complex function of magnetic anisotropy,[22] electron spin relaxation time,[1-3] solubility, and substrate affinity. Our results indicate that the latter characteristic cannot always be ascertained accurately by nmr methods alone and that complementary colligative studies may be helpful in guiding systematic efforts to design more stereoselective shift reagents.

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Complexes of Cyclic 2-Oxacarbenes. II. Kinetics and Thermodynamics of Reactions Forming Complexes of Cyclic 2-Oxacarbenes[1]

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Abstract: When (*pentahaptocyclopentadienyl*)(tricarbonyl)(3-bromo-*n*-butyl)molybdenum reacts with triphenylphosphine, the cis isomer of the cation (*pentahaptocyclopentadienyl*)(dicarbonyl)(triphenylphosphine)(3-methyl-2-oxacyclopentylidene)molybdenum is formed initially followed by isomerization to the trans isomer. However, when the molybdenum complex possesses 4-bromo-*n*-butyl, 5-bromo-*n*-pentyl, 3-chloro-*n*-propyl, or 4-iodo-*n*-butyl groups as the alkyl ligands, reaction with triphenylphosphine affords the trans isomer of the corresponding acyl complexes. The acyl complexes, except for the 6-bromohexanoyl complex, undergo slow equilibration with the trans isomer of the cation formed by internal nucleophilic attack of the acyl oxygen atom on the ω-carbon atom displacing the halide anion. The preparation and characterization of the above complexes are reported along with a kinetic investigation of the different reaction pathways observed within this sequence of reactions. This detailed kinetic investigation provided satisfactory evidence that when the haloalkyl complexes are treated with triphenylphosphine a cis acyl intermediate is formed in a steady-state concentration. Subsequent reactions of this intermediate included either a geometrical isomerization to the thermodynamically more stable trans acyl complex, an intramolecular cyclization reaction forming the cis carbenoid complex, or both of these reactions occurring in parallel. The reaction kinetics of several related reactions are reported also.

In recent years a number of reaction pathways for forming complexes that contain carbenoid ligands have been reported.[4] Concurrent work in three laboratories has suggested that such ligands may be formed *via* an internal cyclization mechanism.

Chisholm and Clark prepared cationic Pt^{II} complexes containing the 2-oxacyclopentylidene ligand by reaction 1,[5] and employed a similar approach in pre-

$$\textit{trans}\text{-PtClMeL}_2 + \text{HC}{\equiv}\text{CCH}_2\text{CH}_2\text{OH} \xrightarrow[\text{AgPF}_6]{\text{MeOH}} \textit{trans}\text{-[PtMeCO(CH}_2)_2\text{CH}_2\text{L}_2]^+\text{PF}_6^- \quad (1)$$

L = PMe_2Ph, $AsMe_3$

paring the first Pt^{IV} alkoxycarbenoid complex (reaction 2).[6] The postulated mechanism involves coordination

$$\text{PtMe}_2\text{CF}_3\text{IL}_2 + \text{AgPF}_6 \xrightarrow{\text{HC}{\equiv}\text{CCH}_2\text{CH}_2\text{OH}} [\text{PtMe}_2\text{CF}_3\text{CO(CH}_2)_2\text{CH}_2\text{L}_2]^+\text{PF}_6^- \quad (2)$$

L = PMe_2Ph

of the acetylene group to the coordinately unsaturated Pt cation forming a Pt-stabilized carbonium ion followed by intramolecular nucleophilic attack of the alcohol substituent.[7]

Casey and Anderson demonstrated that the pentacarbonylmanganate anion, $Mn(CO)_5^-$, can cause "CO insertion" in methyl pentacarbonylmanganese in much the same way as can other more conventional nucleophiles, such as phosphines. The resulting anionic complex was alkylated forming a neutral (alkoxy)(alkyl)–carbenoid complex (reaction 3).[8] This evi-

$$\text{Mn(CO)}_5^- + \text{MeMn(CO)}_5 \rightleftharpoons [(\text{OC})_5\text{MnMn(CO)}_4\text{C(O)Me}]^- \xrightarrow{\text{Me}_3\text{OBF}_4} (\text{OC})_5\text{MnMn(CO)}_4\text{C(OMe)(Me)} \quad (3)$$

dence then suggested that the complex formed when $NaMn(CO)_5$ is treated with 1,3-dibromopropane is actually a carbenoid complex containing the 2-oxacyclopentylidene ligand (reaction 4). The mechanism

$$\text{Br(CH}_2)_3\text{Br} \xrightarrow{\text{Mn(CO)}_5^-} (\text{OC})_5\text{Mn(CH}_2)_3\text{Br} \xrightarrow{\text{Mn(CO)}_5^-} [(\text{OC})_5\text{MnMn(CO)}_4\text{C(O)(CH}_2)_3\text{Br}]^- \longrightarrow (\text{OC})_5\text{MnMn(CO)}_4\text{COCH}_2\text{CH}_2\text{CH}_2 \quad (4)$$

proposed involves the nucleophilic attack of the anion,

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$Mn(CO)_5^-$, on one of the terminal carbon atoms of the 1,3-dibromopropane molecule forming a neutral ω-bromoalkyl complex. A second $Mn(CO)_5^-$ anion initiates acyl formation which is then followed by a rapid intramolecular cyclization which displaces a bromide ion to form the neutral carbenoid complex.[8]

Previously, a similar mechanism was suggested involving a cis acyl intermediate in the formation of cationic molybdenum complexes containing the 2-oxacyclopentylidene ligand (reaction 5).[9] Although

$$(h^5\text{-}C_5H_5)Mo(CO)_3(CH_2)_3Br + L \longrightarrow [cis\text{-}(h^5\text{-}C_5H_5)Mo(CO)_2(L)C(O)(CH_2)_3Br] \xrightarrow{\Delta} cis\text{-}[Mo(h^5\text{-}C_5H_5)(CO)_2(L)\overline{CO(CH_2)_2CH_2}]^+Br^- \quad (5)$$

$L = PPh_3$

the cis carbenoid complex was formed in this case, variation of the haloalkyl group afforded the trans isomer of the corresponding acyl complexes. The preparation and characterization of other carbenoid and acyl derivatives within this series of complexes along with a more detailed kinetic investigation of the above reaction sequence (5) are reported now in order to support the postulation of the cis acyl intermediate.

Experimental Section

The salt, $NaMo(h^5\text{-}C_5H_5)(CO)_3$, was prepared by a literature method.[10] All reactions and other manipulations were performed under dry, prepurified nitrogen at room temperature unless otherwise stated. Solvents used for washing and transfers were reagent grade from freshly opened bottles and were purged with nitrogen. The reaction solvents, acetonitrile and nitromethane, were of Spectrograde quality and were purged with nitrogen.

Proton magnetic resonance spectra were recorded on a Varian Associates T-60 spectrometer and infrared spectra on a Perkin-Elmer 337 spectrometer. Tetramethylsilane was used as an internal standard in all pmr spectra and polystyrene film was used for calibration of the ir spectra. Microanalyses were by Spang Microanalytical Laboratory, Ann Arbor, Mich., and by Meade Microanalytical Laboratory, Amherst, Mass., and are presented in Appendix I.[11]

$(h^5\text{-}C_5H_5)Mo(CO)_3(CH_2)_3Br$ (1). Practical grade 1,3-dibromopropane was distilled before use, and the procedure of King and Bisnette[12] was followed.[9]

[*cis*- and *trans*-$Mo(h^5\text{-}C_5H_5)(PPh_3)(CO)_2(COCH_2CH_2CH_2)]Br$. Both the cis (**2**) and the trans (**14**) geometrical isomers were prepared by a literature procedure.[9]

[*cis*- and *trans*-$Mo(h^5\text{-}C_5H_5)(PPh_3)(CO)_2(\overline{COCH_2CH_2CH_2})]BPh_4$. The tetraphenylborate salt of either the cis (**15**) or the trans (**16**) isomer was prepared from the respective bromide salts (**2** and **14**) by a metathetic reaction using $NaBPh_4$ as reported earlier.[9]

$[(h^5\text{-}C_5H_5)Mo(CO)_3[CH_2CH_2CH(Me)Br]$ (3). A solution of 11.3 g (0.042 mol) of $NaMo(h^5\text{-}C_5H_5)(CO)_3$ in 150 ml of freshly distilled tetrahydrofuran was treated with 10 g (0.046 mol) of reagent grade 1,3-dibromobutane over a 1-min period. The reaction solution was stirred for 21 hr and then the solvent was removed under reduced pressure (20 mm, 25°). The residue was extracted with 50 ml of methylene chloride and filtered, and the solvent was removed under reduced pressure. A similar extraction was performed on this second residue with 50 ml of pentane. The residue resulting from removal of the solvent from the pentane extraction was recrystallized from pentane at −15° affording 1.03 g (6.5% based on Mo) of product as dark yellow, rectangular needles: mp 42–43°; ir (cyclohexane) ν_{CO} 2015 (s), 1930 (vs); pmr (CS_2) τ 8.34 (doublet, 3, Me, $J_{HH} \sim 7$ Hz), 8.14 (broad multiplet, 4, $2CH_2$), 6.14 (quartet, 1, H), 4.74 (singlet, 5, C_5H_5).

[*cis*-$Mo(h^5\text{-}C_5H_5)(PPh_3)(CO)_2(\overline{COC(H)(Me)CH_2CH_2})]Br$ (4). A solution of 0.32 g (0.84 mmol) of **3** in 1 ml of acetonitrile was treated with a solution of 0.46 g (1.75 mmol) of triphenylphosphine in 5 ml acetonitrile over a 30-sec period. The reaction solution was stirred for 20 min and then the solvent was removed under reduced pressure (20 mm, 25°). The yellow residue was washed with 15 ml of 6:1 pentane–methylene chloride and dried for *ca.* 6 min (0.01 mm, 25°) affording 0.535 g (98.5% based on Mo) of a bright yellow solid which was a 97:3 mixture of the cis and trans isomers, respectively: mp 105–110° dec; ir (CH_2Cl_2) ν_{CO} 1980 (vs), 1910 (s); pmr ($CDCl_3$) τ 9.17 (broad multiplet, 3, CH_2 + H), 8.74 (doublet, *ca.* 1.5, Me′, $J_{HH} \sim 7$ Hz), 9.40 (doublet, *ca.* 1.5, Me″, $J_{HH} \sim 7$ Hz), 6.00 (broad multiplet, 2, CH_2), 4.50 (doublet, *ca.* 0.15, C_5H_5 of trans isomer, $J_{P-H} \sim 1.0$ Hz), 4.20 (singlet, 5, C_5H_5 of cis isomer), 2.57 (broad multiplet, 15, PPh_3). The product was recrystallized from a *o*-dichlorobenzene at −15° affording a mixture of cis and trans isomers which was dried for 12 hr (0.01 mm, 25°).

