} = 39$, WH). IR (pentane), cm^{-1}: 2009 s [$\nu(Co(CO)_2)$ and $\nu(WH(CO)_3)$]; 1948 s [$\nu(Co(CO)_2)$]; 1920 s br [$\nu(WH(CO)_3)$].

Reaction of $WCp^*Me(CO)_3$ under CO/H_2. A toluene solution (3 mL) of $WCp^*Me(CO)_3$ (35 mg) was placed under 1060 psi of a 1:2 CO/H_2 gas mixture in a Parr pressure bomb. The bomb was heated in an oil bath maintained at 176 °C. After 11 h, the bomb was allowed to cool to room temperature. Pressure was released, and the solvent was removed in vacuo to leave a yellow solid. An ^{1}H NMR spectrum of a $\mathrm{C_6D_6}$ solution of this solid consisted of peaks for the starting material and $\mathrm{WCp^*H(CO)_3}$[21] in approximately a 1:1 ratio, plus two much smaller unidentifiable resonances. The carbonyl region of the IR spectrum of a pentane solution of the residue consisted of two peaks assigned to $\mathrm{WCp^*Me(CO)_3}$ and $\mathrm{WCp^*H(CO)_3}$, as well as a peak of approximately equal intensity at 1979 cm^{-1} assigned to $\mathrm{W(CO)_6}$.

Test Reactions of $\mathrm{W(CO)_6}$ and $\mathrm{HC_5Me_5}$ under $\mathrm{CO/H_2}$. $\mathrm{W(CO)_6}$ (112 mg, 0.32 mmol), $\mathrm{HC_5Me_5}$ (55 mg, 0.40 mmol), and toluene (7 mL) were placed in a Parr pressure bomb. The bomb was pressurized with 1010 psi of a 1:2 $\mathrm{CO/H_2}$ gas mixture and heated in an oil bath maintained at 165 °C. After 6 h, the bomb was cooled to room temperature, and the pressure was released. Volatile components were removed in vacuo from a 2-mL sample of the solution, leaving only a white solid that was identified as $\mathrm{W(CO)_6}$. An ^{1}H NMR spectrum showed no $\mathrm{WCp^*H(CO)_3}$ to be present, and only toluene and $\mathrm{HC_5Me_5}$ were observed by GLC.

[$\mathrm{WMe(CO)_3}$](η^5-$\mathrm{Me_4C_5CH_2CH_2C{\equiv}CMe}$). $\mathrm{W(CO)_6}$ (5.42 g, 15.4 mmol) and $\mathrm{LiC_5Me_4(CH_2CH_2C{\equiv}CMe)}$ (3.01 g, 15.5 mmol) were combined in THF (35 mL) in a 100-mL Schlenk flask. The suspension was stirred and heated to reflux for 9 h; no solids remained. The brown solution was allowed to cool to room temperature. A solution of MeI (3.3 g, 23.2 mmol) in THF (2 mL) was added dropwise with stirring. After 5 min, the solution was heated to reflux for 6 h. Volatiles were removed, and the brown, tarry residue was extracted with pentane (1 × 120 mL, 3 × 10 mL). The combined extracts were filtered through Celite and placed on a column of alumina (10 × 2.5 cm) made up in pentane. A broad yellow band was easily eluted with pentane, and solvent was removed to leave a fluffy yellow solid (4.86 g, 67%). ^{1}H NMR ($\mathrm{C_6D_6}$): δ 2.29 (t, 2, $\mathrm{C_5C}H_2\mathrm{CH_2}$), 1.95 (tq, 2, $^5J_{\mathrm{HH}}$ = 3.1, $\mathrm{CH_2CH_2C{\equiv}CMe}$), 1.63 and 1.49 (s, 6 each, $\mathrm{C_5Me_4}$), 1.45 (t, 3, $^5J_{\mathrm{HH}}$ = 2.9, $\mathrm{C{\equiv}CMe}$), 0.35 (s, 3, WMe). ^{13}C{^{1}H} NMR ($\mathrm{C_6D_6}$): δ 233.3 and 220.4 (W(CO)), 104.7, 103.9, and 102.8 (ring carbon atoms), 78.2 and 76.6 ($\mathrm{C{\equiv}C}$), 25.7 and 20.8 ($\mathrm{CH_2CH_2}$), 10.2 and 9.9 ($\mathrm{C_5}Me_4$), 3.3 ($\mathrm{C{\equiv}C}Me$), −24.2 (WMe). IR (pentane), cm^{-1}: 2017 s, 1918 s [ν(CO)]. Anal. Calcd for $\mathrm{WC_{18}H_{22}O_3}$: C, 45.98; H, 4.72. Found: C, 46.28; H, 4.81.

