(2) mm/s. The data can be fit by the least-squares method to a straight line: The coefficient of determination r^2 is 0.977. It should be noted that the ΔE_Q value used for ferrocenium triiodide is, obviously, the minimum that could be selected for this ion, as ΔE_Q values of less than ca. 0.15 mm/s are difficult to resolve. The actual point for ferrocenium triiodide will therefore be closer to the line than indicated.

The correlation of Δg with ΔE_Q suggests a continuous change in the properties of such mixed-valence bridged ferrocenes as the systems change from a localized to a delocalized moiety. In the PKS vibronic-coupling model[28] for mixed-valence compounds, three parameters are needed to describe the properties of such species. Electronic coupling between the two metal centers is gauged by ϵ, whereas the vibronic coupling is gauged by the λ parameter, which is directly proportional to the difference in the equilibrium value of the a_{1g} monomer normal coordinate in the two different oxidation states which characterize the mixed-valence compound. The third parameter is W, which gauges the difference in zero-point energy between the two states of a given mixed-valence species. In our opinion it is likely that ϵ changes from one mixed-valence ferrocene to another.

Across the series, the electronic coupling between the Fe(II) and Fe(III) ions in the mixed-valence ion is increasing. For a very localized ion, the **g** tensor is very anisotropic and ΔE_Q is small as with a monomeric ferrocenium ion. An increase in ϵ leads to a slight admixture of some of the electronic properties of the Fe(II) center into those of the Fe(III) center. The mixed-valence ion is still localized, but the Fe(III) ion has an EPR spectrum with less **g**-tensor anisotropy, and a larger ΔE_Q is seen in the Mössbauer spectrum. At some point the ion becomes delocalized. It is obvious from Figure 12 that mixed-valence bridged ferrocenes are needed that bridge the gap in the correlation, that is, ions with intermediate values of the electronic coupling.

Acknowledgment. We are grateful for support from NIH Grant HL13652 and for assistance from R. Emberson with the Mössbauer data collection. The mass spectral data processing equipment was provided by NIH Grants CA 11388 and GM 16864.

Registry No. $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^{10}\text{-C}_5\text{H}_4\text{C}{\equiv}\text{CC}_5\text{H}_4)\text{Fe}(\eta^5\text{-C}_5\text{H}_5)$, 12098-14-5; $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^{10}\text{-C}_5\text{H}_4\text{C}{\equiv}\text{CC}_5\text{H}_4)\text{Fe}(\eta^5\text{-C}_5\text{H}_5)](\text{I}_3)_2$, 73946-44-8; $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^{10}\text{-C}_5\text{H}_4\text{C}{\equiv}\text{CC}_5\text{H}_4)\text{Fe}(\eta^5\text{-C}_5\text{H}_5)](\text{BF}_4)_2$, 74779-52-5; $[\text{Fe}(\eta^{10}\text{-C}_5\text{H}_4\text{C}{\equiv}\text{CC}_5\text{H}_4)_2\text{Fe})]\text{I}_3$, 74779-53-6; $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^{10}\text{-C}_{10}\text{H}_8)\text{Fe}(\eta^5\text{-C}_5\text{H}_5)]\text{I}_3$, 39470-17-2; $(\eta^5\text{-CH}_3\text{COC}_5\text{H}_4)\text{Fe}(\eta^{10}\text{-C}_{10}\text{H}_8)\text{Fe}(\eta^5\text{-C}_5\text{H}_5)$, 59197-46-5; $[(\eta^5\text{-CH}_3\text{COC}_5\text{H}_9)\text{Fe}(\eta^{10}\text{-C}_{10}\text{H}_8)\text{Fe}(\eta^5\text{-C}_5\text{H}_5)]\text{I}_3$, 74779-55-8; $[\text{Co}(\eta^{10}\text{-C}_{10}\text{H}_9)_2\text{Co}](\text{PF}_6)_2$, 39333-80-7; $[\text{Co}(\eta^{10}\text{-C}_{10}\text{H}_8)_2\text{Co}]\text{PF}_6$, 69365-59-9; $[(\eta^5\text{-CH}_3\text{COC}_5\text{H}_4)\text{Fe}(\eta^5\text{-C}_5\text{H}_5)]\text{I}_5$, 74779-56-9; $\text{Fe}(\eta^{10}\text{-C}_5\text{H}_4\text{C}{\equiv}\text{CC}_5\text{H}_4)_2\text{Fe}$, 59187-97-2; $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^{10}\text{-C}_5\text{H}_4\text{–Se–C}_5\text{H}_4)\text{Fe}(\eta^5\text{-C}_5\text{H}_5)]\text{I}_3$, 74779-57-0; $[\text{Co}(\eta^{10}\text{-C}_5\text{H}_4\text{C}{\equiv}\text{CC}_5\text{H}_4)_2\text{Co}](\text{PF}_6)_2$, 74779-59-2; $[\text{Co}(\eta^{10}\text{-C}_5\text{H}_4\text{C}{\equiv}\text{CC}_5\text{H}_4)_2\text{Co}]\text{PF}_6$, 74792-77-1.

Supplementary Material Available: Tables VI (IR data for diferrocenylacetylene and its dioxidized I_3^- salt) and VII (IR data for [2.2]ferrocenophane-1,13-diyne and its I_3^- salt) (2 pages). Ordering information is given on any current masthead page.

