tives which indicated an increased π acidity for phosphorus when $X = PR_2$.[10,11]

Finally, we note that the ease of demethylation of the sp and fsp metal halide complexes increases in the order of nucleophilicity of X, *viz.*, $I^- \gg Br^- > Cl^-$. This order is consistent with a Zeisel-type nucleophilic mechanism for cleavage of the $S-CH_3$ bond in the thioether.[18,28,29] A Zeisel mechanism is also consistent with the fluoro complexes undergoing more facile S demethylation than the sp complexes; the electronegative fluoroaryl ring would increase the positive charge on sulfur, thus increasing the susceptibility for nucleophilic attack by X^-.

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Delineation of Shift Reagent–Substrate Equilibria

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Abstract: The equilibria between $Ln(fod)_3$ (Ln = Pr, Eu, Ho, or Yb; fod = 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyloctanedionate) and the basic substrate (π-C_5H_5)$Fe(CO)_2(CN)$ have been studied by vapor pressure osmometry on benzene solutions. Dimers and, in some cases, higher aggregates of the shift reagents are found in pure $Ln(fod)_3$ solutions. In general, the shift reagent: substrate systems form 1:1 and 1:2 complexes. In the case of $Pr(fod)_3$, 1:3 complex formation is also observed. The relative successive formation constants for 1:2 adduct formation decrease from light to heavy lanthanide. This, as well as the 1:3 formation with $Pr(fod)_3$, is thought to reflect greater steric crowding with the heavier members. The osmometry results are compared with nmr shifts determined under similar conditions, and the factors determining the shapes of plots of substrate shift *vs.* shift reagent to substrate ratio are discussed.

Central to the quantitative application of nmr shift reagents as structural and chemical probes[1–4] are the stoichiometry and equilibria of interaction between lanthanide shift reagent, Ln, and substrate, S. Surprisingly, little is actually known about the identity of the species which exist at ambient temperature in typical reagent–substrate solutions. Crystallographic studies[2,5,6] have identified 1:2 lanthanide: substrate adducts in the solid state; however, the situation in solution is far from clear. Until the recent, elegant experiments of Shapiro and Johnston[7] analyses of substrate chemical shifts as a function of lanthanide: substrate ratio have supported 1:1 adduct formation at room temperature,[1,8–10] and in some cases,[8–10] equilibrium constants have been calculated. Another nmr experiment,[11] which unfortunately may not apply at room temperature, detected only 1:2 adducts in the presence of excess base at −80°. Shapiro and Johnston's precision nmr analysis of $Eu(fod)_3$–substrate equilibria[7] yielded successive formation constants for both 1:1 and 1:2 adduct formation. The inherent possible complexity of the equilibria occurring in these systems indicated to us that an alternative physiochemical technique, in this case vapor pressure osmometry, would be a useful if not necessary supplement to even the most rigorous analysis of substrate nmr shift data. The possibility of extensive shift reagent association or 1:3 (or even 1:4) adduct formation cannot, *a priori*, be ruled out in shift reagent–substrate solutions.

We present here correlated osmometric and pmr studies with the model substrate $(C_5H_5)Fe(CO)_2CN$, which was chosen because it displays a single sharp resonance in the nmr, the site of coordination is known,[4] and it can be accurately weighed. Because of recent interest[2,3,12] in using lanthanides other than europium for shift reagents, we present data on the systems $Ln(fod)_3$,[13] where fod = 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionate and Ln = Pr, Eu, Ho, and Yb. The scope of equilibria occurring is considerably richer than heretofore believed. Some insight is provided into the systematic nature of lanthanide β-diketonate coordination chemistry and into what factors determine the utility of a given shift reagent.

Experimental Section

The substrate $(C_5H_5)Fe(CO)_2CN$ was prepared and purified

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(1) J. K. M. Sanders, S. W. Hanson, and D. H. Williams, *J. Amer. Chem. Soc.*, **94**, 5325 (1972), and references therein.