{[$\mathrm{WCl_4}$](η^5,η^5-$\mathrm{Me_4C_5CH_2CH_2C_5Me_4}$)[$\mathrm{WMe(CO)_3}$]}$_2$ (17). [$\mathrm{WMe(CO)_3}$](η^5-$\mathrm{Me_4C_5CH_2CH_2C{\equiv}CMe}$) (1.71 g, 3.64 mmol) was dissolved in dichloromethane (20 mL) and the solution was cooled to −30 °C. $\mathrm{W(C_3Me_3)Cl_3}$[7] (0.906 g, 2.44 mmol) was added while stirring the solution. The clear red solution was allowed to warm to room temperature, and an orange precipitate formed. After 90 min, the solids were isolated by filtration, washed well with dichloromethane (2 × 6 mL), and dried to give an orange powder (yield 0.875 g, 41% from $\mathrm{W(C_3Me_3)Cl_3}$). The compound is very sparingly soluble in dichloromethane, and could not be purified. The soluble trimethylphosphine adduct could be more completely characterized (vide infra). IR (Nujol), cm^{-1}: 1996 s, 1895 s br [ν(CO)].

Solvent was evaporated from the filtrate of the reaction mixture, leaving a brown tar. This was extracted with toluene (10 mL), leaving a brown oil containing the expected disproportionation product, **16** (eq 9). This complex could be converted to [$\mathrm{WCl_4}$]$_2$($\mathrm{Cp^2}$) by treating it with $\mathrm{PCl_5}$ (vide infra). IR ($\mathrm{CH_2Cl_2}$), cm^{-1}: 2002 s, 1904 s br [ν(CO)]. EPR ($\mathrm{CH_2Cl_2}$): g = 1.94; $w_{1/2}$ = 23 G. This is virtually identical with the EPR data for $\mathrm{WCp^*Cl_2}$(η^2-$\mathrm{C_2Me_2}$)[7] in $\mathrm{CH_2Cl_2}$: g = 1.94; $w_{1/2}$ = 35 G.

[$\mathrm{WCl_4(PMe_3)}$](η^5,η^5-$\mathrm{Me_4C_5CH_2CH_2C_5Me_4}$)[$\mathrm{WMe(CO)_3}$]. [$\mathrm{WCl_4}$]($\eta^5,\eta^5$-$\mathrm{Me_4C_5CH_2CH_2C_5Me_4}$)[$\mathrm{WMe(CO)_3}$] (10 mg, 0.011 mmol) was added to a stirred solution of $\mathrm{PMe_3}$ (5 μL, 0.049 mmol) in dichloromethane (1 mL). A pale green solution immediately formed, and after 5 min the volatiles were removed to leave a green solid. ^{1}H NMR ($\mathrm{CD_2Cl_2}$): δ 2.00 (s) and 1.98 (br sh) ([$\mathrm{WMe(CO)_3}$](η^5-$\mathrm{RC_5}Me_4$), most likely $\mathrm{C_5Me^{\beta}_2}$ and $\mathrm{C_5Me^{\alpha}_2}$, respectively), 0.02 (s, WMe), −3.4 (v br, [$\mathrm{WCl_4(PMe_3)}$](η^5-$\mathrm{RC_5}Me_4$)), −7.6 (v br, $\mathrm{PMe_3}$). EPR ($\mathrm{CD_2Cl_2}$, 25 °C): g = 1.89; $w_{1/2}$ = 44 G (virtually identical with the EPR data for $\mathrm{WCp^*Cl_4(PMe_3)}$[10] in $\mathrm{CH_2Cl_2}$: g = 1.89; $w_{1/2}$ = 52 G). IR ($\mathrm{CH_2Cl_2}$), cm^{-1}: 2002 s, 1905 s br [ν(CO)].