$(h^5\text{-}C_5H_5)Mo(CO)_3(CH_2)_4Br$ (5). The procedure of King and Bisnette was followed.[12] Using 26.8 g (0.10 mol) of $NaMo(h^5\text{-}C_5H_5)(CO)_3$ and 12.8 ml (0.11 mol) of 1,4-dibromobutane, 6.56 g (17.4% based on Mo) was obtained as straw yellow crystals after recrystallization from pentane at −15°: mp 52.0–52.8°; ir (cyclohexane) ν_{CO} 2015 (s), 1930 (vs).

trans-$(h^5\text{-}C_5H_5)Mo(CO)_2(PPh_3)C(O)(CH_2)_4Br$ (7). To a solution of 13.73 g (0.028 mol) of **5** in 30 ml acetonitrile was added a solution of 19.26 g (0.074 mol) of triphenylphosphine in 105 ml of acetonitrile over a 1-min period. Precipitation of a yellow solid occurred within 5 min of mixing the reagents. After 20 min the reaction mixture was filtered and the isolated solid was washed with 5 ml of acetonitrile followed by 20 ml of pentane. The solid was then dried for 0.5 hr (0.01 mm, 25°) affording 12.73 g (55%) of the product. Recrystallization from acetonitrile at −15° gave 7.02 g (34%) of the product as pale lime plates: mp 133–135° dec; ir (CH_2Cl_2) ν_{CO} 1930 (s), 1850 (vs), $\nu_{C=O}$ 1605 (m); pmr (CS_2) τ 8.47 (broad multiplet, 4, $2CH_2$), 7.20 (triplet, 2, CH_2, $J_{HH} \sim 7$ Hz), 6.87 (triplet, 2, CH_2, $J_{HH} \sim 7$ Hz), 5.07 (doublet, 5, C_5H_5, $J_{PH} \sim 1.3$ Hz), 2.67 (broad multiplet, 15, PPh_3).

[*trans*-$Mo(h^5\text{-}C_5H_5)(PPh_3)(CO)_2(\overline{COCH_2CH_2CH_2CH_2})]BPh_4$ (13). A solution of 4.59 g (7.1 mmol) of **7** in 120 ml of nitromethane was added dropwise to a solution of 1.66 g (8.5 mmol) of $AgBF_4$ in 7 ml of nitromethane over a 10-min period. The reaction mixture was stirred for 6 hr under subdued lighting and then filtered. The solvent was removed from the filtrate (20 min, 25°) affording a brown residue to which 50 ml of methanol was added, and the resulting mixture was filtered giving a brown solution. A solution of 4.8 g (14.1 mmol) of $NaBPh_4$ dissolved in a minimum amount of methanol was added to the brown, methanol solution precipitating immediately a light yellow solid. This mixture was kept at −15° for 9 hr and was then filtered; the solid was washed with 50 ml of pentane and dried for 0.3 hr (50 mm, 25°) affording 4.45 g (71%) of a light brown solid. A solution of 0.78 g of this crude product in 5 ml of methylene chloride was chromatographed through a 25 mm × 63 mm Florisil (100–200 mesh)–methylene chloride column. A yellow band was eluted and addition of pentane precipitated a yellow solid which was dried for 1 hr (0.01 mm, 25°) affording 0.47 g (60% recovery) of a yellow powder: mp 139.5–141° dec; ir (CH_2Cl_2) ν_{CO} 1975 (s), 1900 (vs); pmr (CD_2Cl_2) τ 8.33 (broad multiplet, 4, $2CH_2$), 6.66 (broad multiplet, 2, CH_2), 5.60 (broad multiplet, 2, CH_2), 4.74 (doublet 5, C_5H_5, $J_{PH} \sim 1.0$ Hz), 2.80 (broad multiplet, 35, PPh_3 + BPh_4).

Reaction of 13 with Pyridine *N*-Oxide. A previously reported procedure was followed.[9] Thus, a solution of 0.10 g (0.11 mmol) of **13** in 1 ml of methylene chloride was treated with a solution of 0.168 g (1.8 mmol) of pyridine *N*-oxide in 1 ml of methylene chloride giving a dark wine red solution. After stirring for 1.5 hr the volatile components were trap-to-trap distilled with the aid of external heating *via* a hot-air blower giving 1–2 ml of a clear distillate. The infrared spectrum of this distillate exhibited a ketonic stretching vibration at 1725 cm^{-1} (CH_2Cl_2) in agreement with that stretch found in reagent grade δ-valerolactone. A qualitative test for a lactone (or ester) group was performed on a 0.10 ml sample of this distillate

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(10) J. J. Eisch and R. B. King, "Organometallic Syntheses, Transition Metal Compounds," Vol. 1, Academic Press, New York, N. Y., 1965, p 145.

(11) Appendixes I–III will appear at the Editor's request following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number JACS-73-3552. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

(12) R. B. King and M. B. Bisnette, *J. Organometal. Chem.*, 7, 311 (1967).

using the general procedure described by Hall and Schaeffer.[13] A positive test was observed. A yield of *ca.* 17% (based on Mo) for the lactone is estimated from the intensity of the ketonic stretching vibration through comparison to a calibration curve based on the authentic lactone and from the areas of peaks obtained *via* vpc analysis although the efficiency of the trap-to-trap distillation is unknown.

(h^5-C_5H_5)Mo(CO)$_3$(CH_2)$_5$Br (6). To a solution of 26.1 g (0.097 mol) of NaMo(h^5-C_5H_5)(CO)$_3$ in 120 ml of freshly distilled tetrahydrofuran was added 14.0 ml (0.120 mol) of 1,5-dibromopentane, which had been passed through a 10 mm × 20 mm column of Merck acid-washed alumina, over a 30-sec period. The reaction mixture was stirred for 27 hr and then the solvent was removed (20 mm, 25°). The orange residue was extracted with two 120-ml portions of hexane at reflux. The resulting solution was filtered and placed at −15° for 12 hr precipitating an impure solid. Recrystallization from hexane at −15° afforded 9.55 g (25% based on Mo) of caramel-colored diamonds which were dried for 1 hr (0.01 mm, 25°): mp 111–112°; ir (cyclohexane) ν_{CO} 2015 (s), 1925 (vs); pmr (CS_2) τ 8.43 (broad multiplet, 8, 4 CH_2), 6.70 (triplet, 2, CH_2, J_{HH} ~ 7 Hz), 4.73 (singlet, 5, C_5H_5).

***trans*-(h^5-C_5H_5)Mo(CO)$_2$(PPh$_3$)C(O)(CH_2)$_5$Br (8).** A mixture of 4.00 g (0.01 mol) of **6** in 5 ml of acetonitrile was treated with a solution of 5.39 g (0.02 mol) of triphenylphosphine in 17 ml of acetonitrile over a 30-sec period. The reaction solution was stirred for 4.5 hr and then the solvent was removed (20 mm, 25°). The light orange residue was dissolved in 20 ml of methylene chloride forming a yellow solution which was then cooled to 0°. Addition of pentane to this solution with stirring caused precipitation of a yellow powder. Recrystallization of this solid from carbon disulfide at −15° afforded 6.0 g (91%) of a pale lemon yellow powder: mp 115–116°; ir (CH_2Cl_2) ν_{CO} 1930 (s), 1845 (vs); $\nu_{C=O}$ 1610; pmr (CS_2) τ 8.70 (broad multiplet, 6, 3 CH_2), 7.20 (broad triplet, 2, CH_2, J_{HH} ~ 6 Hz), 6.80 (broad triplet, 2, CH_2, J_{HH} ~ 7 Hz), 5.20 (doublet, 5, C_5H_5, J_{PH} ~ 1.5 Hz), 2.60 (broad multiplet, 15, PPh$_3$).

[*trans*-Mo(h^5-C_5H_5)(CO)$_2$(PPh$_3$)$\overline{CO(CH_2)_4CH_2}$]BPh$_4$. Attempted Preparation. To a solution of 1.0 g (1.5 mmol) of **8** in 25 ml of nitromethane at 60° was added dropwise a solution of 0.46 g (2.4 mmol) of $AgBF_4$ in 5 ml of nitromethane over a 10-min period. The reaction mixture was stirred at 60° for 12 hr and filtered, and then the solvent was removed (20 mm, 25°). The black residue was extracted with 15 ml of methanol. The resulting solution was filtered and the filtrate was cooled to 0°. A solution of 0.76 g (4.5 mmol) of $NaBPh_4$ in 5 ml of methanol cooled to 0° was added to the filtrate affording immediate precipitation of a light brown solid. The solid was isolated by filtration, washed with pentane, and dried for 12 hr (0.01, 25°) affording 0.79 g (58%) of a light tan crude product. This solid gave very weak terminal CO stretching frequencies, 2000 (w) and 1920 (w) (CH_2Cl_2), and further purification was not accomplished. Both recrystallization and column chromatography gave irreproducible results. Also, silver ion assisted ring formation at high dilution or thermally initiated ring formation attempts were unsuccessful.

(h^5-C_5H_5)Mo(CO)$_3$(CH_2)$_3$Cl (9). The procedure was very similar to that given for the preparation of complex **6**. Using 21.7 g (0.081 mol) of NaMo(h^5-C_5H_5)(CO)$_3$ and 9.0 ml (0.083 mol) of 1-chloro-3-iodopropane, 9.1 g (35% based on Mo) of product was obtained as light orange plates: mp 81–83°; ir (cyclohexane) ν_{CO} 2015 (s), 1935 (vs); pmr (CS_2) τ 8.30 (broad multiplet, 4, 2 CH_2), 6.67 (triplet, 2, CH_2, J_{HH} ~ 7 Hz), 4.67 (singlet, 5, C_5H_5).

***trans*-(h^5-C_5H_5)Mo(CO)$_2$(PPh$_3$)C(O)(CH_2)$_3$Cl (10).** The procedure followed was similar to that used for complex **8**; however, the reaction period before work-up was only 15 min for this reaction. Thus, 0.50 g (1.15 mmol) of **9** and 0.81 g (3.1 mmol) of triphenylphosphine afforded 0.79 g (87% based on Mo) of product as a light yellow powder which was a 95:5 mixture of trans acyl and trans carbenoid complexes, respectively: mp 131–133°; ir (CH_2Cl_2) ν_{CO} 1930 (s), 1850 (vs); $\nu_{C=O}$ 1605 (m); pmr ($CDCl_3$) τ 8.07 (broad multiplet, 2, CH_2), 6.90 (triplet, 2, CH_2, J_{HH} ~ 7 Hz), 6.60 (triplet, 2, CH_2, J_{HH} ~ 7 Hz), 3.40 (doublet, 5, C_5H_5, J_{PH} ~ 1.5 Hz), 2.64 (broad multiplet, 15, PPh$_3$).

(h^5-C_5H_5)Mo(CO)$_3$(CH_2)$_4$I (11). The procedure followed was similar to that described for complex **6**. Using 19.2 g (0.074 mol) of NaMo(h^5-C_5H_5)(CO)$_3$ and 9.6 ml (0.072 mol) of 1,4-diiodobutane, 7.83 g (25% based on Mo) of the product was obtained as yellow crystals: mp 46–49°; ir (cyclohexane) ν_{CO} 2020 (s), 1930 (vs); pmr (CS_2) τ 8.33 (broad multiplet, 6, 3 CH_2), 6.87 (broad triplet, 2, CH_2, J_{HH} ~ 6 Hz), 4.74 (singlet, 5, C_5H_5).

***trans*-(h^5-C_5H_5)Mo(CO)$_2$(PPh$_3$)C(O)(CH_2)$_4$I (12).** To a solution of 0.50 g (1.2 mmol) of **11** in 2 ml of acetonitrile was added a solution of 0.61 g (2.3 mmol) of triphenylphosphine in 3 ml of acetonitrile over a 30-sec period, giving a clear orange solution. Precipitation of a light yellow solid occurred within 7 min of adding the triphenylphosphine. After 1 min longer the reaction solution was filtered; the isolated solid washed with 2 ml of acetonitrile followed by 20 ml of pentane. The solid was then dried for 0.5 hr (10 mm, 25°), affording 0.397 g (49%) of the product as a lemon yellow powder: mp 124.5–125.5°; ir (CH_2Cl_2) ν_{CO} 1930 (s), 1850 (vs), $\nu_{C=O}$ 1605 (m); pmr ($CDCl_3$) τ 8.44 (broad multiplet, 4, 2 CH_2), 7.00 (broad multiplet, 4, 2 CH_2), 5.17 (doublet, 5, C_5H_5, J_{PH} ~ 1.5 Hz), 2.67 (broad multiplet, 15, PPh$_3$).