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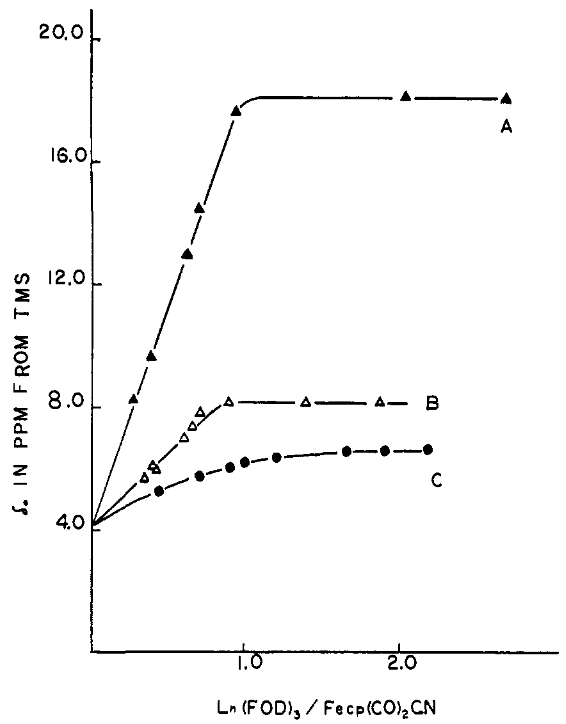

Figure 1. The observed downfield shift of $(C_5H_5)Fe(CO)_2CN$, δ_o, from TMS *vs.* the shift reagent to substrate ratio at 37°: (A) Ln = Yb; (B) Ln = Eu with exclusion of H_2O; (C) Ln = Eu without exclusion of H_2O. For curves A and B [Ln] ≈ 0.4 *M*.

according to the literature;[14] it was stored in a desiccator over $CaSO_4$. The shift reagents $Eu(fod)_3$ and $Pr(fod)_3$ (Pierce Chemical Co.) were recrystallized from methylcyclohexane and dried *in vacuo* over P_2O_5. The complexes $Ho(fod)_3$ and $Yb(fod)_3$ were prepared by the literature procedure,[15] sublimed at 10^{-3} mm, and dried *in vacuo* over P_2O_5. These samples were handled and stored at all times in an atmosphere of dry, purified nitrogen. Benzene was distilled under nitrogen from benzophenone ketyl, and was stored under nitrogen over molecular sieves.

Nmr Measurement. Spectra were recorded on Perkin-Elmer R20-B (60 MHz) or Bruker HFX-10 (90 MHz) instruments. Spectra were calibrated by measuring the position of the C_5H_5 signal relative to internal benzene or TMS, with a frequency counter. All spectra were recorded at +37°, the temperature at which the osmometer operates. Ample time was allowed for each sample to reach equilibrium temperature.

Osmometry. Measurements were performed in benzene on a Mechrolab 302 osmometer at +37°. The instrument was equipped with an inert atmosphere system (argon) and was calibrated with benzil and additionally checked with ferrocene. The time dependence of the thermistor resistance was treated as recommended by the osmometer manufacturer.[16]

Results

Figures 1 and 2 present chemical shift data as a function of the ratio, Ln/S. These curves are similar to numerous ones in the literature, where the inflection in the curve at Ln/S ≈ 1 was ascribed to the formation of 1:1 adducts. Figure 1 also illustrates the effect of neglecting to remove moisture and other impurities from $Eu(fod)_3$. Clearly, shifts are reduced (as has been noted before[1-3]) and the curve does not break as sharply.

Table I presents osmometric molecular weight data on solutions similar to those employed for the nmr

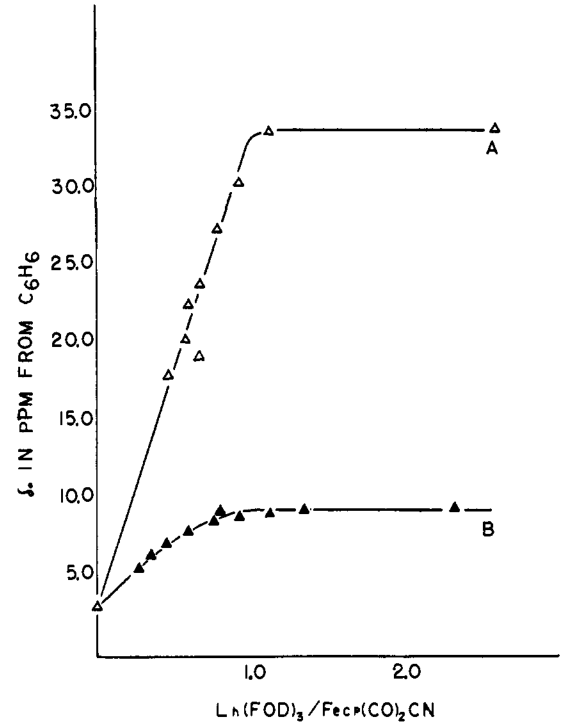

Figure 2. The observed upfield shift of $(C_5H_5)Fe(CO)_2CN$, δ_o, from C_6H_6 *vs.* the shift reagent to substrate ratio at 37°: (A) Ln = Ho; (B) Ln = Pr. [Ln] ≈ 0.4 *M*.