[$\mathrm{WMe_4}$](η^5,η^5-$\mathrm{Me_4C_5CH_2CH_2C_5Me_4}$)[$\mathrm{WMe(CO)_3}$] (18). A 2.8 M solution of MeMgCl (0.85 mL, 2.38 mmol) was diluted to 6 mL with THF and cooled to −30 °C. [$\mathrm{WCl_4}$](η^5,η^5-$\mathrm{Me_4C_5CH_2CH_2C_5Me_4}$)-[$\mathrm{WMe(CO)_3}$] (400 mg, 0.456 mmol) was added as a solid with stirring. The suspension became green-yellow and then yellow as it was allowed to warm to room temperature. After 70 min, the yellow precipitate was isolated by filtration, washed with a THF/ether mixture (1:1, 2 × 3 mL), and dried in vacuo. This solid was extracted with dichloromethane (40 mL), and yellow needles were obtained by standing the extract at −30 °C (151 mg from two crops, 41%). ^{1}H NMR ($\mathrm{CD_2Cl_2}$; see Figure 3): δ 36 (v v br, $\mathrm{WC_5Me_4}$), 17 (v v br, [$\mathrm{WMe_4}$]$\mathrm{C_5C}H_2\mathrm{CH_2}$), 4.0 (v br, [$\mathrm{WMe_4}$]$\mathrm{C_5CH_2C}H_2$), 2.21 (br, [$\mathrm{WMe(CO)_3}$]$\mathrm{C_5Me^{\alpha}_2}$), 2.08 (s, [$\mathrm{WMe(CO)_3}$]$\mathrm{C_5Me^{\beta}_2}$), 0.22 (s, $\mathrm{WMe(CO)_3}$). IR ($\mathrm{CH_2Cl_2}$), cm^{-1}: 2003 s, 1903 s br [ν(CO)]. EPR ($\mathrm{CH_2Cl_2}$, 25 °C): g = 2.01; $w_{1/2}$ = 135 G (virtually identical with the EPR data for $\mathrm{WCp^*Me_4}$[10]). Anal. Calcd for $\mathrm{W_2C_{28}H_{43}O_3}$: C, 42.28; H, 5.45. Found: C, 42.18; H, 5.58.

[$\mathrm{WMe(CO)_3}$](η^5,η^5-$\mathrm{Me_4C_5CH_2CH_2C_5Me_4}$){[$\mathrm{WMe_4}$][$\mathrm{PF_6}$]} (19). [$\mathrm{WMe_4}$]($\eta^5,\eta^5$-$\mathrm{Me_4C_5CH_2CH_2C_5Me_4}$)[$\mathrm{WMe(CO)_3}$] (131 mg, 0.165 mmol) was partially dissolved in dichloromethane (10 mL). [$\mathrm{FeCp_2}$][$\mathrm{PF_6}$] (55 mg, 0.166 mmol) was added as a solid over 5 min with stirring. All [$\mathrm{FeCp_2}$][$\mathrm{PF_6}$] disappeared within 15 min as the mixture became a light brown solution. After 30 min, a small amount of black precipitate was removed by filtration through a piece of glass wool filter paper placed in a disposable pipet. The solvent was evaporated, and $\mathrm{FeCp_2}$ was extracted with ether (8 mL). Solids were isolated by filtration, washed with ether (2 × 2 mL), and dried to leave a dull yellow powder (138 mg, 89%), which was >95% pure as shown by ^{1}H NMR. Recrystallization from a mixture of dichloromethane and ether afforded tan microcrystals that contained 1.0 equiv dichloromethane of crystallization which is not removed in vacuo, as shown by ^{1}H NMR. ^{1}H NMR ($\mathrm{CD_2Cl_2}$): δ 3.4 (v br, 3, axial Me of $\mathrm{WMe_4}$), 2.60 and 2.27 (m, 2 each, $\mathrm{CH_2CH_2}$), 2.09, 2.06, 2.05, and 1.99 (s, 6 each, $Me_4\mathrm{C_5CH_2CH_2C_5}Me_4$), 1.65 (br, 9, equatorial methyl groups of $\mathrm{WMe_4}$), 0.16 (s, 3, $\mathrm{WMe(CO)_3}$). ^{19}F NMR ($\mathrm{CD_2Cl_2}$): δ 72.81 (d, J_{FP} = 719, $\mathrm{PF_6}$). IR ($\mathrm{CH_2Cl_2}$), cm^{-1}: 2002 s, 1905 s br [ν(CO)]. Anal. Calcd for $\mathrm{W_2C_{29}H_{45}PCl_2O_3F_6}$ (includes 1.0 $\mathrm{CH_2Cl_2}$ of crystallization): C, 33.97; H, 4.42; F, 11.12; Cl, 6.92. Found: C, 34.26; H, 4.43; F, 11.28; Cl, 7.41.

