

Ligand Substitution Kinetics of Mo(CO)(RC≡CR')(S₂CNMe₂)₂ Complexes

Richard S. Herrick, D. Mark Leazer, and Joseph L. Templeton*

W. R. Kenan, Jr. Laboratory, Department of Chemistry, University of North Carolina,
Chapel Hill, North Carolina 27514

Received December 28, 1982

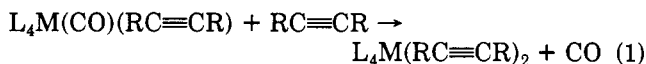
Kinetics of the conversion of Mo(CO)(RC≡CR')(S₂CNMe₂)₂ to Mo(RC≡CR')(S₂CNMe₂)₂ have been followed by visible spectroscopy. Both the reagents and products in this reaction are formally 16-electron complexes. The observed rate law is first order in metal complex and independent of free alkyne concentration when the reaction is run under an inert atmosphere. The reaction is inhibited in the presence of carbon monoxide gas, and the rate expression under 1 atm of carbon monoxide has a first-order dependence on alkyne. Reversible dissociation of carbon monoxide to generate a steady-state intermediate provides a simple mechanistic scheme which is compatible with the experimental results. The relative rate of carbon monoxide substitution corresponds qualitatively with the relative electron-withdrawing ability of the bound alkyne as reflected in the order PhC₂Ph > PhC₂H > PhC₂Me > HC₂-*n*-Bu > EtC₂Et. When the free alkyne differs from the bound alkyne, a rapid alkyne-exchange reaction can be monitored for Mo(CO)(RC≡CR')(S₂CNMe₂)₂ complexes by low-temperature ¹H NMR spectroscopy. The second-order rate expression observed for alkyne exchange is consistent with an associative mechanism. Reactions of Mo(CO)(RC≡CR')(S₂CNMe₂)₂ with nucleophiles (L = CO, P(OMe)₃, PET₃) to form Mo(CO)L₂(S₂CNMe₂)₂ occur rapidly at room temperature. General features of associative and dissociative substitution mechanisms accessible to six-coordinate d⁴ Mo(CO)(RC≡CR')(S₂CNMe₂)₂ complexes are discussed in light of these results.

Introduction

Six-coordinate d⁴ complexes containing both π-acid and π-base ligands constitute an important class of organometallic compounds. These complexes are formally electron deficient in terms of simple electron counting schemes. A number of 16-electron molybdenum (II) complexes have been isolated including Mo(CO)₂(PPh₃)₂X₂ (X = Cl, Br, I),¹ Mo(CNR)₄(SR)₂(R = *t*-Bu),² Mo(CO)₂(py)₂(O-*t*-Bu)₂,³ and Mo(CO)₂(S₂CNR₂)₂.⁴ A subclass of formally electron-deficient group 6 d⁴ complexes consists of monomers containing one or more alkyne ligands. Representative examples include M(CO)(RC≡CR)(S₂CNR')₂ (M = Mo,⁵ W⁶), Mo(RC≡CR)₂(S₂CNR')₂,^{5,7} (π-C₅H₅)M(CO)(RC≡CR)X (M = Mo, W),⁸ (π-C₅H₅)M(RC≡CR)₂X (M = Mo, W),⁹ [(π-C₅H₅)M(CO)(RC≡CR)₂]⁺,¹⁰ and Mo(CO)(RC≡CR)(PR')₂X₂.¹¹

The reactivity patterns of these complexes remain to be explored. Some complexes readily undergo ligand addition to form seven-coordinate 18-electron products in accord with chemical expectations for unsaturated compounds. Available data indicate that it may be prudent to consider the reactivity of the alkyne complexes separately. Substitution reactions dominate the chemistry of d⁴ alkyne derivatives reported to date while ligand addition to form

an 18-electron product is rare. Formation of bis(alkyne) complexes occurs via substitution of the carbonyl ligand in mono(carbonyl) mono(alkyne) complexes as in eq 1.



(a) L₄ = (S₂CNR')₂;^{5,7} (π-C₅H₅)Cl; M = Mo, W⁹

(b) L₄ = (π-C₅H₅)(CO); M = V, Nb, Ta¹²

A satisfactory qualitative molecular orbital picture of the metal-alkyne bond in these formally electron-deficient complexes has emerged.¹³ The physical properties of these alkyne complexes are compatible with vacant alkyne π_{||}* acceptance and filled alkyne π_⊥ donation in bonding to filled and vacant dπ orbitals, respectively. Given the molecular orbital scheme of these formally electron-deficient alkyne monomers and the diverse reactivity they display toward nucleophiles, a question arises concerning the mechanism of these reactions. The standard substitution route for 18-electron reagents invokes dissociation to an unsaturated intermediate followed by ligand addition to form product.¹⁴ Unsaturated transition-metal alkyne complexes conceivably have two distinct pathways available for substitution reactions. Ligand association to form a saturated complex could precede ligand loss to form the final 16-electron product. This would correspond with established 18-electron reagent mechanisms with the free energy of the saturated and unsaturated species inverted to exchange their roles as reagents, intermediates, and products. Alternatively one could envision ligand dissociation generating a formal 14-electron intermediate followed by ligand addition to form the final substituted product.

To address this question a kinetic study of reactions of mono(carbonyl)mono(alkyne)bis(dithiocarbamate)molyb-

(1) (a) Drew, M. G. B.; Tomkins, I. B.; Colton, R. *Aust. J. Chem.* **1970**, *23*, 2517. (b) Colton, R.; Tomkins, I. B. *Ibid.* **1966**, *19*, 1519.

(2) Kamata, M.; Hirotsu, K.; Higuchi, T.; Tatsumi, K.; Hoffmann, R.; Yoshida, T.; Otsuka, S. *J. Am. Chem. Soc.* **1981**, *103*, 5772.

(3) Chisholm, M. H.; Huffman, J. C.; Kelly, R. L. *J. Am. Chem. Soc.* **1979**, *101*, 7615.

(4) (a) Ward, B. C.; Templeton, J. L. *J. Am. Chem. Soc.* **1980**, *102*, 6568. (b) Colton, R.; Scollary, G. R.; Tomkins, I. B. *Aust. J. Chem.* **1968**, *21*, 15.

(5) McDonald, J. W.; Newton, W. E.; Creedy, C. T. C.; Corbin, J. L. *Organomet. Chem.* **1975**, *92*, C25.

(6) Ricard, L.; Weiss, R.; Newton, W. E.; Chen, G. J.-J.; McDonald, J. W. *J. Am. Chem. Soc.* **1978**, *100*, 1318.

(7) Herrick, R. S.; Templeton, J. L. *Organometallics* **1982**, *1*, 842.

(8) Davidson, J. L.; Green, M.; Stone, F. G. A.; Welch, A. J. *J. Chem. Soc., Dalton Trans.* **1976**, 738.

(9) Davidson, J. L.; Sharp, D. W. A. *J. Chem. Soc., Dalton Trans.* **1975**, 2531.

