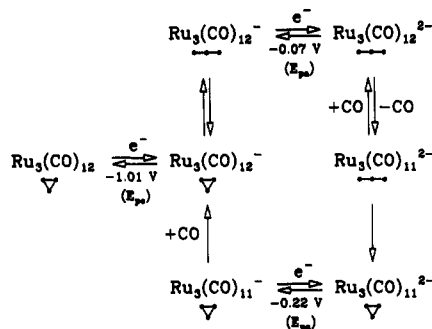


Scheme I



bonding. Thus the fate of the short-lived^{15,16} *triangulo*- $\text{Ru}_3(\text{CO})_{12}^{\cdot-}$ plausibly could be either ring opening to linear $\text{Ru}_3(\text{CO})_{12}^{\cdot-}$ or CO loss to form *triangulo*- $\text{Ru}_3(\text{CO})_{11}^{\cdot-}$. In either case, further reduction to a dianion is expected to be highly exoergic when the electrode potential is -1.01 V. The reverse of the CO loss pathway is responsible for the formation of $\text{Ru}_3(\text{CO})_{12}$ when $\text{Ru}_3(\text{CO})_{11}^{2-}$ is oxidized in the presence of CO. However, since only the linear dianion is formed at low temperature and the product ratio dependence on scan rate suggests that *triangulo*- $\text{Ru}_3(\text{CO})_{11}^{2-}$ is a secondary product, *triangulo*- $\text{Ru}_3(\text{CO})_{12}^{\cdot-}$ must decay via metal-metal bond cleavage with loss of CO subsequent to formation of the linear dianion. Since CO pressure significantly influences the dianion product ratio, CO loss is apparently reversible. On the other hand, the linear dianion is not formed from *triangulo*- $\text{Ru}_3(\text{CO})_{11}^{2-}$ under 1 atm of CO pressure so that we are led to postulate a two-step process involving reversible loss of CO to form linear $\text{Ru}_3(\text{CO})_{11}^{2-}$, followed by irreversible ring closure to give *triangulo*- $\text{Ru}_3(\text{CO})_{11}^{2-}$. The various processes are summarized in Scheme I.

Unlike most other ETC processes involving transition-metal clusters, chemical and electrochemical initiation of Lewis base substitution on $\text{Ru}_3(\text{CO})_{12}$ do not give equivalent results. Electrochemical initiation results in much lower yields and poorer product specificity than when a catalytic amount of a chemical reducing agent is used. Although some nucleophilic substitution product is obtained, the current efficiency is low and the dominant products are $\text{Ru}_3(\text{CO})_{11}^{2-}$ and $\text{Ru}_3(\text{CO})_{12}^{2-}$. These results are consistent with the cyclic voltammetry studies discussed above and fit into the general scheme for competition between ETC catalysis and an ECE process presented by Saveant.¹⁷ The reason for the success of ETC catalysis as a synthetic method for Lewis base derivatives of $\text{Ru}(\text{CO})_{12}$ is apparently that reduction to the dianion

does not occur under the usual synthetic conditions.³ When a catalytic amount of benzophenone ketyl is used as an initiator, $\text{Ru}_3(\text{CO})_{12}^{\cdot-}$ reacts with nucleophile and completes the chain before another molecule of reducing agent is encountered. Studies are in progress on the electrochemistry of the $\text{Ru}_3(\text{CO})_{12}$ system in the presence of Lewis bases.

Preparation and Reaction Dynamics of $(\eta^4\text{-C}_5\text{H}_6)\text{Re}(\text{PPh}_3)_2\text{H}_3$. A Structurally Characterized η^4 -Cyclopentadiene Complex

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Summary: The complex $(\eta^4\text{-C}_5\text{H}_6)\text{Re}(\text{PPh}_3)_2\text{H}_3$ has been prepared by the reaction of $\text{Re}(\text{PPh}_3)_2\text{H}_7$ with cyclopentadiene at 25°C , isolated, and structurally characterized. Variable-temperature ^1H NMR shows at least two distinct fluxional processes. Spin-saturation NMR spectroscopy reveals a process in which the endo hydrogen exchanges with the hydride ligands.