[$\mathrm{WCl_4}$]$_2$(η^5,η^5-$\mathrm{Me_4C_5CH_2CH_2C_5Me_4}$). [$\mathrm{WMe(CO)_3}$]($\eta^5$-$\mathrm{Me_4C_5CH_2CH_2C{\equiv}CMe}$) (3.34 g, 7.10 mmol) was dissolved in dichloromethane (40 mL) in a 100-mL Schlenk flask and cooled to ~0 °C. $\mathrm{W(C_3Me_3)Cl_3}$[7] (1.76 g, 4.74 mmol) was added with stirring, and the mixture was allowed to warm to room temperature. An orange precipitate formed, and after 60 min, the mixture was cooled to ~0 °C. $\mathrm{PCl_5}$ (6.0 g, 28.8 mmol) was added with stirring, and the suspension was allowed to warm to room temperature. The mixture was refluxed for 46 h under the pressure of a mercury bubbler (860 Torr). The dark suspension was allowed to cool, and the precipitate was collected by filtration. The solids were washed well with dichloromethane (5 × 12 mL) and dried in vacuo to an orange-brown powder. This powder was combined with $\mathrm{PCl_5}$ (2.03 g, 9.7 mmol) in chloroform (40 mL) and refluxed with stirring for 40 h. The suspension was allowed to cool, and solids were collected by filtration. [The finely divided powder caused filtration to be very slow.] The solids were transferred to a flask and stirred with dichloromethane (25 mL) for 5 min. The orange solids were isolated by filtration, washed with dichloromethane (2 × mL) and dried in vacuo to an orange powder (3.38 g, 78%). The product is insoluble in organic solvents, as it most likely has an oligomeric or polymeric structure due to intermolecular bridging chlorides. Chlorination was considered to be complete as an IR spectrum exhibited no ν(CO) signals. The product could also be obtained from similar reaction of $\mathrm{PCl_5}$ with the dichloromethane reaction solution of [$\mathrm{WMe(CO)_3}$](η^5-$\mathrm{Me_4C_5CH_2CH_2C{\equiv}CMe}$) and $\mathrm{Cl_3W(C_3Me_3)}$, after separating the precipitate of [$\mathrm{WCl_4}$]($\mathrm{Cp^2}$)-[$\mathrm{WMe(CO)_3}$]. IR (Nujol), cm^{-1}: 1070 w, 1016 s [ν($\mathrm{C_5}$ ring)].

[$\mathrm{WMe_4}$]$_2$(η^5,η^5-$\mathrm{Me_4C_5CH_2CH_2C_5Me_4}$). A 2.8 M solution of MeMgCl (2.1 mL, 5.88 mmol) was diluted to 8 mL with THF and cooled to ~0 °C. [$\mathrm{WCl_4}$]$_2$(η^5,η^5-$\mathrm{Me_4C_5CH_2CH_2C_5Me_4}$) (0.48 g, 0.81 mmol) was added with stirring, and a dark yellow suspension developed upon warming to room temperature. After 3 h, the yellow precipitate was collected by filtration, washed with a THF/ether mixture (1:1, 2 × 4 mL), and dried in vacuo. Extraction with dichloromethane (~30 mL) and recrystallization from this solution at −30 °C afforded analytically pure orange microcrystals (0.20 g from two crops, 48%): ^{1}H NMR ($\mathrm{CD_2Cl_2}$, $w_{1/2}$ values in parentheses): δ 44 (1170 Hz) and 36 (980 Hz) (v v br, $\mathrm{C_5Me_4}$), 18.5 (510 Hz) (v v br, $\mathrm{CH_2CH_2}$). EPR ($\mathrm{CD_2Cl_2}$, 25 °C): g = 2.01; $w_{1/2}$ = 210 (similar to the EPR data of $\mathrm{WCp^*Me_4}$[10]). Anal. Calcd for $\mathrm{W_2C_{28}H_{52}}$: C, 44.46; H, 6.93. Found: C, 44.04; H, 6.90.