(10) Watson, P. L.; Bergman, R. G. *J. Am. Chem. Soc.* **1980**, *102*, 2698.

(11) Winston, P. B.; Burgmayer, S. J. N.; Templeton, J. L. *Organometallics* **1983**, *2*, 167.

(12) (a) Nesmeyanov, A. N.; Anisimov, K. N.; Kolobova, N. E.; Pasyanskii, A. A. *Dokl. Akad. Nauk SSSR* **1968**, *182*, 112. (b) Nesmeyanov, A. N.; Anisimov, K. N.; Kolobova, N. E.; Pasyanskii, A. A. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1969**, 100.

(13) Tatsumi, K.; Hoffmann, R.; Templeton, J. L. *Inorg. Chem.* **1982**, *21*, 466.

(14) Tolman, C. A. *Chem. Soc. Rev.* **1972**, *1*, 337.

Table I. Visible Absorption Parameters for Mo(CO)(RC₂R)(S₂CNMe₂)₂ Complexes in Toluene at 25 °C

alkyne	λ_{max} , nm	ϵ , L mol ⁻¹ cm ⁻¹
PhC ₂ H	700	230
Ph ₂ C ₂	705	140
PhC ₂ Me	677	230
1-hexyne	688	83
3-hexyne	673	85

denum(II) with added alkyne was undertaken. Both carbonyl substitution and alkyne-exchange reactions have been probed. In concert with products formed when these molybdenum alkyne complexes react with CO, P(OMe)₃, or PEt₃ a general hypothesis concerning the nucleophilic reactivity patterns characterizing these six-coordinate d⁴ reagents can be formulated.

Experimental Section

Spectroscopic Measurements. Infrared spectra were recorded on a Beckman IR 4250 spectrophotometer and calibrated with a polystyrene standard. Proton NMR spectra were recorded on a Varian XL-100, and chemical shifts are reported as parts per million downfield from SiMe₄. NMR sample temperatures were measured directly with an alcohol thermometer placed in the probe. Electronic spectra were recorded on Varian 634 and Perkin-Elmer 552 spectrophotometers.

General Procedures. Molybdenum hexacarbonyl, chlorine gas, sodium dialkyldithiocarbamate salts, alkynes, and tertiary phosphines were obtained from commercial sources and used as received. Solvents used for the preparation of starting materials were degassed with nitrogen prior to use. Fisher alumina (80–200 mesh) was used as received for chromatographic purifications. A dry oxygen-free nitrogen atmosphere was used for the preparative and kinetic aspects of this work. Carbon monoxide gas was purified by passage through chromous acid solution followed by calcium chloride to remove water. Reagent Mo(CO)(RC≡CR')(dmtc)₂ complexes (dmtc = -S₂CNMe₂) were prepared from Mo(CO)₄Cl₂¹⁵ according to published methods⁵ and purified by chromatography on alumina with toluene as eluent.

Alkyne Addition Reactions. Kinetic studies were performed under pseudo-first-order conditions with the alkyne present in excess. Substitution reactions of mono(carbonyl) mono(alkyne) complexes with added alkyne to form bis(alkyne) complexes were carried out under nitrogen or carbon monoxide in 100-mL Schlenk flasks fitted with serum caps. A carefully weighed sample of the metal reagent was added to the reaction flask first. Approximately 50 mL of distilled toluene (potassium/benzophenone) was transferred to the previously tared flask that was weighed again in order to calculate the volume of toluene from the density ($\rho = 0.867$ g/mL). The green solution was placed in a constant temperature bath and after thermal equilibrium had been established a known amount of alkyne was added. Reaction progress was followed by monitoring the decrease in the visible absorption due to starting material near 700 nm (Table I). The bright orange product has an intense visible absorption near 400 nm and negligible absorption in the 700 nm region. The solution remains homogeneous throughout the reaction. Initial reactions were followed for more than 3 half-lives to establish linearity of the pseudo-first-order plots. All reactions were monitored a minimum of 2 half-lives. Reaction solutions were warmed to 80 °C for 1 h to take the reactions to completion in order to obtain A_{∞} . A full visible spectrum was recorded when the A_{∞} reading was taken in order to check for absorption due to potential oxidation products. Oxidation of Mo(CO)(RC≡CR')(dmtc)₂ produces OMo(dmtc)₂, which exhibits an intense transition near 510 nm.¹⁶ In the few cases where oxidation was indicated, the data from that kinetic run were discarded.

Reactions of Mo(CO)(PhC₂Ph)(dmtc)₂ with PhC₂Ph under a CO atmosphere were performed in a similar manner. As CO(g) was introduced into the evacuated reaction vessel, the solution

of Mo(CO)(PhC₂Ph)(dmtc)₂ changed from green to orange and solution infrared spectra indicated that formation of Mo(CO)₃(dmtc)₂ had occurred. Addition of the alkyne reagent in excess returned the solution to its original green color, but visible spectroscopy revealed the presence of residual Mo(CO)₃(dmtc)₂. The flask was evacuated and backfilled with CO twice, and solutions were stirred continuously to maintain a CO-saturated liquid phase. One experiment was carried out under a mixed atmosphere with a CO:N₂ ratio of 41:59 determined by measuring the flow rate of each gas individually and then combining the two gas lines with a Y-tube.

Alkyne-Exchange Reactions. Approximately 33 mg (0.067 mmol) of Mo(CO)(HC₂-*n*-Bu)(dmtc)₂ was placed in each of two 5-mm NMR tubes. Deoxygenated CDCl₃ (1 mL) containing 2 drops of CH₂Cl₂ as an internal standard was added; green homogeneous solutions resulted. The NMR tube was cooled to -37 °C in the probe. An initial spectrum was taken to measure the relative integration ratios of the bound 1-hexyne terminal proton (δ 12.14):CH₂Cl₂. Precooled phenylacetylene diluted with CDCl₃ to prevent freezing was added. The NMR tube was vigorously agitated before the sample was replaced in the probe. Reactions were followed by monitoring the integration ratios of the terminal alkyne protons of the starting material (δ 12.14) and the phenylacetylene product (δ 12.48). The amount of free alkyne was determined by integrating the phenyl protons relative to the methylene chloride standard. The ratios of HC₂Ph:Mo(CO)(HC₂-*n*-Bu)(dmtc)₂ for the two kinetic experiments were 5.70:1.00 and 32.8:1.00. Both reactions were followed for 2 half-lives. Only reagents and products were spectroscopically detected during the course of the reaction. A_{∞} values (integration areas at $T = \infty$) were obtained 1 h after the sample was warmed to room temperature.

Treatment of Kinetic Data. Absorbance data from visible spectroscopy and integration ratios from ¹H NMR spectroscopy were used to obtain pseudo-first-order rate constants, k_{obsd} , from $\ln(A_{\infty} - A_t)$ vs. t plots (correlation coefficients <-0.990 for experiments under nitrogen). Data for reactions under CO gave plots showing upward curvature when PhC₂Ph was present in less than 40-fold excess. Rate constants for these experiments were calculated from the first half-life, $t_{1/2}$, and represent the average rate constant during the early part of the reaction. An Eyring plot yielded values of ΔH^{\ddagger} and ΔS^{\ddagger} .