Table I. Osmometric Data for Shift Reagents

Metal	Ln_{tot}[a]	M_{tot}[a]	Ln[a]	$(Ln)_2$[a]	K_D[b]
Pr					
1	0.0306	0.0208	0.0110	0.0098	81.0
2	0.0536	0.0314	0.0092	0.0222	262
3	0.0779	0.0407	0.0035	0.0372	3040
Eu					
1	0.0371	0.0255	0.0140	0.0116	59.4
2	0.0214	0.0152	0.0090	0.0062	76.5
3	0.0742	0.0451	0.0160	0.0291	(114)
4	0.0216	0.0158	0.0100	0.0058	58.0
5	0.0475	0.0326	0.0177	0.0149	49.6
6	0.0890	0.0485	0.0080	0.0405	(632)
Av					60.9 ± 18
Dy					
1	0.0494	0.0385	0.0276	0.0109	14.3
2	0.0989	0.0716	0.0443	0.0273	13.9
3	0.0197	0.0170	0.0143	0.0022	13.2
Av					13.8 ± 4.0
Ho					
1	0.0453	0.0370	0.0287	0.0083	10.1
2	0.0208	0.0173	0.0138	0.0035	18.4
3	0.0627	0.0519	0.0411	0.0108	6.4
Av					11.6 ± 3.8
Yb					
1	0.0479	0.0396	0.0313	0.0083	8.5
2	0.0601	0.0506	0.0411	0.0095	5.6
3	0.0242	0.0207	0.0172	0.0035	11.7
Av					8.6 ± 3.6

[a] In mol/l.: Ln_{tot} = total added concentration of $Ln(fod)_3$, M_{tot} = total measured concentration of solute. Ln = concentration of monomeric $Ln(fod)_3$. $(Ln)_2$ = concentration of dimeric $Ln(fod)_3$. [b] In M^{-1}. The magnitude of error in a molecular weight measurement was independently established from the root mean square deviation between observed and theoretical values of the molecular weight of ferrocene. This plus the less significant weighing and volume errors were used to calculate errors in the *K*'s and $\delta_{1:2}$. These results are thought to be quite generous and for example are much greater than the standard deviation in the measurements. K_D values in parentheses have estimated errors >100% and have been neglected in calculating average values.

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(15) K. J. Eisentraut and R. E. Sievers, *Inorg. Syn.*, 11, 94 (1968).

(16) Model 302 Instruction Manual, Mechrolab Inc., Technical Bulletin No. 10.

Table II. Osmometric Data for Shift Reagent and Substrate[e]

Metal	S_{tot}[a]	Ln_{tot}[a]	M_{tot}[a]	S[a]	LnS_2[a]	LnS_3[a]	$K_{1:1}$[b]	$K_{1:2}$[b]	$K_{1:3}$[b]	$\delta_{1:1}$[c]
Pr	$CpFe(CO)_2CN$									
1	0.0175	0.0408	0.0295				>10³	>10³		762.5
2	0.0357	0.0402	0.0343							
3	0.0500	0.0402	0.0357							
4	0.0625	0.0403	0.0385							
5	0.0578	0.0402	0.0392							
6	0.0432	0.0399	0.0348							
7	0.0672	0.0401	0.0399							
8	0.0880	0.0401	0.0476							
9	0.0720	0.0404	0.0416							
10	0.0913	0.0395	0.0505	0.0110	0.0382	0.0013	>10³	>10³	(3.1)	
11	0.1036	0.0390	0.0551	0.0161	0.0295	0.0095	>10³	>10³	20.0	
12	0.1273	0.0398	0.0686	0.0288	0.0209	0.0189	>10³	>10³	31.4	
Av							>10³	>10³	25.7 ± 13	

