completion of the addition, the chloroform and other volatiles were pumped off at 80°. The remaining liquid was identified as methylneophylbenzyltin iodide from its nmr spectrum (Table I). Integration of the spectrum confirmed the ratio methyl:neophyl methyl:neophyl methylene:benzyl:aromatic of 3:6:2:2:10.

Benzylmethylneophyltin Chloride. Benzylmethylneophyltin iodide (5.0 g) was dissolved in 100 ml of ether. The ether solution was shaken with 50 ml of a 5 *M* aqueous solution of potassium hydroxide. The KOH layer was separated and the ether layer shaken with 50 ml of 3 *M* hydrochloric acid for 10 min. The ether layer was separated, dried over calcium chloride, and filtered. The ether was removed on a rotary evaporator. The resulting product was identified by its nmr spectrum (Table II). Integration of the spectrum confirmed the ratio methyl:neophyl methyl:neophyl methylene:benzyl:aromatic of 3:6:2:2:10.

Acknowledgment. We thank Dan Netzel for obtaining the 90-MHz spectra.

Complexes of Cyclic 2-Oxacarbenes. I. A Spontaneous Cyclization to Form a Complex of 2-Oxacyclopentylidene[1]

F. A. Cotton* and C. M. Lukehart[2]

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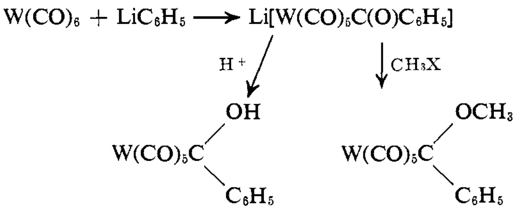
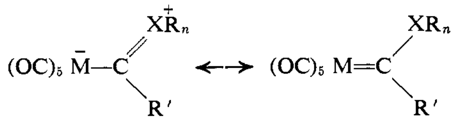
Abstract: When (*pentahapto*cyclopentadienyl)(tricarbonyl)(3-bromo-*n*-propyl)molybdenum (**1**) reacts with triphenylphosphine, the cis and trans isomers of the cation (*pentahapto*cyclopentadienyl)(dicarbonyl)(triphenylphosphine)(2-oxacyclopentylidene)molybdenum (**2**) are formed. Closer observation indicates that the cis isomer is produced under kinetic control as the initial product and that this rearranges unimolecularly to the trans isomer. The equilibrium constant, [trans]/[cis], at 27° in chloroform has the value 42 ± 5, and the rate constant for the cis-to-trans conversion is 1.3×10^{-5} sec^{-1}. It appears that the preparative reaction involves attack by $P(C_6H_5)_3$ on Mo to form the acyl derivative $BrCH_2CH_2CH_2C(O)Mo(h^5\text{-}C_5H_5)(PPh_3)(CO)_2$ in the cis configuration, which promptly and spontaneously undergoes internal nucleophilic attack of the acyl oxygen atom on the γ-carbon atom to displace Br^- and generate the cis form of the cation. The presence of the coordinated carbene, 2-oxacyclopentylidene, $:\overline{COCH_2CH_2CH_2}$, is demonstrated by infrared and pmr spectra and by the formation of γ-butyrolactone when **2** is treated with pyridine *N*-oxide.

The possibility of stabilizing carbenes by causing them to be coordinated to low-valent metal atoms appears to have been first knowingly accomplished by Fischer and Maasbol[3] in 1964 by way of reaction sequences such as



Subsequent chemical studies[4] showed that the –OR group of the carbene can be replaced by –NR′R″ groups. X-Ray crystallographic studies[5] of several chromium compounds containing the :C(OR)R′ and :C(NRR′)R″ types of carbenes have validated the idea that these compounds can realistically be regarded as carbene complexes whose electronic structures may be represented as resonance hybrids of I and II. The relative contributions of I and II vary significantly as the group XR_n is changed, but in all cases the contribution of I is substantial. Indeed, the only complexes so far reported are those in which an XR_n group capable of participating in a structure such as I is present. More recently, the attack of alcohols or primary amines on isocyanides coordinated to platinum(II) has been shown to afford complexes of the type $PtX_2(PR_3)[C(R)NHR']$, where R = OCH_3, OC_2H_5, OC_3H_7, NHC_6H_5, and $NHC(CH_3)C_2H_5$ and R′ = C_6H_5.[6] An X-ray crystallographic examination of the compound $PtCl_2[P(C_2H_5)_3][C(OC_2H_5)NH(C_6H_5)]$ confirmed the structural formulation of these compounds.