Formation of 13 from 12. The procedure followed was similar to that reported for the preparation of **13** from **7**. Thus, 0.19 g (0.27 mmol) of **12** and 0.058 g (0.30 mmol) of $AgBF_4$ followed by 0.20 g (0.58 mmol) of $NaBPh_4$ afforded 0.18 g (74%) of product as a yellow powder. Infrared, pmr, and elemental analysis identified the product as compound **13**, mp 140–145° dec.

Kinetic Measurements. All kinetic experiments were conducted in Spectrograde acetonitrile which was dried over 4 A Linde molecular sieves and purged with nitrogen. The organometallic reactants were prepared as stated above and purified further by recrystallization when necessary. Freshly opened triphenylphosphine was used and infrared analysis did not reveal any triphenylphosphine oxide. Silver tetrafluoroborate was recrystallized from acetonitrile and isolated as a white solid which was identified by pmr and gravimetric silver ion analysis as the adduct Ag(CH_3CN)$_4$$BF_4$. All kinetic data were recorded on a Hitachi Perkin-Elmer R-20B high-resolution nmr spectrometer equipped with a Model R-202VT variable temperature unit using the h^5-C_5H_5 resonance of the organometallic complexes as a probe to the reaction studied. Rate data were obtained by following the change in intensity, estimated by peak height times peak width at half-height, of the h^5-C_5H_5 resonances of the reactant and product complexes over at least 60% of the reaction. All rate constants were determined in triplicate for reactions involving only one reactant and in triplicate for each of three different relative reactant concentrations for those reactions between a haloalkyl complex and triphenylphosphine. The reaction between Ag(CH_3CN)$_4$$BF_4$, which was transferred in a glove bag under nitrogen, and a haloalkyl complex was studied at seven different relative concentrations of the silver ion. All reactions were studied at three different temperatures over a *ca.* 20° range.

The products were identified in most cases by isolation and characterization. In solution the product was identified by the chemical shift of the h^5-C_5H_5 pmr resonance. If the chemical shift of the h^5-C_5H_5 resonance in a haloalkyl complex is considered as an internal reference, then the h^5-C_5H_5 resonance of the trans isomer of the corresponding acyl complex lies 22 Hz to higher field and the h^5-C_5H_5 resonances of the trans and cis isomers of the corresponding carbenoid complexes lie at 8 and 20 Hz to lower field, respectively. The stereochemistry of the complexes is determined from the presence or absence of splitting of the h^5-C_5H_5 resonance by the phosphorus nucleus.[9,14]

The kinetic data were treated by standard methods,[15a] and the activation parameters were calculated from the Eyring equation for reactions performed in solution[15b]

$$k_{soln} = e\frac{kt}{h}e^{-E_a/RT}e^{\Delta S^{\pm}/R}$$

where E_a is the experimental activation energy and all values for

$$\Delta H^{\pm} = E_a - RT$$

the reported activation parameters are normalized to 298°K.

Results

It was demonstrated previously that a haloalkyl ligand could be converted directly into a cyclic carbenoid

(13) R. T. Hall and W. E. Schaeffer in "Organic Analyses," Vol. 2, Interscience, New York, N. Y., 1954, p 55.

(14) R. J. Mawby and G. Wright, *J. Organometal. Chem.*, 21, 169 (1970).

(15) (a) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, Wiley, New York, N. Y., 1961. (b) S. Glasstone, K. J. Laidler, and H. Eyring, "Theory of Rate Processes," 1st ed, McGraw-Hill, New York, N. Y., 1941, p 199.

ligand when treated with triphenylphosphine as was shown for the 3-bromo-*n*-propyl complex (**1**) (reaction 6), probably *via* a "CO insertion" step forming a cis

$$(h^5\text{-}C_5H_5)Mo(CO)_3(CH_2)_3Br + PPh_3 \xrightarrow[\sim 25^\circ]{CH_3CN}$$

1

$$cis\text{-}[Mo(h^5\text{-}C_5H_5)(CO)_2(PPh_3)\overline{COCH_2CH_2CH_2}]Br \quad (6)$$

2

acyl intermediate which underwent an intramolecular ring closure forming the cis isomer of the cationic carbenoid complex **2**.[9] A substituted cyclopentylidene ligand is shown now to be prepared in a similar manner (**4**) (reaction 7).[16]

$$BrC(H)(Me)CH_2CH_2Br + NaMo(h^5\text{-}C_5H_5)(CO)_3 \xrightarrow{THF}$$

$$(h^5\text{-}C_5H_5)Mo(CO)_3CH_2CH_2C(H)(Me)Br$$

3

$$cis\text{-}[Mo(h^5\text{-}C_5H_5)(CO)_2(PPh_3)\overline{COC(H)(Me)CH_2CH_2}]Br \xleftarrow{CH_3CN \mid PPh_3} \quad (7)$$

4

However, when this reaction with triphenylphosphine was extended to complexes containing bromoalkyl ligands in which the metal and bromine atoms are separated by more than three carbon atoms or with the 3-chloro-*n*-propyl ligand, the cis carbenoid complex was not isolated. For example, both the 4-bromo-*n*-butyl (**5**) and 5-bromo-*n*-pentyl (**6**) complexes reacted with triphenylphosphine affording the trans isomers of the 5-bromopentanoyl (**7**) and 6-bromohexanoyl (**8**) complexes, respectively (reaction 8).

$$(h^5\text{-}C_5H_5)Mo(CO)_3(CH_2)_nBr + PPh_3 \longrightarrow$$

5, $n = 4$
6, $n = 5$

$$trans\text{-}(h^5\text{-}C_5H_5)Mo(CO)_2(PPh_3)C(O)(CH_2)_nBr \quad (8)$$

7, $n = 4$
8, $n = 5$

These results are understandable in terms of the proposed mechanism. If a cis haloacyl complex were formed as a reactive intermediate, there appear to be two pathways for further reaction. Either a rapid intramolecular cyclization occurs within the haloacyl ligand forming the cis isomer of the cationic carbenoid complex or an intramolecular geometrical isomerization occurs forming the neutral trans haloacyl complex. Complexes of the type $(h^5\text{-}C_5H_5)Mo(CO)_3R$ (R = Me, Et, CH_2Ph, C_3H_5), where the R group does not possess a halogen atom, react with phosphines and phosphites forming the corresponding trans acyl complexes.[17,18] This result is expected since the intramolecular cyclization pathway is not possible.

However, when the alkyl ligand possesses a bromine atom on the γ-carbon atom, a rapid cyclization occurs forming the cis isomer of the cyclopentylidene complex. When the bromine atom is further removed from the metal atom, formation of the trans haloacyl complex becomes the favored process due to the retardation in the rate of ring closure for rings containing greater than five members.

Another qualitative check on this mechanism is provided through alteration of the halogen atom in the haloalkyl ligand. Since the cyclization reaction probably proceeds *via* an S_N2 attack of the acyl oxygen atom on the carbon atom possessing the halogen atom, it was expected that the rate of cyclization would depend on the identity of the halogen atom since the rates of S_N2 reactions at a halocarbon center decrease in the order C–I > C–Br > C–Cl.[19]

Indeed, the 3-chloro-*n*-propyl complex (**9**) when treated with triphenylphosphine, formed the trans 4-chlorobutanoyl complex (**10**) presumably by decreasing the rate of cyclization below the rate of the competing cis-to-trans geometrical isomerization of the haloacyl complex (reaction 9).

$$(h^5\text{-}C_5H_5)Mo(CO)_3(CH_2)_3Cl + Ph_3P \xrightarrow{CH_3CN}$$

9

$$trans\text{-}(h^5\text{-}C_5H_5)Mo(CO)_2(PPh_3)C(O)(CH_2)_3Cl \quad (9)$$

10

However, the similar reaction with the 4-iodo-*n*-butyl complex (**11**) afforded the trans 5-iodopentanoyl complex (**12**) as found with the analogous bromoalkyl ligand (reaction 8) and no cis cyclohexylidene complex was isolated (reaction 10). Presumably, the S_N2 closure reaction was not accelerated sufficiently to permit the rapid occurrence of the cyclization pathway.

$$(h^5\text{-}C_5H_5)Mo(CO)_3(CH_2)_4I + Ph_3P \xrightarrow{CH_3CN}$$

11

$$trans\text{-}(h^5\text{-}C_5H_5)Mo(CO)_2(PPh_3)C(O)(CH_2)_4I \quad (10)$$

12

As anticipated,[9] the trans isomers of the 5-iodo- and 5-bromopentanoyl complexes (**12** and **7**) were converted readily into the trans isomer of the cationic cyclohexylidene complex **13** through silver ion assistance (reaction 11). A similar reaction occurred with the 6-bromohexanoyl complex (**8**) although the product was not completely characterized.

$$trans\text{-}(h^5\text{-}C_5H_5)Mo(CO)_2(PPh_3)C(O)(CH_2)_4X \xrightarrow[2.\ NaBPh_4\text{-}MeOH]{1.\ AgBF_4\text{-}MeNO_2}$$

12, X = I
7, X = Br

$$trans\text{-}[Mo(h^5\text{-}C_5H_5)(CO)_2(PPh_3)\overline{CO(CH_2)_3CH_2}]BPh_4 \quad (11)$$

13

To obtain quantitative data concerning the competitive formation of acyl and carbenoid complexes, a kinetic study was undertaken. The results of this study will be presented in two parts, pertaining to reactions in which the alkyl ligand contains either three or four carbon atoms in the carbon chain.

The $[CH_2]_3$ System. The reaction of the 3-bromo-

(16) Complex **4** possesses two optical centers: one at the molybdenum atom and another at the cyclopentylidene carbon atom containing the methyl substituent as demonstrated by the diastereotopic methyl resonances in the pmr spectrum. These resonances, doublets due to coupling to the geminal hydrogen atom, were separated by 40 Hz in $CDCl_3$ solution with an intensity ratio of *ca.* 60:40. The $h^5\text{-}C_5H_5$ resonance was a singlet in both $CDCl_3$ and a *o*-dichlorobenzene solution; however, a diastereotopic splitting of *ca.* 1.2 Hz was observed in the polar solvents CH_3CN, MeOD, DMF-d_7 and DMSO-d_6. Recrystallization from *o*-dichlorobenzene afforded the same ratio of diastereomers, and the optical center at the molybdenum atom racemized slowly, if at all, on the pmr time scale up to 90° in a DMSO-d_6 solution at which point the geometrical isomerization became rapid enough to prevent measurement of the $h^5\text{-}C_5H_5$ resonance of the cis isomer.

(17) P. J. Craig and M. Green, *J. Chem. Soc. A*, 1978 (1968).

(18) P. J. Craig and M. Green, *ibid.*, 157 (1969).