The η^5 -cyclopentadienyl ligand is one of the most versatile and perhaps most important ligands in organometallic chemistry. While the ligand is observed to behave as a spectator group in many reactions, its variation in coordination number has led to many discoveries of the importance of reduced hapticity (η^1 or η^3) in substitution reactions involving $\eta^5\text{-C}_5\text{H}_5$ complexes.¹ Several reports of the related $\eta^4\text{-C}_5\text{H}_6$ complexes have appeared in the literature, either in the preparation of $\eta^5\text{-C}_5\text{H}_5$ complexes or as proposed reactive intermediates.²⁻⁵ Only a few substituted derivatives of the type $(\eta^4\text{-C}_5\text{H}_5\text{R})\text{M}$ have been

(15) Alkali-metal reduction of $\text{Ru}_3(\text{CO})_{12}$ in THF solution has been reported¹⁶ to produce an ESR-active radical species which was originally thought to be $\text{Ru}_3(\text{CO})_{12}^{\cdot-}$. We have found that when $\text{Ru}_3(\text{CO})_{12}$ in THF is exposed to a Na or K mirror at room temperature and then quickly cooled to dry ice-acetone temperature, a weak spectrum ($g = 1.986$) is observed which shows $^{99}\text{Ru}/^{101}\text{Ru}$ satellites ($a^{\text{Ru}} \approx 24$ Gauss) with amplitudes consistent with three equivalent Ru sites in the radical species, but whether this is due to $\text{Ru}_3(\text{CO})_{12}^{\cdot-}$, $\text{Ru}_3(\text{CO})_{11}^{\cdot-}$, or some other species is uncertain. When $\text{Ru}_3(\text{CO})_{12}$ was reduced at low temperature with Na, K or with an electrode or when $\text{Ru}_3(\text{CO})_{12}^{2-}$ was oxidized electrochemically at low temperatures, no ESR spectrum could be detected. At present we have no explanation for these results.

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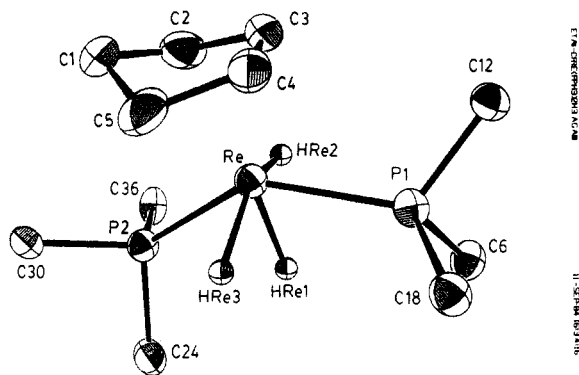
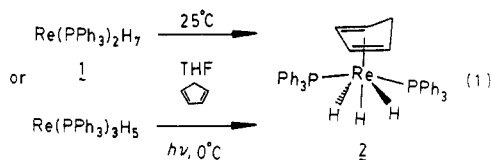


Figure 1. ORTEP drawing of $(\eta^4\text{-C}_5\text{H}_6)\text{Re}(\text{PPh}_3)_2\text{H}_3$, **2**. Ellipsoids are shown at the 50% probability level. Hydrogens and phenyl carbons not attached to phosphorus have been omitted for clarity.

characterized structurally.⁵ In this paper, the preparation and first structural characterization of a compound containing the parent $\eta^4\text{-C}_5\text{H}_6$ ring is described and the dynamic behavior of the endo C_5H_6 hydrogen in the complex reported.