I II

While the work reported here was in progress, still another route leading to *in situ* formation of coordinated carbene moieties was reported.[7] Attack of an alcohol on a coordinated acetylene leads, apparently through a coordinated vinyl ether intermediate, to a C(OR)-CHR′R″ type of carbene complex. Of direct relevance to the studies we are reporting here was Chisholm and Clark's observation of the following particular reaction (where L = $As(CH_3)_3$ or $P(CH_3)_2C_6H_5$), in which an intramolecular cyclization has occurred.

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(1) Supported in part by the National Science Foundation.

(2) National Science Foundation Trainee, 1969–1970.

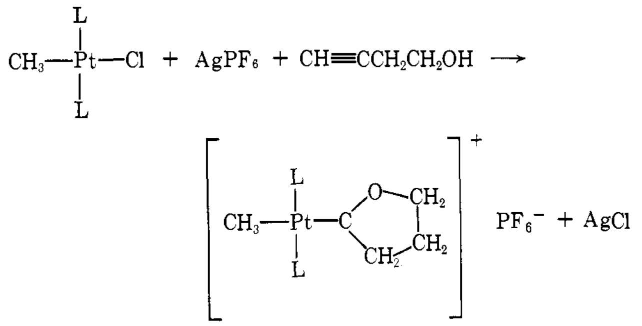
(3) E. O. Fischer and A. Maasbol, *Angew. Chem., Int. Ed. Engl.*, **3**, 580 (1964).

(4) U. Klabunde and E. O. Fischer, *J. Amer. Chem. Soc.*, **89**, 7141 (1967).

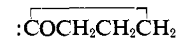
(5) *Cf.* J. A. Connor and O. S. Mills, *J. Chem. Soc. A*, 335 (1969), and references therein to earlier work by Mills and his coworkers.

(6) M. E. Badley, J. Chatt, R. L. Richards, and G. R. Sim, *Chem. Commun.*, 1322 (1969).

(7) M. H. Chisholm and H. C. Clark, *ibid.*, 763 (1970).



We have been attempting to devise deliberate and flexible methods for the synthesis of complexes containing as ligands carbenes which may be thought of as derived from cyclic ethers by loss of two geminal α-hydrogen atoms. We have found that this can be accomplished by intramolecular cyclizations though under circumstances quite different from those in Chisholm and Clark's work. In this paper we describe the preparation and characterization of isomeric complex cations containing the coordinated carbene



$:\overline{COCH_2CH_2CH_2}$

2-oxacyclopentylidene. In subsequent reports more details about the mechanism of formation of the complexes of this carbene as well as accounts of the preparation and characterization of complexes containing carbenes derived from other cyclic ethers will be presented.

Experimental Section

The salt, $NaMo(h^5\text{-}C_5H_5)(CO)_3$, was prepared by a literature method.[8] 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 solvent, acetonitrile, was of Spectrograde quality and was 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. Mass spectra were recorded on a Hitachi Perkin-Elmer RMU-6D mass spectrometer with a Varian Aerograph Series 1200 gas chromatograph attached to the inlet system. A 5% QF-1 column was used and calibration was provided by known background peaks. Conductivity measurements were performed on a Serfass bridge using a cell calibrated with a 0.1 *M* aqueous potassium chloride solution. Microanalyses were by Spang Microanalytical Laboratory, Ann Arbor, Mich.

$(h^5\text{-}C_5H_5)Mo(CO)_3(CH_2)_3Br$ (1). Practical grade 1,3-dibromopropane was distilled before use, and the procedure of King and Bisnette[9] was followed. Using 29.6 g (0.11 mol) of $NaMo(h^5\text{-}C_5H_5)(CO)_3$ and 14.2 ml (0.14 mol) of 1,3-dibromopropane, 10.4 g (26% based on Mo) of product was obtained as straw-yellow plates, mp 90–92°; ir (cyclohexane) 2025 (s), 1945 (vs).