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Metal Clusters. 26.[1] Hydrogenation of Bridging Alkyne Ligands in Dinuclear Molybdenum Complexes

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At temperatures above 100 °C, hydrogen reacts with $(\eta^5\text{-C}_5\text{H}_5)_2\text{Mo}_2(\text{CO})_4(\text{RC}_2\text{R})$ to form *cis*-RCH=CHR and $(\eta^5\text{-C}_5\text{H}_5)_2\text{Mo}_2(\text{CO})_4$. In the presence of excess alkyne, the reaction is catalytic with turnover rates of ~0.03/min at 150 °C. In the catalytic reaction, the product olefin was the cis isomer; no trans isomer was detected in the 2-butyne, 3-hexyne, and $\text{C}_2\text{H}_2(+\text{D}_2)$ reactions. Alkyne exchange between free alkyne and complexed alkyne occurred above 100 °C. At higher temperatures, additional reactions became significant, primarily acetylene insertions to form complex metallacyclic species. This competing insertion reaction was notable for reaction systems with C_2H_2 and with 2-butyne as the free or complexed ligand. Slow thermal dissociation of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Mo}_2(\text{CO})_4(\text{C}_2\text{H}_2)$ to $(\eta^5\text{-C}_5\text{H}_5)_2\text{Mo}_2(\text{CO})_4$ and C_2H_2 was demonstrated at 150 °C; none was detected for the substituted acetylene derivatives. The new $(\eta^5\text{-C}_5\text{H}_5)_2\text{Mo}_2(\text{CO})_3[\text{P(OCH}_3)_3](\text{RC}_2\text{R})$ complex was prepared and shown to be a catalyst precursor for acetylene hydrogenation to cis olefins. This complex was more active than the parent complexes by at least 1 order of magnitude. Disproportionation of the complex occurred under catalytic conditions to form $(\eta^5\text{-C}_5\text{H}_5)_2\text{Mo}_2(\text{CO})_4(\text{RC}_2\text{R})$ and presumably $(\eta^5\text{-C}_5\text{H}_5)_2\text{Mo}_2(\text{CO})_2[\text{P(OCH}_3)_3]_2$. To test for fragmentation in the $(\eta^5\text{-C}_5\text{H}_5)_2\text{Mo}_2(\text{CO})_4(\text{RC}_2\text{R})$ hydrogenation reaction and in the acetylene-exchange reaction, we used a mixture of the $(\text{C}_5\text{H}_5)_2\text{Mo}_2$ complex and the $(\text{CH}_3\text{C}_5\text{H}_4)_2\text{Mo}_2$ complex. Ligand label interchange was not detected. Thus, fragmentation is not an integral part of these reaction cycles. Carbon monoxide inhibited the hydrogenation reaction and the acetylene-interchange reaction. Exchange between ^{13}CO and the molybdenum–acetylene complexes was fast at the temperatures (110–150 °C) of the hydrogenation and acetylene-exchange reactions, but CO and the molybdenum–acetylene compounds did not form a spectroscopically detectable complex at 110 °C and 2 atm. Kinetic studies of the acetylene-exchange reaction established the rate law to be of the form $k_1[(\text{C}_5\text{H}_5)_2\text{Mo}_2(\text{CO})_4(\text{RC}_2\text{R})]$. For both the hydrogenation reaction and the alkyne-exchange reaction, the first step must comprise CO dissociation to give $(\eta^5\text{-C}_5\text{H}_5)_2\text{Mo}_2(\text{CO})_3(\mu_x\text{-RC}_2\text{R})$. In the cocompetition of CO for this intermediate, acetylenes are more effective than is hydrogen.

Introduction

Interactions of acetylenes with metal atoms in polynuclear metal complexes are complex and rarely comprise simple σ–π complex formation centered at a single metal atom in the polynuclear assembly. Illustrated in **1**–**4** are representative interactions[2] rendered in skeletal form without depiction of acetylene substituent atoms and other metal ligand atoms. Earlier, we described the reactivity of typical representatives

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[1] M. Tachikawa and E. L. Muetterties, *J. Am. Chem. Soc.*, **102**, 4541 (1980).

[2] For a discussion of polynuclear metal–alkyne complexes see E. L. Muetterties, T. N. Rhodin, E. Band, C. F. Brucker, and W. R. Pretzer, *Chem. Rev.*, **79**, 91 (1979).

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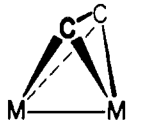

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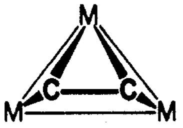

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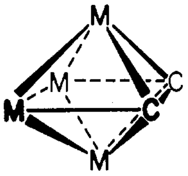

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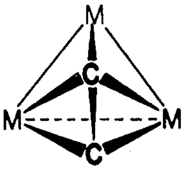

4

of these four structural classes.[3,4] Only one of those investigated, $Ni_4(CNR)_4(RC_2R)_3$, was shown to be reactive and to be a catalyst precursor for acetylene hydrogenation to cis olefins.[3,4] Here we describe a slightly reactive acetylene complex, $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4(RC_2R)$, of structural form **1**.[5] Presented are the chemical and catalytic properties, the alkyne-exchange reaction and the associated kinetic parameters, and labeling studies that assess the proclivity of the dinuclear complex to fragmentation. Mechanistic features of the catalytic hydrogenation reaction and the alkyne-exchange reaction are defined by these studies.

Experimental Section

Reagents and Procedures. All hydrocarbon solvents were refluxed in the presence of sodium metal and were distilled prior to use with the exceptions of (1) the alkylacetylenes which were dried with calcium hydride and generally were passed through a grade 1 alumina packed column, (2) diphenylacetylene which was crystallized from diethyl ether, and (3) C_2H_2 (Liquid Carbonics) which was used (a) directly from the cylinder for synthesis reactions and (b) after passage through a −78 °C cold trap to remove acetone before use in catalytic reactions. Dichloromethane was dried over P_4O_{10} and then distilled. All synthetic, kinetic, and catalytic procedures were effected (1) in an argon atmosphere in a Vacuum Atmospheres Dribox with a Model HE Dri-Train, (2) with a conventional vacuum line, or (3) with a modified Schlenk system.

All the molybdenum–acetylene carbonyl complexes with the one exception of the diphenylacetylene derivative were synthesized by the procedure of Bailey et al.[6] The diphenylacetylene derivative was prepared from $\eta^5\text{-}C_5H_5Mo(CO)_3H$ and diphenylacetylene[7] and was recrystallized by very slowly removing the methylene chloride from a methylene chloride–heptane solution of the complex. The $(\eta^5\text{-}C_5H_5)_2W_2(CO)_4(C_2H_5C_2C_2H_5)$ derivative was prepared by the procedure of Ginley et al.[8] The analogous $CH_3C_5H_4Mo$ complexes were prepared by the same procedures and were primarily characterized by mass spectrometric analysis.

