Heterobimetallic Complexes Connected by Peralkylated Cyclopentadienyl Rings

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Received January 6, 1987

Heterobimetallic complexes can be prepared in which the metals (tungsten and rhodium or cobalt) are linked by a ligand system of the type η^5,η^5-$C_5Et_4CH_2CH_2C_5Me_4$ (Cp^2). [W(O-*t*-Bu)O_2](Cp^2)[Rh$(CO)_2$] (1) was prepared by treating the tungstacyclobutadiene complex W(C_3Et_3)($OCMe_2CMe_2O$)(O-*t*-Bu) with Rh(η^5-$C_5Me_4CH_2CH_2C{\equiv}CEt$)$(CO)_2$. The best route to the analogous cobalt complex (2) consists of the reaction between [W(O-*t*-Bu)O_2](η^5-$C_5Et_4CH_2CH_2C_5Me_4H$) (3, obtained as a mixture of isomers of the C_5Me_4H ring) and $Co_2(CO)_8$ in neat *tert*-butylethylene. Addition of 2 equiv of Cl_2 to 1 yields [WO_2Cl](Cp^2)[$RhCl_2$] (4). Treatment of 4 with 2 equiv of PCl_5 yields [WCl_4](Cp^2)[$RhCl_2$] (5), a soluble adduct of which, [W(PMe_3)Cl_4](Cp^2)[Rh(PMe_3)Cl_2] (6), can be obtained upon addition of PMe_3. Treating 6 with excess dimethylzinc yields [WMe_4](Cp^2)[Rh(PMe_3)Me_2], which upon reaction with CO at 1000 psi yields [W$(CO)_3$Me](Cp^2)[Rh(PMe_3)Me_2].

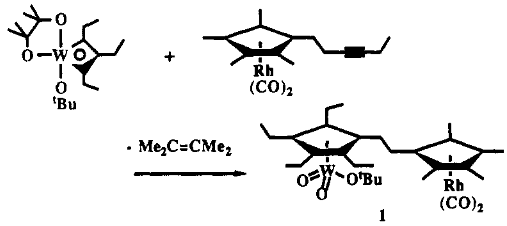
Introduction

Bimetallic complexes that contain cyclopentadienyl rings linked by one or more bridging atoms are relatively rare. The most common type contains C_5H_4 rings linked by $SiMe_2$[1] or CH_2[2] groups. Other reported bridging groups include CMe_2CMe_2,[3] $CHNMe_2CHNMe_2$,[4] linked azulenyl[5] and related[6] systems, *m*-xylyl,[1b,7] and —C≡C—.[8] No examples of bimetallic complexes containing peralkylated cyclopentadienyl rings have been reported, although permethylated rings connected by $SiMe_2$[9] or CH_2CH_2[10] groups have been prepared (the latter in low yield) and bound to a single metal. Heterobimetallic complexes containing linked cyclopentadienyl complexes are unknown, in part probably because it is inherently difficult to add one metal selectively to one ring and a different metal to the second.

The relatively recent discovery that peralkylated cyclopentadienyl tungsten complexes could be prepared by treating a tungstacyclobutadiene complex with an acetylene[11] opened up the possibility of preparing ditungsten complexes or heterobimetallic complexes containing one tungsten atom. Heterobimetallic complexes containing linked cyclopentadienyl rings would be unique and inherently interesting as a result of the possibility that reactions could become favorable that would not be favorable in analogous systems consisting of a mixture of the two analogous (unlinked) complexes. Here we report in detail the preparation of tungsten/rhodium and tungsten/cobalt bimetallics containing the η^5,η^5-$C_5Et_4CH_2CH_2C_5Me_4$ ligand and some chemistry of the tungsten/rhodium system. A portion of this work has appeared in preliminary form.[12]

Results and Discussion

The preparation of [W(O-*t*-Bu)O_2](Cp^2)[Rh$(CO)_2$] (1; Cp^2 = η^5,η^5-$C_5Et_4CH_2CH_2C_5Me_4$; the tungsten is connected to the C_5Et_4 end of the ligand system) is shown in eq 1.



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(1)

It had been known that the tungstacyclobutadiene complex W(C_3Et_3)($OCMe_2CMe_2O$)(O-*t*-Bu) reacts cleanly with internal acetylenes RC≡CR to give cyclopentadienyl complexes of the type W(η^5-$C_5Et_3R_2$)(O-*t*-Bu)O_2[11] and with the diyne $EtC{\equiv}CCH_2CH_2C{\equiv}CEt$ to give analogous ditungsten complexes linked by a CH_2CH_2 unit.[13] The reaction shown in eq 1 is also quite clean. Although we originally obtained 1 only as an orange oil,[12] we now find that it can be obtained in crystalline form in 67% yield if the reaction is carried out on a sufficiently large scale with Rh(η^5-$C_5Me_4CH_2CH_2C{\equiv}CEt$)$(CO)_2$ that has been purified by column chromatography on alumina (see Experimental Section).

The ^{1}H and ^{13}C NMR spectra of 1 are shown in Figure 1. In each case there is no feature that is not found in spectra of the analogous monomeric species; i.e., there is no evidence that the two ends of the molecule are connected through a bridging ligand other than the ring system itself. In Figure 1A the methylene protons of the two types of ethyl groups appear as two overlapping quartets at 2.5 ppm, even though each methylene group should actually contain inequivalent protons (four in all). The assignments shown in Figure 1B were made on the basis of chemical shifts in closely similar species; e.g., the signals at 124.1, 123.7, and 121.5 ppm are in the region where the ring carbon atom signals are found in the spectrum of [W(O-*t*-Bu)O_2]$_2$(η^5,η^5-$C_5Et_4CH_2CH_2C_5Et_4$)[13]