[*cis*- and *trans*-$Mo(h^5\text{-}C_5H_5)(PPh_3)(CO)_2(C_4H_6O)$]Br (2). A. Cis. To a mixture of 0.76 g (1.9 mmol) of **1** in 3.0 ml of acetonitrile was added a solution of 1.1 g (4.7 mmol) of triphenylphosphine in 10.0 ml of acetonitrile over a 1-min period, giving a clear orange solution. Precipitation of a yellow solid occurred within 3 min of adding the triphenylphosphine. After 15 min the reaction mixture was filtered and the isolated solid washed with 1 ml of acetonitrile followed by 20 ml of pentane. The solid was then dried for 0.5 hr (0.01 mm, 25°), affording 0.91 g (71%) of the bright yellow cis isomer: mp 140–143° dec; ir (CH_2Cl_2) ν_{CO} 1980 (vs), 1910 (s); pmr ($CDCl_3$) τ 8.40 (broad multiplet, 2, CH_2), 6.33 (complex sextet, 2, CH_2), 5.39 (complex sextet, 2, CH_2), 4.17 (singlet, 5, C_5H_5), 2.54 (multiplet, 15, PPh_3).

B. Trans. A solution of 0.46 g (1.2 mmol) of **1** in 12 ml of acetonitrile was treated with a solution of 0.65 g (2.8 mmol) of triphenylphosphine in 11 ml of acetonitrile over a 1-min period. The reaction solution was stirred for 62 hr and then the solvent was removed under reduced pressure (20 mm, 25°). The yellow residue was washed with two 25-ml portions of 1:1 hexane–methylene chloride and then one 20-ml portion of pentane and dried for *ca.* 0.5 hr (50 mm, 25°), affording 0.61 g (78%) of a pale lemon-yellow powder: mp 150–160° dec; ir (CH_2Cl_2) ν_{CO} 1985 (s), 1910 (vs); pmr ($CDCl_3$) τ 7.84 (broad quintet, 2, CH_2), 5.94 (broad triplet, 2, CH_2), 4.77 (broad triplet, 2, CH_2), 4.44 (doublet, 5, C_5H_5, $J_{P-H} \sim 1.1$ Hz), 2.55 (multiplet, 15, PPh_3).

Anal. Calcd for $C_{29}H_{26}PMoBrO_3$: C, 55.34; H, 4.16; P, 4.92; Mo, 15.24; Br, 12.69; O, 7.94. Found: C, 55.0, H, 4.27; P, 5.00; Mo, 15.04; Br, 12.3; O (by difference), 8.4.

[$Mo(h^5\text{-}C_5H_5)(PPh_3)(CO)_2(C_4H_6O)$]$BPh_4$, Cis or Trans. Addition of a concentrated methanol solution of $NaBPh_4$ to a concentrated methanol solution of either isomer immediately precipitated the corresponding tetraphenylborate salt which was filtered in air, washed with methanol, and air dried, affording essentially quantitative yields.

Trans. Mp 159–161°; ir ($CHCl_3$) ν_{CO} 1985 (s), 1910 (vs); pmr ($CDCl_3$) τ 8.54 (broad quintet, 2, CH_2), 6.94 (broad triplet, 2, CH_2), 5.65 (broad triplet, 2, CH_2), 4.90 (doublet, 5, C_5H_5, $J_{P-H} \sim 1.0$ Hz), 2.80 (multiplet, 35, $BPh_4 + PPh_3$).

Cis. Mp 152–153°; ir (CH_2Cl_2) ν_{CO} 1990 (vs), 1930 (s); pmr ($CDCl_3$) τ 7.67 (complex triplet, 2, CH_2), 6.54 (broad multiplet, 2, CH_2), 5.90 (broad multiplet, 2, CH_2), 4.84 (singlet, 5, C_5H_5), 2.84 (multiplet, 35, $BPh_4 + PPh_3$).