Reactions of Mo(CO)(RC₂R)(dmtc)₂ with Other Lewis Bases. (a) Carbon Monoxide. Mo(CO)(HC₂H)(dmtc)₂ (0.400 g, 1.02 mmol) was dissolved in 10 mL of CH₂Cl₂. Carbon monoxide gas was bubbled through the solution. Within a few minutes the solution was orange. After 20 min a solution IR spectrum indicated that conversion of Mo(CO)(HC₂H)(dmtc)₂ to Mo(CO)₃(dmtc)₂ was complete: IR (CH₂Cl₂) $\nu(\text{CO})$ 2028 (s), 1943 (s) cm⁻¹.

(b) Trimethyl Phosphite. Mo(CO)(MeC₂Me)(dmtc)₂ (0.13 g, 0.31 mmol) was dissolved in toluene (10 mL). Trimethyl phosphite (2.25 equiv) was added to the solution, which immediately changed from green to cherry red. After the solution was stirred for 45 min, the only $\nu(\text{CO})$ band observed was at 1825 cm⁻¹. Petroleum ether was added to precipitate a pink solid. The solution was filtered and solvent was removed. The orange oil was triturated with ether/MeOH (1/1) and produced Mo(CO)[P(OMe)₃]₂(dmtc)₂ as a red solid: IR (KBr) 1841 (s), 1829 (sh) cm⁻¹; ¹H NMR (CDCl₃) δ 3.61 (d, 18 H, OMe, ³J_{HP} = 11 Hz), 3.27 (s, 12 H, NCH₃).

(c) Triethylphosphine. Mo(CO)(EtC₂Et)(dmtc)₂ (0.200 g, 0.448 mmol) was dissolved in 10 mL of CH₂Cl₂, and a slight excess of PEt₃ (0.059 g, 0.62 mL, 0.50 mmol) was added. The solution color immediately changed from green to reddish brown. Solution IR showed a decrease in intensity of the starting material $\nu(\text{CO})$ absorption, and a new band of similar intensity at 1770 cm⁻¹ was present, which was assigned to Mo(CO)(PEt₃)₂(dmtc)₂.

Decomposition of Mo(CO)(HC₂Ph)(dmtc)₂ in the Absence of Nucleophiles. Mo(CO)(HC₂Ph)(dmtc)₂ (0.200 g, 0.429 mmol) was dissolved in 25 mL of toluene. The solution was held at a temperature of 90 °C for 30 min while purified N₂ gas was bubbled through the solution. After 20 min the solution color had changed from green to orange-brown. The solution volume was reduced, and a brown powder was isolated. IR and ¹H NMR spectroscopy indicated that no carbonyl or alkyne ligands had been retained in the solid decomposition product.

(15) Colton, R.; Tomkins, I. B. *Aust. J. Chem.* 1966, 19, 1143.

(16) Newton, W. E.; Corbin, J. L.; Bravard, D. C.; Searles, J. E.; McDonald, J. W. *Inorg. Chem.* 1974, 13, 1100.

Table II. Rate Constants for the Reaction of $\text{Mo}(\text{CO})(\text{PhC}_2\text{Ph})(\text{S}_2\text{CNMe}_2)_2$ with added PhC_2Ph at 25 °C under Nitrogen^a

alkyne excess, equiv	$10^5 k_{\text{obsd}},^b$ s ⁻¹	alkyne excess, equiv	$10^5 k_{\text{obsd}},^b$ s ⁻¹
10 ×	2.1 (2)	20 ×	2.1 (2)
20 ×	2.3 (2)	40 ×	2.4 (2)

^a $[\text{Mo}(\text{CO})(\text{PhC}_2\text{Ph})(\text{dmtc})_2]_0 = (5.0 \pm 0.1) \times 10^{-3}$ M.

^b The estimated error in the last digit is indicated in parentheses.

Table III. Rate Constants for the Reactions of $\text{Mo}(\text{CO})(\text{RC}_2\text{R}')(\text{S}_2\text{CNMe}_2)_2$ with $\text{RC}_2\text{R}'$ under Nitrogen

$\text{RC}_2\text{R}'$	$T, ^\circ\text{C}$	$10^5 k_{\text{obsd}},^a$ s ⁻¹
PhC_2Ph	25.0	2.2 (2)
PhC_2Ph	40.0	14 (1)
PhC_2H	25.0	0.42 (3)
PhC_2Me	25.0	0.23 (2)
PhC_2Me	40.0	2.0 (1)
PhC_2Me	57.4	20 (1)
$\text{HC}_2\text{-}n\text{-Bu}$	40.0	0.79 (4)
$\text{HC}_2\text{-}n\text{-Bu}$	57.4	8.5 (1)
EtC_2Et	57.4	4.8 (5)

^a The estimated error in the last digit is indicated in parentheses.

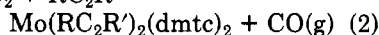
Table IV. Activation Parameters for the Reaction of $\text{Mo}(\text{CO})(\text{RC}_2\text{R}')(\text{S}_2\text{CNMe}_2)_2$ with $\text{RC}_2\text{R}'$

$\text{RC}_2\text{R}'$	$\Delta H^\ddagger,^a$ kcal mol ⁻¹	$\Delta S^\ddagger,^a$ eu
PhC_2Ph	24.2 (6)	1 (2)
PhC_2CH_3	26.4 (4)	4 (1)
$\text{HC}_2\text{-}n\text{-Bu}$	27.5 (5)	6 (2)

^a The estimated error in the last digit is indicated in parentheses.

Results

Bis(Alkyne) Formation Reactions. Reactions of $\text{Mo}(\text{CO})(\text{RC}_2\text{R}')(\text{dmtc})_2$ ($\text{dmtc} = \text{-S}_2\text{CNMe}_2$; $\text{RC}_2\text{R}' = \text{PhC}_2\text{Ph}, \text{PhC}_2\text{H}, \text{PhC}_2\text{Me}, \text{HC}_2\text{-}n\text{-Bu},$ and EtC_2Et) with added free alkyne to form $\text{Mo}(\text{RC}_2\text{R}')_2(\text{dmtc})_2$ proceed according to eq 2 at temperatures ranging from 25.0 to 57.4 °C.