Proton NMR spectra were obtained with a Varian EM390 spectrometer system with tetramethylsilane reference and deuteriotoluene or deuteriobenzene solvent. Gas chromatography was extensively employed for quantitative separation and identification of organic products; identifications were confirmed with GC–mass spectrometric analyses. With a Perkin-Elmer gas chromatograph, the columns used were (1) dimethylsulfolane (12 ft, 15% on Chrom P) for the separation of butane and the isomeric butenes and (2) dimethylsulfolane in series with β,β'-oxydipropionitrile (25 ft, 25% on Chrom P) for the separation of hexane and the isomeric hexenes. For GC–mass spectrometric studies, a Finnegan 4000 system interfaced with an INCOS data system was used, and for the analysis of the molybdenum complexes, an AEI MS-12 system interfaced with an INCOS data system was used.

Preparation of $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_3[P(OCH_3)_3](C_2H_5C_2C_2H_5)$. $[\eta^5\text{-}C_5H_5Mo(CO)_2]_2(C_2H_5C_2C_2H_5)$ (0.5990 g, 1.609×10^{-3} mol) was dissolved in 20 mL of toluene, and then $P(OCH_3)_3$ (0.28 mL, 2.3755 $\times 10^{-3}$ mol) was added. The mixture was photolyzed at 0 °C for 30 min after which the solvent was vacuum removed. The residue was dissolved in a 3:7 toluene–heptane mixture, and the solution was placed on a silica column. Elution with the 3:7 toluene–heptane mixture developed and removed a red band (starting material). The product was then eluted from the column with toluene. Removal of the toluene solvent and recrystallization of the residue from 1:19 toluene–heptane mixture provided crystals. Anal. Calcd for $C_{22}H_{29}Mo_2O_6P$: C, 43.16; H, 4.77; P, 5.06. Found: C, 43.30; H, 4.83; P, 5.12. ^1H NMR (benzene-d_6): δ 0.88 (t, 3, J = 7.0 Hz), 1.22 (t, 3, J = 7.5 Hz), 2.60 (q, 2, J = 7.5 Hz), 3.05 (q, 2, J = 7.0 Hz), 3.15 (d, 9, J_{P-H} = 9 Hz), 4.86 (d, 5, J = 0.6 Hz), 4.94 (s, 5). IR (toluene solution): 1933 (m), 1901 (sh), 1877 (s), 1808 cm^{-1} (m).

Thermal Dissociation of the Acetylene Complexes. Solutions of the $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4(RC_2R)$ complexes (~60 mmol) in 20 mL of mesitylene were heated at 150 °C for 2 h in a Schlenk flask fitted with a reflux condenser and a gas inlet through which a slow argon purge was maintained throughout the reaction period. Then the solvent was removed under vacuum, and the residue was characterized by ^1H NMR analysis. The 2-butyne and 3-hexyne adducts showed no sign of decomposition. The acetylene, C_2H_2, adduct decomposed very slowly to form initially $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4$. With longer reaction times, the latter complex underwent decomposition to yield two unidentified complexes that had proton resonances at ~4.8 (A) and 5.5 ppm (B), respectively. The relative amounts of products after 2-, 4.5-, 6-, and 8-h reaction periods were respectively 99, 84, 78, and 45% for $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4(C_2H_2)$, 1, 6, 3, and 7% for $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4$, 0, 10, 12, and 33% for complex A, and 0, 0, 7, and 15% for complex B. The dissociation of the C_2H_2 complex was completely suppressed in a CO atmosphere (CO purge).

Acetylene-Exchange Reactions. Exchange reactions between $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4$(alkyne) (50–60 mmol) and alkyne′ (500–600 mmol) or carbon monoxide were examined in mesitylene (20 mL) or C_7D_8 (0.5 mL) solution at 120–180 °C in a closed Schlenk vessel (procedure A), under flow conditions (alkyne′ or CO) in a three-necked flask fitted with a reflux condenser and a gas inlet tube (procedure B) or in a sealed NMR tube (procedure C). At the completion of the attempted exchange reaction for procedures A and B, the mesitylene solvent was removed under vacuum, and the residue was analyzed by ^1H NMR spectroscopy. For procedure C, the products were analyzed directly by NMR spectroscopy. Results are summarized in Table I. A carbon monoxide atmosphere reduced the rate of acetylene exchange by at least a factor of 10 for the diphenylacetylene–hexyne complex system.

To determine the molecularity of the exchange reaction, we heated weighed amounts of $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4(C_2H_5C_2C_2H_5)$ (~3×10^{-2} mmol) and $C_6H_5C_2C_6H_5$ in 0.5 mL of toluene at 110 °C for up to 3 h in a sealed NMR tube under an argon atmosphere. At 15-min intervals, the NMR tube was removed from the heating bath and immediately chilled. The contents of the tube were analyzed by ^1H NMR spectroscopy; the relative amounts of 3-hexyne and diphenylacetylene adducts were determined by integration. In one of the above kinetic runs, a carbon monoxide atmosphere was used in lieu of an argon atmosphere. In this latter experiment, the tube was heated for 3 h at 110 °C. Results are summarized in Figure 1 and Table II (complete experimental data are presented as supplementary material, Table V). The linear plot shown in Figure 1 was generated from a least-squares analysis of the data. Larger reactant ratios of diphenylacetylene to the molybdenum–hexyne complex could not be used because of the low solubility of diphenylacetylene.

The above exchange reaction was also examined on the analogous tungsten compound. However, the tungsten–alkyne complex was unreactive up to 150 °C, where a myriad of ^1H NMR resonances began to appear. Because of the lack of a clean exchange reaction, this exchange reaction was not examined in detail.