Reaction of 2 with Pyridine *N*-Oxide. A. Qualitative Lactone Test. A solution of 2.1 g (3.33 mmol) of the trans isomer of compound **2** in 45 ml of methylene chloride was treated with 0.65 g (6.6 mmol) of pyridine *N*-oxide in 7 ml of methylene chloride, giving a dark wine-red solution. After stirring at room temperature for 0.5 hr the volume was reduced to *ca.* 1 ml under reduced pressure (20 mm, −20°). The residue was extracted with 50 ml of distilled ether and the resulting mixture was filtered, yielding a red-orange solid which when recrystallized from methylene chloride afforded 1.5 g (78%) of *trans*-$(h^5\text{-}C_5H_5)Mo(CO)_2PPh_3Br$ which was identified by melting point, ir, and pmr.[10,11]

The volume of the filtrate was slowly reduced to *ca.* 2 ml (20 mm, −20°) and then trap-to-trap distilled, giving a clear distillate having the characteristic smell of free pyridine. Methanol was added to the distillate to give a total volume of *ca.* 5 ml. A qualitative test for a lactone (or ester) by conversion to the hydroxamic acid which in turn gives a purple ferric complex was performed using the general procedure described by Hall and Shaeffer.[12] A positive test was observed for the "unknown solution" obtained from the pyridine *N*-oxide degradation. Under the experimental conditions used, ethyl acetate also gave a strong positive test, while an ether–methanol blank and a blank solution containing added pyridine gave a negative test.

B. Product Identification. A solution of 0.51 g (0.83 mmol) of compound **2**, a mixture of both isomers, in 2 ml of chloroform was treated with a solution of 0.16 g (1.65 mmol) of pyridine *N*-oxide in 1 ml of chloroform to give an immediate reaction (slightly exothermic) with a change in color to a dark wine-red. This solution was stirred at room temperature for 15 min and then trap-to-trap distilled. The resulting distillate was reduced to less than 1 ml total volume (20 mm, 25°). Injection of this solution onto a 5% QF-1 gas chromatography column (temperature program: 45° → 245°, 20°/min) produced three components. Identification was accomplished by allowing each component to pass into a RMU-6D mass spectrometer and then comparing the experimental spectra with published standard spectra.[13–15]

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

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

[10] P. M. Treichel and R. L. Shubkin, *Inorg. Chem.*, 6, 1328 (1967).

[11] P. M. Treichel, K. W. Barnett, and R. L. Shubkin, *J. Organometal. Chem.*, 7, 449 (1967).

[12] R. T. Hall and W. E. Shaeffer in "Organic Analysis," Vol. 2, Interscience, New York, N. Y., 1954, p 55.

[13] E. Stenhagen, S. Abrahamsson, and F. W. McLafferty, "Atlas of Mass Spectral Data," Interscience, New York, N. Y., 1969, pp 103, 445.

[14] L. Friedman and F. A. Long, *J. Amer. Chem. Soc.*, 75, 2832 (1953).

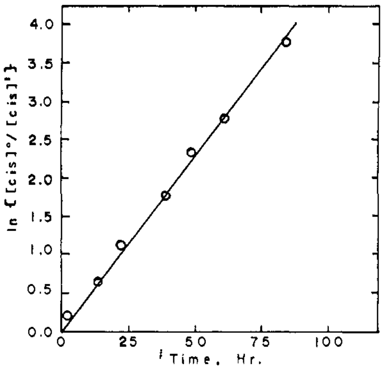


Figure 1. A plot of kinetic data for the isomerization of **2** at 30° showing conformity to unimolecular kinetics.

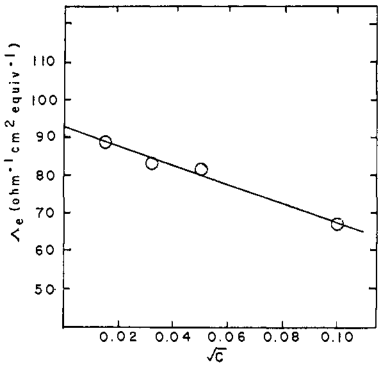


Figure 2. Conductance data for a mixture of cis and trans isomers of **2**, confirming its nature as a 1 : 1 electrolyte.

The first component proved to be chloroform, the second was free pyridine, and the third component was identified as γ-butyrolactone. A crude yield analysis, based on chromatogram peak areas, indicated nearly a quantitative yield of the lactone.