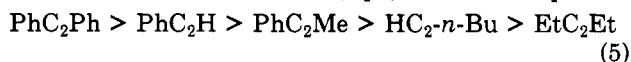
A pseudo-first-order rate law was obeyed (eq 3) as

$$\frac{-d[\text{Mo}(\text{CO})(\text{RC}_2\text{R}')(\text{dmtc})_2]}{dt} = k_{\text{obsd}}[\text{Mo}(\text{CO})(\text{RC}_2\text{R}')(\text{dmtc})_2] \quad (3)$$

illustrated in Figure 1 by the $\ln(A_t - A_\infty)$ vs. t plot for the reaction of $\text{Mo}(\text{CO})(\text{PhC}_2\text{Me})(\text{dmtc})_2$ with PhC_2Me at 57.4 °C. The rate constant, k_{obsd} , is independent of alkyne concentration (Table II) in accord with a first-order rate law as in eq 4. A comparison of first-order rate constants,

$$\frac{-d[\text{Mo}(\text{CO})(\text{RC}_2\text{R}')(\text{dmtc})_2]}{dt} = k_1[\text{Mo}(\text{CO})(\text{RC}_2\text{R}')(\text{dmtc})_2]^1[\text{RC}_2\text{R}']^0 \quad (4)$$

k_1 , for various alkyne derivatives is presented in Table III. Electron-withdrawing alkyne ligands promote more rapid carbon monoxide substitution (eq 5). Activation param-



eters for $\text{PhC}_2\text{Ph}, \text{PhC}_2\text{Me},$ and $\text{HC}_2\text{-}n\text{-Bu}$ derivatives are compiled in Table IV, each exhibiting a small positive value of ΔS^\ddagger .

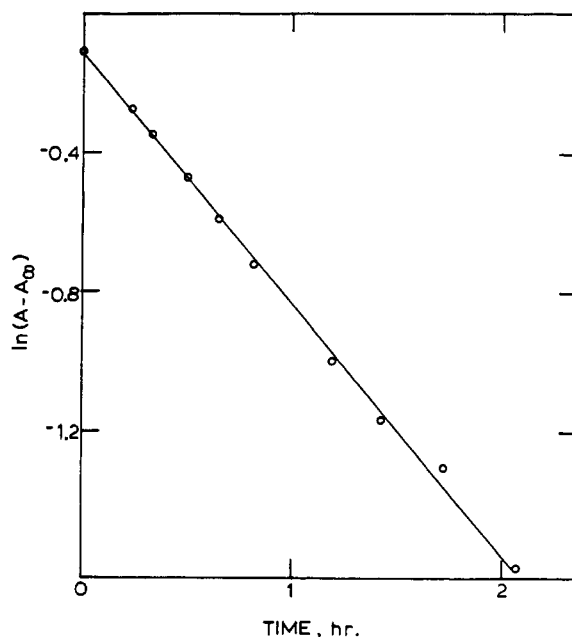


Figure 1. Pseudo-first-order plot of $\ln(A - A_\infty)$ vs. t for the reaction of $\text{Mo}(\text{CO})(\text{PhC}_2\text{Me})(\text{dmtc})_2$ with PhC_2Me (20 equiv) at 57.4 °C under 1 atm of dinitrogen.

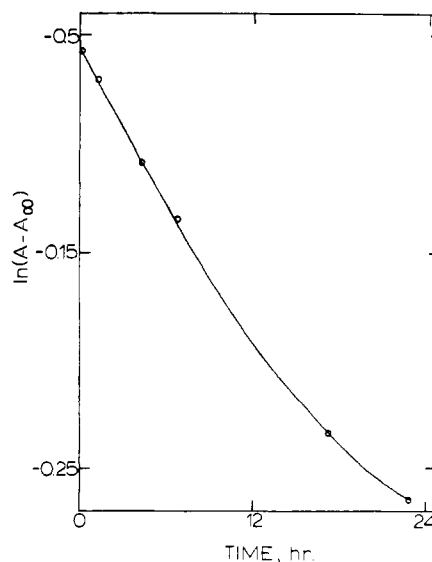


Figure 2. Pseudo-first-order plot of $\ln(A - A_\infty)$ vs. t for the reaction of $\text{Mo}(\text{CO})(\text{PhC}_2\text{Ph})(\text{dmtc})_2$ with PhC_2Ph (40 equiv) at 40.0 °C under 1 atm of carbon monoxide.

Carbon monoxide inhibition experiments were performed with $\text{Mo}(\text{CO})(\text{PhC}_2\text{Ph})(\text{dmtc})_2$ and excess diphenylacetylene at 40.0 °C. The solution concentration of dissolved CO at 1 atm of pressure was calculated by established methods.¹⁷ Under these conditions $\text{Mo}(\text{CO})(\text{PhC}_2\text{Ph})(\text{dmtc})_2$ is in rapid equilibrium with $\text{Mo}(\text{CO})_3(\text{dmtc})_2$ with up to 15% of the metal reagent present as the tricarbonyl. Since this is a rapid equilibrium with the bulk of the reagent present as the carbonyl alkyne complex, the kinetics can be analyzed in terms of the rate of disappearance of $\text{Mo}(\text{CO})(\text{PhC}_2\text{Ph})(\text{dmtc})_2$. Kinetic runs with 10.0-, 100-, and 200-fold excess alkyne gave linear plots of $\ln(A_t - A_\infty)$ vs. t ($r < -0.990$) while 20.0- and 40.0-fold excess diphenylacetylene experiments under carbon monoxide curved upward as shown in Figure 2. Rate constants for these runs were calculated as described

Table V. Rate Constants for the Reaction of Mo(CO)(PhC₂Ph)(S₂CNMe₂)₂ with PhC₂Ph at 40.0 °C under Carbon Monoxide^a

alkyne excess, equiv	10 ³ [CO], M	[PhC ₂ Ph], M	10 ⁵ k _{obsd} , ^b s ⁻¹
20.0	7.92	0.108	1.6 (2)
40.0	7.92	0.216	3.4 (3)
100.0	7.92	0.490	5.4 (5)
200.0	7.92	0.794	7.9 (8)
10.0	3.25	5.97 × 10 ⁻²	2.3 (2)

^a [Mo(CO)(PhC₂Ph)(dmtc)₂]₀ = (5.5 ± 0.5) × 10⁻³ M.

^b The estimated error in the last digit is indicated in parentheses.

Table VI. Rate Constants for Alkyne-Exchange Reactions at -37 °C

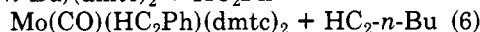
Mo(CO)(HC ₂ - <i>n</i> -Bu)(dmtc) ₂ + HC ₂ Ph = Mo(CO)(HC ₂ Ph)(dmtc) ₂ + HC ₂ - <i>n</i> -Bu ^a	
[PhC ₂ H] ₀ / [Mo(CO)(HC ₂ - <i>n</i> -Bu)(dmtc) ₂] ₀	10 ³ k _{obsd} , ^b s ⁻¹
5.70	0.26 (3)
32.8	1.8 (2)

^a [Mo(CO)(HC₂-*n*-Bu)(dmtc)₂]₀ = 0.10 ± 0.01 M.

^b k_{obsd} = k_{ex}[HC₂Ph]; k_{ex} = (5.0 ± 0.5) × 10⁻⁵ L mol⁻¹ s⁻¹.

in the Experimental Section and are listed in Table V. A doubling of k_{obsd} resulted when the PhC₂Ph concentration was increased from 20.0- to 40.0-fold excess under CO. At higher alkyne concentrations the observed rate constant increased, although the increase was no longer linear with the alkyne concentration.