(19) Bimolecular substitution rates for alkyl halides show that an alkyl bromide undergoes substitution about 30–40 times faster than the corresponding chloride, while the iodide reacts about 2.0–2.5 times faster than the bromide; see C. I. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p 339.

n-propyl complex (**1**) with triphenylphosphine went to completion forming the cis isomer of the cyclopentylidene complex (**2**) (reaction 12). The concentration

$$\underset{\mathbf{1}}{(h^5\text{-}C_5H_5)Mo(CO)_3(CH_2)_3Br} + Ph_3P \xrightarrow[CH_3CN]{k_1} \underset{\mathbf{2}}{cis\text{-}[Mo(h^5\text{-}C_5H_5)(CO)_2(PPh_3)\overline{COCH_2CH_2CH_2}]Br} \quad (12)$$

of the bromoalkyl complex **1** was followed as a function of time, temperature, and relative triphenylphosphine concentration. The disappearance of the bromoalkyl complex followed first-order kinetics and was independent of triphenylphosphine concentration as shown in Table I of Appendix II.[11] The calculated

Table I. Reaction Rate Constants and Activation Parameters

Reaction	k_i	$^{298}k_i$, sec^{-1}	$\Delta H^{\pm}$, kcal/mol	$\Delta S^{\pm}$, eu
		$[CH_2]_3$ System		
12	k_1	$4.28 \pm 0.60 \times 10^{-3}$	11.6 ± 2.4	-31 ± 8
13	k_5	$1.17 \pm 0.17 \times 10^{-5}$	22.4 ± 1.0	-5 ± 4
14	k_5'	$3.43 \pm 0.42 \times 10^{-6}$	24.1 ± 1.1	-3 ± 3
		$[CH_2]_4$ System		
16	k_1	$4.96 \pm 0.60 \times 10^{-3}$	15.5 ± 1.5	-18 ± 5
18	k_7	$1.22 \pm 0.60 \times 10^{-2}$ l./mol sec	11.7 ± 2.7	-28 ± 8

kinetic parameters for reaction 12 are shown in Table I of this text.

The geometrical isomerization of the cis cyclopentylidene complex (**2**) to the trans isomer **14** was followed also. The cis isomer isomerizes completely into the trans isomer (reaction 13). The rate data for this reaction are shown in Table II of Appendix II and the calculated kinetic parameters for this first-order reaction are shown in Table I.

$$\underset{\mathbf{2}}{cis\text{-}[Mo(h^5\text{-}C_5H_5)(CO)_2(PPh_3)\overline{COCH_2CH_2CH_2}]Br} \xrightarrow[CH_3CN]{k_5} \underset{\mathbf{14}}{trans\text{-}[Mo(h^5\text{-}C_5H_5)(CO)_2(PPh_3)\overline{COCH_2CH_2CH_2}]Br} \quad (13)$$

In order to detect any influence from the counterion on this intramolecular isomerization, a kinetic analysis of the isomerization of the tetraphenylborate salt **15** was performed (reaction 14). The reaction followed first-order kinetics and went to completion. The rate data are shown in Table III of Appendix II and the calculated kinetic parameters are shown in Table I.

$$\underset{\mathbf{15}}{cis\text{-}[Mo(h^5\text{-}C_5H_5)(CO)_2(PPh_3)\overline{COCH_2CH_2CH_2}]BPh_4} \xrightarrow[CH_3CN]{k_5'} \underset{\mathbf{16}}{trans\text{-}[Mo(h^5\text{-}C_5H_5)(CO)_2(PPh_3)\overline{COCH_2CH_2CH_2}]BPh_4} \quad (14)$$

The tetraphenylborate anion appears to exert some influence upon the rate of geometrical isomerization at the molybdenum center. This effect is probably significant, though small, since the minimum value for the ratio, $k_5:k_5'$, allowing for an error of one standard deviation in each rate constant is 2.6.

When the 3-chloro-*n*-propyl complex (**9**) was treated with triphenylphosphine at room temperature, the corresponding trans 4-chlorobutanoyl complex (**10**) was isolated as the major product (reaction 9). However, kinetic examination of this reaction at temperatures of 0, +11, and +20° revealed a complex, though informative, rate process. Figure 1 shows the mole fraction of each observed species as a function of time at each temperature. The graph at each temperature represents the average of nine kinetic data sets since at each temperature three runs were recorded in triplicate at three different molar ratios of [PPh_3]:[chloroalkyl]. There was no observed effect on the reaction rates from varying the concentration of the phosphine relative to the concentration of the chloroalkyl complex. The graph of the experimental data recorded at 0° represents an average of triplicate runs for a *ca.* 0.075 *M* solution of the chloroalkyl complex **9** in acetonitrile at 0° under the reactant molar ratios, [PPh_3]:[chloroalkyl], of 1.00, 1.60, and 2.06. The same concentration of the chloroalkyl complex was utilized in the other two experiments; however, the temperatures (reactant molar ratios) for these runs were respectively

+11°	1.15	1.56	2.09
+20°	1.10	1.54	2.08

In each graph the 3-chloro-*n*-propyl complex (**9**) decreased in concentration with increasing time after addition of the triphenylphosphine with the concurrent formation of the trans 4-chlorobutanoyl complex (**10**) as the major kinetically favored product and with the appearance followed by the disappearance of the cis cyclopentylidene complex as the minor kinetically formed product. The slow appearance of the trans cyclopentylidene complex results from both geometrical isomerization of the cis cyclopentylidene complex and from ring closure of the trans 4-chlorobutanoyl complex. A separate study confirmed the isomerization and equilibration between the trans 4-chlorobutanoyl and trans cyclopentylidene complexes. Figure 2 shows an example of the experimental data obtained for this reaction at 11°.

The dashed lines in Figure 1 indicate the range of the values of the experimental data. A reaction sequence, to be discussed later, was chosen as a model for this rather complex system of reactions, and the rate equations were integrated analytically giving expressions representing the time dependence of the mole fraction of each of the species observed. The calculated mole fractions based on a set of rate constants are shown by the points marked "×." A set of rate constants was thus determined at each temperature.

A separate kinetic investigation of the equilibration of the trans 4-chlorobutanoyl complex (**10**) with the trans isomer of the cyclopentylidene complex (**17**) was undertaken to determine independently the forward and reverse rate constants, thus also determining the value of the equilibrium constant (reaction 15).

$$\underset{\mathbf{10}}{trans\text{-}(h^5\text{-}C_5H_5)Mo(CO)_2(PPh_3)C(O)(CH_2)_3Cl} \underset{\Delta}{\overset{k_6}{\rightleftharpoons}} \underset{\mathbf{17}}{trans\text{-}[Mo(h^5\text{-}C_5H_5)(CO)_2(PPh_3)\overline{COCH_2CH_2CH_2}]Cl} \quad (15)$$

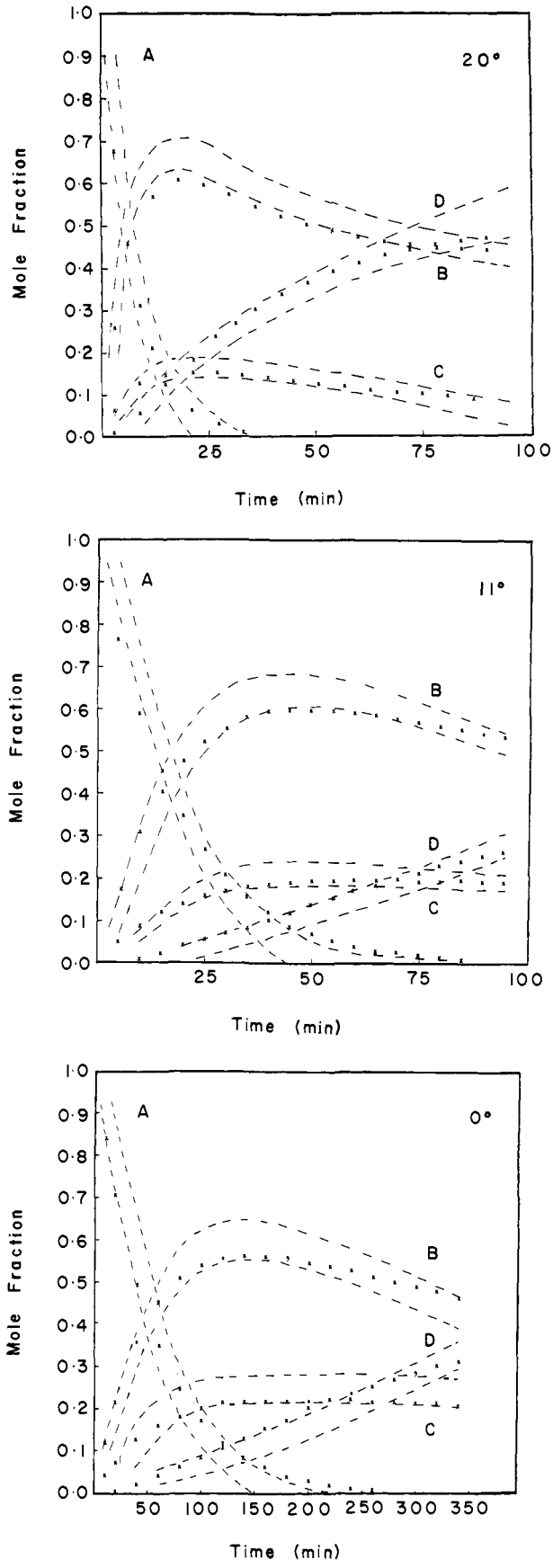


Figure 1. Kinetic data for the reaction of $(h^5\text{-}C_5H_5)Mo(CO)_3(CH_2)_3Cl$ with Ph_3P at 20, 11, and 0°: A, $(h^5\text{-}C_5H_5)Mo(CO)_3(CH_2)_3Cl$; B, *trans*-$(h^5\text{-}C_5H_5)Mo(CO)_2(Ph_3P)(COCH_2CH_2CH_2Cl)$; C, *cis*-$(h^5\text{-}C_5H_5)Mo(CO)_2(Ph_3P)(\overline{COCH_2CH_2CH_2})^+$; D, *trans*-$(h^5\text{-}C_5H_5)Mo(CO)_2(Ph_3P)(\overline{COCH_2CH_2CH_2})^+$.

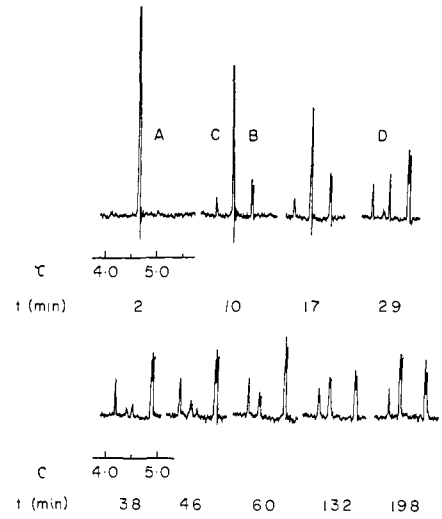


Figure 2. Representative time-dependent pmr spectra of the type which provided the data shown in Figure 1 of the reaction run at 11°. The labeling of the resonances corresponds with the labeling of the curves in Figure 1.

Although the trans 4-chlorobutanoyl complex (**10**) was only sparingly soluble in acetonitrile, *ca.* 0.02 *M*, the reaction was followed at 35, 46, and 56°. However, the rate data were not of sufficient precision to reveal whether the reverse reaction, governed by k_{-6}, deviates from first-order kinetics. Therefore, the data were treated assuming first-order kinetics in both directions.[20] The equilibrium constant remains unchanged at 2.0 ± 0.5 in the temperature range studied. The kinetic data are shown in Table IV of Appendix II and the calculated kinetic parameters for the forward reaction along with the thermodynamic parameters for the equilibrium are $^{298}k_6 = (6.13 \pm 0.63) \times 10^{-4}$ sec^{-1}, $^{298}k_{-6} = (3.06) \pm 0.33) \times 10^{-4}$ sec^{-1}, $\Delta H^{\pm} = 16.9 \pm 1.1$ kcal/mol, $\Delta S^{\pm} = -19.3 \pm 6.6$ eu, $K = 2.0 \pm 0.5$ (35–56°), $\Delta H^{\circ} \approx 0$ kcal/mol, and $\Delta S^{\circ} \approx +2 \pm 0.6$ eu.