The thermolysis of the complex $\text{Re}(\text{PPh}_3)_2\text{H}_7$ (**1**)⁶ in the presence of dienes is known to produce $(\eta^4\text{-diene})\text{Re}(\text{PPh}_3)_2\text{H}_3$ complexes,⁷ and the reaction of a similar complex, $\text{Re}(\text{PPh-}i\text{-Pr}_2)_2\text{H}_7$, with ethylene in the presence of $\text{Pt}(\text{C}_2\text{H}_4)_2(\text{PPh-}i\text{-Pr}_2)_2$, gives $\text{Re}(\text{C}_2\text{H}_4)_2(\text{PPh-}i\text{-Pr}_2)_2\text{H}_3$.⁸ Reaction of **1** with cyclopentadiene at 60 °C has also been reported to produce the dihydride complex $\text{CpRe}(\text{PPh}_3)_2\text{H}_2$ in 60% yield based upon **1**, and spectroscopic evidence for the intermediacy of the complex $(\eta^4\text{-C}_5\text{H}_6)\text{Re}(\text{PPh}_3)_2\text{H}_3$ was presented.⁷

We have found that **1** (0.12 M) reacts with cyclopentadiene at 25 °C in THF solution (1:4, v/v) upon standing for 12 h. Addition of ether produces a white crystalline solid formulated as $(\eta^4\text{-C}_5\text{H}_6)\text{Re}(\text{PPh}_3)_2\text{H}_3$ (**2**) in 56% yield (eq 1). Alternatively, irradiation (Pyrex



filter) of a cyclopentadiene/THF solution (1:4) of $\text{Re}(\text{PPh}_3)_3\text{H}_3$ (**1**) (1.5 M) at 0 °C for 15 min produces $(\eta^4\text{-C}_5\text{H}_6)\text{Re}(\text{PPh}_3)_2\text{H}_3$ in 23% yield upon precipitation with ether. Heating a C_6D_6 solution of pure **2** at 60 °C results in the first-order formation of $\text{CpRe}(\text{PPh}_3)_2\text{H}_2$, **3**, with a rate constant of $1.26(2) \times 10^{-4} \text{ s}^{-1}$.

The ^1H NMR spectrum of **2** at -50 °C in toluene- d_8 shows four peaks at δ 5.764 (dd, $J = 20.0, 9.1 \text{ Hz}$, 1 H), 3.943 (br s, 2 H), 3.353 (d, $J = 8.0 \text{ Hz}$, 1 H), and 2.723 (br s, 2 H) for an $\eta^4\text{-C}_5\text{H}_6$ group, two triplets at δ -2.358 ($J = 38.8 \text{ Hz}$, 1 H) and -7.087 ($J = 19.4 \text{ Hz}$, 2 H) for the hydride ligands, and a multiplet at δ 7.06 (18 H) and two singlets at δ 8.093 (6 H) and 7.718 (6 H) for the phosphine meta and para and distinct ortho hydrogens, respectively.

The structure of **2** shown in Figure 1 displays an overall geometry that can best be described as a grossly distorted pentagonal bipyramid in which the pentagonal plane

Table I. Selected Distances (Å) and Angles (deg) in $(\eta^4\text{-C}_5\text{H}_6)\text{Re}(\text{PPh}_3)_2\text{H}_3$

| Bond Distances | | | |
|--------------------------|------------|--------------|------------|
| Re-P1 | 2.381 (2) | Re-C4 | 2.215 (6) |
| Re-P2 | 2.370 (2) | Re-C5 | 2.345 (7) |
| Re-HRe1 ^a | 1.60 | C1-C2 | 1.487 (10) |
| Re-HRe2 ^a | 1.38 | C2-C3 | 1.422 (9) |
| Re-HRe3 ^a | 1.73 | C3-C4 | 1.426 (9) |
| Re-C2 | 2.267 (7) | C4-C5 | 1.491 (9) |
| Re-C3 | 2.195 (6) | C5-C1 | 1.515 (10) |
| Bond Angle | | | |
| P1-Re-P2 | 139.69 (6) | P2-Re-CEN | 112.7 (2) |
| HRe1-Re-CEN ^b | 176.6 | HRe1-Re-HRe2 | 85.4 |
| P1-Re-CEN | 107.6 (2) | HRe1-Re-HRe3 | 81.7 |

^aHydrides not refined. Located on difference Fourier map.
^bCEN is the C2-C3-C4-C5 centroid.