Metal	S_{tot}	Ln_{tot}	M_{tot}	S	LnS	LnS_2[a]	$K_{1:1}$	$K_{1:2}$	$\delta_{1:1}$[d]	$\delta_{1:2}$[d]
Eu	$CpFe(CO)_2CN$									
1	0.0483	0.0396	0.0374				>10³		736.0	
2	0.0688	0.0396	0.0451	0.0055	0.0159	0.0237	>10³	271	736.0	626.9
3	0.0744	0.0383	0.0482	0.0098	0.0120	0.0263	>10³	224	736.0	620.0
4	0.0625	0.0401	0.0428	0.0027	0.0204	0.0197	>10³	358	736.0	615.1
5	0.0530	0.0404	0.0386				>10³		736.0	
6	0.0852	0.0408	0.0530	0.0122	0.0086	0.0322	>10³	307	736.0	608.4
Av							>10³	290 ± 145	736.0	618 ± 57

Metal	S_{tot}	Ln_{tot}	M_{tot}	S	LnS	LnS_2	$K_{1:1}$	$K_{1:2}$	$\delta_{1:1}$[c]	$\delta_{1:2}$[c]
Ho	$CpFe(CO)_2CN$									
1	0.0153	0.0397	0.0342				>10³		3072.0	
2	0.0358	0.0402	0.0347				>10³		3072.0	
3	0.0513	0.0402	0.0423				>10³		3072.0	
4	0.0618	0.0413	0.0576	0.0163	0.0371	0.0042	>10³	(6.95)	3072.0	
5	0.0582	0.0392	0.0447	0.0055	0.0257	0.0135	>10³	95.5	3072.0	1691.2
6	0.0735	0.0428	0.0542	0.0114	0.0235	0.0193	>10³	72.0	3072.0	1543.7
7	0.0427	0.0394	0.0375				>10³		3072.0	
8	0.0663	0.0400	0.0488	0.0088	0.0225	0.0175	>10³	88.4	3072.0	1826.2
9	0.0846	0.0397	0.0612	0.0215	0.0163	0.0234	>10³	66.8	3072.0	1751.0
Av							>10³	80.7 ± 40	3072.0	1703 ± 158

Metal	S_{tot}	Ln_{tot}	M_{tot}	S	LnS	LnS_2	$K_{1:1}$	$K_{1:2}$	$\delta_{1:1}$[d]	$\delta_{1:2}$[d]
Yb	$CpFe(CO)_2CN$									
1	0.0501	0.0399	0.0426	0.0027	0.0324	0.0075	>10³	(85.7)	1630.7	1147
2	0.0545	0.0402	0.0421	0.0019	0.0278	0.0124	>10³	(235)	1630.7	1083
3	0.0793	0.0394	0.0597	0.0203	0.0198	0.0196	>10³	48.8	1630.7	1098
4	0.0613	0.0403	0.0499	0.0096	0.0289	0.0114	>10³	41.1	1630.7	1138
5	0.0680	0.0399	0.0566	0.0167	0.0285	0.0114	>10³	24.0	1630.7	1165
6	0.0787	0.0397	0.0575	0.0178	0.0225	0.0172	>10³	43.0	1630.7	1109
							>10³	39.2 ± 20	1630.7	1123 ± 104

Metal	S_{tot}	Ln_{tot}	M_{tot}	S	LnS	LnS_2	$K_{1:2}$
Eu	Cholesterol						
1	0.0498	0.0400	0.0444	0.0043	0.0347	0.0054	36.2
2	0.0686	0.0402	0.0503	0.0101	0.0219	0.0183	82.7
3	0.0487	0.0390	0.0426	0.0036	0.0329	0.0061	51.5
4	0.0787	0.0396	0.0512	0.0116	0.0121	0.0275	195.9
5	0.0902	0.0394	0.0625	0.0231	0.0117	0.0277	102.5

[a] In mol/l. [b] In M^{-1}. [c] In Hz upfield from C_6H_6. [d] In Hz downfield from TMS. Values in parentheses have errors >100% and have been neglected in calculating average values. [e] Cp = h^5-C_5H_5. S_{tot} = total added concentration of substrate. S = concentration of free substrate. LnS = concentration of 1:1 adduct. LnS_2 = concentration of 1:2 adduct. The errors were calculated as described in the footnote to Table I.