Alkyne-Exchange Reactions. The alkyne exchange reaction (eq 6) yielded linear plots of ln(A_t - A_∞) vs. t for Mo(CO)(HC₂-*n*-Bu)(dmtc)₂ + HC₂Ph →



both experiments¹⁸ in agreement with a pseudo-first-order rate law (eq 7). A linear k'_{obsd} response to HC₂Ph con-

$$\frac{-d[\text{Mo(CO)(HC}_2\text{-}n\text{-Bu)(dmtc)}_2]}{dt} = k'_{\text{obsd}}[\text{Mo(CO)(HC}_2\text{-}n\text{-Bu)(dmtc)}_2] \quad (7)$$

centration (Table VI) implies a second-order rate law as in eq 8.

$$\frac{-d[\text{Mo(CO)(HC}_2\text{-}n\text{-Bu)(dmtc)}_2]}{dt} = k_{\text{ex}}[\text{Mo(CO)(HC}_2\text{-}n\text{-Bu)(dmtc)}_2][\text{HC}_2\text{Ph}] \quad (8)$$

Reactions with Other Nucleophiles. Reactions of Mo(CO)(RC₂R')(dmtc)₂ with nucleophiles other than alkynes lead to rapid loss of alkyne with concomitant formation of Mo(CO)L₂(dmtc)₂ complexes. These reactions proceeded at room temperature, and no loss of the carbonyl ligand was observed. The reaction of Mo(CO)(HC₂H)(dmtc)₂ with carbon monoxide quantitatively produces Mo(CO)₃(dmtc)₂ as the acetylene is swept out of the system by the CO gas stream. Trimethyl phosphite reacted cleanly to yield Mo(CO)[P(OMe)₃]₂(dmtc)₂, but reaction with PEt₃ did not produce a single product even in the presence of excess phosphine. An equilibrium was established between Mo(CO)(EtC₂Et)(dmtc)₂ and Mo-

(CO)(PEt₃)₂(dmtc)₂ as judged by comparison of solution infrared spectra with published data.¹⁹

Discussion

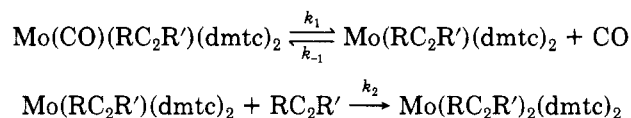
Carbon Monoxide Substitution Reactions. The observed first-order rate law for conversion of Mo(CO)(RC≡CR')(S₂CNMe₂)₂ to the bis(alkyne) derivative (eq 4) suggests that the rate-determining step is either isomerization of the metal reagent or ligand dissociation. In either case the simple first-order rate expression is inconsistent with an associative pathway. The substitution of carbon monoxide by alkyne does not proceed by alkyne addition followed by loss of the carbonyl ligand. That this pathway is not operative is important since conversion of the formal 16-electron reagent to an 18-electron intermediate with two alkynes each serving as a two-electron-donor ligand would offer an intuitively attractive mechanism that would be complementary to the 18-16-18-electron pathways commonly invoked for saturated reagents and products.

The experimental rate law is consistent with a dissociative process proceeding through a formal 14-electron intermediate. The small positive values observed for ΔS[‡] are compatible with bond weakening in the transition state. A vacant coordination site could be provided either by dechelation of a dithiocarbamate sulfur or by carbon monoxide dissociation as the rate determining step. Dechelation of one end of a dithiocarbamate ligand has been postulated to occur in W(O)(RC≡CR)(dmtc)₂ to form a fluxional five-coordinate intermediate.²⁰ The feasibility of attaining a formal 14-electron intermediate is supported by the recent isolation and structural characterization of a five-coordinate molybdenum(II) alkyne porphyrin complex, [Mo(PhC₂Ph)TTP]·C₆H₅CH₃ (TTP = *meso*-tetra-*p*-tolylporphyrin).²¹

In an effort to differentiate between Mo-S and Mo-CO bond cleavage the reaction was monitored under a CO atmosphere. The observed rate inhibition by free carbon monoxide suggests a reversible CO dissociation precedes the rate-determining step under these conditions. Since no monodentate dithiocarbamate species was trapped by CO to form a detectable amount of Mo(CO)₂(PhC₂Ph)(dmtc)(η¹-SC(=S)NMe₂), the sulfur dissociation pathway can be eliminated as a possible mechanism for formation of the bis(alkyne) products.²² Indirect support for relatively facile CO dissociation is provided by the decomposition of Mo(CO)(RC≡CR')(dmtc)₂ at 90 °C as no carbonyl-containing material remains after 30 min.

The rate dependence on alkyne concentration in the presence of carbon monoxide indicates the rate-determining step changes as the CO/PhC₂Ph ratio increases. The simplest mechanism suggested by these results is presented in Scheme I. Application of the steady-state

Scheme I



(19) Crichton, B. A. L.; Dilworth, J. R.; Pickett, C. J.; Chatt, J. J. *Chem. Soc., Dalton Trans.* 1981, 892.

(20) Templeton, J. L.; Ward, B. C.; Chen, G. J.-J.; McDonald, J. W.; Newton, W. E. *Inorg. Chem.* 1981, 20, 1248.

(21) DeCian, A.; Cobin, J.; Schappacher, M.; Ricard, L.; Weiss, R. J. *Am. Chem. Soc.* 1981, 103, 1850.

(22) If the bis(alkyne) product forms from a dechelated dithiocarbamate intermediate, then carbon monoxide inhibition by trapping the intermediate would lead to a buildup of the intermediate since the reaction proceeds to completion even under a CO atmosphere. No such carbonyl adduct was spectroscopically observed.

(18) Although the experiment using 5.70 equiv of HC₂Ph does not have enough excess HC₂Ph to be rigorously considered a pseudo-first-order experiment, essentially the same value for the rate constant, k_{obsd}, was obtained by plotting the data using a mixed second-order rate law.

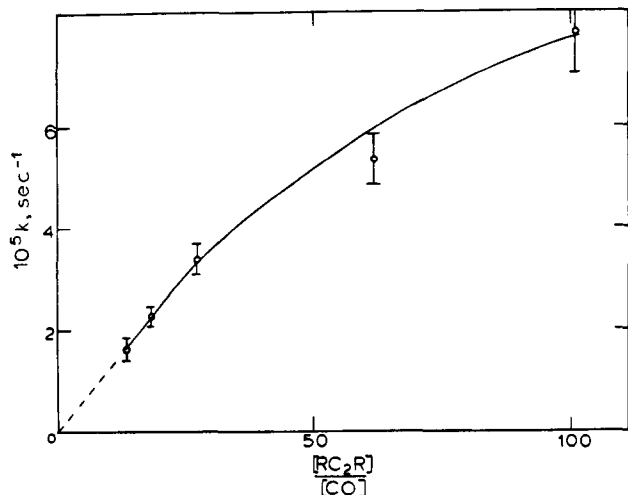


Figure 3. A graph of k_{obsd} vs. $[\text{RC}_2\text{R}]/[\text{CO}]$ illustrating the rate variation from first order to zero order in alkyne concentration.