contains the three hydride ligands and the two C_5H_6 double-bond centers.¹⁰ The axial phosphines form the distorted P1-Re-P2 axial vector of 139.7°. The centroid of the four olefinic C_5H_6 carbons lies directly opposite (176.6°) one of the rhenium hydride ligands. The dihedral angle formed by the C1-C2-C5 and C2-C3-C4-C5 planes is 143.8°, compared with 180° in free cyclopentadiene¹¹ and 143.5° in $\text{CpCo}(\eta^4\text{-C}_5\text{H}_5\text{Ph})$.⁵ Some important bond angles and distances are given in Table I. The pentagonal-bipyramid structure was also expected from the spectroscopic data reported by Baudry, Ephritikhine, and Felkin.⁷ Curiously, the IR spectrum of **2** shows $\nu_{\text{C-H}}$ bands at 2755 and 3060 cm^{-1} , yet the Re-H_{endo} distance is 3.18 Å. The suggestion that an M-H interaction is responsible for the lower $\nu_{\text{C-H}}$ stretching energy, as was put forth for $(\eta^4\text{-C}_5\text{H}_6)\text{CoCp}$, is not supported by the structural results determined here.^{3a,c}

The variable-temperature ^1H NMR of **2** displays fluxional behavior of all of its resonances. Upon warming a toluene- d_8 solution of **2** from -50 °C, the distinct ortho phenyl resonances at δ 8.093 and 7.718 are first observed to collapse and coalesce at -15 °C. At 400 MHz, this corresponds to a rate for interconversion of 333 s^{-1} , or $\Delta G^\ddagger = 12.1 \text{ Kcal/mol}$.¹² Variable-temperature $^{31}\text{P}\{^1\text{H}\}$ NMR spectra (162 MHz) also show dynamic behavior, with two doublets being observed (δ 35.03, 33.75, $J = 74 \text{ Hz}$) at -60 °C. Coalescence occurs at -30 °C to produce a singlet at δ 33.34 at 30 °C.

The two hydride triplets at δ -2.358 and -7.087 collapse to a single resonance at δ -5.67 at 60 °C. At the coalescence temperature of 20 °C a rate constant of 4200 s^{-1} can be calculated. The ΔG^\ddagger is 12.3 kcal/mol for this process and is not experimentally different from the barrier to the phosphine exchange, although a single mechanism is not rigorously required to account for these two processes. The mechanism for phosphine interconversion probably in-

(10) Recrystallization of **2** from THF/hexane affords crystals in the monoclinic space group $P2_1/n$ space with $Z = 4$, $d_{\text{calc}} = 1.549 \text{ g/cm}^3$, and crystal parameters $a = 16.4834(93) \text{ Å}$, $b = 9.2964(108) \text{ Å}$, $c = 22.1861(78) \text{ Å}$, and $\beta = 100.34(4)^\circ$. Collection of 3178 unique data with $F_o > 3\sigma$ from $2 < 2\theta < 45^\circ$ followed by a Patterson map solution of the structure revealed the η^4 structure for **2** shown in Figure 1. Following placement of the hydrogen atoms on the phenyl groups in idealized locations, a difference Fourier map revealed all of the hydrogens bound to the C_5H_6 group as well as three peaks near the rhenium. The latter three peaks were located in the appropriate positions to correspond to the symmetry anticipated for the hydride ligands from the low-temperature ^1H NMR spectrum. Final anisotropic refinement of all non-hydrogen atoms with data $> 3\sigma$ converged with $R_1 = 0.0243$, $R_w = 0.0285$, and $\text{GOF} = 0.97$.

(11) An angle of 180° can be calculated for C_5H_6 using the MM2 program of N. L. Allinger, available from the Quantum Chemistry Program Exchange, Indiana University (#318). MNDO refinement also gives a planar molecule.

(12) For exchanging resonances at coalescence, $k = \pi\delta\nu/(2)^{1/2}$. ΔG^\ddagger is computed from the Eyring equation $\Delta G^\ddagger = -RT \ln(kA_0h/k_B T)$.