Stoichiometric Hydrogenation of $(\eta^5\text{-}C_5H_5)_2M_2(CO)_4(C_2H_5C_2C_2H_5)$ (M = Mo, W). $(\eta^5\text{-}C_5H_5)_2M_2(CO)_4(C_2H_5C_2C_2H_5)$ (M = Mo, W) (4.69×10^{-5} mol) in 20 mL of mesitylene was placed in a reaction

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[6] W. I. Bailey, M. H. Chisholm, F. A. Cotton, and L. A. Rankel, *J. Am. Chem. Soc.*, **100**, 5764 (1978).

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Table I. Alkyne-Exchange Reactions for $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4(RC_2R')$

acetylene complex						
R	R′	reactant	T, °C	time, h	procedure	results
H	H	CO	150	2	A, B	no reactn
H	H	3-hexyne	120	2	A	complex reactn mixture
H	H	3-hexyne	100	2	A	no reactn
CH_3	CH_3	3-hexyne	150	2	A	~50% exchange[a]
CH_3	CH_3	3-hexyne	150	4	A	95% exchange[a]
CH_3	CH_3	2-butyne	150	4	A	complex reactn mixture
C_2H_5	C_2H_5	$C_6H_5C_2C_6H_5$	150	2	A	75% exchange[b]
C_2H_5	C_2H_5	2-butane	150	0.5	B	~50% exchange – complex reactn mixture
C_2H_5	C_2H_5	CO	150	6	A	no reactn
C_2H_5	C_2H_5	C_2H_2	150	2	B	complex reactn mixture
C_2H_5	C_2H_5	3-hexyne	150	2	A	96% hexyne complex
C_2H_5	C_2H_5	3-hexyne	180	2	A	complex reactn mixture
C_2H_5	C_2H_5	1-hexyne	120	2	C	~50% exchange + other products
C_6H_5	C_6H_5	1-hexyne	120	2	C	~70% reactant + 7 other products
$n\text{-}C_4H_9$	H	1-hexyne	120	2	C	~53% reactant + other products
$n\text{-}C_4H_9$	H	3-hexyne	120	2	C	84% reactant + other products

[a] ~5% of three other products formed. [b] ~10% of at least two other products formed.

Table II. Kinetics of the Alkyne-Exchange Reaction

mole ratio[a]	n_0[b]	slope × 10^3	intercept	correlation	std dev	variance
5:1	3.411	3.46	7.81×10^{-2}	0.995	0.173	0.0272
10:1	3.333	3.53	8.68×10^{-2}	0.997	0.176	0.0282
20:1	2.888	3.64	8.95×10^{-2}	0.990	0.183	0.0305
30:1[c]	3.200	3.85	1.15×10^{-1}	0.974	0.180	0.0290
30:1[c]	3.120	3.52	1.30×10^{-1}	0.994	0.176	0.0282
40:1[c]	3.023	3.84	1.18×10^{-1}	0.973	0.179	0.0289
40:1[c]	3.062	3.72	1.08×10^{-1}	0.996	0.186	0.0313

[a] Alkyne:alkyne complex. [b] n_0 = the number of moles of the $(C_5H_5)_2Mo_2(CO)_4$(acetylene) complex multiplied by 10^5. [c] These [c] These reactions were done twice, with use of the denoted quantities.

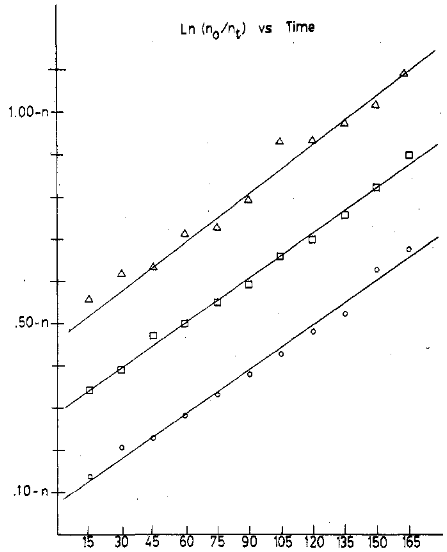

Figure 1. Plot of rate data for the acetylene-exchange reaction between $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4$(3-hexyne) and diphenylacetylene to produce $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4(C_6H_5C_2C_6H_5)$. n_0 represents the initial number of moles of the hexyne complex and n_t the number of moles of the hexyne complex at time t in minutes. The abscissa has a sliding scale derived by substituting n = 0, 0.1, and 0.2, respectively.

tube. The tube was then cooled to −196 °C, evacuated, and filled with H_2 to 1 atm. After allowing the tube and contents to warm up to room temperature, we placed the tube in a heating bath at 150 °C for 2 h. The volatile product, collected and then analyzed by gas chromatography, was *cis*-3-hexene. The residues were analyzed by ^1H NMR spectroscopy and shown to be a mixture of the starting acetylene complex and $(\eta^5\text{-}C_5H_5)_2M_2(CO)_4$ for M = W and only $(\eta^5\text{-}C_5H_5)_2M_2(CO)_4$ for M = Mo.

Table III. Catalytic Hydrogenations for $(\eta^5\text{-}C_5H_5)_2M_2(CO)_3L(C_2H_5C_2C_2H_5)$[a]

catalyst			
M	L	T, °C	turnover rate[b]
Mo	CO	150	2.62×10^{-2}
Mo	CO	100	4.40×10^{-2}
Mo	$P(OCH_3)_3$	100	5.63×10^{-3}
W	CO	170	7.39×10^{-4}

[a] The product is *cis*-3-hexene for each case. [b] Units of the turnover rates are mol of 3-hexene (mol of catalyst)$^{-1}$ min^{-1}.

Catalytic Hydrogenations. These procedures comprised reaction of weighed quantities (~5 × 10^{-5} mol) of the alkyne complexes and of alkyne (~1.2 × 10^{-3} mmol) in 20 mL of mesitylene in a glass reaction vessel fitted with a Kontes stopcock. The vessel with the nongaseous reactants was cooled to −196 °C, evacuated, and filled with hydrogen to 1 atm. The vessel was closed and then heated to the reaction temperature for a set period of time. Characterization comprised gas chromatography of the volatile products and NMR analysis of the nonvolatile residues. Results are presented in Table III. For the $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_3P(OCH_3)_3(C_2H_5C_2C_2H_5)$ catalytic reaction, NMR analysis of the residue showed the presence of the phosphite complex (~60%), $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4(C_2H_5C_2C_2H_5)$, and other resonances, one set of which was consistent with the structure $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_2[P(OCH_3)_3]_2$ (doublet C_5H_5 resonances). In the 2-butyne and 3-hexyne reaction systems, no *trans*-2-butene or -3-hexene, respectively, was detected by GC analysis.