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Registry No. **1**, 102342-00-7; **2**, 120905-76-2; **3**, 120905-77-3; **4**, 120905-78-4; **5**, 120905-79-5; **6**, 120905-80-8; **7**, 120905-81-9; **8**, 120905-83-1; **9**, 120905-84-2; **10**, 120905-85-3; **11**, 120906-13-0; **12** (isomer 1), 120905-86-4; **12** (isomer 2), 120905-87-5; **12** (isomer 3), 120905-88-6; (**12**)($\mathrm{PF_6}$) (isomer 1), 120905-90-0; (**12**)($\mathrm{PF_6}$) (isomer 3), 120905-94-4; **13** (isomer 1), 120905-95-5; **13** (isomer 2), 120905-96-6; **13** (isomer 3), 120905-97-7; **14**, 120905-98-8; **15**, 120905-99-9; **16**, 120906-11-8; **17**, 120906-00-5; **18**, 120906-01-6; **19**, 120906-03-8; $\mathrm{HC_5Me_4(CH_2CH_2C{\equiv}CMe)}$ (isomer 1), 120905-72-8; $\mathrm{HC_5Me_4(CH_2CH_2C{\equiv}CMe)}$ (isomer 2), 120905-74-0; $\mathrm{HC_5Me_4(CH_2CH_2C{\equiv}CMe)}$ (isomer 3), 120905-75-1; $\mathrm{LiC_5Me_4(CH_2CH_2C{\equiv}CMe)}$, 120905-73-9; [$\mathrm{Rh(CO)_2Cl}$]$_2$, 14523-22-9; [$\mathrm{WCl_4}$]($\eta^5,\eta^5$-

$Me_4C_5CH_2CH_2C_5Me_4)[RhCl_2]$, 120906-04-9; PMe_3, 594-09-2; $[WH_5(PMe_3)](\eta^5,\eta^5\text{-}Me_4C_5CH_2CH_2C_5Me_4)\{[RhMe(CO)(PMe_3)][O_3SCF_3]\}$, 120906-06-1; $[FeCp_2][PF_6]$, 11077-24-0; $Co_2(CO)_8$, 10210-68-1; $WCp^*Me(CO)_3$, 34807-90-4; $W(CO)_6$, 14040-11-0; $[WMe(CO)_3](\eta^5\text{-}Me_4C_5CH_2CH_2C{\equiv}CMe)$, 120906-07-2; $[WCl_4(PMe_3)](\eta^5,\eta^5\text{-}Me_4C_5CH_2CH_2C_5Me_4)[WMe(CO)_3]$, 120906-08-3; $[WCl_4]_2(\eta^5,\eta^5\text{-}Me_4C_5CH_2CH_2C_5Me_4)$, 120906-09-4; $[WMe_4]_2(\eta^5,\eta^5\text{-}Me_4C_5CH_2CH_2C_5Me_4)$, 120906-10-7.