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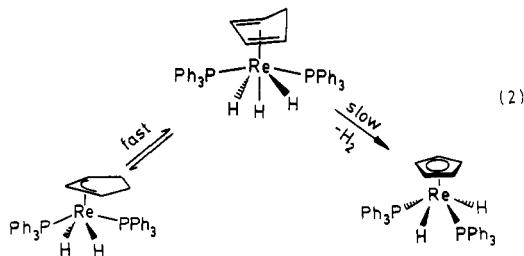
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volves rotation of the $\eta^4\text{-C}_5\text{H}_6$ group. The hydride exchange can be accounted for as a pairwise exchange that might only occur with the cyclopentadiene rotated 90° from its most stable orientation.

A third fluxional process shows broadening of both the hydride ligands and the four C_5H_6 resonances beginning at $\sim 50^\circ\text{C}$. Complete collapse of the C_5H_6 resonances occurs at 80°C as a resonance begins to grow in at δ 3.57. At 90°C the hydride resonance disappears into the base line, but decomposition to form **3** occurs rapidly at this temperature before the limiting high-temperature spectrum can be attained.

The nature of this process is revealed by irradiating the hydride resonance at δ -5.67 at temperatures above 40°C and observing the complete collapse of only the C_5H_6 resonance at δ 3.353. This latter resonance can be confidently assigned to the endo hydrogen of the $\eta^4\text{-C}_5\text{H}_6$ group, which apparently undergoes exchange with the hydride ligands on the time scale of relaxation processes ($\sim 1\text{--}5\text{ s}^{-1}$). This corresponds to a ΔG^\ddagger of about 18.5 kcal/mol and is clearly a separate process from the other exchanges. In the fast-exchange limit, resonances would have been expected at δ 3.82 (5 H) and -3.30 (4 H).

While the exact nature of the latter exchange process is not known, a mechanism involving reversible reductive elimination of H_2 followed by migration of the endo $\eta^4\text{-C}_5\text{H}_6$ hydrogen to the metal can be ruled out since the formation of **3** is observed to be irreversible, even under 1000 psi of H_2 . Reversible loss of phosphine followed by endo-hydrogen migration would produce $\text{CpRe}(\text{PPh}_3)\text{H}_4$, which does not react with PPh_3 .¹³ One possibility is shown in eq 2, involving reversible migration of a hydride ligand



to the C_5H_6 ring to form a symmetrical η^3 -allyl intermediate. Such reversible migrations have been observed in the related η^4 -cyclohexadiene system, which was also characterized structurally,¹⁴ and in the related bis(ethylene) derivative.⁵ Bercaw has also used a reversible metal to Cp ring hydrogen migration to account for H/D exchange in zirconium hydride complexes.¹⁵ Further studies of this and related processes are under way.¹⁶

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Supplementary Material Available: Tables of data collection parameters, positional and thermal parameters, least-squares planes, bond angles and distances, and tables of structure factors (43 pages). Ordering information is given on any current masthead page.

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Simple Routes to Mono(η^5 -pentamethylcyclopentadienyl) Complexes of Molybdenum(V) and Tungsten(V)

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Summary: Addition of $\text{W}(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_3\text{Me}$ to PCl_5 in dichloromethane produces sparingly soluble $\text{W}(\eta^5\text{-C}_5\text{Me}_5)\text{Cl}_4$ as a bright orange powder in $\sim 80\%$ yield. $[\text{NEt}_4][\text{W}(\eta^5\text{-C}_5\text{Me}_5)\text{Cl}_5]$ and $\text{W}(\eta^5\text{-C}_5\text{Me}_5)\text{Cl}_4(\text{PMe}_3)$ can be prepared readily. Addition of excess ZnMe_2 to $\text{W}(\eta^5\text{-C}_5\text{Me}_5)\text{Cl}_4(\text{PMe}_3)$ produces yellow $\text{W}(\eta^5\text{-C}_5\text{Me}_5)\text{Me}_4$ in good yield. The reaction between $\text{Mo}(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_3\text{Me}$ and PCl_5 in dichloromethane produces purple $\text{Mo}(\eta^5\text{-C}_5\text{Me}_5)\text{Cl}_4$. Addition of PMe_3 yields $\text{Mo}(\eta^5\text{-C}_5\text{Me}_5)\text{Cl}_4(\text{PMe}_3)$, but attempted preparations of $\text{Mo}(\eta^5\text{-C}_5\text{Me}_5)\text{Me}_4$ so far have failed. PCl_5 has also been used to prepare $\text{W}(\eta^5\text{-C}_5\text{Et}_5)\text{Cl}_4$ from $\text{W}(\eta^5\text{-C}_5\text{Et}_5)(\text{O})\text{Cl}_3$.