approximation leads to rate law 9, and eq 10 defines k_{obsd} for the pseudo-first-order conditions employed. In the

$$-\frac{d[\text{Mo}(\text{CO})(\text{RC}_2\text{R}')(\text{dmtc})_2]}{dt} = \frac{k_1 k_2 [\text{Mo}(\text{CO})(\text{RC}_2\text{R}')(\text{dmtc})_2] [\text{RC}_2\text{R}']}{k_{-1} P_{\text{CO}} + k_2 [\text{RC}_2\text{R}']} \quad (9)$$

$$k_{\text{obsd}} = \frac{k_1 k_2 [\text{RC}_2\text{R}']}{k_{-1} P_{\text{CO}} + k_2 [\text{RC}_2\text{R}']} \quad (10)$$

absence of added carbon monoxide gas $k_2 [\text{RC}_2\text{R}'] \gg k_{-1} P_{\text{CO}}$ and the rate simplifies to the observed first-order expression with $k_{\text{obsd}} = k_1$. With a carbon monoxide pressure of 1 atm, doubling the diphenylacetylene concentration from 20- to 40-fold excess approximately doubles the magnitude of k_{obsd} and suggests a first-order alkyne dependence in the numerator in accord with eq 10 when $k_{-1} P_{\text{CO}} \gg k_2 [\text{RC}_2\text{R}']$. In an effort to determine the order of the carbon monoxide term in the denominator, an experiment was run with an intermediate pressure of CO (312 torr) and a 10-fold alkyne concentration. The k_{obsd} of $2.3 \times 10^{-5} \text{ s}^{-1}$ can be compared to the value of $1.6 \times 10^{-5} \text{ s}^{-1}$ observed with a 20-fold alkyne excess at $P_{\text{CO}} = 1 \text{ atm}$ and indicates an inverse first-order dependence on P_{CO} .

Both terms in the denominator contribute to k_{obsd} at high alkyne concentrations under a carbon monoxide atmosphere since the condition $k_{-1} P_{\text{CO}} \gg k_2 [\text{RC}_2\text{R}']$ no longer applies. This is graphically illustrated in Figure 3. Graphing the data in terms of k_{obsd}^{-1} vs. $P_{\text{CO}}/[\text{RC}_2\text{R}']$ produces the plot shown in Figure 4 in agreement with eq 11. The slope and intercept allow one to calculate the

$$\frac{1}{k_{\text{obsd}}} = \frac{1}{k_1} + \frac{k_{-1}}{k_1 k_2} \frac{P_{\text{CO}}}{[\text{RC}_2\text{R}']} \quad (11)$$

ratio of k_{-1} to k_2 , but a more useful comparison is to calculate the molar concentration of CO in order to cancel units and determine the relative ability of CO and PhC_2Ph to trap the electron-deficient intermediate for which they compete. The resulting ratio of 130 indicates that carbon monoxide is a better nucleophile than diphenylacetylene by more than 2 orders of magnitude in this case.

The influence of the bound alkyne on the rate of carbon monoxide substitution can be reconciled with the π acidity of the alkyne ligands. The three-center two-electron bond involving one filled $d\pi$ orbital, one CO π^* , and the alkyne π_{\parallel}^* has been described previously.²³ The more electron-

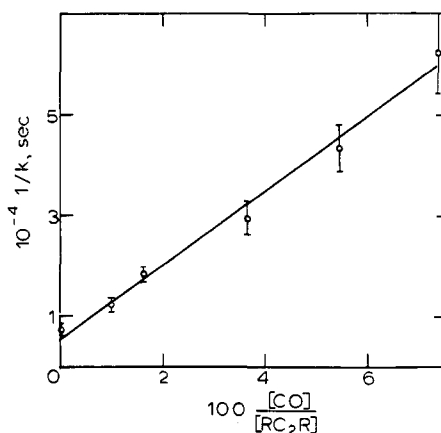


Figure 4. A plot of $(k_{\text{obsd}})^{-1}$ vs. $[\text{CO}]/[\text{RC}_2\text{R}]$ showing a linear dependence and an intercept of $(k_1)^{-1}$ in accord with the mechanism postulated in Scheme I.

Table VII. Carbonyl Stretching Frequencies for $\text{Mo}(\text{CO})(\text{RC}_2\text{R}')(\text{S}_2\text{CNMe}_2)_2^a$

RC_2R	$\nu(\text{C}=\text{O}), \text{cm}^{-1}$	RC_2R	$\nu(\text{C}=\text{O}), \text{cm}^{-1}$
PhC_2Ph	1940	$\text{HC}_2\text{-}n\text{-Bu}$	1926
PhC_2H	1937	EtC_2Et	1925
PhC_2Me	1928		

^a CH_2Cl_2 solution.

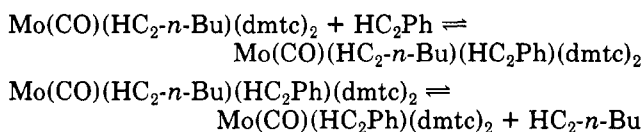
withdrawing alkynes compete more effectively with the carbon monoxide for available $d\pi$ electron density. This effect is evident in the infrared $\nu(\text{CO})$ data listed in Table VII where higher carbonyl frequencies characterize electron-withdrawing alkyne complexes. The qualitative agreement between the carbonyl stretching frequencies and the order of reactivity rates (eq 5) is consistent with a ground-state weakening of the Mo-CO bond altering the activation energy associated with k_1 of Scheme I. A stabilization of the transition state could also be responsible for the rate differences, but it is difficult for us to conceive of an effect in which an electron-poor intermediate is favored by more electron-withdrawing alkyne ligands. The π -donor abilities of alkyne ligands and dithiocarbamates are well established and are no doubt important in the electron-deficient intermediate.

Alkyne-Exchange Reactions. Replacement of a bound $\text{HC}_2\text{-}n\text{-Bu}$ by HC_2Ph in $\text{Mo}(\text{CO})(\text{HC}_2\text{R})(\text{dmtc})_2$ was chosen for kinetic analysis because the terminal acetylenic protons of the bound alkyne ligands provide a convenient ^1H NMR probe. Neither the infrared nor electronic spectra of reagents and products differ enough to monitor reaction progress by these techniques. These exchange reactions were considerably faster at -37°C than any of the carbon monoxide substitution reactions studied at temperatures above 25°C . No bis(alkyne) products were detected during these low-temperature alkyne-exchange reactions.