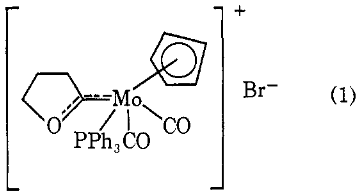
Isomerization Reaction. Kinetics and Equilibrium. The conversion of *cis*-**2** to *trans*-**2** was followed by pmr intensity ratios as a function of time at 27 ± 1°. The decrease of the cis isomer followed first-order kinetics, as shown in Figure 1. A *ca.* 0.3 *M* solution in $CDCl_3$ was used. A least-squares fitting of a straight line to a plot of ln $\{[\mathrm{cis}]^0/[\mathrm{cis}]^t\}$ *vs.* t yielded $k = 1.3 \pm 0.1 \times 10^{-5}$ sec^{-1}, and the limit of [cis]/[trans] as $t \rightarrow \infty$ was 0.025. The half-time of the reaction is 14.8 hr.

Conductance Measurements. The conductance of a mixture of the cis and trans isomers of **2** was measured in reagent grade methanol solution in the concentration range of 10^{-2}–10^{-4} equiv/l. The equivalent conductance (ohm^{-1} cm^2 equiv^{-1}) for a 10^{-3} *M* solution was $\Lambda_e = 82.7$. The concentration dependence of the equivalent conductance was measured at 30° and analyzed by means of the Onsager limiting law, as described previously.[16] The equivalent ionic conductance of the bromide ion under these conditions was obtained from the literature.[17] The compound was found to be a 1:1 electrolyte by comparing the experimental slope (Λ_e *vs.* $\sqrt{C}$), see Figure 2, to that calculated from the Onsager limiting law for 1:1 and 2:1 electrolytes, as follows: **2**, Λ_0, 92.5; experimental slope, 250 ± 10; calculated 1:1 slope, 247; calculated 2:1 slope, 466.

Results

The synthetic procedure employs only one new reaction, *viz.*

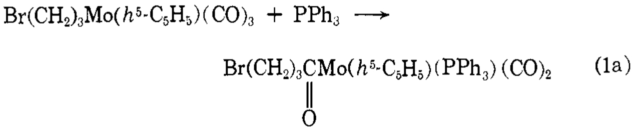
$$\mathrm{BrCH_2CH_2CH_2Mo}(h^5\text{-}\mathrm{C_5H_5})\mathrm{(CO)_3} + \mathrm{PPh_3} \longrightarrow$$



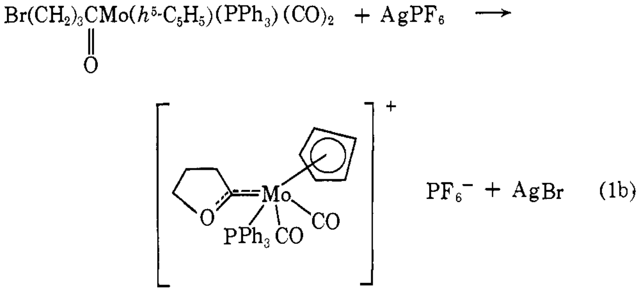
(1)

2

It was our initial assumption that two distinct steps, 1a and 1b, would be required, with the assistance in step 1b of a silver salt to remove Br^- and replace it with a noncoordinating anion such as BF_4^- or PF_6^-, *i.e.*, as shown. Other studies[18] show that in general the two steps do occur as distinct reactions, and the ω-bromoacyl derivatives can be isolated. In this case, however, it appears that a spontaneous cyclization, reaction 1c, immediately follows (1a).