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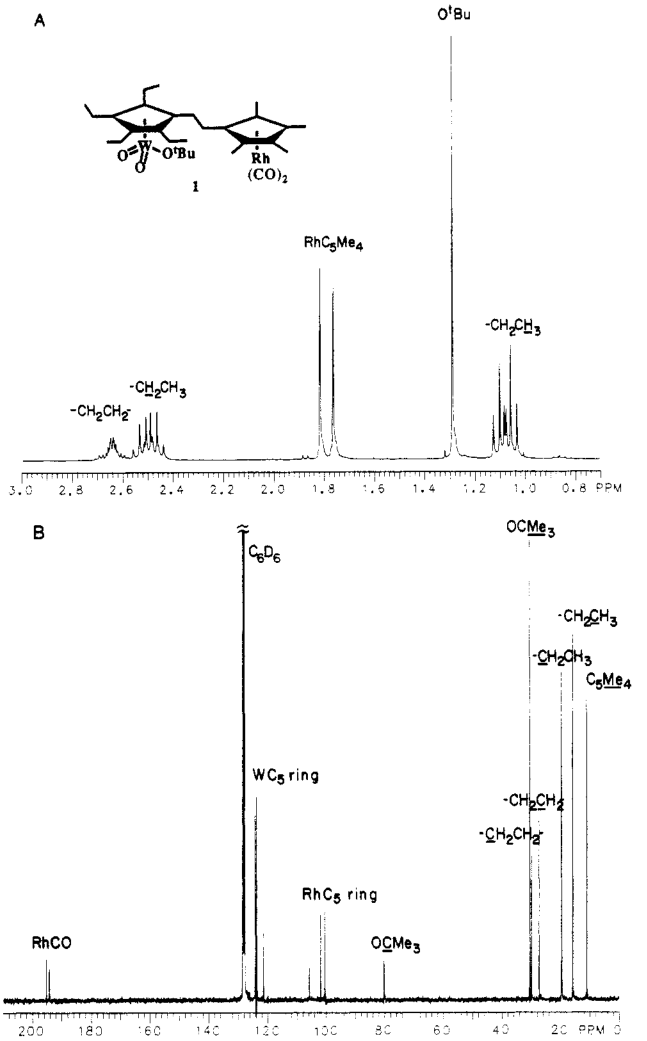
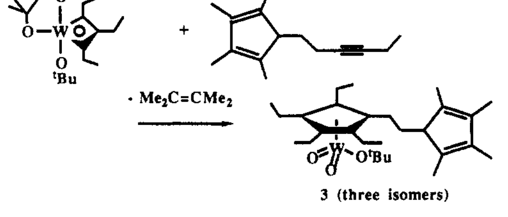


Figure 1. (A) ^{1}H NMR spectrum of 1 in C_6D_6. (B) ^{13}C NMR spectrum of 1 in C_6D_6.

(124.3, 124.0, and 120.8 ppm). The signals at 105.9, 101.9, and 100.4 ppm are found at virtually the same positions as those in the spectrum of Rh(η^5-$C_5Me_4CH_2CH_2C{\equiv}CEt$)(CO)$_2$, and each displays coupling to ^{103}Rh of ~6 Hz. The resonances at 19.3 and 15.5 ppm actually can be resolved into two each (at 19.4 and 19.2 ppm, 15.6 and 15.4 ppm); it is on this basis that they have been assigned (respectively) to the two methylene carbon atoms and two methyl carbon atoms of the two different types of ethyl groups on the C_5Et_4 ring.

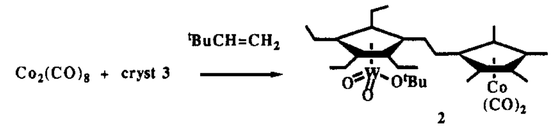
The reaction between W(C_3Et_3)($OCMe_2CMe_2O$)(O-*t*-Bu) and Co(η^5-$C_5Me_4CH_2CH_2C{\equiv}CEt$)(CO)$_2$ proceeds analogously to yield [W(O-*t*-Bu)O$_2$](Cp^2)[Co(CO)$_2$] (2). Unfortunately, we have not been able to prepare Co(η^5-$C_5Me_4CH_2CH_2C{\equiv}CEt$)(CO)$_2$ in adequate yield, and therefore only 10–20 mg of 2 has been prepared in this manner. A much better route, and one that has the potential of greater generality, begins with the reaction shown in eq 2. Three isomers of 3 are possible, depending on what carbon atom the ring proton is bound to. In fact, the ^{1}H NMR spectra of crude 3 are extremely complex. At least some of this complexity could result from the presence of two or more of these isomers. Only one white, microcrystalline compound can be isolated from the reaction mixture in 35–40% yield. Its ^{1}H NMR spectrum is somewhat simpler than that of the crude mixture and consistent with the proposal that the crystalline product contains only two isomers of 3. The ratio of the two isomers varies from experiment to experiment. The major one appears to be one of the two unsymmetric possibilities while the minor component appears to be the symmetric species, the one in which the proton is bound to the same carbon atom as a carbon atom in the CH_2CH_2 link. Recrystallization of the mixture of isomers of 3 yields a mixture that contains only ~10% of the symmetric isomer, but the yield of recovered 3 is not high. The fact that isolated, crystalline 3 is a mixture of two isomers does not appear to influence the course of the next step (see below); there is no reason to expect that it would. However, use of *crude* 3 in the next step results in a poor yield of 2, a fact that suggests there *may* be a significant amount of some species present in crude 3 other than the three isomers we would expect.



(2)

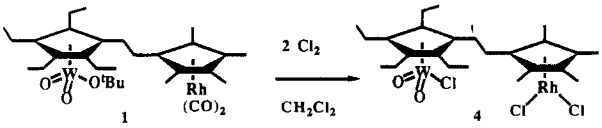
3 (three isomers)

On the basis of the reported reaction of $Co_2(CO)_8$ with excess pentamethylcyclopentadiene to give Co(η^5-C_5Me_5)(CO)$_2$,[14] we attempted to prepare 2 by the reaction between crystalline 3 and $Co_2(CO)_8$. The reaction between 3 and 0.5 equiv of $Co_2(CO)_8$ does yield 2, but only in ~65% yield. We suspected that some of the double bonds in the unbound ring of 3 were being hydrogenated in the process of forming the cyclopentadienyl cobalt complex 2. Therefore we tried using *tert*-butylethylene as the *solvent* in the reaction between $Co_2(CO)_8$ and a stoichiometric amount of crystalline 3 in the hope that *tert*-butylethylene would be hydrogenated selectively.[15] This approach appears to work well (eq 3). 2 can be isolated readily as red plates in a yield of ~80%. Its ^{1}H and ^{13}C NMR spectra and its IR spectrum are virtually identical with those of 1; again there is no evidence that the two ends of the molecule are interacting in any fashion except through the Cp^2 ligand.



(3)

So far we have found it to be relatively difficult to control reactions of species such as 1 and 2 at both metals simultaneously. We have had some success in reactions involving 1. As shown in eq 4, 1 reacts with 2 equiv of chlorine gas to give an orange powder that is soluble in dichloromethane, but not other common solvents. All attempts to obtain a crystalline sample have failed, but a powder sample analyzes correctly for C, H, and Cl. The formulation of 4 is also fully consistent with its ^{1}H NMR



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[15] It has been known for several years that *tert*-butylethylene will act as a sink for molecular hydrogen. See: (a) Crabtree, R. H.; Felkin, H.; Morris, G. E. *J. Organomet. Chem.* **1977**, *141*, 205. (b) Baudry, D.; Ephritikhine, M.; Felkin, H. *J. Chem. Soc., Chem. Commun.* **1980**, 1243. (c) Crabtree, R. H.; Mihelcic, J. M.; Quirk, J. M. *J. Am. Chem. Soc.* **1979**, *101*, 7738.