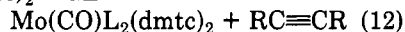
The second-order rate law observed for alkyne exchange (eq 8) is consistent with an associative mechanism which generates a saturated mono(carbonyl) bis(alkyne) intermediate as in Scheme II. Although other mechanisms that fit the rate expression are conceivable, the rapid formation of an 18-electron species followed by loss of one of the two 2-electron donor alkyne ligands merges nicely with qualitative reactivity patterns observed with other nucleophiles (vide infra). The feasibility of a seven-coordinate bis-

(alkyne) intermediate is supported by Davidson's synthesis of the triphenylphosphine adduct of $(\pi\text{-C}_6\text{H}_5)\text{Mo}(\text{CF}_3\text{C}\equiv\text{CCF}_3)_2\text{Cl}$.²⁴

Scheme II

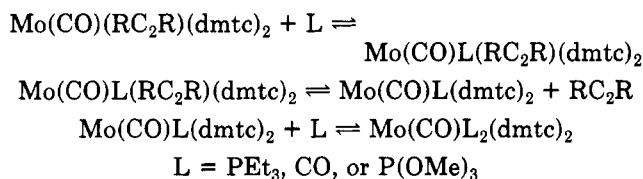


Alkyne Substitution Reactions. Reactions of $\text{Mo}(\text{CO})(\text{RC}_2\text{R}')(\text{dmtc})_2$ with three nucleophiles were explored spectroscopically. Addition of excess carbon monoxide, trimethyl phosphite, or triethylphosphine leads to formation of $\text{Mo}(\text{CO})\text{L}_2(\text{dmtc})_2$ as in eq 12. These reactions



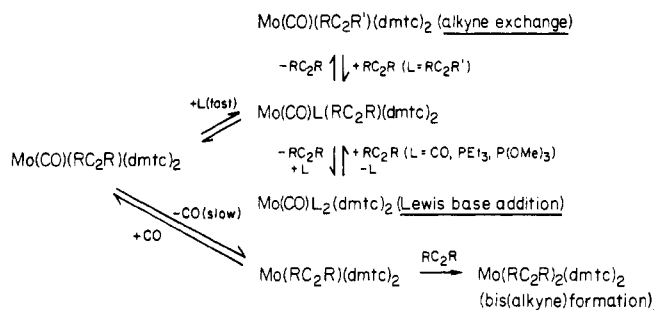
occur in minutes at room temperature. The most attractive mechanism for replacement of the alkyne ligand by the two-electron donor ligands is through an associative process reminiscent of the alkyne exchange reaction pathway. Formation of an 18-electron intermediate by ligand addition could promote alkyne loss prior to addition of a second ligand to form the observed product as speculated in Scheme III. No kinetic studies of these reactions were attempted.

Scheme III



Summary. Reactions of $\text{Mo}(\text{CO})(\text{RC}_2\text{R}')(\text{dmtc})_2$ with selected nucleophiles are compatible with the reactivity patterns depicted in Scheme IV. Substitution of the bound alkyne by either another alkyne or by two Lewis base donor ligands can be postulated to proceed by initial ligand association to generate an 18-electron intermediate. Regardless of the ligand added the saturated species that results is unstable with respect to alkyne dissociation. The absence of vacant metal $d\pi$ orbitals in the putative $\text{Mo}(\text{CO})\text{L}(\text{RC}_2\text{R})(\text{dmtc})_2$ intermediate restricts the alkyne to donation from the π_{\parallel} orbital and acceptance into the π_{\perp}^* orbital. Elimination of ligand-to-metal π_{\perp} donation will tend to weaken the metal-alkyne bond, and in fact the Dewar-Chart-Duncanson olefin bonding model²⁵ should provide an adequate description of the alkyne bonding in these species. Olefins have been shown to form seven-coordinate complexes when added in excess to $\text{Mo}(\text{CO})_2(\text{S}_2\text{CNR}_2)_2$,²⁶ but the formation constants are small and olefin loss occurs readily. Facile loss of the alkyne ligand from $\text{Mo}(\text{CO})\text{L}(\text{RC}_2\text{R})(\text{dmtc})_2$, where the attractive π_{\perp} -metal $d\pi$ interaction has been nullified, would conform to the reactivity pattern established by the olefin analogue. If the added L is the same alkyne as bound in the metal reagent, a degenerate alkyne exchange has transpired, and no net chemistry results. If the free alkyne differs from the bound, an alkyne exchange has been accomplished. If the added ligand is CO, $\text{P}(\text{OMe})_3$, or PET_3 the 16-electron $\text{Mo}(\text{CO})\text{L}(\text{dmtc})_2$ intermediate formed by alkyne disso-

Scheme IV



ciation rapidly adds another L to give the observed 18-electron product.

Carbon monoxide substitution is only realized when the rapid associative route leads to no net chemistry. In other words, in the presence of nucleophiles other than alkynes the associative pathway leads rapidly to products that retain the carbonyl ligand. The much slower route involving CO dissociation to form a formal 14-electron intermediate siphons the rapidly exchanging $\text{Mo}(\text{CO})(\text{RC}_2\text{R})(\text{dmtc})_2$ reagent to bis(alkyne) products only when excess alkyne is the sole available nucleophile.

Carbon monoxide dissociation from the $\text{Mo}(\text{CO})(\text{RC}_2\text{R})(\text{dmtc})_2$ reagent is promoted by both the alkyne's π -acid character (π_{\parallel}^*) that inhibits metal $d\pi$ to CO π^* back-bonding and its π -base character (π_{\perp}) that can provide additional electron density to stabilize the electron-deficient $\text{Mo}(\text{RC}_2\text{R})(\text{dmtc})_2$ intermediate. Support for the labilization of CO by an adjacent alkyne ligand can be gleaned by comparison with $\text{M}(\text{CO})_2\text{L}(\text{dmtc})_2$ ($\text{M} = \text{Mo}, \text{W}$) complexes that form readily from tricarbonyl reagents but resist further carbon monoxide substitution even under rigorous reaction conditions.²⁷ In the few cases where $\text{Mo}(\text{CO})\text{L}_2(\text{dmtc})_2$ complexes have been prepared the carbonyl stretching frequencies are between 130 and 180 cm^{-1} lower than in the mono(carbonyl) mono(alkyne) complexes,¹⁹ reflecting the π -acidity of the bound alkyne. Substitution of the carbon monoxide in $\text{Mo}(\text{CO})\text{L}_2(\text{dmtc})_2$ compounds has not yet been reported, a fact which is consistent with the strong multiple Mo-CO bond in these d^4 complexes containing a lone π -acid ligand.

This work indicates that $\text{Mo}(\text{CO})(\text{RC}_2\text{R})(\text{dmtc})_2$ complexes can undergo ligand substitution reactions by both associative and dissociative mechanisms. In the reactions studied here the associative processes occur much more rapidly than ligand dissociation, in accord with intuitive expectations for 16-electron molybdenum(II) monomers. At the same time the complete absence of saturated seven-coordinate products from reactions with excess alkyne underscores the role of alkyne π_{\perp} donation in stabilizing six-coordinate complexes of the type $\text{Mo}(\text{CO})(\text{RC}_2\text{R})(\text{dmtc})_2$ and $\text{Mo}(\text{RC}_2\text{R})_2(\text{dmtc})_2$. In summary no simple electron-counting formalism adequately conveys the chemical properties of these unusual alkyne complexes. Their reactivity ranges from that expected for electron-deficient complexes to that anticipated for saturated complexes. A convenient model for describing these complexes is to consider them as formal 16-electron complexes that are stabilized by π donation from the filled alkyne π_{\perp} orbital into the vacant $d\pi$ orbital, which would be filled for an analogous 18-electron species. This destabilized $d\pi$ orbital constitutes the LUMO while the remaining two levels from the original nest of three $d\pi$ orbitals are sta-

(24) Davidson, J. L.; Green, M.; Sharp, D. W. A.; Ston, F. G. A.; Welch, A. J. *J. Chem. Soc., Chem. Commun.* 1974, 706.