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Electronic Structure of Piano-Stool Dimers. 8. Electronically Induced Conformational Changes in High-Valent Bimetallic Chalcogen Complexes of the Type $[CpML]_2(\mu\text{-}L)_2$ (M = Mo, Re; L = S, O)[1]

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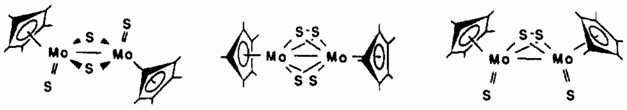
Fenske–Hall molecular orbital calculations have been applied to a series of bimetallic chalcogen complexes that adhere to the general formula $Cp_2M_2L_4$, where M = Mo, Re and L = O, S. In the case of M = Mo and L = S three geometric isomers were considered: $[CpMoS]_2(\mu\text{-}S)_2$ (**1**), $[CpMo]_2(\mu\text{-}S)_2(\mu\text{-}S_2)$ (**2**), and $[CpMoS]_2(\mu\text{-}S_2)$ (**3**). Series of calculations were performed in order to create a potential surface modeling an isomerization pathway among the three isomers. It was found that the conversion from **1** to **2** is a photochemically allowed process, whereas the conversion from **2** to **3** is allowed thermally. In the related oxo compound $[CpMoO]_2(\mu\text{-}O)_2$ (**4**), the reason for the puckering of the central Mo_2O_2 core was found to be due to a more favorable Mo–(μ-O) π interaction in the slightly folded geometry. In addition, folding the μ-oxo ligands of **4** toward the cis Cp rings, rather than away from the Cp rings in a sterically less congested environment, was found to be the electronically preferred geometry. Further puckering of the μ-oxo ligands of **4** to form a μ-peroxo structure was calculated to be a significantly higher energy process than the same distortion coordinate associated with the sulfide analogue. Calculations on the d^2–d^2 complex $[CpReO]_2(\mu\text{-}O)_2$ (**5**) at Re–Re distances varying from 2.74 to 3.54 Å indicate the most stable configuration to be at 3.14 Å. This stable geometry at 3.14 Å appears to be the result of the generation of two nonbonding, Re-based orbitals that are then able to hold the four metal-based electrons. At both longer and shorter Re–Re distances, the μ-oxo ligands destabilize one of the two nonbonding orbitals to generate a high-energy HOMO.

Discrete bimetallic organotransition-metal chalcogen complexes have recently been the subject of extensive research. Compounds of this type represent a link between ionic, solid-state metal chalcogenides and low-valent organometallic systems. Of particular interest are sulfur-containing species of this type that serve as models for heterogeneous desulfurization catalysts used in the purification of petroleum products.[3,4] An interesting series of bimetallic chalcogen complexes is that which adheres to the general formula $(\eta^5\text{-}C_5R_5)_2M_2L_4$, where L = O, S. Crystallographically characterized members of this high-valent piano-stool dimer series have been prepared for a variety of transition metals including V,[5] Cr,[6] Mo,[7–11] Re,[12] Fe,[13,14] and Co.[14] Not surprisingly, the structures of these compounds are highly dependent upon the oxidation state and corresponding electronic requirements of the metal. Moreover, even within the series of Mo complexes where L = S, three different structure types have been observed, viz. $[Cp^*MoS]_2(\mu\text{-}S)_2$ (**1**), $[Cp^*Mo]_2(\mu\text{-}S)_2(\mu\text{-}S_2)$ (**2**), and $[Cp^*MoS]_2(\mu\text{-}S_2)$ (**3**) ($Cp^* = \eta^5\text{-}C_5Me_5$), two of which (**1**, **2**) have been characterized crystallographically.[10,11] These three isomers are illustrated in A. The chemistry of these species is also relevant to the understanding of the coordination of sulfur ligands to molybdenum in biological systems.[15,16] The tetraoxo analogues of this system are also known for the metals Cr, Mo, and Re, and in each case their structures resemble the basic structure of **1**. To date, there has been no evidence for peroxo analogues of structure types **2** and **3** in the piano-stool dimer class.



1 **2** **3**

A

Because this series of compounds displays such a plethora of structure types and alternating metal d counts, and because of its close relationship to important heterogeneous and homogeneous systems, the need for a thorough understanding of the electronic structure and bonding operating within this system is obvious. We have found previously, in calculational treatments of piano-stool dimers containing π-acid ligands, that the Fenske–Hall method provides reliable results for such complexes and can be used to explain certain anomalous reactivity patterns as well as conformational preferences in these low-valent systems.[1,17,18] In this contribution we have extended this approach to include the high-valent bimetallic series $Cp_2M_2L_4$, where M = Mo, L = S, O and M = Re, L = O. These results will be used to examine

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