$(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4(HC_2H)$ (0.0310 g, 6.74 × 10^{-5} mol) was dissolved in 20 mL of mesitylene contained in a glass reaction vessel. The vessel was cooled to −196 °C, evacuated, and then allowed to warm to room temperature. The tube was then filled with a 1:1 C_2H_2–D_2 mixture to 1 atm. The tube was then placed in a heating bath at 150 °C for 1.5 h. A sample of the gases above the solution was taken and analyzed by IR spectroscopy. Only the absorptions due to *cis*-$C_2H_2D_2$ were observed; the characteristic vibration is at 841.5 cm^{-1}. There was no detectable absorption in the 988-cm^{-1} region characteristic for the *trans*-$C_2H_2D_2$ isomer.[9]

Labeled C_5H_5 Ligand-Exchange Reactions. Mixtures of the $(\eta^5\text{-}CH_3C_5H_4Mo)_2$ and $(\eta^5\text{-}C_5H_5Mo)_2$ complexes ((0.6–2.5) × 10^{-5} mol each) were dissolved in 20 mL of toluene and reacted alone or reacted in combination with other reagents in argon or in CO atmospheres for varying time periods at 25–150 °C. The complexes were recovered and analyzed by mass spectroscopy for label interchange, i.e., formation of $(\eta^5\text{-}C_5H_5Mo)(\eta^5\text{-}CH_3C_5H_4Mo)$ dinuclear complexes. All reactions listed in Table IV led to dinuclear products that contained apparent trace to 1% amounts of the dinuclear complex with one C_5H_5 and one $CH_3C_5H_4$ ligand, with the exception of the 25 °C exchange between the molybdenum tricarbonyl dimers where

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(9) Infrared reference data for *cis*- and *trans*-$C_2H_2D_2$ were obtained from Professor J. Thomas: *cis*-$C_2H_2D_2$, 843 cm^{-1}; *trans*-$C_2H_2D_2$, 988 cm^{-1}.

Table IV. Ligand (C_5H_5-$CH_3C_5H_4$) Interchange in Dinuclear Molybdenum Complexes

Mo reactants[a]	other reactants	atmosphere	T, °C	time, h	product[a,b] detected	% label interchange
A + B		argon	25	3	A, B, C	25
D + E	3-hexyne[c]	argon	25	2	F, G, H	~1
F + G		argon	25	3	F, G, H	~1
F + G		argon	110	2	F, G, H	~1
F + G		argon	110	12	F, G, H	~1
F + G		argon	150[d]	2	F, G, H	~1
F + G		CO	110	2	F, G, H	~1
F + G		CO	150[d]	2	F, G, H	~1
F + G	diphenylacetylene[e]	*f*	110	2	F, G, H, I, K	~1
F + G	3-hexyne[g]	H_2	150	2	F, G, H	~1
A + B[h]					A, B	0
F + G[h]					F, G	0
F + G	diphenylacetylene	argon	0 (UV)	0.5	F, G, I, J	0

[a] A = $(C_5H_5)_2Mo_2(CO)_6$, B = $(CH_3C_5H_4)_2Mo_2(CO)_6$, C = $(C_5H_5)(CH_3C_6H_4)Mo_2(CO)_6$, D = $(C_5H_5)_2Mo_2(CO)_4$, E = $(CH_3C_5H_4)_2Mo_2(CO)_4$, F = $(C_5H_5)_2Mo_2(CO)_4$(3-hexyne), G = $(CH_3C_5H_4)_2Mo_2(CO)_4$(3-hexyne), H = $(C_5H_5)(CH_3C_5H_4)Mo_2(CO)_4$(3-hexyne), I = $(C_5H_5)_2Mo_2(CO)_4(C_6H_5C_2C_6H_5)$, J = $(CH_3C_5H_4)_2Mo_2(CO)_4(C_6H_5C_2C_6H_5)$, and K = $(C_5H_5)(CH_3C_5H_4)Mo_2(CO)_4(C_6H_5C_2C_6H_5)$. [b] Complexes analyzed by mass spectrometric analyses. [c] Mole ratio of acetylene to Mo dimers ≅ 6. [d] Mesitylene solvent. [e] Mole ratio of acetylene to Mo dimers ≅ 80. [f] Sealed-tube reaction. [g] Mole ratio of acetylene to Mo dimers ≅ 200. [h] Blank experiments using physical mixtures or mixtures obtained by dissolution and removal of solvent followed by the mass spectrometric analysis.

the exchange was ~25% complete within 2 h. The apparent interchange in the $(C_5H_5)_2Mo_2(CO)_4(RC_2R)$ reactions were artifacts. First, increase in reaction times did not lead to increases in apparent interchange, and second, the observed intensity profiles at the masses characteristic of the mixed species did not match the calculated profiles. Experimental blanks in which physical mixtures of the C_5H_5 and $CH_3C_5H_4$ dinuclear complexes were subjected to mass spectrometric analysis established that no detectable scrambling occurred under analysis conditions.

Carbonyl Ligand Exchange in $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4(RC_2R)$. A solution of $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4(C_2H_5C_2C_2H_5)$ (0.03 g, 8.81×10^{-5} mol) in 10 mL of toluene was placed in a reaction tube of approximately 100-mL volume. The tube was then cooled to −78 °C, evacuated, and filled to a pressure of 58 cmHg with ^{13}CO (90%). The tube and contents were allowed to warm up to room temperature. The tube was then placed in a heating bath at 110 or 150 °C for a period of time. After this period, the carbon monoxide was removed by evacuation after cooling of the tube and its contents to −78 °C. The resulting solution was then analyzed by infrared spectroscopy. At 150 °C, the exchange was complete within 8 h, whereas the extent of the exchange was low (~10%) at 110 °C after 3 h.