The discovery of $[\text{Ta}(\eta^5\text{-C}_5\text{Me}_4\text{R})(\mu\text{-H})\text{Cl}_2]_2$ ($\text{R} = \text{Me}, \text{Et}$) complexes¹ and their reaction with carbon monoxide to give μ -hydride μ -formyl complexes of the type $[\text{Ta}(\eta^5\text{-C}_5\text{Me}_4\text{R})\text{Cl}_2]_2(\mu\text{-H})(\mu\text{-CHO})^2$ led to a search for related chemistry of the less oxophilic metals Mo and W. Unfortunately, suitable high oxidation state mono($\eta^5\text{-C}_5\text{Me}_4\text{R}$) starting materials such as $\text{M}(\eta^5\text{-C}_5\text{Me}_5)\text{Cl}_4$ were unknown. A tungsten complex with the formula $[\text{W}(\eta^5\text{-C}_5\text{Me}_4\text{-}t\text{-Bu})\text{Cl}_4]_2$ was prepared via a reaction between the tungstenacyclobutadiene complex $\text{W}[\text{C}(t\text{-Bu})\text{C}(\text{Me})\text{C}(\text{Me})]\text{Cl}_3$ and 2-butyne,³ but a more direct route to analogous, simpler, $\eta^5\text{-C}_5\text{Me}_5$ complexes was clearly needed before the chemistry could be explored in detail. We report here simple, high-yield routes to molybdenum and tungsten complexes of the type $\text{M}(\eta^5\text{-C}_5\text{Me}_5)\text{Cl}_4$ ($\text{M} = \text{Mo}, \text{W}$).

All attempts to prepare $\text{M}(\eta^5\text{-C}_5\text{Me}_5)\text{Cl}_4$ complexes directly from MCl_x ($x = 5$ or 6) and a mild $\eta^5\text{-C}_5\text{Me}_5$ source such as $\text{SnBu}_3(\text{C}_5\text{Me}_5)$, a type of reaction that has yielded complexes such as $\text{Ta}(\eta^5\text{-C}_5\text{Me}_5)\text{Cl}_4$,⁴ so far have failed. Therefore we chose to prepare a lower oxidation state complex containing one $\eta^5\text{-C}_5\text{Me}_5$ ring and subsequently oxidize it. A solution of $\text{W}(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_3\text{Me}^5$ dissolved in dichloromethane was added dropwise at 25°C to 2.5 equiv of PCl_5 partially dissolved in dichloromethane. The PCl_5 dissolved as the solution rapidly changed color to orange and gas (presumably CO) evolved. After the mixture was refluxed overnight, an almost iridescent orange powder was filtered off and washed liberally with dichloromethane. It could be sublimed at 200°C and $<0.1\ \mu\text{m}$. Elemental analysis^{6a} and subsequent reactions (vide

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(6) (a) Anal. Calcd for $\text{WC}_{10}\text{H}_{15}\text{Cl}_4$: C, 26.06; H, 3.28; Cl, 30.77. Found: C, 26.30; H, 3.38; Cl, 29.27. (b) Anal. Calcd for $\text{WC}_{15}\text{H}_{25}\text{Cl}_5\text{N}$: C, 34.50; H, 5.63; Cl, 28.29. Found: C, 34.85; H, 5.81; Cl, 27.68. (c) Anal. Calcd for $\text{WC}_{15}\text{H}_{24}\text{Cl}_4\text{P}$: C, 29.08; H, 4.51; Cl, 26.41. Found: C, 29.42; H, 4.48; Cl, 25.64.