The $[CH_2]_4$ System. The reaction of the 4-bromo-*n*-butylalkyl complex (**5**) with triphenylphosphine in acetonitrile went to completion forming the corresponding trans 5-bromopentanoyl complex (**7**) (reaction 16). The disappearance of the bromoalkyl reactant followed first-order kinetics and was independent of ligand concentration as shown in Table V of Appendix II. The calculated kinetic parameters are shown in Table I.

$$\underset{\mathbf{5}}{(h^5\text{-}C_5H_5)Mo(CO)_3(CH_2)_4Br} + PPh_3 \xrightarrow[CH_3CN]{k_1} \underset{\mathbf{7}}{trans\text{-}(h^5\text{-}C_5H_5)Mo(CO)_2(PPh_3)C(O)(CH_2)_4Br} \quad (16)$$

The trans 5-bromopentanoyl complex (**7**) equilibrated slowly with the trans isomer of the cyclohexylidene complex (**18**), and a kinetic study of this reaction was undertaken using a *ca.* 0.02 *M* solution of the 5-bromopentanoyl complex (**7**) in acetonitrile (reaction 17). The values for the rate constant, k_6, and the

(20) This assumption would hold if the carbenoid complexes formed ion pairs with the anions. Such an association is supported by the immeasurably low conductivity of a mixture of the complexes **2** and **4** of a 0.01 *M* solution in CH_3CN at 25°.

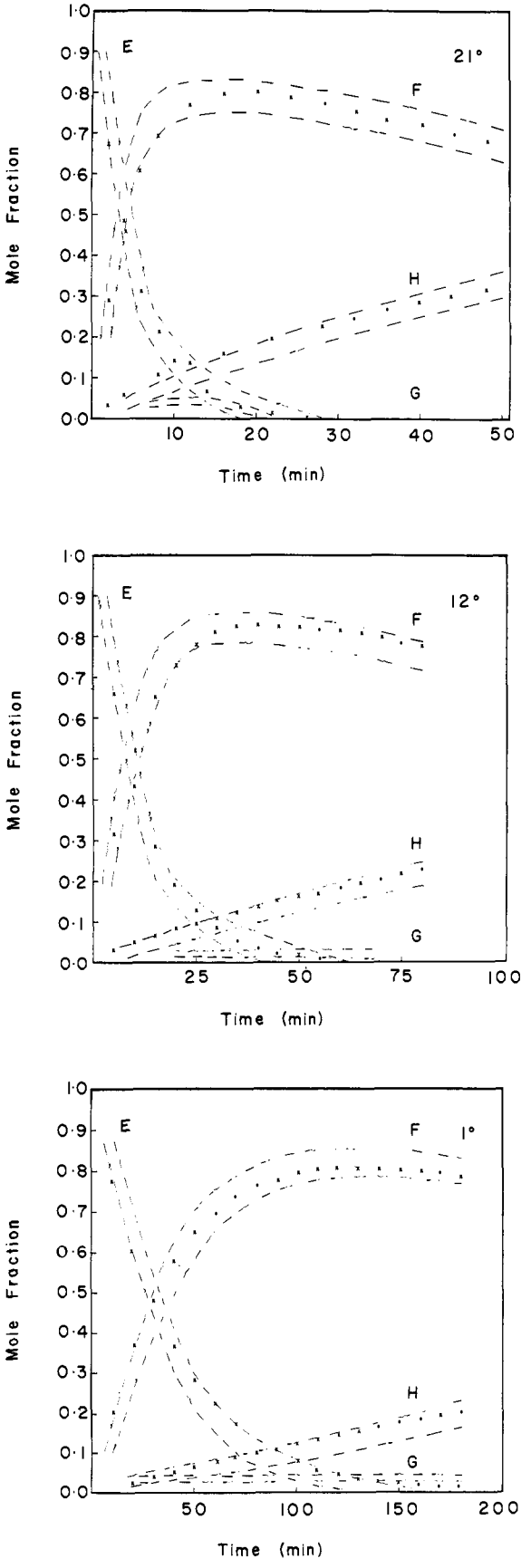


Figure 3. Kinetic data for the reaction of $(h^5\text{-}C_5H_5)Mo(CO)_3(CH_2)_4I$ with Ph_3P at 21, 12, and 1°: E, $(h^5\text{-}C_5H_5)Mo(CO)_3(CH_2)_4I$; F, *trans*-$(h^5\text{-}C_5H_5)Mo(CO)_2(Ph_3P)(COCH_2CH_2CH_2CH_2I)$; G, *cis*-$(h^5\text{-}C_5H_5)Mo(CO)_2(Ph_3P)(\overline{COCH_2CH_2CH_2CH_2})^+$; H, *trans*-$(h^5\text{-}C_5H_5)Mo(CO)_2(Ph_3P)(\overline{COCH_2CH_2CH_2CH_2})^+$.

$$\textit{trans}\text{-}(h^5\text{-}C_5H_5)Mo(CO)_2(PPh_3)C(O)(CH_2)_4Br \underset{k_{-6}}{\overset{k_6}{\rightleftharpoons}} \underset{\mathbf{8}}{\textit{trans}\text{-}[Mo(h^5\text{-}C_5H_5)(CO)_2(PPh_3)\overline{CO(CH_2)_3CH_2}]Br} \quad (17)$$
$$\mathbf{7} \qquad\qquad CH_3CN$$

equilibrium constant calculated assuming first-order kinetics for the forward and reverse reaction are shown in Table VI of Appendix II. The kinetic parameters calculated for the forward reaction, k_6, and the thermodynamic parameters for the equilibrium are $^{298}k_6 = (5.05 \pm 2.36) \times 10^{-5}$ sec^{-1}, $\Delta H^{\ddagger} = 15.0 \pm 2.1$ kcal/mol, $\Delta S^{\ddagger} = -27.6 \pm 7.6$ eu, $\Delta H°_{298} = -7.68 \pm 0.24$ kcal/mol, $\Delta S°_{298} = -25.8 \pm 0.8$ eu, $\Delta G°_{298} = +0.02 \pm 0.07$ kcal/mol, and $^{298}K = 1.0 \pm 0.25$.

In accord with the original expectation for a reaction sequence leading from haloacyl complexes to cyclic carbenoid complexes,[9] the trans 5-bromo- and trans 5-iodopentanoyl complexes were converted into the trans isomer of the corresponding cationic cyclohexylidene complexes when treated with $AgBF_4$. A typical reaction involving silver ion assistance in ring formation was studied kinetically (reaction 18).

$$\underset{\mathbf{7}}{\textit{trans}\text{-}(h^5\text{-}C_5H_5)Mo(CO)_2(PPh_3)C(O)(CH_2)_4Br} + AgBF_4 \cdot 4MeCN \xrightarrow[CH_3CN]{k_7} \textit{trans}\text{-}[Mo(h^5\text{-}C_5H_5)(CO)_2(PPh_3)\overline{CO(CH_2)_3CH_2}]BF_4 \quad (18)$$

The reaction went to completion and the rate was measured at various concentrations of the silver-containing compound at three temperatures.

It was found that the rate depended markedly on the concentration of $AgBF_4 \cdot 4CH_3CN$, as shown by the data in Table VII of Appendix II. A plot of these data gave a straight line with a nonzero intercept. This line was described by the two-term rate law

$$-\frac{d[acyl]}{dt} = (k_7 + k_7'[Ag])[acyl] \quad (19)$$

with $k_7 = (3.0 \pm 1.0) \times 10^{-4}$ sec^{-1} and $k_7' = (1.65 \pm 0.15) \times 10^{-2}$ l. mol^{-1} sec^{-1} at 34°.

The value of k_7 pertains to the same thermally initiated ring closure as that in reaction 17. The rate constant obtained independently in a study of that reaction, $(1.23 \pm 0.05) \times 10^{-4}$ sec^{-1} at 34°, is within two standard deviations of the value estimated for k_7.

Additional rate data were gathered for reaction 18 at 45 and 55° and are presented in Table VIII of Appendix II. The calculated activation parameters for the silver-assisted ring closure are shown in Table I.

As described previously, when the 4-iodo-*n*-butyl complex (**11**) is treated with triphenylphosphine, the trans 5-iodopentanoyl complex (**12**) was isolated (reaction 10). However, when this reaction was investigated kinetically at temperatures below room temperature, four species were observed as in the analogous reaction of the 3-chloro-*n*-propyl complex (reaction 9). Figure 3 represents the mole fraction of each species as a function of time where the curves refer to the iodoalkyl, cis cyclohexylidene, trans 5-iodopentanoyl, and trans cyclohexylidene complexes. The major kinetically controlled product was the trans 5-iodo-

pentanoyl complex as was the major product isolated *via* the preparative route (reaction 10). However, the change from a bromine atom (reaction 16) to an iodine atom sufficiently accelerated the rate of ring formation relative to the rate of trans acyl formation that 4–5% of a cis carbenoid species was formed. As was found in the reaction of the 3-chloro-*n*-propyl complex with triphenylphosphine, the reaction rate was independent of relative ligand concentration. Thus, each graph in Figure 3 represents an average of nine spectra at a given temperature. The concentration of the 4-iodo-*n*-butyl complex was *ca.* 0.038 *M*, and at each temperature triplicate runs were recorded at three triphenylphosphine concentrations as shown below.

T, °C	[PPh_3]/[iodoalkyl]
+1	1.08, 1.47, 1.96
+12	1.05, 1.57, 2.08
+21	1.07, 1.53, 2.04

The dashed curves indicate the range of the values of the experimental data. A calculated curve is shown by the "×" points. These calculated values were obtained by assuming a model for the reaction scheme followed by analytical integration of the rate laws giving the mole fraction–time dependency for each species. This model was identical with the one used for the analysis of the reaction of the 3-chloro-*n*-propyl compound with triphenylphosphine, except that here the cis carbenoid species was assumed to be in a steady-state concentration.

The thermally initiated ring closure and equilibration of the trans 5-iodopentanoyl complex (**12**) to the trans isomer of the cyclohexylidene complex (**19**) were examined independently (reaction 20). The values for

$$\underset{\mathbf{12}}{trans\text{-}(h^5\text{-}C_5H_5)Mo(CO)_2(PPh_3)C(O)(CH_2)_4I} \underset{k_{-6}}{\overset{k_6}{\rightleftharpoons}} \underset{\mathbf{19}}{trans\text{-}[Mo(h_5\text{-}C_5H_5)(CO)_2(PPh_3)\overbrace{CO(CH_2)_3CH_2}]I} \quad (20)$$

the forward rate constant, k_6, obtained at three temperatures are shown in Table IX of Appendix II. Over this temperature range the value of the equilibrium constant, 4.0 ± 0.6, was independent of temperature within the errors of measurement. By treating the forward and reverse reactions (20) as first-order processes, the kinetic parameters for the forward step and the thermodynamic parameters for the equilibrium are $^{298}k_6 = (1.51 \pm 0.16) \times 10^{-4}$ sec^{-1}, $\Delta H^{\pm} = 17.4 \pm 2.0$ kcal/mol, $\Delta S^{\pm} = -16.7 \pm 6$ eu, $K = 4.0 \pm 0.6$, $\Delta H^{\circ} \approx 0 \pm 2$ kcal/mol, $\Delta S^{\circ} \approx 2.75 \pm 0.31$ eu.

Since the 5-iodopentanoyl complex (**12**) was more soluble in acetonitrile and had a larger value for the equilibrium constant, *K*, for reaction 21 than the other

$$[\text{trans haloacyl}] \overset{K}{\rightleftharpoons} [\text{trans carbene}]X \quad (21)$$

trans haloacyl complexes, an attempt was made to test whether extensive ion pairing exists in the salts of the carbenoid complexes. If most of the carbenoid cations form ion pairs with the halide anions, then the assumption of first-order kinetics for the reverse reaction, k_{-6}, is justified. This system is described by

$$\text{trans acyl} \overset{K_1}{\rightleftharpoons} \underset{\text{ion pair}}{\{+\ -\}} \overset{K_2}{\rightleftharpoons} \text{dissociated ions}$$

where K_1 and K_2 are equilibrium constants.