(25) (a) Dewar, M. J. S. *Bull. Soc. Chim. Fr.* 1951, 18, C71. (b) Chatt, J.; Duncanson, L. H. *J. Chem. Soc.* 1953, 2939. (c) Albright, T. A.; Hoffmann, R.; Thibeault, J. C.; Thorn, D. L. *J. Am. Chem. Soc.* 1979, 101, 3801.

(26) Templeton, J. L.; Burgmayer, S. J. N. *Organometallics* 1982, 1, 1007.

(27) Templeton, J. L.; Ward, B. C. *J. Am. Chem. Soc.* 1981, 103, 3743.

bilized by back-bonding with π -acid ligands and house the four metal-based electrons. This classification has the advantage of maintaining a simple electron counting procedure while still suggesting the importance of ligand-to-metal donation into vacant $d\pi$ orbitals.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American

Chemical Society, for support of this research.

Registry No. Mo(CO)(PhC₂Ph)(S₂CNMe₂)₂, 81476-50-8; Mo(CO)(PhC₂H)(S₂CNMe₂)₂, 74456-79-4; Mo(CO)(PhC₂Me)(S₂CNMe₂)₂, 84943-89-5; Mo(CO)(HC₂Bu-n)(S₂CNMe₂)₂, 84943-90-8; Mo(CO)(EtC₂Et)(S₂CNMe₂)₂, 84943-91-9; PhC₂Ph, 501-65-5; PhC₂H, 536-74-3; PhC₂Me, 673-32-5; HC₂Bu-n, 693-02-7; EtC₂Et, 928-49-4; CO, 630-08-0; P(OMe)₃, 121-45-9; PET₃, 554-70-1.

Homogeneous Catalysis of Arene Hydrogenation by Cationic Rhodium Arene Complexes

Clark R. Landis and Jack Halpern*

Department of Chemistry, The University of Chicago, Chicago, Illinois 60637

Received October 19, 1982

Arenes react with [Rh(DIPHOS)(MeOH)₂]⁺ to form 1:1 [Rh(DIPHOS)(arene)]⁺ adducts. Equilibrium constants for the formation of such adducts in methanol were determined for benzene, naphthalene, and 9-methylantracene, and the adducts were characterized by ¹H and ³¹P NMR spectroscopy. The adducts of anthracene and of 9-substituted derivatives thereof catalyze the hydrogenation of the anthracenes to the corresponding 1,2,3,4-tetrahydroanthracenes under relatively mild conditions (50–75 °C (1 atm H₂)). The results of kinetic measurements on such catalytic hydrogenation reactions are reported.

Introduction

Cationic rhodium complexes containing phosphine ligands, notably [Rh(DIPHOS)(MeOH)₂]⁺ (where DIPHOS = 1,2-bis(diphenylphosphino)ethane), have previously been reported to catalyze the hydrogenation of a variety of substrates including alkenes, alkynes, and ketones.¹ We now report that such complexes also are effective as catalysts for the hydrogenation of arenes, notably of anthracenes to the corresponding 1,2,3,4-tetrahydroanthracenes. The formation and characterization of [Rh(DIPHOS)(arene)]⁺ complexes, which apparently are the effective catalysts in these hydrogenation reactions, are described, together with some kinetic measurements on the catalytic reactions.

Experimental Section

[Rh(DIPHOS)(norbornadiene)]BF₄ was prepared by adaptation of the procedure described for preparation of the corresponding perchlorate.^{1b} [Rh(DIPHOS)(MeOH)₂]⁺ was generated in situ by hydrogenation of [Rh(DIPHOS)(norbornadiene)]⁺ as previously described.²

Equilibrium constants for the formation of [Rh(DIPHOS)(arene)]⁺ complexes were determined in methanol by spectral titrations at ca 500 nm similar to those described previously for [Rh(DIPHOS)(benzene)]⁺.²

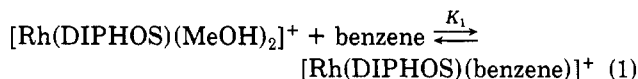
¹H NMR spectra were determined with a Bruker HS-270 spectrometer and ³¹P NMR spectra with a Bruker HFX-90 spectrometer.

Kinetic measurements were made on catalytic hydrogenation reactions performed in Fisher-Porter bottles. Initial reaction rates were determined by periodic sampling and analysis of the solution using a Varian 1400 gas chromatography equipped with a flame ionization detector and a 1/8 in. × 10 ft 20% DEGS on Chrom W (60/80) column. The identification of the products was substantiated by ¹H NMR spectroscopy. The isotopic composition of the products of reaction with D₂ was determined mass spec-

trometrically. All equilibrium and kinetic measurements were made in methanol solution.

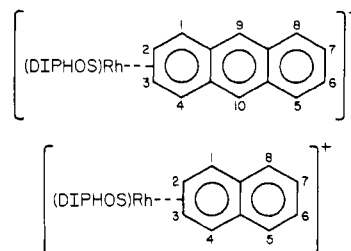
Results and Discussion

Formation and Characterization of [Rh(DIPHOS)(arene)]⁺ Complexes. The formation of [Rh(DIPHOS)(benzene)]⁺ according to reaction 1 and the characterization of this complex have previously been described.²



These studies were extended to the corresponding naphthalene and anthracene complexes including (a) determination of the ¹H and ³¹P NMR spectra of the complexes and (b) determination of the equilibrium constants (K_1) for the formation of the complexes according to eq 1. Because of the low solubility of anthracene in methanol, the equilibrium constant K_1 was determined for the adduct of 9-methylantracene.

The NMR parameters of the [Rh(DIPHOS)(arene)]⁺ complexes are listed in Table I using the numbering systems shown below. Where appropriate, the assignments were confirmed by using selective decoupling to identify adjacent protons. Some NMR data for [Rh(DIPHOS)(diene)]⁺ complexes also are listed in Table I for comparison.



The structure of the [Rh(DIPHOS)(benzene)]⁺ adduct has previously been inferred to involve symmetrical η^6

(1) (a) R. R. Schrock and J. A. Osborn, *Chem. Comm.* 567 (1970); (b) *J. Am. Chem. Soc.*, **93**, 2397 (1971); (c) *Ibid.* **98**, 2134, 4450 (1976).

(2) (a) J. Halpern, D. P. Riley, A. S. C. Chan, and J. J. Pluth, *J. Am. Chem. Soc.*, **99**, 8056 (1977); (b) J. Halpern, A. S. C. Chan, D. P. Riley, and J. J. Pluth, *Adv. Chem. Ser.*, **No. 173**, 16 (1979).