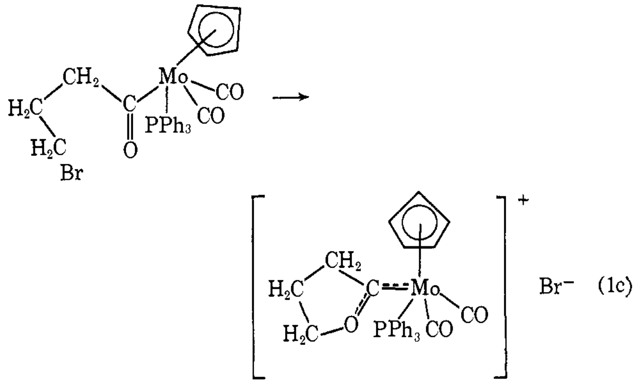
$$\mathrm{Br(CH_2)_3Mo}(h^5\text{-}\mathrm{C_5H_5})\mathrm{(CO)_3} + \mathrm{PPh_3} \longrightarrow \mathrm{Br(CH_2)_3}\underset{\overset{\|}{\mathrm{O}}}{\mathrm{C}}\mathrm{Mo}(h^5\text{-}\mathrm{C_5H_5})(\mathrm{PPh_3})(\mathrm{CO})_2 \qquad (1a)$$



$$\mathrm{Br(CH_2)_3}\underset{\overset{\|}{\mathrm{O}}}{\mathrm{C}}\mathrm{Mo}(h^5\text{-}\mathrm{C_5H_5})(\mathrm{PPh_3})(\mathrm{CO})_2 + \mathrm{AgPF_6} \longrightarrow$$

(1b)

2



(1c)

Initially, reaction 1 was carried out using dilute solutions, from which no product separates, and the reaction mixture was allowed to stand for about 20 hr. Essentially pure trans cation was then obtained as either the bromide or BPh_4 salt. The long reaction time was employed to ensure as complete a reaction as possible; the overall color change is very slight and gives no clear indication as to when the reaction might be complete. Later, when concentrated solutions of the reactants were used there was an almost immediate precipitate of [*cis*-Mo(h^5-C_5H_5)(PPh_3)$(CO)_2$(C_4H_6O)]Br. Since rate and equilibrium studies (*vide infra*) show that the trans isomer is thermodynamically favored in solution and that the half-time for conversion of the cis to the trans isomer is about 15 hr, the suspicion arose that reaction 1 directly produces at least a considerable fraction of

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[15] W. H. McFadden, E. A. Day, and M. J. Diamond, *Anal. Chem.*, **37**, 89 (1965).

[16] A. Davison, D. V. Howe, and E. T. Shawl, *Inorg. Chem.*, **6**, 458 (1967).

[17] P. Walden and E. J. Birr, *Z. Phys. Chem.*, **144**, 269 (1929).

[18] C. M. Lukehart, unpublished results.

the product in the cis configuration. It was then shown by pmr spectroscopic examination of the homogeneous reaction mixture, commencing immediately on addition of the $P(C_6H_5)_3$ solution to the solution of **1**, that **2** is initially formed entirely (within the sensitivity limits of the spectrometer) in the cis configuration.

On the basis of these observations, optimal procedures for obtaining salts of pure cis and pure trans cation **2** were easily devised. The bromide of cation **2** in the cis form is only sparingly soluble, so that by use of concentrated solutions it can be caused to precipitate from the reaction mixture as it forms, once the concentration in solution reaches the saturation point. The trans isomer which has formed by rearrangement remains in solution. To obtain the pure trans isomer, solutions of the cis isomer may be left to stand for long periods whence almost complete rearrangement to the trans isomer takes place.

To establish quantitatively the time required to achieve maximum conversion of the cis to the trans isomer and to ascertain the equilibrium proportions of the isomers, a kinetic and equilibrium study was carried out. As shown in Figure 1, the cis → trans reaction follows first-order kinetics. The rate constant is 1.3×10^{-5} sec^{-1} at 27° in $CDCl_3$ solution and the equilibrium ratio, [trans]/[cis], obtained after long periods of time, is 42 ± 5.

The identification of the cis and trans isomers was accomplished by means of infrared and pmr spectra, using criteria previously developed by others.[19–21] Both the cis and trans isomers of **2** show two carbonyl stretching bands in the infrared spectrum. The frequencies are virtually identical in the two isomers (1910, 1985 cm^{-1} for the trans and 1910, 1980 cm^{-1} for the cis in CH_2Cl_2), but they are distinguished by their different intensity ratios. In one case (trans) the higher frequency band is about half as intense as the lower frequency one, whereas in the other (cis) the reverse intensity ratio is found. In each case the higher frequency band should be assigned to the antisymmetric stretch[22] and the intensity ratios can be qualitatively correlated with the geometry on the basis of simple arguments, as explained by Manning.[20]