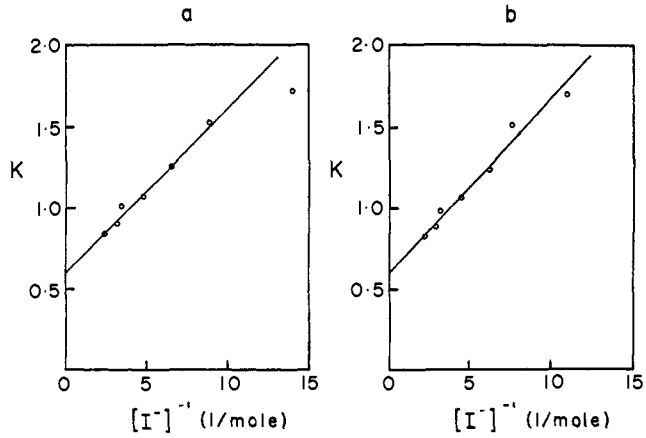


Figure 4. A plot of the equilibrium constant of the ring closure reaction of *trans*-(h^5-C_5H_5)$Mo(CO)_2(PPh_3)C(O)(CH_2)_4I$ as a function of iodide concentration: (a) assuming no dissociation of the ion pair, (b) assuming partial dissociation of the ion pair.

Pmr intensity measurements of the h^5-C_5H_5-resonance in the trans acyl and trans carbenoid complexes gives the ratio of the concentrations of these two species, *i.e.*, *K;* however, the trans carbenoid resonance represents the sum of the carbenoid cations in both the ion pair and the dissociated ions. Therefore, *K* is given by

$$K = \frac{\text{carbenoid resonance intensity}}{\text{acyl resonance intensity}} = \frac{[\{+\ -\}] + [+]}{[\text{acyl}]} = K_1 + K_1K_2\frac{1}{[-]}$$

and a plot of *K vs.* 1/[−], where [−] is the molar concentration of the "free" halide anion, should give a straight line having a slope of K_1K_2 and an intercept of K_1.

The equilibrium constant, *K*, was measured at various iodide concentrations, by adding known amounts of (n-Bu)$_4$NI to a 0.035 *M* solution of the trans 5-iodopentanoyl complex (**12**) in acetonitrile at 25° after equilibrium was established. The following measurements were recorded.

[I^-] (added)	*K*	[I^-] (added)	*K*
0	3.94	0.20	1.07
0.07	1.71	0.28	1.00
0.11	1.52	0.34	0,89
0.146	1.25	0.39	0.83

Figure 4a shows a plot of *K vs.* 1/[I^-]$_{added}$ for which the initial amount of free iodide resulting from partial dissociation of the ion pair in the absence of added iodide was taken as zero. Clearly this assumption is not good as reflected by the poor fit of the point at lowest added iodide concentration. A better fit is obtained by correcting for some dissociation into free iodide as shown in Figure 4b giving $K_1 = 0.64$ and $K_2 = 0.14$ mol/l. From K_2 the degree of dissociation of the ion pair into free ions was only 31% thereby substantiating the assumption that the reverse reaction, k_{-6}, occurs predominantly by a first-order process.

Discussion

In addition to reaction 6, which was reported previously,[9] the reaction of the 3-bromo-*n*-butyl complex (**3**) with triphenylphosphine provided another example

of the direct formation of a cationic cyclopentylidene complex as the cis isomer from an alkyl complex. However, when the bromine atom of the alkyl ligand is separated from the molybdenum atom by a carbon chain having more than three carbon atoms, reaction with triphenylphosphine affords the corresponding trans acyl complex as shown in reaction 8. By judicious variation of the halogen atom the reactivities of the *n*-propyl- and *n*-butylhaloalkyl complexes were altered in such a way that both cis carbenoid and trans acyl complexes were formed. In general, the cis carbenoid complexes isomerized completely to the thermodynamically more stable trans isomers. The trans acyl complexes equilibrated thermally with the corresponding trans carbenoid complexes *via* intramolecular ring formation resulting from attack by the acyl oxygen atom on the carbon atom containing the halogen atom. The trans acyl complexes are driven quantitatively to the cyclic trans carbenoid complexes when treated with Ag^+ ion.

These synthetic results suggested strongly that an intermediate species is formed when the haloalkyl complexes are treated with triphenylphosphine and that this intermediate collapses forming two different products depending upon the relative rates of reaction for the alternative pathways. The kinetic studies described above were undertaken to elucidate the details of such a mechanism.

The formation of the cyclic ylidene ligand is one of the few reactions that have been examined in kinetic detail in which a carbenoid complex is formed directly. Only two such reactions have previously been investigated kinetically. The nucleophilic attack of methyllithium on a carbon monoxide ligand in the following complexes was examined by the stopped-flow technique.[21]

$$LM(CO)_5 + CH_3Li \xrightarrow[25°]{\text{ether}} Li[(OC)_4M(L)(COCH_3)]$$

M = Cr, Mo, W; L = CO
M = W; L = $P(C_6H_5)_3$, $As(C_6H_5)_3$, $P(OC_6H_5)_3$

The rate data are consistent with the rate law

$$\text{rate} = k[\text{substrate}][CH_3Li]^{1/4}$$

and with a mechanism involving a dissociation of the methyllithium tetramer into monomeric units which then attack the carbon ligand in the slow step of the reaction.

$$(CH_3Li)_4 \overset{K}{\rightleftharpoons} 4CH_3Li$$

$$M(CO)_5L + CH_3Li \xrightarrow{k_2} \left[(OC)_4(L)MC(\overset{\delta+}{=}O)\cdots CH_3\text{--}Li \right]^{\delta-\ \delta+}$$

$$\xrightarrow{\text{fast}} Li[(OC)_4M(L)(COCH_3)]$$

The rates of reaction of the substituted carbonyl complexes are more than 100 times smaller than the rates for the hexacarbonyl compounds, presumably due to the steric inhibition of the nucleophilic attack at a carbonyl ligand cis to the ligand, L. Only the cis carbenoid complex is formed from the substituted carbonyl complexes. The rates of reaction within the hexacarbonyl series decrease as W > Mo > Cr. This is the same trend estimated for M–C bond strengths and probably reflects an increasing positive charge on the carbonyl carbon atom in going from Cr to W.

The following analogous reactions using Grignard reagents proceeded at more convenient rates and a classical kinetic study was performed at 27.9°.[22]

$$W(CO)_6 + PhCH_2MgCl \xrightarrow{\text{THF}} W(CO)_5[C(O^-Mg^+Cl)(CH_2Ph)]$$

$$W(CO)_5PPh_3 + PhCH_2MgCl \xrightarrow{\text{THF}} cis\text{-}W(CO)_4PPh_3[C(O^-Mg^+Cl)(CH_2Ph)]$$

The reactions are first order in the Grignard reagent although some deviations occur at low Grignard concentrations. As found with the methyllithium reactions above, the phosphine-substituted complex reacts about an order of magnitude more slowly than the pure carbonyl complex presumably due to steric effects or to the less electrophilic character of the carbon atoms of the coordinated carbon monoxide molecules. The other reaction pathway observed involves the formation of an acyl ligand by treating an alkyl complex with triphenylphosphine.

In contrast to the paucity of kinetic investigations involving the formation of carbenoid complexes, the "CO insertion" reaction has been investigated for several systems.

Noack and Calderazzo observed that the reaction of $MeMn(CO)_5$ with ^{13}C labeled carbon monoxide formed the cis isomer of the acetyl complex (**20**) (reaction 22).[23] Product analysis of the thermally ini-

$$MeMn(CO)_5 + {}^{13}CO \longrightarrow cis\text{-}MeC(O)Mn(CO)_4({}^{13}CO) \quad (22)$$
20

tiated decarbonylation reaction of **20** and the carbonylation reaction of *cis*-$MeMn(CO)_4(^{13}CO)$ with unlabeled carbon monoxide provided conclusive evidence that the reaction mechanism is described best as a methyl migration and not as a carbon monoxide insertion.

Noack, *et al.*, examined a similar reaction where the incoming nucleophile was triphenylphosphine (reaction 23).[24] The kinetically formed product was the

$$MeMn(CO)_5 + Ph_3P \longrightarrow cis\text{-}MeC(O)Mn(CO)_4Ph_3P \quad (23)$$
21

cis isomer of the acetyl complex (**21**) which subsequently isomerized to and equilibrated with the trans isomer. Although the detailed reaction mechanism was not established, a kinetic study by Calderazzo and Cotton showed that the rate of reaction was independent of triphenylphosphine concentration and that the rate constant had a value of 6.6×10^{-4} sec^{-1} at 30.5°.[25]

Mawby and Glyde studied "CO insertion" reactions of iridium(III)–alkyl complexes of the type[26,27]

(21) J. R. Paxson and G. R. Dobson, *J. Coord. Chem.*, 1, 321 (1972).

(22) D. J. Darensbourg and M. Y. Darensbourg, *Inorg. Chim. Acta*, 5, 247 (1971).

(23) K. Noack and F. Calderazzo, *J. Organometal. Chem.*, 10, 101 (1967).

(24) K. Noack, M. Ruck, and F. Calderazzo, *Inorg. Chem.*, 7, 345 (1968).

(25) F. Calderazzo and F. A. Cotton, *Chim. Ind. (Milan)*, 46, 1165 (1964).

(26) R. W. Glyde and R. J. Mawby, *Inorg. Chim. Acta*, 4, 331 (1970).

(27) R. W. Glyde and R. J. Mawby, *ibid.*, 5, 317 (1971).

$$IrCl_2R(CO)_2L + L' \longrightarrow IrCl_2(CO)LL'C(O)R$$
$$R = Me, Et$$
$$L = L' = As(Ph)_{3-x}(Me)_x \quad x = 1, 2$$

in which the rate of reaction was independent of both the concentration of L′ and the nature of the solvent. These facts coupled with the small values for the entropy of activation, +1.8 to −6.7 eu, supported a postulated mechanism involving a five-coordinate intermediate, **22**, formed *via* a combination of CO insertion and alkyl migration

$$[Ir(CO)_2Cl_2RL] \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{\mathbf{22}}{[Ir(CO)Cl_2LC(O)R]} \xrightarrow[L']{k_2} \underset{\mathbf{23}}{trans\text{-}[Ir(CO)Cl_2LL'C(O)R]}$$

The product, **23**, was formed initially as the trans isomer and preliminary evidence suggested a subsequent isomerization to the cis isomer. A similar mechanism was postulated recently for CO insertion into platinum(II)–alkyl bonds.[28]

Green and Westlake investigated the kinetics of reaction 24 in acetonitrile at various temperatures.[29] The

$$\underset{\mathbf{24}}{(h^5\text{-}C_5H_5)Fe(CO)_2R} + L \xrightarrow{k} \underset{\mathbf{25}}{(h^5\text{-}C_5H_5)Fe(CO)LC(O)R} \quad (24)$$
$$R = Me, Et, i\text{-}Pr; \; L = Ph_3P, PhMe_2P$$
$$R = Et; \; L = Ph_2MeP, (MeO)_3P, (PhO)_3P$$

rate of reaction, k, increased linearly with an increase in the concentration of L and approached a limiting value suggesting a mechanism involving an intermediate, I, in steady-state concentration (reaction 25). This

$$\mathbf{24} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} I \xrightarrow[L]{k_2} \mathbf{25} \quad (25)$$

mechanism is substantiated, by the approach toward first-order kinetics, *i.e.*, $k = k_1$, at high ligand concentrations and by the linear relationship obtained when $1/k$ is plotted as a function of 1/[L]. The activation parameters for the reactions having L = Me_2PhP in acetonitrile were

R	$\Delta H^{\pm}$ (±0.5) kcal/mol	$\Delta S^{\pm}$ (±2.0) eu
Me	18.2	−19
Et	14.4	−30
i-Pr	12.5	−33

The increased reactivity for the series *i*-Pr > Et > Me is reflected in the decrease in the values for the enthalpy of activation and was related to the probable decrease in the Fe–C bond strength for this series of alkyl complexes. The large negative values for the entropy of activation and the observed dependence of the rate on solvent indicated a highly ordered transition state having some type of solvent participation.