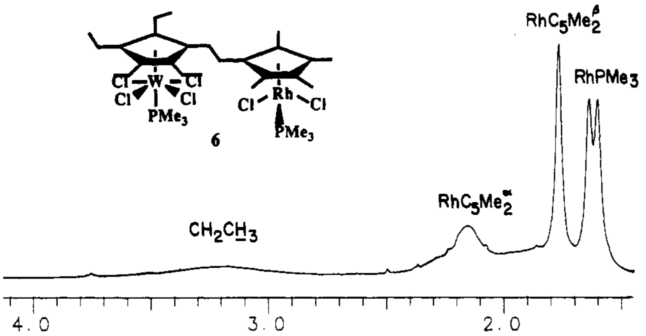
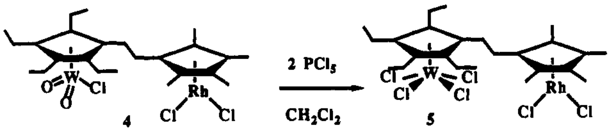


Figure 2. The partial ^{1}H NMR spectrum of **6** in CD_2Cl_2.

spectrum and its IR spectrum. It is clear that the *tert*-butoxide ligand and the carbonyl ligands are absent and that the two oxo ligands are still present (strong, sharp peaks at 900 and 939 cm^{-1}).

Further reaction of **4** with PCl_5 gives rise to a totally insoluble orange powder whose IR spectrum shows no evidence of $\nu(W{=}O)$ peaks. Since an analogous reaction between $W(\eta^5\text{-}C_5Et_5)O_2Cl$ and PCl_5 has been shown to give rise to $W(\eta^5\text{-}C_5Et_5)Cl_4$ virtually quantitatively[16] and since $M(\eta^5\text{-}C_5Me_5)(CO)_3Me$ (M = Mo or W) has been shown to react with PCl_5 to give $M(\eta^5\text{-}C_5Me_5)Cl_4$ (probably a dimer),[17] we propose that the insoluble orange powder is the perchloride complex **5** shown in eq 5. Undoubtedly it is a polymer, since neither $W(\eta^5\text{-}C_5Me_5)Cl_4$ nor $Rh(\eta^5\text{-}C_5Me_5)Cl_2$ is monomeric. The best evidence that **5** is what we believe it to be is its reaction with 2 equiv of PMe_3 to give brown, crystalline **6** (eq 6) in 85–90% crude yield. The EPR spectrum of **6** in dichloromethane shows a signal at g = 1.89 with a width at half-height of 27 G that is indistinguishable from the EPR signal for $W(\eta^5\text{-}C_5Me_5)Cl_4(PMe_3)$.[17,18] It also has an ^{1}H NMR spectrum, in spite of the presence of the W(V) d^1 center. Since this spectrum is not routine and the discussion is somewhat tedious, we will first discuss the spectra of two models.



(5)

$$[WCl_4](Cp^2)[RhCl_2] \xrightarrow{2\ PMe_3} [W(PMe_3)Cl_4](Cp^2)[Rh(PMe_3)Cl_2] \quad (6)$$

The ^{1}H NMR spectrum of $W(\eta^5\text{-}C_5Me_5)Cl_4(PMe_3)$ shows two broad signals ($w_{1/2} \approx 500$ Hz) at −5.75 and −7.42 ppm that can be ascribed to the $\eta^5\text{-}C_5Me_5$ and PMe_3 ligands, respectively, on the basis of their relative intensities.[18] $W(\eta^5\text{-}C_5Et_5)Cl_4(PMe_3)$ was prepared from $W(\eta^5\text{-}C_5Et_5)(O\text{-}t\text{-}Bu)O_2$[11] as shown in eq 7. An ^{1}H NMR spectrum in

$$W(\eta^5\text{-}C_5Et_5)(O\text{-}t\text{-}Bu)O_2 \xrightarrow[2.\ PMe_3]{1.\ 2.5\ PCl_5/CH_2Cl_2} W(\eta^5\text{-}C_5Et_5)Cl_4(PMe_3) \quad (7)$$

CD_2Cl_2 consists of progressively broader peaks at 2.60 ($w_{1/2} \approx 60$ Hz), 0.05 ($w_{1/2} \approx 300$ Hz), and −8.0 ppm ($w_{1/2} \approx 650$ Hz) that can be assigned on the basis of $w_{1/2}$ and by comparison with the spectrum of $W(\eta^5\text{-}C_5Me_5)Cl_4(PMe_3)$[18] to the CH_2CH_3, CH_2CH_3, and PMe_3 protons, respectively.

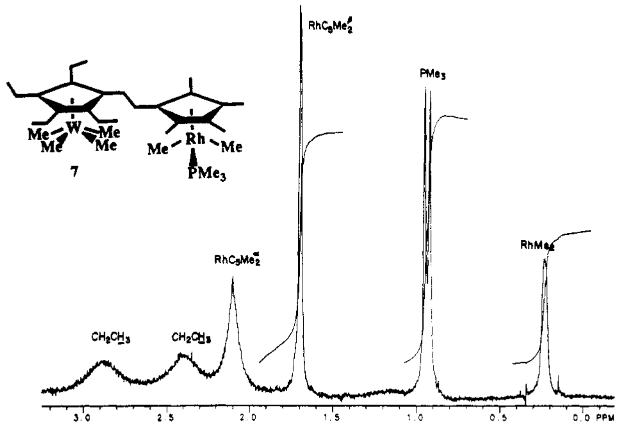
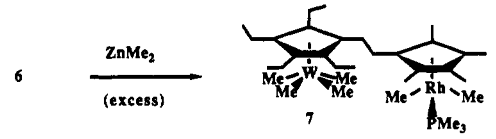


Figure 3. The partial ^{1}H NMR spectrum of **7** in C_6D_6.

The partial ^{1}H NMR spectrum of **6** is shown in Figure 2. Most signals can be assigned on the basis of their width and chemical shift. We assign the two at 1.62 (d) and 1.77 ppm to the $RhPMe_3$ and $RhC_5Me^{\beta}_2$ protons (where Me^{β}_2 refers to the two methyl groups furthest away from the C_2H_4 bridge). The signal for the two Me^{α} groups is probably that at ~2.15 ppm. The resonance for the PMe_3 protons can be observed at −7.7 ppm ($w_{1/2} \approx 400$ Hz; not shown in Figure 2), and what is probably the resonance for one or both types of CH_2CH_3 protons can be observed at ~3.2 ppm ($w_{1/2} \approx 200$ Hz). Resonances for the methylene protons in the two types of ethyl groups and the C_2H_4 bridge, however, are not as obvious. In addition to broad features in the part of the spectrum shown in Figure 2, there is a relatively weak and broad resonance at −1.8 ppm. Therefore we feel that there is too much uncertainty involved to allow any further assignments to be made. Nevertheless the spectrum is useful as a means of identifying **6** since it does not appear to change significantly with concentration in the range of 10–50 mg/0.5 mL of CD_2Cl_2.