It is even possible to apply the principles involved semiquantitatively, whereby the ratios of the integrated intensities can be used to estimate the OC–Mo–CO angles. We calculate these angles to be 78 and 121° for the cis and trans isomers, respectively, both of which are very plausible values. For example, in the compound *trans*-$(h^5\text{-}C_5H_5)Mo(CO)_2(PPh_3)C(O)CH_3$, the observed[23] OC–Mo–CO angle is 108°. The relatively high values of the CO stretching frequencies (as compared to frequencies of about 1940 and 1985 cm^{-1} in neutral compounds such as $Mo(h^5\text{-}C_5H_5)(CO)_2(RCO)(PPh_3)$) may be attributed to the charge on the cation, which lessens the degree of Mo ($d\pi$) → CO (π^*) back bonding.

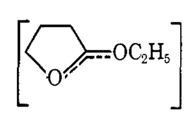
Independent of the infrared criterion, but in complete accord with it, is the isomer assignment based on the empirical nmr criterion that ^{31}P splitting of the $h^5\text{-}C_5H_5$ proton resonance is usually observable (~1 Hz) for the trans isomers, but unresolvably small for cis isomers of $Mo(h^5\text{-}C_5H_5)(CO)_2XL$ species in general.

Electrolytic conductance measurements demonstrate that **2** is a 1:1 electrolyte. The observed slope of Λ_e *vs.* $\sqrt{C}$ is 250 ± 10, while that calculated from the Onsager limiting law for a 1:1 electrolyte is 247.

Discussion

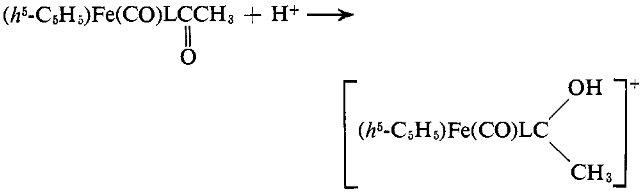
The cyclization reaction which we report here is reminiscent of certain other known reactions. Thus, the following Meerwein intramolecular cyclization[24] is broadly similar, though assistance by Ag^+ is required.

$$BrCH_2CH_2CH_2COOC_2H_5 + AgBF_4 \longrightarrow$$



$$BF_4^- + AgBr$$

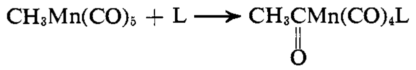
There is also a similarity to the following protonation reaction.[25]



$$(h^5\text{-}C_5H_5)Fe(CO)L\underset{\underset{O}{\|}}{C}CH_3 + H^+ \longrightarrow \left[(h^5\text{-}C_5H_5)Fe(CO)LC\begin{matrix}OH\\CH_3\end{matrix}\right]^+$$

Despite these broad similarities, the reaction reported here, and also those preparations to be described later, where reactions of types 1a and 1b occur as separate stages with Ag^+ assistance required in the step resembling 1b, represents a new synthetic method for carbenes stabilized by coordination to metal atoms.

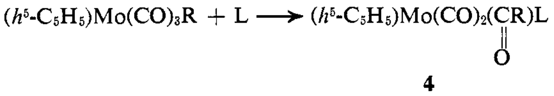
The stereospecific formation of the product cation **2** in its cis configuration bears comparison with the steric course of the reactions



$$CH_3Mn(CO)_5 + L \longrightarrow CH_3\underset{\underset{O}{\|}}{C}Mn(CO)_4L$$

Noack and Calderazzo have shown[26] that when L = CO a cis substitution occurs by way of a methyl shift. When L = $P(C_6H_5)_3$ the initial product has again been shown[27] to be cis and there are indirect reasons to favor an alkyl migration mechanism, though conclusive evidence on the latter point is lacking.

The present work also should be compared with results obtained by Craig and Green[28] in their study of the reaction



$$(h^5\text{-}C_5H_5)Mo(CO)_3R + L \longrightarrow (h^5\text{-}C_5H_5)Mo(CO)_2(\underset{\underset{O}{\|}}{C}R)L$$

4

$R = CH_3, C_2H_5$
$L = P(C_6H_5)_3, PR_3, P(OR)_3$

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[19] M. J. Mays and S. M. Pearson, *J. Chem. Soc. A*, 2291 (1968).