measurements. It should be borne in mind that such determinations measure the concentration of solute particles; we shall refer to this quantity as the *measured* solute concentration. In cases of association of Ln and S, measured concentrations will be less than the sum of the nominal concentrations, since there will be fewer particles when Ln and S combine. Beginning with the shift reagents alone, it can be seen (Table I) that significant association takes place. This result is in accord with some solid-state lanthanide β-diketonate structural data[17] and other molecular weight measurements[9,18] in other noncoordinating solvents. As progressively larger concentrations of $(C_5H_5)Fe(CO)_2CN$ are placed in solution (Table II), the measured solute concentration lags far behind the sum of the nominal concentrations. Up to S/Ln ≈ 1, the mea-

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sured concentrations are invariably less than or equal to (Ln + S)/2, indicating strong 1:1 adduct formation, and competing shift reagent association. Even more interesting, increasing S/Ln beyond 1 does not monotonically increase the measured solute concentration. It is apparent that added S is still being consumed and that 1:2 Ln:S complexes are being formed. In the case of Ln = praseodymium, measured concentrations remain anomalously small even up to $S/Ln \approx 3$, indicating that 1:3 Ln:S complexes are also present.

The following sets of mass balance equations were employed to analyze the osmometric data in a more quantitative fashion. The subscript tot denotes the total quantity in solution. M_{tot} denotes total solute.

$$M_{tot} = Ln + (Ln)_2 \qquad (1)$$

$$Ln_{tot} = Ln + 2(Ln)_2$$

$$K = [(Ln)_2]/[(Ln)]^2 \qquad (2)$$

Since the first equilibrium constant for substrate–shift reagent interaction was immeasurably large ($K_{1:1} > 10^3$), data could only be analyzed in the region where $Ln/S < 1$. Equilibrium constant data

$$S_{tot} = S + LnS + 2LnS_2$$

$$Ln_{tot} = LnS + LnS_2 \qquad (3)$$

$$M_{tot} = S + LnS + LnS_2$$

$$K_{1:1} = [LnS]/[Ln][S] > 10^3 \qquad (4)$$

$$K_{1:2} = [LnS_2]/[LnS][S] \qquad (5)$$

for the Eu, Ho, and Yb systems along with estimated errors, are given in Table II. As can be seen in the table, the osmometric data for $Pr(fod)_3$ indicate a considerably greater propensity for association. Indeed, both $K_{1:1}$ and $K_{1:2}$ were immeasurably large. However, $K_{1:3}$ could be determined in the region $Ln/S < 0.5$. Also, it appears (Table I) that the praseodymium

$$S_{tot} = S + 2LnS_2 + 3LnS_3$$

$$Ln_{tot} = LnS_2 + LnS_3 \qquad (6)$$

$$M_{tot} = S + LnS_2 + LnS_3$$

$$K_{1:3} = [LnS_3]/[LnS_2][S] \qquad (7)$$

shift reagent alone forms aggregates of higher molecular weight than dimers.

For the Eu, Ho, and Yb systems, it is also possible to calculate the resonance position of S in LnS and in LnS_2 by combining the osmometric results with the pmr data.[19] The result is presented in Table II. Invariably, the C_5H_5 protons are shifted to a greater extent in the 1:1 adducts.

Such stoichiometric determinations are by no means restricted to $(C_5H_5)Fe(CO)_2CN$ as the substrate. The last entry in Table II is for solutions of $Eu(fod)_3$ and cholesterol, which demonstrates the unexpected[20] presence of 1:2 Ln:S adducts in this particular system.