Alkylation of **6** with excess dimethylzinc gave **7** as ether-soluble yellow needles (eq 8). (The reaction between



(8)

$W(\eta^5\text{-}C_5Me_5)(PMe_3)Cl_4$ and excess $ZnMe_2$ to give $W(\eta^5\text{-}C_5Me_5)Me_4$ has been reported.[17,18]) The ^{1}H NMR spectrum of $W(\eta^5\text{-}C_5Me_5)Me_4$ does not show any resonance that can be ascribed to the methyl groups directly attached to W, but a resonance for the $\eta^5\text{-}C_5Me_5$ methyl groups can be observed at 39.70 ppm ($w_{1/2} \approx 580$ Hz).[18] In the ^{1}H NMR spectrum of $W(\eta^5\text{-}C_5Et_5)Me_4$ a broad signal ($w_{1/2} \approx 600$ Hz) is observed at 18.5 ppm that can be assigned to the methylene protons and a narrower signal ($w_{1/2} \approx 35$ Hz) at 2.68 ppm that can be ascribed to the methyl protons in the ethyl groups. The resonances in the spectrum of **7** (Figure 3) therefore can be assigned with some degree of certainty. What is not shown in Figure 3 is a very broad ($w_{1/2} \approx 1000$ Hz), unsymmetric peak at ~17 ppm that we assign to the several types of methylene protons in the ring ethyl groups. Most of the remaining resonances are assigned as shown in the figure; the resonances at 2.4 and 2.9 ppm are assigned to the two different methyl groups in the ethyl groups on the basis of their similar widths and chemical shifts (cf. $W(\eta^5\text{-}C_5Et_5)Me_4$ above). Again we cannot locate signals for the methylene protons in the C_2H_4 bridge with any degree of certainty, although in this case some of the intensity at 17 ppm could be ascribed to at

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[16] Murray, R. C., unpublished observations.

[17] Murray, R. C.; Blum, L.; Liu, A. H.; Schrock, R. R. *Organometallics* **1985**, *4*, 953.

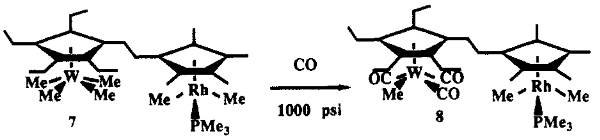
[18] Liu, A. H.; Murray, R. C.; Dewan, J. C.; Santarsiero, B. D.; Schrock, R. R., submitted for publication.

Table I. Chemical Shift (ppm) and Width (Hz) of Assignable Resonances of Ligands Bound to W in the Spectra of 6, 7, and Model Compounds in CD_2Cl_2

compd	CH_2CH_3	CH_2CH_3	PMe_3
$W(\eta^5\text{-}C_5Et_5)Cl_4(PMe_3)$	2.60 (60)	0.05 (300)	−8.0 (650)
6	3.18 (250)		−7.7 (400)
$W(\eta^5\text{-}C_5Et_5)Me_4$	2.68 (35)	18.5 (600)	
7	2.88 (65) 2.40 (65)	~17 (1000)	

least one set of them. For convenience some of the relevant assignable resonances in **6**, **7**, and models are listed in Table I.

We have shown that **7** reacts with carbon monoxide cleanly at 1000 psi as shown in eq 9. (At 40 psi the reaction is very slow, but **8** is still the primary product.) This now completely diamagnetic species has ^1H and ^{13}C NMR spectra and an IR spectrum that are totally consistent and analogous to those observed for $W(\eta^5\text{-}C_5Me_5)(CO)_3Me$ and $Rh(\eta^5\text{-}C_5Me_5)(PMe_3)Me_2$ separately. Since we also have observed that $W(\eta^5\text{-}C_5Me_5)Me_4$ reacts with CO under similar conditions to give $W(\eta^5\text{-}C_5Me_5)(CO)_3Me$,[16] the reaction shown in eq 9 probably does not involve the Rh center at all. The fate of the methyl ligands in either case has not yet been determined. Again we have no evidence that the Rh and W are connected in any way other than through the Cp^2 ligand.



(9)

Conclusion

We have shown that it is possible to prepare some heterobimetallic complexes containing the $\eta^5,\eta^5\text{-}C_5Et_4CH_2CH_2C_5Me_4$ ring system relatively straightforwardly. We will be exploring reactions of recently prepared trimethyltungstacyclobutadiene complexes[19] in an effort to prepare analogous, simpler $\eta^5,\eta^5\text{-}C_5Me_4CH_2CH_2C_5Me_4$ complexes. In addition to exploring the chemistry of W/Rh and W/Co complexes, we hope to prepare and study heterobimetallic species containing tungsten and metals other than rhodium or cobalt (e.g., ruthenium). Eventually we hope to collect a set of reactions that will answer the question as to whether there is any significant advantage to tethering metals together, i.e., are there any types of reactions of such bimetallic species that could not be competitive in a system involving the analogous (unlinked) complexes?

Experimental Section

General Details. All experiments were performed under a nitrogen atmosphere in a Vacuum Atmospheres HE43-2 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. 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.

NMR data are listed in parts per million relative to Me_4Si for ^1H and ^{13}C 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.

Preparation of Compounds. $HC_5Me_4(CH_2CH_2C{\equiv}CEt)$. A solution of *tert*-butyllithium (26.2 mL of a 1.7 M solution in pentane) was added dropwise over 30 min to a solution of 1-iodo-3-hexyne[20] (4.63 g, 22.3 mmol) in ether (100 mL) at −78 °C under argon. After the solution was stirred for an additional 30 min, 2,3,4,5-tetramethyl-2-cyclopentenone (3.04 g, 22.0 mmol) was added dropwise over 10 min at −78 °C. The mixture was allowed to warm to room temperature and was poured onto a mixture of concentrated hydrochloric acid (30 mL) and ice (100 g). After the hydrolysis reaction was shaken for 10 min, the organic layer was separated and the aqueous layer extracted with 3 × 30 mL of ether. The combined organic layers were neutralized by washing with saturated sodium bicarbonate solution and dried over sodium sulfate. After filtration and evaporation of the ether, the resultant oil was distilled at 1 torr and 82–85 °C, yielding a yellow oil (3.3 g, 73%). The product probably is a mixture of the three possible isomers. ^1H NMR: δ 2.65 (m), 2.54 (q), and 2.41 (q) (ring proton in three isomers); 2.17, 1.90, and 1.66 (m, $CpCH_2CH_2C{\equiv}CCH_2CH_3$); 1.84, 1.81, 1.79, 1.76, and 1.74 (s, ring Me groups); 1.08 (m, $C{\equiv}CCH_2CH_3$), 1.00 (d, aliphatic ring methyl group). ^{13}C NMR: δ 141.2, 139.4, 138.4, 138.0, 137.9, 136.2, 135.8, 134.6, 134.2, and 133.6 (s, olefinic carbons); 81.8, 81.6, 81.3, 80.3, 79.9, and 79.6 (s, alkyne carbons); 56.0, 51.9, and 49.8 (d, J = 122, 120, and 122, respectively, aliphatic ring carbons); 28.2, 26.7, 26.2, 24.2, and 20.5 (t, $CH_2CH_2C{\equiv}CCH_2CH_3$); 14.6, 14.5, 14.3, 14.2, 13.7, 13.6, 12.9, 11.8, 11.7, 11.2, and 11.1 (q, methyl groups).