Photochemically Initiated Acetylene Exchange. A solution of $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4(C_2H_5C_2C_2H_5)$ (0.0191 g, 3.702×10^{-5} mol) and diphenylacetylene (0.1328 g, 7.46×10^{-4} mol) in 0.5 mL of C_7D_8 was sealed in an NMR tube and photolyzed with quartz-filtered radiation from a Hanovia 450-W medium-pressure lamp for 30 min at 0 °C. After this period, the products were analyzed spectroscopically. Analysis showed the presence of $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4(C_2H_5C_2C_2H_5)$ (53.4%), $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4(C_6H_5C_2C_6H_5)$ (30.7%), and other C_5H_5 resonances at δ ~4.3 (s, 2.5%), ~4.6 (s, 2.5%), ~5.0 (d, 6%), and ~5.4 (s, 5%).

Results and Discussion

All the molybdenum- and tungsten-acetylene complexes, $(\eta^5\text{-}C_5H_5)_2M_2(CO)_4(RC_2R)$, reacted with hydrogen at 100 °C or above to form $(\eta^5\text{-}C_5H_5)_2M_2(CO)_4$ and *cis*-RCH=CHR. Small amounts (trace to 1%) of the trans olefin were detected in the stoichiometric reaction only with the 2-butyne system. With long reaction times, other products were formed due to the thermal reactivity of the $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4$ product in a hydrogen atmosphere. No striking difference in reactivity of the acetylene adducts was evident in the molybdenum series although the parent C_2H_2 derivative appeared to be most reactive. Hydrogenation rate was substantially lower (10^2–10^3) for tungsten than for molybdenum. In the presence of excess alkyne, the reactions were catalytic although low in rate (Table II) even at 150–170 °C. Hydrogenation products consisted only of the derivative olefin; no olefin isomerization product and no alkane were detected by gas chromatographic analysis. The stereochemistry of the product olefin was wholly cis; no trans isomers were detected in the 2-butyne, 3-hexyne, and $C_2H_2(+D_2)$ reaction systems although very small amounts could have been present and escaped detection by GC and infrared analysis. Catalytic reaction rate was significantly suppressed by the presence of carbon monoxide.

A more facile reaction than hydrogenation was alkyne exchange which occurred at modest rates at temperatures as low as 110 °C. This exchange reaction was also sharply reduced in rate by the presence of carbon monoxide. Acetylene dissociation of the complexes was detected only for the C_2H_2 complex, and the rate was low at 150 °C. Carbon monoxide completely blocked the acetylene dissociation reaction in this complex. A reaction sequence consistent with all data and conclusions is

$$(C_5H_5)_2Mo_2(CO)_4(\mu_2\text{-}C_2H_2) \rightleftharpoons (C_5H_5)_2Mo_2(CO)_3(\mu_1\text{-}C_2H_2) + CO$$

$$(C_5H_5)_2Mo_2(CO)_3(\mu_1\text{-}C_2H_2) \rightleftharpoons (C_5H_5)_2Mo_2(CO)_3 + C_2H_2$$

Substitution of trimethyl phosphite for carbon monoxide in the acetylene complexes led to higher initial activity in the catalyzed acetylene hydrogenation reactions. However, the complex $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_3[P(OCH_3)_3]$(3-hexyne) rapidly underwent a redistribution process to yield the parent $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4$(3-hexyne) complex and a $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_2[P(OCH_3)_3]_2$ complex which was unreactive to acetylene addition.

The significance of this molybdenum-alkyne chemistry is not the catalytic alkyne hydrogenation reaction per se since such homogeneous and heterogeneous reactions are legion but rather the mechanistic features of the catalytic reaction and the basic chemistry of these dinuclear molybdenum complexes with μ_2-acetylene ligands. An obvious fundamental issue is whether the dinuclear complex undergoes fragmentation to mononuclear metal species at some point during the reaction cycle.[10] We addressed this issue by labeling the cyclopentadienyl ring, namely, the use of $(C_5H_5Mo)_2$ and $(CH_3C_5H_4Mo)_2$ complexes and a mass spectrometric assay for a cross-labeled $(C_5H_5)(CH_3C_5H_4)Mo_2$ species in the reaction products. A number of basic reactions were then examined (Table IV). Curtis and Klinger[11] in their seminal studies of the molybdenum carbonyl dimer chemistry showed label interchange between $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_6$ and $(\eta^5\text{-}CH_3C_5H_4)_2Mo_2(CO)_6$ at 110 °C. We showed that substantial fragmentation in this system occurs at 25 °C within 2 h; this reflects the relatively low Mo–Mo bond energy[12a] in this di-

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(10) The stereochemistry of the product olefin in the catalytic reaction is wholly consistent with catalysis by a mononuclear metal complex (if the steps comprise $L + M \xrightarrow{+H_2} L + MH_2 \xrightarrow{RC_2R} L + MH_2(RC_2R) \rightarrow L + M(H)(-CR{=}CRH)$, only cis olefin would be formed). If the catalytic intermediate is polynuclear, cis olefin *could* also again be the product (see ref 3 and 4 and also E. L. Muetterties, W. R. Pretzer, M. G. Thomas, B. F. Beier, D. L. Thorn, V. W. Day, and A. B. Anderson, *J. Am. Chem. Soc.*, **100**, 2090 (1978)).

(11) M. D. Curtis and R. J. Klinger, *J. Organomet. Chem.*, **161**, 23 (1978).

nuclear complex which has a formal bond order of 1. All other reaction systems based on the dinuclear molybdenum–acetylene complexes (Table IV), including the catalytic hydrogenation reaction, examined for fragmentation through the C_5 ring labels showed apparent trace to 1% formation of cross-labeled product. None of these apparent exchanges was time dependent; in fact, an increase of the reaction time by a factor of 6 did not lead to a detectable increased level of interchange. We conclude that cluster fragmentation to mononuclear fragments is not a step integral to the catalytic hydrogenation reaction or to the acetylene-exchange reaction of $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4(\mu_2\text{-}RC_2R)$ complexes.