Discussion

The shape of the curve for nmr shift *vs.* Ln/S ratio has been the source of much confusion with respect to the stoichiometry of lanthanide–substrate interaction. Superficially, a typical curve such as that presented in Figures 1 and 2 might be interpreted in terms of simple 1:1 interaction of Ln and S. However, the osmometry results clearly reveal the formation of 1:2 and in some cases higher complexes. In contrast to the familiar titration curve of a polyprotic acid, our δ *vs.* Ln/S curves and all of those which we have inspected in the literature do not exhibit clear breaks at 1:2 and 1:1 stoichiometry. There are several reasons for this relatively simple shape of the nmr shift curves. Most important is the fact that the measured shift is an average of shifts for the various substrate-containing species, S, LnS, LnS_2, etc. In addition, the combination of osmometry and nmr data shows that for the present case the successive formation constants decrease markedly from $K_{1:1}$ to $K_{1:2}$, and that the chemical shifts for the 1:1 adduct are equal to or somewhat greater than the shift for the 1:2 adduct. As a result, the progression from the low Ln/S ratio represents (for Eu, Ho, and Yb) initially the formation of LnS_2, which upon addition of Ln is converted to LnS with a smooth increase in the observed average chemical shift. When $K_{1:1}$ is large and $K_{1:2}$ is significantly less, the curve eventually will level off around Ln/S = 1:1 because around this point all of the substrate is present as 1:1 and no further change occurs upon addition of shift reagent. (We are neglecting the formation of $Ln_2 \cdot S$, for which there appears to be some evidence in the case of Pr.) When $K_{1:2}$ is fairly large the break will occur before the 1:1 point as, for example, with $Eu(fod)_3$ (Figure 1). Our results appear to be in reasonable agreement with the most detailed nmr analysis to date[7] (which employed a different substrate). The rather featureless character of shift *vs.* Ln/S curves, combined with the large number of unknowns, requires extremely accurate nmr data and a rather formidable numerical analysis to obtain information for successive 1:1 and 1:2 complex formation. The strength of osmometry lies in the possibility of recognizing the formation of higher adducts (*e.g.*, LnS_3) in addition to 1:1 and 1:2 species. The determination of very large equilibrium constants is beyond the capability of the osmometry method.

The osmometry data also reveal some interesting periodic aspects of lanthanide tris(β-diketonate) coordination chemistry. The trend in $K_{1:2}$ (and $K_{1:3}$) at first appears opposite to that commonly observed for the interaction of lanthanides with organic ligands; *viz.*, formation constants generally increase with increasing atomic number.[21] However, most of the equilibria studied were for 1:1 Ln:S interaction in aqueous solution. It is apparent from the available data[2,17] that steric interactions are important factors in the structural chemistry of shift reagent systems. Our equilibrium results are in close accord with changes in ionic radius[21] across the lanthanide series, namely that the heavier metals less readily undergo expansion of the coordination sphere.

The effectiveness of a given shift reagent system is a

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(19) The observed shift of the S resonance in any mixture is simply the average of the S shifts in the individual components, with the contributions weighted by their mole fractions.

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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.

Acknowledgments. This research was supported by the NSF through Grants GP-28878 and GP-30623X. R. Porter is the recipient of an NDEA fellowship.

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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 (*pentahapto*cyclopentadienyl)(tricarbonyl)(3-bromo-*n*-butyl)molybdenum reacts with triphenylphosphine, the cis isomer of the cation (*pentahapto*cyclopentadienyl)(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 preparing the first Pt^{IV} alkoxycarbenoid complex (reaction 2).[6] The postulated mechanism involves coordination 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]

$$trans\text{-}PtClMeL_2 + HC{\equiv}CCH_2CH_2OH \xrightarrow[AgPF_6]{MeOH} trans\text{-}[PtMe\overline{CO(CH_2)_2C}H_2L_2]^+PF_6^- \quad (1)$$
$$L = PMe_2Ph,\ AsMe_3$$

$$PtMe_2CF_3IL_2 + AgPF_6 \xrightarrow{HC{\equiv}CCH_2CH_2OH} [PtMe_2CF_3\overline{CO(CH_2)_2C}H_2L_2]^+PF_6^- \quad (2)$$
$$L = PMe_2Ph$$

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 evidence 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 proposed involves the nucleophilic attack of the anion,

$$\begin{tikzcd}
Mn(CO)_5^- + MeMn(CO)_5 \arrow[r, shift left] & {[(OC)_5MnMn(CO)_4C(O)Me]^-} \arrow[l, shift left] \arrow[dl, "Me_3OBF_4"] \\
(OC)_5MnMn(CO)_4C(OMe)(Me) &
\end{tikzcd} \quad (3)$$

$$Br(CH_2)_3Br \xrightarrow{Mn(CO)_5^-} (OC)_5Mn(CH_2)_3Br \xrightarrow{Mn(CO)_5^-} [(OC)_5MnMn(CO)_4C(O)(CH_2)_3Br]^- \longrightarrow (OC)_5MnMn(CO)_4\overline{COCH_2CH_2C}H_2 \quad (4)$$

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