$LiC_5Me_4(CH_2CH_2C{\equiv}CEt)$. *n*-Butyllithium (6.5 mL of 2.5 M solution in hexane) was added to a solution of $HC_5Me_4(CH_2CH_2C{\equiv}CEt)$ (3.31 g, 16.4 mmol) in ether (50 mL) that had been cooled to −20 °C. The mixture was allowed to warm to room temperature, and the white precipitate was collected by filtration and dried in vacuo (yield 3.03 g, 89%). ^{1}NMR (THF-d_8): δ 2.31, 2.04, and 1.78 (m, 2 each, $C_5CH_2CH_2C{\equiv}CCH_2Me$); 1.66 (s, 12, C_5Me_4); 1.00 (t, 3, CH_2CH_3). $^{13}C\{^1H\}$ NMR (THF-d_8): δ 111.3, 106.6, and 106.0 (ring carbons); 81.7 and 80.4 (alkyne carbons); 27.7 and 22.8 ($C_5CH_2CH_2$); 14.9 and 13.1 (CH_2CH_3); 11.0 and 10.8 (C_5Me_4).

$Rh(CO)_2(\eta^5\text{-}Me_4C_5CH_2CH_2C{\equiv}CEt)$. $[RhCl(CO)_2]_2$ (0.82g, 2.1 mmol) was dissolved in THF (25 mL) at −20 °C, and $LiC_5Me_4(CH_2CH_2C{\equiv}CEt)$ (0.88 g, 4.2 mmol) was added with stirring. The solution became dark as it warmed to room temperature, and after 20 min the THF was removed in vacuo. The resulting brown oil was extracted with pentane. The extracts were concentrated and placed on an alumina column (2.5 × 12 cm) made up in pentane. A broad orange band was eluted easily with pentane. The pentane was removed in vacuo to give an orange oil (1.21 g, 80%). ^1H NMR: δ 2.48 (t, 2, $C_5CH_2CH_2$); 2.18 (tt, 2, $C_5CH_2CH_2$); 2.00 (tq, 2, CH_2CH_3); 1.73 and 1.71 (s, 6 each, C_5Me_4); 0.98 (t, 3, CH_2CH_3). ^{13}C NMR: δ 194.8 (d, J_{CRh} = 84, CO); 106.0, 101.5, and 100.4 (d, $J_{CRh} \approx 6$, ring carbons); 82.2 and 78.9 (s, $C{\equiv}C$); 25.4 and 23.0 (t, CH_2CH_2); 14.4 (q, CH_2CH_3); 12.8 (t, CH_2CH_3); 11.0 and 10.9 (q, C_5Me_4). IR (in pentane, cm^{-1}): 2025 s, 1967 s [ν(CO)].

$[W(O\text{-}t\text{-}Bu)O_2](\eta^5,\eta^5\text{-}C_5Et_4CH_2CH_2C_5Me_4)[Rh(CO)_2]$ (1). $Rh(CO)_2(\eta^5\text{-}C_5Me_4CH_2CH_2C{\equiv}CEt)$ (1.15 g, 3.19 mmol) was added to a solution of $W(C_3Et_3)(OCMe_2CMe_2O)(O\text{-}t\text{-}Bu)$[11] (1.61 g, 3.21 mmol) in pentane (30 mL). After 24 h the solvent was removed in vacuo. Recrystallization from pentane at −40 °C yielded orange plates (1.65 g, 67%). ^1H NMR: δ 2.64 (m, 4, CH_2CH_2); 2.52 and 2.47 (q, 4 each, CH_2CH_3); 1.81 and 1.76 (s, 6 each, C_5Me_4); 1.29 (s, 9, $OCMe_3$); 1.10 and 1.06 (t, 6 each, CH_2CH_3); ^{13}C NMR: δ 194.9 (d, J_{CRh} = 82, CO), 124.1, 123.7, and 121.5 (s, W ring carbons); 105.9, 101.9, and 100.4 (d, $J_{CRh} \approx 6$, Rh ring carbons); 79.9 (s $OCMe_3$); 30.2 (q, $OCMe_3$); 29.6 and 26.8 (t, $C_5CH_2CH_2C_5$); 19.4 and 19.2 (t, CH_2CH_3); 15.6 and 15.4 (q, CH_2CH_3); 10.8 (q, C_5Me_4).

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IR (Nujol mull, cm^{-1}): 2021 s, 1965 s [ν(CO)]; 940 s, 900 s [ν(W=O)]; 915 s [ν(WO-*t*-Bu)]. Anal. Calcd for $WRhC_{30}H_{45}O_5$: C, 46.65; H, 5.87. Found: C, 46.71; H, 5.80.

$[WO_2Cl](\eta^5,\eta^5\text{-}C_5Et_4CH_2CH_2C_5Me_4)[RhCl_2]$ (4). $[W(O\text{-}t\text{-}Bu)O_2](\eta^5,\eta^5\text{-}C_5Et_4CH_2CH_2C_5Me_4)[Rh(CO)_2]$ (0.77 g, 1.00 mmol) was dissolved in dichloromethane (20 mL) in a 500-mL Schlenk flask. Chlorine gas (54 mL at 25 °C and 1 atm, 2.24 mmol) was injected via a gas-tight syringe into the closed flask through a septum. The solution became deep orange. After the solution was stirred for 30 min, excess chlorine was removed in vacuo. Solvent was removed in vacuo to yield an orange powder (0.65 g). ^1H NMR (CD_2Cl_2): δ 2.62 and 2.59 (q, 4 each, CH_2CH_3); 2.52 (m, 4, $C_5CH_2CH_2C_5$); 1.64 and 1.58 (s, 6 each, C_5Me_4); 1.36 and 1.29 (t, 6 each, CH_2CH_3). IR (Nujol mull, cm^{-1}): 939 s, 900 s (of equal intensity) [ν(W=O)]. The sample submitted for elemental analysis consisted of the crude product that had been rinsed several times with THF. Anal. Calcd for $WRhC_{24}H_{36}O_2Cl_3$: C, 38.45; H, 4.84; Cl, 14.19. Found: C, 38.22; H, 4.96; Cl, 14.51.