Of particular interest to the work reported here are the kinetic studies of CO insertion reactions of the methyl-, ethyl-[17] and the benzyl-, allyltricarbonyl-(*pentahaptocyclopentadienyl*)molybdenum[18] complexes (reaction 26). The observed rate, k_{obsd}, in acetonitrile solution is virtually independent of the type of ligand, L, and the ligand concentration implying the rate-determining formation of a reactive intermediate of the type postulated above (reaction2 5). The ethyl com-

$$(h^5\text{-}C_5H_5)Mo(CO)_3R + L \xrightarrow[CH_3CN]{k_{obsd}} trans\text{-}(h^5\text{-}C_5H_5)Mo(CO)_2LC(O)R \quad (26)$$

R	L
Me	PPh_3, $P(OMe)_3$, $P(OCH_2)_3CMe$, $P(OPh)_3$, $P(n\text{-}Bu)_3$
Et	PPh_3, $P(OMe)_3$, $P(OCH_2)_3CMe$
$PhCH_2$, C_3H_5	PPh_3, $P(OPh)_3$

plex reacted with the ligands, L, much more rapidly than the methyl complex in acetonitrile solution, although only a qualitative trend was reported for this difference in rate. In chloroform solution the ethyl complex reacted at a more convenient rate at 30.5°; however, a contribution from a second-order process occurred. A similar effect was observed for the reaction of the methyl complex with $(n\text{-}Bu)_3P$ in *n*-hexane.[30] The reactivity sequence Et > Me > $PhCH_2$ > C_3H_5 suggested that little or no charge separation is involved in the rate-determining step. Although there were insufficient data to obtain activation parameters, the rate, k_{obsd}, for the reaction of the methyl complex with triphenylphosphine in acetonitrile solution at 30.5° was 4.38×10^{-4} sec^{-1}. The acyl complexes were isolated in the trans configuration which is presumably the thermodynamically more stable isomer since no isomerization to a cis configuration occurred.

The reaction of the methyl complex with $P(n\text{-}C_4H_9O)_3$ in THF followed first-order kinetics and the calculated activation parameters are $\Delta H^{\pm} = 16.1 \pm 0.6$ kcal/mol and $\Delta S^{\pm} -25 \pm 2$ eu. Hart-Davis and Mawby estimated for this reaction that a bimolecular reaction with the solvent would lower the value for the entropy of activation to -30 ± 2 eu.[30] The present consensus regarding the nature of the intermediate, I, reaction (25), invokes some degree of solvent participation, although the exact nature of the species is not known.

Also, anionic acyl complexes have been prepared by treating σ-alkyl complexes with potassium cyanide.[31] The insertion reaction of the methyl–molybdenum complex with cyanide was followed by pmr and demonstrated that the kinetically controlled product is the

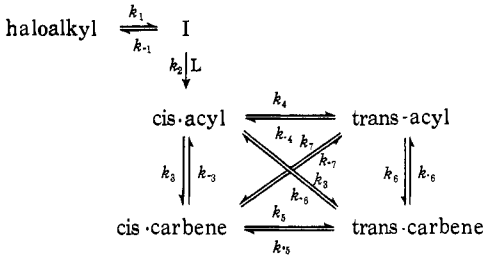
$$(h^5\text{-}C_5H_5)M(CO)_nR + KCN \xrightarrow{CH_3OH} K[(h^5\text{-}C_5H_5)M(CO)_{n-1}(COR)(CN)]$$
$$M = Fe; \; n = 2 \qquad R = CH_3, C_2H_5$$
$$M = Mo, W; \; n = 3$$

cis isomer of the anionic, acetyl complex. This cis isomer isomerizes slowly to the trans isomer in direct analogy to our results concerning the formation of cis and trans cationic, carbenoid complexes from haloalkyl complexes.

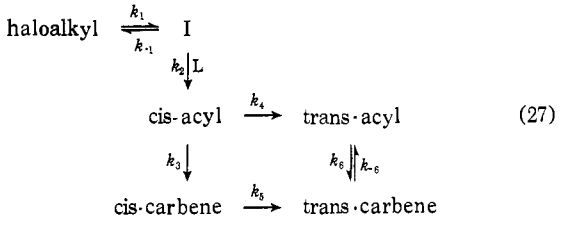
Examination of the present results in the light of these literature reports initially suggested the very general reaction scheme (Scheme I) where I represents a solvent-assisted intermediate which reacts with the ligand, L, forming a cis acyl complex. However, this model can be simplified since: (1) the trans carbenoid complex is formed through isomerization of the trans acyl and cis carbenoid complexes only, therefore, there is no need to invoke pathway 8; (2) the trans acyl complex isomerized to and equilibrated with the trans carbenoid complex *only*, thus establishing, independently, k_6 and k_{-6}, while eliminating k_7 and k_{-7} and

(28) R. W. Glyde and R. J. Mawby, *Inorg. Chem.*, 10, 854 (1971).
(29) M. Green and D. J. Westlake, *J. Chem. Soc. A*, 367 (1971).
(30) A. J. Hart-Davis and R. J. Mawby, *ibid.*, 2403 (1969).
(31) T. Kruck, M. Hofler, and L. Liebig, *Chem. Ber.*, 105, 1174 (1972).

Scheme I



implying that $k_4 \gg k_{-4}$; (3) independent study of the geometrical isomerization of the cis carbenoid complex to the trans isomer demonstrated that no equilibrium is established; therefore, k_{-5} and k_{-8} are *ca.* zero. The simplified, working model is therefore reaction 27,[32]

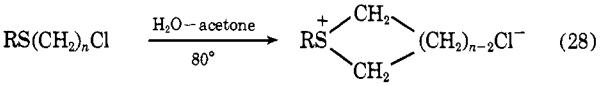


(27)

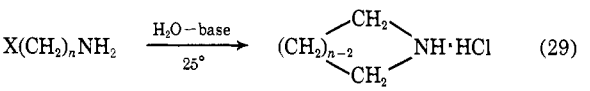
where the haloalkyl complex reacts with the solvent by a slow step forming the intermediate, I, which reacts with the ligand, L, in a fast step forming the cis acyl intermediate which then has available two pathways for further reaction.

The reaction of the 3-bromo-*n*-propyl (**12**) and 4-bromo-*n*-butyl (**16**) complexes with triphenylphosphine support this mechanism in that both reaction rates were independent of triphenylphosphine concentration and had the same value, $4.62 \pm 0.34 \times 10^{-3}$ sec^{-1}, within one standard deviation. Under these conditions the observed rate corresponds to k_1, *i.e.*, k_2 [L] $\gg k_{-1}$, with $k_3 > k_4 > k_1$ in the first reaction and $k_4 > k_3 > k_1$ in the second. This value for k_1 is greater than that value observed by Craig and Green, *ca.* 5×10^{-4} sec^{-1}, for the reaction of the methyl complex with triphenylphosphine, reaction 26, at 30.5°.[17] However, it was reported that the analogous ethyl complex reacted with triphenylphosphine under the same conditions at such a rate that the reaction could not be followed conveniently. This qualitative observation appears to be correct since the haloalkyl complexes, **1**, **5**, **9**, and **11**, react with triphenylphosphine at a rate which is followed conveniently only at temperatures below 20°. The values for $\Delta H^{\pm}$, 14.8 kcal/mol, and $\Delta S^{\pm}$, *ca.* −20 eu, for these latter reactions agree with those values of the activation parameters for the formation of a solvent-assisted intermediate.[30]

The observed trend in the k_3/k_4 ratio is, as expected, based on the rate of cyclization as a function of ring size. Bennett, *et al.*, examined the rate of cyclization of phenyl-δ-chlorobutyl and phenyl-ε-chloroamyl sulfides (reaction 28) and found that the rate of five-membered ring formation was *ca.* 76 times the rate of formation of a six-membered ring.[33] Similarly, Freundlich and coworkers studied the cyclization of chloro-[34] and bromoaliphatic[35] amines (reaction 29)



(28)



(29)

X	*n*	rate (min^{-1})
Cl	4	0.45
	5	0.0065
Br	4	*ca.* 30.0
	5	0.5

and found values of 69 and *ca.* 60, respectively, for the same ratio. Salomon obtained a good correlation to these experimental trends by regarding ring closure as arising from statistical factors.[36,37] Therefore, k_3 in the 4-bromo-*n*-butyl reaction might be reduced by a factor of 70–80 relative to k_3 in the 3-bromo-*n*-propyl reaction permitting the formation of the trans acyl complex in the former reaction if k_3 becomes less than k_4. Since the cis acyl complex was not observed and the overall rate was determined by k_1, independent measurement of k_4 was not possible.

The forward rate, k_6, of reaction 17 represents ring closure forming the cyclohexylidene ligand. This rate is $(5.05 \pm 2.36) \times 10^{-5}$ sec^{-1}, and one might expect that the rate of formation of a cyclopentylidene ligand might be *ca.* 75 times this or $(3.79 \pm 1.77) \times 10^{-3}$ sec^{-1} for k_3 in the reaction of the 3-bromo-*n*-propyl complex thus making k_3 as much as 1.5 times k_1 in this reaction. However, there could be an additional rate enhancement due to the differences in geometrical isomerization at the metal center when using the value of k_6 to estimate k_3.

Also, the kinetic data for the cyclization of the chloro- and bromoaliphatic amines (reaction 29) indicate a rate enhancement of *ca.* 80 when changing the ω-halogen atom from chlorine to bromine. If k_3 in the 3-bromo-*n*-propyl reaction could be reduced by a factor of *ca.* 80 by using the 3-chloro-*n*-propyl ligand, then the trans acyl pathway, k_4, might become the predominant reaction forming the trans acyl complex completely or a mixture of the trans acyl and cis carbenoid complexes. The results indicate that such

(32) The reaction of the 3-chloro-*n*-propyl complex (**9**) with triphenylphosphine, which will be discussed in the following paragraphs, formed both the trans acyl and the cis carbenoid complexes as kinetically controlled products. In this case the significance of the reverse step, k_{-3}, in the decay of the cis carbenoid complex could be determined from the experimental data obtained at 0°. The rates of appearance of these two products during the first 50 min of the reaction were analyzed according to this simplified scheme *including* the step characterized by k_{-3}. During this time interval the reaction rates are linear with time and any effect from the step characterized by k_5 is negligible. The value of k_{-3} was only 4% of k_3, thus, confirming the approximation, $k_3 \gg k_{-3}$.

(33) G. Bennett, *et al.*, *J. Chem. Soc.*, 2567 (1929).

(34) H. Freundlich and A. Krestounikoff, *Z. Phys. Chem.*, **76**, 79 (1911).

(35) H. Freundlich and H. Kraepelin, *ibid.*, **122**, 44 (1926).

(36) G. Salomon, *Trans. Faraday Soc.*, **32**, 153 (1936).