Since the catalytic reaction does not involve mononuclear molybdenum and since the $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4$(alkyne) catalyst precursors are coordinately saturated, the first step in the catalytic cycle must comprise the dissociation of a ligand, specifically carbon monoxide, or the intramolecular rearrangement of the alkyne ligand from a μ_2 (bridging) to a μ_1 (nonbridging) configuration, or of the cyclopentadienyl ligand from an η^5 to an η^3 configuration. The observed suppression of the hydrogenation rate by the presence of carbon monoxide argues convincingly for a first step comprising CO dissociation. Carbon monoxide inhibition of the catalytic hydrogenation reaction would require, if the catalytic reaction sequence involved as a first step an intramolecular rearrangement process, that the CO complex with such a rearranged species be more stable than the original complex.[12b] This requirement was not realized in experiments described below in the related acetylene exchange reaction. Because the rates of catalytic hydrogenation were very low and because the reaction temperature was so high and one of the reactants, hydrogen, was gaseous, establishment of a full rate expression for the hydrogenation reactions did not seem feasible. However, in the studies of the related reaction, alkyne exchange, of the dinuclear molybdenum complex, a first step of CO dissociation has been established, and this reaction step should be integral to the catalytic hydrogenation reaction. Since the rates of hydrogenation were lower than alkyne-exchange rates, hydrogen addition to the $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_3(\mu_x\text{-alkyne})$ intermediate is presumed to be rate determining in the hydrogenation cycle.

For the reactions of the $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4(\mu_2\text{-alkyne})$ complexes with free acetylene, exchange was observed for all reaction systems at 110–150 °C, but only one was clean, devoid of formation of other complexes, and this was the exchange between diphenylacetylene and $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4(\mu_2\text{-3-hexyne})$. A kinetic analysis of this exchange reaction established a first-order rate dependence upon the dinuclear molybdenum complex concentration with no evidence of a dependence upon free alkyne concentration within the limits of the experimental conditions. Hence, a rate-determining step of fragmentation, rearrangement (to a coordinately unsaturated complex), or carbonyl or alkyne ligand dissociation must be operative. A fragmentation process based on Mo–Mo or Mo–C_5H_5 bond scission is excluded by the labeling reactions (Table IV). Rearrangement to a coordinately unsaturated complex either by a μ_2-alkyne $\rightleftharpoons$ μ_1-alkyne process, by an $\eta^5\text{-}C_5H_5Mo \rightleftharpoons \eta^3\text{-}C_5H_5Mo$ process, or by alkyne dissociation as a first step is not consistent with the observation that the exchange reaction was slowed by about a factor of 10 by the presence of carbon monoxide. Rate inhibition by CO could be accommodated in a "rearrangement" first step only if the CO complex with the rearranged complex was more stable than the starting acetylene complex.[12b] NMR studies of solutions of $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4$(3-hexyne) in a CO atmosphere (1–2 atm) were indistinguishable from those of the complex alone at 25–110 °C, and there was no evidence of CO reaction with the acetylene complex over a wide range of conditions.[13] An acetylene dissociation reaction, although established for the C_2H_2 derivative, was not detected in either the 3-hexyne or 2-butyne derivative up to 150 °C. In addition, the CO inhibition of the exchange rate is inconsistent with such a rate-determining step for the reason discussed above. A first step, in the alkyne exchange reaction, of CO dissociation to give $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_3$(alkyne), is fully consistent with the kinetic data and with the added CO inhibition effect. Experimentally, CO ligand exchange between ^{13}CO and $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4$(3-hexyne) was observed to be fast at 150 °C and slow at 110 °C, a result fully required in the apparently operative CO dissociation mechanism for alkyne exchange in the molybdenum complex.

Initially, we anticipated that the key step in the $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4$(alkyne)(alkyne′) exchange reactions and catalyzed-acetylene hydrogenation reaction was a μ_2-alkyne $\rightleftharpoons$ μ_1-alkyne rearrangement in the dinuclear molybdenum complex. Formation of $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4(\mu_1\text{-alkyne})$ would allow for formation of $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4(\mu_1\text{-alkyne})H_2$ in the hydrogenation reaction and $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4(\mu_1\text{-alkyne})(\mu_1\text{-alkyne}')$ in the exchange reaction. In addition, the latter species could account for the formation of complex metallacyclic complexes (side-reaction products observed in most of the alkyne-exchange reaction systems and species isolated and structurally characterized by Stone and co-workers[14]). However, metallacycles could also be generated from the $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_3(\mu_x\text{-alkyne})$ intermediate through initial formation of $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_3(\mu_x\text{-alkyne})(\mu_1\text{-alkyne}')$. Furthermore, fragmentation would be an expectedly facile reaction for an unbridged species like $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4(\mu_1\text{-alkyne})$ but an unlikely reaction for the postulated $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_3$(alkyne) intermediate which would have either a μ_2-acetylene bridging ligand or a μ_1-acetylene ligand and a Mo–Mo triple bond. The latter intermediate is fully consistent with all our data and with coordination chemistry principles for the hydrogenation (stoichiometric and catalytic) and acetylene-exchange reactions.