$[W(PMe_3)Cl_4](\eta^5,\eta^5\text{-}C_5Et_4CH_2CH_2C_5Me_4)[Rh(PMe_3)Cl_2]$ (6). PCl_5 (0.44 g, 2.1 mmol) was added to a stirred solution of $[WO_2Cl](\eta^5,\eta^5\text{-}C_5Et_4CH_2CH_2C_5Me_4)[RhCl_2]$ (0.63 g, 0.84 mmol) in dichloromethane (10 mL). The solution was refluxed for 15 h and then allowed to cool. The orange precipitate that had formed was collected by filtration, washed with dichloromethane (3 × 5 mL), and dried in vacuo. This highly insoluble orange powder is believed to have the composition $[WCl_4](\eta^5,\eta^5\text{-}C_5Et_4CH_2CH_2C_5Me_4)[RhCl_2]$ (0.63 g, 91%). The IR spectrum (Nujol mull) shows no ν(W=O) peaks. It was suspended in dichloromethane (25 mL), and PMe_3 (0.19 mL, 1.9 mmol) was added. After the solution was stirred for 3 h, it was filtered and the solvent was removed to leave a brown microcrystalline solid (crude yield, 0.64 g, 86%). This solid can be recrystallized from a mixture of dichloromethane and ether. ^1H NMR (CD_2Cl_2): δ 3.18 (br, CH_2CH_3); 2.15 (br, $RhC_5Me^{\alpha}{}_2$); 1.77 (br s, $RhC_5Me^{\beta}{}_2$); 1.62 (d, $J_{HP} = 8.4$, $RhPMe_3$), −7.7 (br, $WPMe_3$). Other resonances could not be assigned with certainty (see text). EPR (CH_2Cl_2, 25 °C): $g = 1.89$, $w_{1/2} = 27$ G (identical with the EPR of $(\eta^5\text{-}C_5Et_5)WCl_4(PMe_3)$). Anal. Calcd for $WRhC_{30}H_{54}Cl_6P_2$: C, 36.91; H, 5.58. Found: C, 36.38; H, 5.37.

$[WMe_4](\eta^5,\eta^5\text{-}C_5Et_4CH_2CH_2C_5Me_4)[Rh(PMe_3)Me_2]$ (7). $[W(PMe_3)Cl_4](\eta^5,\eta^5\text{-}C_5Et_4CH_2CH_2C_5Me_4)[Rh(PMe_3)Cl_2]$ (98 mg, 0.100 mmol) was suspended in toluene (7 mL), and the solution was cooled to −20 °C. Dimethylzinc (68 μL, 0.99 mmol) was added with stirring. The mixture was allowed to warm to room temperature, and after 90 min the excess dimethylzinc and toluene were removed in vacuo. The residue was extracted with pentane (15 mL), and the solvent was evaporated to leave a yellow solid. This solid was recrystallized from ether to give yellow needles (35 mg, 45%). ^1H NMR: δ ~17 (v v br, various CH_2 protons); 2.88 and 2.40 (br, CH_2CH_3); 2.10 (br, $RhC_5Me^{\alpha}{}_2$); 1.69 (s, $RhC_5Me^{\beta}{}_2$); 0.93 (br d, $J_{HP} = 9.3$, PMe_3); 0.23 (br s, $RhMe_2$). $^{31}P\{^1H\}$ NMR: δ 15.1 (d, $J_{PRh} = 171$). EPR (CH_2Cl_2, 25 °C): $g = 2.02$ (identical with that of $W(\eta^5\text{-}C_5Et_5)Me_4$). Anal. Calcd for $WRhC_{33}H_{63}P$: C, 50.97; H, 8.17. Found: C, 51.13; H, 8.29.

$[W(CO)_3Me](\eta^5,\eta^5\text{-}C_5Et_4CH_2CH_2C_5Me_4)[Rh(PMe_3)Me_2]$ (8). $[WMe_4](\eta^5,\eta^5\text{-}C_5Et_4CH_2CH_2C_5Me_4)[Rh(PMe_3)Me_2]$ (75 mg, 0.096 mmol) was dissolved in toluene (10 mL), and the solution was placed in a Parr pressure bomb. The bomb was cooled to −78 °C and pressurized with carbon monoxide to 1000 psi. The bomb was allowed to warm to −20 °C over 1 h, and the pressure was then released. Solvent was removed in vacuo, and the brown residue was dissolved in pentane and placed on a short column of alumina. Elution with pentane gave a pale yellow band. The solvent was removed from the yellow solution, and the residue was recrystallized from pentane/ether (1:1) to give light yellow needles (30 mg, 38%). ^1H NMR: δ 2.36 (m, 4, $C_5CH_2CH_2C_5$); 2.20 and 2.27 (m, 4 total, $CH_AH_BCH_3$); 2.00 (q, 4, CH_2CH_3); 1.69 and 1.65 (d, 6 each, $J_{HP} = 2.3$, C_5Me_4); 1.04 and 0.90 (t, 6 each, CH_2CH_3); 0.89 (d, 9, $J_{HP} = 9.0$, PMe_3); 0.45 (s, 3, $J_{HW} = 5.2$, WMe); 0.13 (dd, 6, $J_{HP} = 5.2$, $J_{HRh} = 2.5$, $RhMe_2$). ^{13}C NMR: δ 233.6 and 219.9 (s, W(CO)); 109.5, 109.1, and 107.3 (s, W ring carbons); 97.9, 96.9, and 96.8 (s, Rh ring carbons); 28.3 and 26.9 (t, $C_5CH_2CH_2C_5$); 19.2 and 19.0 (t, CH_2CH_3); 17.3 and 16.7 (q, CH_2CH_3); 15.2 (dq, $J_{CP} = 28.4$, PMe_3); 9.4 and 9.3 (q, C_5Me_4), −6.1 (ddq, J_{CRh} and J_{CP} = 28.3 and 16.2 (not respectively), $RhMe_2$), −24.3 (q, $J_{CW} = 31$, WMe). $^{31}P\{^1H\}$ NMR: δ 8.8 (d, $J_{PRh} = 170$). IR (in pentane, cm^{-1}): 1915 br, 2010 s [ν(CO)]. Anal. Calcd for $WRhC_{33}H_{54}O_3P$: C, 48.54; H, 6.67. Found: C, 48.73; H, 6.69.