(37) A more refined calculation on the probability of ring formation of short chain molecules based on Monte Carlo statistics gave the following probabilities for closure

ring size	probability for closure
5	0.09
6	0.062

if it is assumed that ring closure occurs when the ends of the chain come within 1.6–2.4 Å of each other.[38] The calculated probability of forming a six-membered ring is presumed to be too large by a factor of four due to the nonequal energy of all conformations of the ring. These results are in qualitative agreement to the experimental data observed in the rates of cyclization of the haloalkylamines. A discussion of other factors which might influence these rates is presented by Salomon.[36]

(38) F. A. Cotton and F. E. Harris, *J. Phys. Chem.*, **60**, 1451 (1956).

a parallel reaction does occur as shown in Figure 1. When the reaction model, reaction 27, is examined kinetically by treating the intermediates I and the cis acyl complex as steady-state species, the resulting rate laws for each observed species are integrated analytically giving expressions for the mole fraction–time dependence of each species. These expressions are presented in Appendix III.[11]

These expressions give directly the calculated points, "×," in Figure 1. The values of the rate constants were determined by a computed least-squares fit of the analytical expression for the curve of the cis cyclopentylidene complex to the corresponding experimental data followed by an iterative fit to the curves of the trans acyl and trans cyclopentylidene complexes with k_1 determined directly from the experimental data for the chloroalkyl complex.[39] The set of rate constants was determined at three temperatures and the calculated kinetic parameters are shown in Table II.

Table II. Kinetic Parameters for the Chloroalkyl Complex

i	$^{298}k_i \times 10^{-4}$, sec^{-1}	$\Delta H^{\pm}$, kcal/mol	$\Delta S^{\pm}$, eu
1	35.4 ± 5.2	16.0 ± 1.7	−16 ± 5
3	4.31 ± 0.65	11.2 ± 1.1	−38 ± 3
4	17.5 ± 8.0	14.5 ± 1.3	−22.5 ± 4.5
5	1.53 ± 0.30	15.2 ± 1.3	−25 ± 5
6	4.28 ± 0.73	15.7 ± 0.70	−21 ± 3
−6	3.65 ± 0.63	17.2 ± 1.0	−17 ± 4

The rate constant for ring closure forming the cis cyclopentylidene complex, $k_3 = 4.3 \times 10^{-4}$ sec^{-1}, is reasonably close to that value estimated by correcting the observed rate of formation of the trans cyclohexylidene bromide complex for ring size and halogen atom substitution, (75/80) ($5.05 \pm 2.36 \times 10^{-5}$ sec^{-1}) = *ca.* 4.7×10^{-5} sec^{-1}. This error could easily arise from the estimation of the conversion factor and from the assumption that the cis and trans isomers of the acyl complexes have identical rates from a given reaction type, although this latter assumption is fairly good for this system since k_3 and k_6 are identical within one standard deviation. However, the cis carbenoid complex isomerizes to the trans isomer *ca.* 10 times more slowly than the geometrical isomerization of the cis acyl complex resulting, apparently, from the differences in the entropy of activation rather than from an activation energy difference. The rate of trans acyl formation, k_4, is *ca.* four times the rate of cis cyclopentylidene ligand formation, k_3.

Similarly, it was expected that the rate enhancement of ring closure when going to the 4-iodo-*n*-butyl ligand would permit the formation of a cis cyclohexylidene species. Indeed, a trace of this species, *ca.* 4–5%, was observed, see Figure 3. Using kinetic reaction scheme 27 and assuming steady-state conditions for the intermediate, I, the cis acyl, and the cis cyclohexylidene complexes, the expressions for the mole-fraction–time dependency of each major species were derived and are presented in Appendix III.

The rate constants were determined at each temperature by fitting the calculated curves to the experimental curves by iterative variation of the individual rate constants. The calculated kinetic parameters are shown in Table III. The rate constant, k_5, was not a variable due to the application of the steady-state approximation to the cis cyclohexylidene complex. However, the rate processes, k_5 and k_3, are of similar magnitude since the cis cyclohexylidene complex maintained a small and effectively constant concentration throughout the reaction decay of the iodoalkyl complex. In this reaction, the trans acyl complex was formed at *ca.* ten times the rate of formation of the cis cyclohexylidene complex. Also, k_6 and k_3 are identical within one standard deviation indicating little, if any, effect on the rate of cyclization due to the geometrical isomerization at the metal center.

Table III

i	$^{298}k_i \times 10^{-4}$, sec^{-1}	$\Delta H^{\pm}$, kcal/mol	$\Delta S^{\pm}$, eu
1	48.0 ± 7.2	16.0 ± 1.2	−16 ± 4
3	4.90 ± 0.60	21.0 ± 1.6	−5 ± 5
4	54.2 ± 13.5	18.3 ± 1.6	−10 ± 8
6	2.77 ± 0.95	17.8 ± 1.8	−13 ± 9
−6	0.53 ± 0.14	21.3 ± 2.3	−10 ± 5

When comparing these kinetic data of the reaction forming the cyclopentylidene complex from the 3-chloro-*n*-propyl ligand and that reaction forming the cyclohexylidene complex from the 4-iodo-*n*-butyl ligand to the kinetic data for the other systems reported here, several internal consistencies are observed. (1) The observed rate, k_1, for the reaction of any haloallyl complex with triphenylphosphine was independent of the ligand concentration and had the same value, (4.39 ± 0.85) $\times 10^{-3}$ sec^{-1} at 25°, for all of the systems examined. The average values for the activation parameters, $\overline{\Delta H^{\pm}} = 14.8 \pm 2.3$ kcal/mol and $\overline{\Delta S^{\pm}} \sim -20$ eu, and the zero-order dependence of the rate on the ligand concentration suggests strongly the formation of the intermediate, I. The negligible dependence of the formation of the cis acyl compound upon the chain length of the $-(CH_2)_nX$ group for $n = 3$ or 4 and on the identity of X (Cl, Br, or I) seems reasonable. (2) The forward and reverse rate constants, k_6 and k_{-6}, and the values of the activation parameters for the conversion of the trans 4-chlorobutanoyl and 5-iodopentanoyl complexes into the corresponding trans carbenoid complexes obtained from the analysis of the total system starting from the haloalkyl complexes were identical, usually within one standard deviation, with those values obtained from the independent study of this interconversion. (3) The rate constant for formation of the cyclohexylidene ligand, k_6, from the trans 5-iodopentanoyl complex is *ca.* 2–3 times greater than k_6 for the trans 5-bromopentanoyl complex in complete agreement with previously observed rate enhancement for bimolecular reactions occurring at a carbon center when going from a bromo to an iodo leaving group.[19] (4) Although the rate of ring closure to form the cis carbenoid ligands, k_3, follows the expected dependence on ring size and on variation of the halogen atom, only rough estimates can be made when relating the rate data for one system to that of another system be-

(39) The least-squares program was based on the Marquardt algorithm and adapted by Dr. D. A. Ucko. It is a pleasure to acknowledge the assistance of Dr. J. R. Pipal and Dr. D. A. Ucko in using the computer facilities.

cause of the uncertainty involved in choosing the correction factors. (5) The values of the activation parameters for the steps 3 and 6, which represent a cyclization reaction forming the ionic carbenoid complexes from the neutral haloacyl complexes, are similar to the values observed for similar SN2 reactions.[40] (6) The rates of the geometrical isomerizations of the cis isomer of the cyclopentylidene complexes to the trans isomers, k_5, decrease in the order $Cl^- > Br^- > {}^-BPh_4$ by an overall factor of at least 26. This effect appears to arise mainly from the enthalpy of activation term, although the cause of the relatively large negative value for the entropy of activation of the chloride salt is unknown. This kinetic effect of the anion on k_5 was unexpected and may reflect different changes in the degree of ion pairing between the reactant and the activated complex for the different cases. The values of the activation parameters for the steps (5) correlate well with those values reported for the cis and trans geometrical isomerization of the complexes, $(h^5\text{-}C_5H_5)Mo(CO)_2(Me)(L)$.[41]

L	$\Delta H^{\pm}$ kcal/mol	$\Delta S^{\pm}$, eu
PPh_3	20.9 ± 0.2	−0.2 ± 0.6
$P(OMe)_3$	19.6 ± 0.4	−0.9 ± 1.3
$P(OPh)_3$	17.7 ± 0.3	−4.7 ± 0.7

The reactions involving the 3-chloro-*n*-propyl and 4-iodo-*n*-butyl complexes have particular importance since the "internal" rate constants, k_3 and k_4, were measured. Since the model (reaction 27) correctly explains the kinetic behavior of these complex reactions and since the rate constants k_3 and k_4 are influenced by the nature of the haloalkyl ligand, it is felt that there is satisfactory evidence for the existence of a cis haloacyl intermediate in all cases.

(40) See ref 12, p 138 and ref 13, p 418.

(41) J. W. Faller and A. S. Anderson, *J. Amer. Chem. Soc.*, **92**, 5852 (1970).

Kinetics of Complexation of Vanadate Anions by Ethylenediaminetetraacetic Acid and 1,2-Dihydroxyanthraquinone

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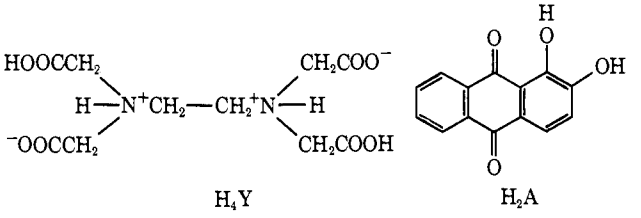
Abstract: The stopped-flow technique has been utilized in kinetics studies of the formation of 1:1 complexes between vanadium(V) anions and EDTA (H_4Y) as well as 1,2-dihydroxyanthraquinone (H_2A). These studies have been conducted at 25° in weakly alkaline media at an ionic strength of 0.5 *M* (NH_4Cl). Reaction schemes for formation of the 1:1 complexes which account for the observed hydrogen ion dependences of the forward rate constants are presented. The rate constants for complex formation are essentially independent of the identity of the complexing ligands used in this study and agree with the previously determined rate constant for vanadate dimerization. The experimentally determined rate constants for complexation of $VO_2(OH)_2^-$ and $VO_2(OH)_3^{2-}$ by H_2Y^{2-} are $(2.34 \pm 0.05) \times 10^4$ and $(2.4 \pm 0.1) \times 10^3$ M^{-1} sec^{-1}, respectively. For complexation of $VO_2(OH)_2^-$ and $VO_2(OH)_3^{2-}$ by HA^-, rate constants of $(2.28 \pm 0.08) \times 10^4$ and $(1.2 \pm 0.3) \times 10^3$ M^{-1} sec^{-1}, respectively, were determined. The value of the stability constant for the HA^-–$VO_2(OH)_2^-$ complex was found to be $(1.0 \pm 0.2) \times 10^4$ *M*.

Few studies of the kinetics of complexation of vanadium(V) ions have been undertaken. This is due, in part, to the number and complexity of vanadate species present in aqueous media, where monomeric cationic and anionic as well as dimeric, trimeric, and decameric species can be found as the acidity of the media and concentration of V(V) are varied.[1] Furthermore, the complexation and polymerization[2] reactions of vanadate ions occur too rapidly to be studied by conventional kinetics methods. During the course of our investigations into the *in vivo* complexation of V(V) by specific marine urochordates (*e.g.*, *Ascidia*), we have utilized the stopped-flow technique to study the kinetics of complexation of monomeric vanadate ions by EDTA and alizarin (1,2-dihydroxyanthraquinone).



Experimental Section

A stock solution of V(V) was prepared by dissolution of sodium vanadate hydrate in distilled water. Hydrochloric acid was used to adjust the pH to an approximate value of 9 whereupon the solution assumed an intense yellow color. The solution was then allowed to stand until the bright color of decavanadate had entirely faded.[2] Total vanadium in the solution was determined spectrophotometrically as the V(V)–H_2O_2 complex.[3] The concentration of

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(3) R. Guenther and R. G. Linck, *J. Amer. Chem. Soc.*, **91**, 3769 (1969).