An obvious extension from our finding and conclusions for the thermal reactions of $(\eta^5\text{-}C_5H_5)_2M_2(CO)_4$(alkyne) complexes is photoactivation of these complexes, specifically photodissociation of a carbonyl ligand to give $(\eta^5\text{-}C_5H_5)_2M_2(CO)_3$(alkyne) in some electronic state. In fact, we found that photoassisted acetylene exchange between $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4$(3-hexyne) and diphenylacetylene was rapid

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(12) (a) The analogous chromium complex appears to be partially dissociated in solution; cf. W. I. Bailey, Jr., F. A. Cotton, J. D. Jamerson, and J. R. Kolb, *J. Organomet. Chem.*, **121**, C23 (1976); Lai-Yoong Goh, M. J. D'Aniello, Jr., S. Slater, E. L. Muetterties, I. Tavanaiepour, M. I. Chang, M. F. Frederich, and V. W. Day, *Inorg. Chem.*, **18**, 192 (1979). (b) If an intermediate, I, of any other type other than $(C_5H_5)_2Mo_2(CO)_3$(acetylene) is postulated as a first reaction step in either the catalytic hydrogenation or the alkyne exchange reaction, the observed CO inhibition step requires substantial diversion of the intermediate, I, to a new complex, (I–CO):

step 1 $$(C_5H_5)_2Mo_2(CO)_4(\text{alkyne}) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{I}$$

step 2

$$\text{I} + \text{alkyne} \xrightarrow{k_2} \text{products} \qquad \text{or I} + H_2 \xrightarrow{k_2'} \text{products}$$

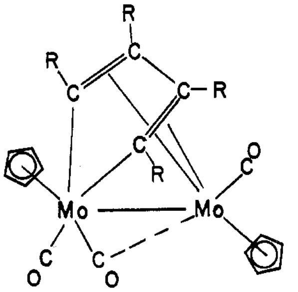
inhibition step $$\text{I} + \text{CO} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} (\text{I–CO})$$

The rate expression for these hypothetical schemes with step 1 rate determining nominally would be $d[\text{products}]/dt = k_1[(C_5H_5)_2Mo_2(CO)_4(\text{alkyne})]$. If CO were to substantially affect the rate, then $K_3 = k_3/k_{-3}$ must be relatively large (equal to 1 or greater) and therefore (I–CO) must be an easily detectable species.

(13) A solution of $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4$(3-hexyne) in toluene-$d_8$ sealed in an NMR tube with a CO atmosphere. This reaction system was monitored by NMR from 25 to 110 °C, and the complex was recovered unchanged from the reaction solutions.

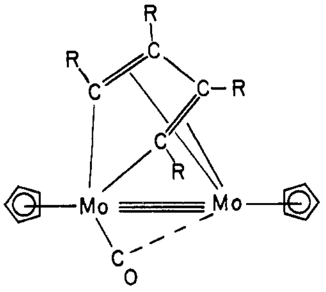
(14) S. A. R. Knox, R. F. D. Stanfield, F. G. A. Stone, M. J. Winter, and P. W. Woodward, *J. Chem. Soc., Chem. Commun.*, 221 (1978).

at 0 °C; the exchange was ~30% complete in 30 min (~20 turnovers/h). No fragmentation of the dinuclear molybdenum–acetylene complex to mononuclear species occurred under the photolysis conditions: the only dinuclear μ_2-acetylene products were $(C_5H_5)_2Mo_2(CO)_4$(diphenylacetylene) and $(CH_3C_5H_4)_2Mo_2(CO)_4$(diphenylacetylene) from the photolysis at 0 °C of a mixture of the C_5H_5 and $CH_3C_5H_4$ molybdenum–3-hexyne complexes in the presence of excess diphenylacetylene (Table IV). Nevertheless, these experiments do not establish that the intermediates in the thermal and the photoassisted alkyne exchange reactions are the same. In fact, the two reactions are not identical; the photochemical reaction produced another type of product characterized as **5**. This type of product is however structurally related to the metallacycles produced in the thermal exchange reactions involving C_2H_2 or 2-butyne as discussed above. Attempts to photoassist the catalytic hydrogenation process were unsuccessful for the $(C_5H_5)_2Mo_2(CO)_4$(3-hexyne), 3-hexyne, and H_2 system. This reaction, effected under hydrogen flow conditions, led to CO loss, consistent with the above-proposed first step of CO-photodissociation. No acetylene hydrogenation took place, and no reactant, $(C_5H_5)_2Mo_2(CO)_4$(3-hexyne), was recovered. The major molybdenum product was a derivative of **5** wherein the two terminal CO ligands had been lost to give a triply bonded dinuclear complex, **6**,[15] which has a precedent in the R = C_6H_5 analogue reported by Knox et al.[14] In addition, there are chromium analogues for R = C_6H_5 and for R = H and C_6H_5.[14,16]



R = C_2H_5

5



R = C_2H_5

6

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Registry No. $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_3[P(OCH_3)_3](C_2H_5C_2C_2H_5)$, 74482-79-4; $[(\eta^5\text{-}C_5H_5)Mo(CO)_2]_2(C_2H_5C_2C_2H_5)$, 61373-51-1; $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4$, 56200-27-2; $(\eta^5\text{-}C_5H_5)_2W_2(CO)_4(C_2H_5C_2C_2H_5)$, 74482-80-7; $(\eta^5\text{-}C_5H_5)_2W_2(CO)_4$, 62853-03-6; $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_2[P(OCH_3)_3]_2$, 74482-81-8; $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4(HC_2H)$, 56200-29-4; $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4(CH_3C_2CH_3)$, 68079-61-8; $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4(C_6H_5C_2C_6H_5)$, 68079-59-4; $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4(n\text{-}C_4H_9C_2H)$, 74482-82-9; $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_6$, 12091-64-4; $(\eta^5\text{-}CH_3C_5H_4)_2Mo_2(CO)_6$, 33056-03-0; $(\eta^5\text{-}C_5H_5)(\eta^5\text{-}CH_3C_5H_4)Mo_2(CO)_6$, 74482-83-0; $(\eta^5\text{-}CH_3C_5H_4)_2Mo_2(CO)_4$, 69140-73-4; $(\eta^5\text{-}CH_3C_5H_4)_2Mo_2(CO)_4(C_2H_5C_2C_2H_5)$, 74482-84-1; *cis*-3-hexene, 13269-52-8.

Supplementary Material Available: Table V, a full listing of experimental data for the kinetic study of the acetylene exchange reaction (1 page). Ordering information is given on any current masthead page.

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[15] The full characterization of these photochemical reactions will be described in a separate paper.

[16] J. S. Bradley, *J. Organomet. Chem.*, **150**, C1 (1978).