$[W(O\text{-}t\text{-}Bu)O_2](\eta^5\text{-}C_5Et_4CH_2CH_2C_5Me_4H)$ (3). $W(C_3Et_3)(OCMe_2CMe_2O)(OCMe_3)$[11] (3.58 g, 7.14 mmol) was dissolved in pentane (40 mL). $HC_5Me_4(CH_2CH_2C{\equiv}CEt)$ (1.46 g, 7.21 mmol) was added. After 30 h the solvent was removed leaving a brown oil (2.5 g), which was dissolved in pentane (4 mL). Standing this solution at −40 °C yielded a white powder (1.70 g, 39%) consisting of a mixture of two of the possible three isomers. The mixture can be enriched in the major isomer by slow crystallization from a more dilute solution. ^1H NMR (major isomer): δ 2.8–2.4 (m, 13, CH_2CH_3, $C_5CH_2CH_2C_5$, and $C_4C(H)Me$); 1.79 and 1.74 (s, 3 and 6, respectively, C_5Me_4 groups); 1.29 (s, 9, $OCMe_3$); 1.18, 1.16, and 1.08 (t, 3, 3, and 6, respectively, $CHCH_3$); 1.02 (s, 3, C_4CHMe). ^1H NMR (minor isomer): δ 2.8–2.4 (m, 13, CH_2CH_3, $C_5CH_2CH_2C_5$, and $C_4C(H)CH_2CH_2$); 1.86 and 1.73 (6 each, C_5Me_4 groups); 1.23 (s, 9, $OCMe_3$); 1.15 and 1.05 (t, 6 each, CH_2CH_3). $^{13}C\{^1H\}$ NMR (mixture of two isomers): δ 141.4, 138.5, 136.7, 135.5, and 134.3 (free ring carbons); 124.2, 124.1, 123.8, 123.4, 122.6, and 122.1 (W ring carbons); 79.9 ($OCMe_3$); 56.6 and 49.6 ($\overline{C{=}C{-}\mathit{C}{-}C{=}C}$); 30.3 and 30.1 ($OCMe_3$); 28.9, 28.4, 27.7, and 20.1 ($C_5CH_2CH_2C_5$); 19.6, 19.9, and 19.3 (CH_2CH_3); 15.8 and 15.6 (CH_2CH_3); 14.2 (C_4CHMe); 11.9, 11.7, 11.3, and 11.1 (olefinic Me groups). IR (Nujol mull, cm^{-1}): 938 s, 900 s [ν(W=O)], 912 s [ν(WO-*t*-Bu)].

$[W(O\text{-}t\text{-}Bu)O_2](\eta^5,\eta^5\text{-}C_5Et_4CH_2CH_2C_5Me_4)[Co(CO)_2]$ (2). A crystalline sample of $[W(O\text{-}t\text{-}Bu)O_2][\eta^5\text{-}C_5Et_4CH_2CH_2C_5Me_4H)$ (1.54 g, 2.51 mmol) was dissolved in 3,3-dimethyl-1-butene (35 mL), and $Co_2(CO)_8$ (0.43 g, 1.26 mmol) was added. After the reaction mixture was stirred for 20 h, the solvent was removed leaving a dark red oil. This oil was dissolved in pentane (10 mL), and the solution was cooled to −40 °C to give red plates (1.49 g in two crops, 82%). ^1H NMR: δ 2.59 (m, 4, $C_5CH_2CH_2C_5$); 2.51 and 2.47 (q, 4 each, CH_2CH_3); 1.67 and 1.63 (s, 6 each, C_5Me_4); 1.28 (s, 9, $OCMe_3$); 1.10 and 1.06 (t, 6 each, CH_2CH_3). ^{13}C NMR: δ 208.2 (s, CO), 124.2, 123.6, and 121.1 (s, W ring carbons); 100.6, 97.5, and 96.4 (s, Co ring carbons); 79.9 (s, $OCMe_3$); 30.2 (q, $OCMe_3$); 28.2 and 27.0 (t, $C_5CH_2CH_2C_5$); 19.4 and 19.2 (t, CH_2CH_3); 15.6 and 15.5 (q, CH_2CH_3); 10.4 and 10.3 (q, C_5Me_4). IR (KBr pellet, cm^{-1}); 1990 s, 1930 s [ν(CO)]; 960 br, 896 s [ν(W=O)]; 922 s [ν(WO-*t*-Bu)]. Anal. Calcd for $WCoC_{30}H_{45}O_5$: C, 49.46; H, 6.23. Found: C, 49.61; H, 6.19.

$W(\eta^5\text{-}C_5Et_5)Cl_4$. $W(\eta^5\text{-}C_5Et_5)(O\text{-}t\text{-}Bu)O_2$[11] (0.52 g, 1.05 mmol) was added to a solution of PCl_5 (0.55 g, 2.64 mmol) in dichloromethane (10 mL), and the mixture was heated to reflux for 12 h. Solvent was removed in vacuo and the orange solid recrystallized from dichloromethane to yield orange crystals (0.41 g, 74%). EPR (CH_2Cl_2, 25 °C): $g = 1.92$, $w_{1/2} = 53$ G (identical with the EPR of $W(\eta^5\text{-}C_5Me_5)Cl_4$.[18]) Anal. Calcd for $WC_{15}H_{25}Cl_4$: C, 33.93; H, 4.75; Cl, 26.70. Found: C, 33.99; H, 4.99; Cl, 26.62.

$W(\eta^5\text{-}C_5Et_5)Cl_4(PMe_3)$. A solution of $W(\eta^5\text{-}C_5Et_5)Cl_4$ (0.19 g, 0.18 mmol) in dichloromethane (5 mL) was cooled to 0 °C, and PMe_3 (55 μL, 0.54 mmol) was added. The solution was allowed to warm to room temperature. After 30 min, the solvent was removed in vacuo leaving a green solid (0.20 g, 91%). EPR (CH_2Cl_2, 25 °C); $g = 1.89$, $w_{1/2} = 45$ G (virtually identical with the EPR of $W(\eta^5\text{-}C_5Me_5)Cl_4(PMe_3)$[18]). See Table I for NMR results.

$W(\eta^5\text{-}C_5Et_5)Me_4$. A 2.8 M solution of MeMgCl (0.46 mL, 1.29 mmol) was diluted to 5 mL with THF. $W(\eta^5\text{-}C_5Et_5)Cl_4$ (0.17 g, 0.16 mmol) was added while stirring this solution. A yellow color formed immediately. After 30 min the solvent was removed in vacuo and the residue was extracted with pentane. The extract was filtered and the solvent removed in vacuo to leave a yellow crystalline solid (0.12 g, 83%). EPR (CH_2Cl_2, 25 °C) $g = 2.01$ (identical with the EPR of $W(\eta^5\text{-}C_5Me_5)Me_4$[18]). See Table I for NMR results.

Acknowledgment. This work was supported by the Director, Office of Basic Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy, under Grant DE-FG02-86ER13564. J.F.B. thanks the National Science Foundation for a predoctoral fellowship. We thank A. Liu for the preparation and analysis of $[W(\eta^5\text{-}C_5Et_5)Cl_4]_2$.

Registry No. 1, 108347-32-6; 2, 108347-33-7; 3 (major isomer), 108347-44-0; **3** (minor isomer), 108347-41-7; **4**, 108347-34-8; **5**, 108347-35-9; **6**, 108347-36-0; **7**, 108347-37-1; **8**, 108347-38-2; $HC_5Me_4(CH_2CH_2C{\equiv}CEt)$, 95069-26-4; $LiC_5Me_4(CH_2CH_2C{\equiv}CEt)$, 95045-06-0; $[RhCl(CO)_2]_2$, 14523-22-9; $Rh(CO)_2(\eta^5\text{-}C_5Me_4CH_2CH_2C{\equiv}CEt)$, 95045-03-7; $W(C_3Et_3)(OCMe_2CMe_2O)(O\text{-}t\text{-}Bu)$, 83487-40-5; $W(\eta^5\text{-}C_5Et_5)Me_4$, 108347-39-3; $W(\eta^5\text{-}C_5Et_5)Cl_4(PMe_3)$, 108347-40-6; $Co_2(CO)_8$, 10210-68-1; $W(\eta^5\text{-}C_5Et_5)Cl_4$, 108347-42-8; $W(\eta^5\text{-}C_5Et_5)(O\text{-}t\text{-}Bu)O_2$, 91230-65-8; 1-iodo-3-hexyne, 102998-71-0; 2,3,4,5-tetramethyl-2-cyclopentenone, 54458-61-6.