[20] A. R. Manning, *ibid.*, *A*, 1984 (1967).

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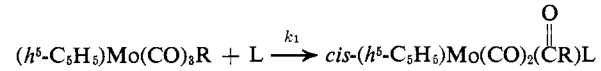
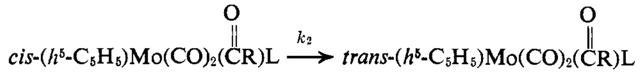
It was found that only trans isomers of the species of type **4** could be *isolated.* Indeed, it was stated that no evidence for even the transient occurrence of the cis isomers was obtained when the reacting systems were observed in the nmr spectrometer. Craig and Green then concluded that the *trans*-acyl complexes are probably formed directly, *i.e.*, by kinetic control. This conclusion is in direct contrast to our observations on reaction 1, and we are led to suggest a different interpretation of their observations.

If reactions of type 1a where we have CH_3 or C_2H_5 in place of $Br(CH_2)_3$ proceed directly, under kinetic control, to the *trans*-acyl compound, as proposed by Craig and Green, it would seem virtually necessary to believe that reaction 1a itself follows the same course. The exclusive appearance of the cis isomer of **2** would then have to result from a subsequent reaction step in which cyclization and trans → cis isomerization take place simultaneously and rapidly. This seems distinctly unlikely both of itself and when compared to the alternative interpretation to be proposed below. It is to be emphasized that cyclization of a *trans*-acyl compound to *trans*-**2** cannot account for the results since the trans isomer of **2** is the thermodynamically stable one and by such a path no significant quantity of *cis*-**2** would ever be seen.

We propose that in the following sequence of reactions



$$(h^5\text{-}C_5H_5)Mo(CO)_3R + L \xrightarrow{k_1} cis\text{-}(h^5\text{-}C_5H_5)Mo(CO)_2(\overset{\overset{O}{\|}}{C}R)L$$



$$cis\text{-}(h^5\text{-}C_5H_5)Mo(CO)_2(\overset{\overset{O}{\|}}{C}R)L \xrightarrow{k_2} trans\text{-}(h^5\text{-}C_5H_5)Mo(CO)_2(\overset{\overset{O}{\|}}{C}R)L$$

the ratio k_2/k_1 is appreciably greater than unity. Thus when $R = CH_3$ or C_2H_5, and $k_2/k_1 \geq 10$, detection of the cis intermediate by nmr would be unlikely since its mole fraction would never be >0.1; thus the trans isomer might *appear* to be the primary product. On the other hand, when $R = Br(CH_2)_3$ we must assume that the unimolecular rate constant, k_3, for cyclization of the *cis*-acyl compound to the *cis*-carbene, **2**, is such that $k_3/k_2 \geq 10$, based on a rough estimate of detectability limits in the nmr spectrum. Since for $R = CH_3$ in CH_3CN Craig and Green find $k_1 \approx 5 \times 10^{-4}$, we would have to assume that lower limits for k_2 and k_3 are 5×10^{-3} and 5×10^{-2}, respectively. Experiments to test these tentative proposals are being carried out.[29]

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(29) NOTE ADDED IN PROOF. Further spectroscopic and chemical evidence indicating a coordinated 2-oxacyclopentylidene ligand and providing assignment of the carbene methylene groups has now been provided by the enhanced rate of hydrogen–deuterium exchange on the carbon atom α to the carbene carbon atom, as demonstrated in known alkoxy carbene molecules [C. G. Kreiter, *Angew. Chem., Int. Ed. Engl.*, 7, 390 (1968)] and in a postulated 2-oxacyclopentylidene ligand [C. P. Casey, *Chem. Commun.*, 1220 (1970)]. Thus, when a catalytic amount of sodium methoxide-d_3 was added to a methanol-d_4 solution of *trans*-**2** in an nmr tube at room temperature the broad triplet at τ *ca.* 6.0 immediately disappeared, with the high-field broad quintet (τ *ca.* 8.0) becoming a broad triplet with no change in the multiplicity of the lower field broad triplet (τ *ca.* 4.0).