Photochemistry of η^4-Cyclopentadiene Iron Tricarbonyl Complexes: Transfer of the 5-Endo Substituent to the Iron Center Following Dissociative Loss of Carbon Monoxide

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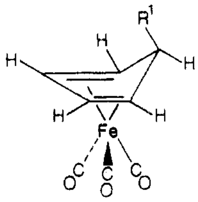
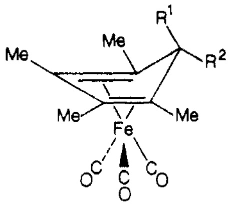
Received August 29, 1985

Near-UV irradiation of the complexes $(\eta^4\text{-}C_5H_5R^1)Fe(CO)_3$ (R^1 = *exo*-H, Ia; *exo*-CH_2Ph (*exo*-Bz), Ib) and $(\eta^4\text{-}C_5Me_4R^1R^2)Fe(CO)_3$ (R^1 = *exo*-Me, R^2 = *endo*-Me, IIa; R^1 = *exo*-Me, R^2 = *endo*-H, IIb; R^1 = *exo*-Bz; R^2 = *endo*-Me, IIc) where R^1 and R^2 are on the doubly allylic carbon, C-5, in an exo and endo position, respectively, results in the dissociative loss of CO. For all complexes the prompt photoproduct is a coordinatively unsaturated, 16e $(\eta^4\text{-cyclopentadiene})Fe(CO)_2$ that can be detected by IR at low temperature, ~77 K. Irradiation ($\lambda > 420$ nm) of the 16e species at low temperature (~77 K) results in transfer of the 5-endo substituent to form $(\eta^5\text{-cyclopentadienyl})Fe(CO)_2R^2$ (R^2 = H, Me) products. Transfer of the 5-endo substituent can also occur thermally upon warmup, but the transfer of the 5-endo group is not very competitive with back-reaction of the 16e species and CO to regenerate the starting $(\eta^4\text{-cyclopentadiene})Fe(CO)_3$ complexes. The 366-nm quantum yield (at 10^{-7} einstein/min) for CO loss at 298 K in alkane solution is ~0.1; the formation quantum yields for the $(\eta^5\text{-cyclopentadienyl})Fe(CO)_2H$ species are also ~0.1, but the formation quantum yields for the $(\eta^5\text{-cyclopentadienyl})Fe(CO)_2Me$ species are $<10^{-2}$. All results are consistent with thermal or light-activated transfer of the 5-endo substituent (H or Me) following light-induced loss of CO from the parent $(\eta^4\text{-cyclopentadiene})Fe(CO)_3$. The thermal rate of the transfer of a 5-*endo*-Me vs. a 5-*endo*-H is much slower on the basis of the thermal rates of reactions of $(\eta^4\text{-}C_5Me_5R^2)Fe(CO)_2(1\text{-pentene})$ (R^2 = *endo*-H or *endo*-Me) which give $(\eta^5\text{-}C_5Me_5)Fe(CO)_2R^2$.

In this paper we wish to report our findings regarding the photochemistry of some $(\eta^4\text{-cyclopentadiene})Fe(CO)_3$ complexes. Near-UV photoexcitation of various $(\eta^4\text{-cyclopentadiene})Fe(CO)_3$ species, I and II, is found to induce dissociative loss of CO as the primary photochemical event followed by transfer of the 5-endo group, H or Me, to form η^5-cyclopentadienyl complexes.



Ia: R^1 = H
b: R^1 = $CH_2C_6H_5$



IIa: R^1 = R^2 = Me
b: R^1 = Me; R^2 = H
c: R^1 = $CH_2C_6H_5$; R^2 = Me

It is known that irradiation of $(\eta^4\text{-1,3-butadiene})Fe(CO)_3$ at ambient temperatures leads to both loss of CO, eq 1, and η^4- → η^2-binding of the olefin, eq 2, as evidenced by

$$(\eta^4\text{-1,3-butadiene})Fe(CO)_3 \xrightarrow{h\nu} (\eta^4\text{-1,3-butadiene})Fe(CO)_2 + CO \quad (1)$$

$$(\eta^4\text{-1,3-butadiene})Fe(CO)_3 \xrightarrow{h\nu} (\eta^2\text{-1,3-butadiene})Fe(CO)_3 \quad (2)$$

formation of both $(\eta^4\text{-1,3-butadiene})Fe(CO)_2L$ and $(\eta^2\text{-diene})Fe(CO)_3L$ (L = $P(OMe)_3$) when the $(\eta^4\text{-1,3-butadiene})Fe(CO)_3$ is irradiated in the presence of L.[1] The 366-nm quantum yields for CO loss are in the range 0.01–0.20 for a variety of $(\eta^4\text{-1,3-diene})Fe(CO)_3$ complexes while the 366-nm quantum yield for the η^4- → η^2-binding of the olefin was reported to be much smaller, 0.001–0.007.[1] The low quantum efficiency for the η^4- → η^2-olefin binding was attributed to competition for the vacant coordination site between the uncoordinated double bond to regenerate the η^4-diene complex and the incoming $P(OMe)_3$ to yield the $P(OMe)_3$ substitution product. Both the CO loss product and the η^2-1,3-butadiene complexes from irradiation of $(\eta^4\text{-1,3-butadiene})Fe(CO)_3$ have been observed in low-temperature matrices.[2] For example, $(\eta^4\text{-1,3-butadiene})Fe(CO)_3$ yields both $(\eta^4\text{-1,3-butadiene})Fe(CO)_2$ and $\eta^2\text{-1,3-butadiene})Fe(CO)_3$ when irradiated in Ar or N_2 matrices at 10 K. For $(\eta^4\text{-2,3-diMe-1,3-butadiene})Fe(CO)_3$, however, only the CO loss product was detected by IR. The difference in reactivity is attributed to the presence of the bulky Me groups which hinder rotation about the C_2–C_3 bond of the 2,3-dimethyl-1,3-butadiene ligand that is required for an *s-cis*-diene → *s-trans*-diene rearrangement, eq 3. For an η^2-1,3-diene complex to form, it is postulated that such a rearrangement must occur,[2] oth-

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[1] Jaenicke, P.; Kerber, R. K.; Kirsch, P.; Koerner von Gustorf, E. A.; Rumin, R. *J. Organomet. Chem.* **1980**, *187*, 361.

[2] Ellerhorst, G.; Gerhartz, W.; Grevels, F. W. *Inorg. Chem.* **1980**, *19*, 67.

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