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Studies on Main Group Metal–Transition Metal Bonded Compounds. 4. Solution and Exchange Studies on $[\eta^5\text{-}C_5H_5(CO)_3Mo]_2Zn$, $\eta^5\text{-}C_5H_5(CO)_3MoZnBr$, and Their Exchange Products

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Nuclear magnetic resonance and infrared spectral studies on solutions of $\eta^5\text{-}C_5H_5(CO)_3MoZnBr$ (TmZnBr) and $[\eta^5\text{-}C_5H_5(CO)_3Mo]_2Zn$ (Tm_2Zn) with tetra-*n*-butylammonium bromide, $ZnBr_2$, and $\eta^5\text{-}C_5H_5(CO)_3Mo^-$ (Tm^-) have established the existence of two intermediate ionic species, $[\eta^5\text{-}C_5H_5(CO)_3Mo]_3Zn^-$ (Tm_3Zn^-) and $[\eta^5\text{-}C_5H_5(CO)_3Mo]_2ZnBr^-$ (Tm_2ZnBr^-). The rapid equilibrium processes established include the steps $Tm_2Zn + Tm^- \rightleftarrows Tm_3Zn^-$ and $TmZnBr + Tm^- \rightleftarrows Tm_2ZnBr^-$ for which the equilibrium constants have been estimated as 125 (32), and 5.9 (14), respectively. The slow exchange in solutions of $ZnBr_2$ and Tm_2Zn has been studied by variable-temperature ^1H NMR line-shape analysis. The rate law is consistent with a bimolecular exchange of a Tm moiety, $Tm_2Zn + Tm^*ZnBr = Tm^*ZnTm + TmZnBr$, in which E_a = 6.59 (25) kcal/mol, $\Delta H^{\ddagger}_{25°}$ = 6.00 (25) kcal/mol, and $\Delta S^{\ddagger}_{25°}$ = −26.2 (11) cal/(deg mol). Reactions involving analogous mercury and cadmium derivatives are discussed.

Introduction

Recently, we reported the preparation and characterization of the compounds $\eta^5\text{-}C_5H_5(CO)_3MZnX$ (M = Mo, W; X = Cl, I)[1] and examined single-crystal structures of $(\eta^5\text{-}C_5H_5(CO)_3MoZnCl\cdot Et_2O)_2$,[1,2a] $\eta^5\text{-}C_5H_5(CO)_3MoZnBr\cdot 2THF$,[3] and $[Bu_4N]^+[\eta^5\text{-}C_5H_5(CO)_3Mo]^-$,[3] which provide additional information on the structures of transition metal–group 2B compounds now known.[4–9] There is, however, only limited quantitative information with regards the behavior of these species in solution.

Burlitch[5] has shown that many transition metal–group 2B compounds, including Tm_2Zn,[2a] ionize in the presence of basic solvents such as DMF or in the presence of halide ions. Displacement of the metal carbonyl anion, Tm^-, from a metal–metal bonded compound is due to competition for the acidic sites on the group 2B metal. Strongly basic metal moieties, e.g., $\eta^5\text{-}C_5H_5(CO)_2Fe^-$, are not displaced by DMF[5] while the weakly basic $(CO)_4Co^-$ is displaced completely from Zn, Cd, and Hg. Likewise, weaker transition metal bases are displaced in the presence of stronger transition metal bases.[12] Thus, $\eta^5\text{-}C_5H_5(CO)_2Fe^-$ will displace $(CO)_4Co^-$ from $[(CO)_4Co]_2M$ (M = Zn, Cd, and Hg) to form the asymmetric complexes.

Anions of the type $[(CO)_4Co]_2HgX^-$ (X = halide or $(CO)_4Co^-$)[11,12] have been reported as products of the weak base $(CO)_4Co^-$ acting on the mercury compound. However, no complexes were observed when amines, halides, or $(CO)_4Co^-$ were reacted with $[(CO)_5Mn]_2Hg$, Tm_2Hg, or $[\eta^5\text{-}C_5H_5(CO)_2Fe]_2Hg$.

Mays and co-workers[6] report formation of Tm_2Hg from reactions of Me_4NI and TmHgI (eq 1) while the analogous

$$2Me_4NI + 2TmHgI = Tm_2Hg + (Me_4N)_2HgI_4 \qquad (1)$$

$$Tm_2Hg + HgX_2 = 2TmHgX \qquad (2)$$

cadmium compounds are shown to form 1:1 and 1:2 adducts with Me_4NI. Reaction of HgX_2 with Tm_2Hg leads to the exchange product TmHgX,[7] eq 2.

More recently, Pannell and Jackson[10] have studied solutions on $Na[\eta^5\text{-}C_5H_5(CO)_2Fe]$ by infrared methods. These studies indicated that the sodium atom can participate in three structural configurations with respect to the metal moiety: directly bonded, bonded through a carbonyl bridge, or as solvent-separated ion pairs.

In this study the complex formation reactions of TmZnBr and Tm_2Zn with both Br^- and Tm^- have been investigated. The kinetics of the slow exchange in the Tm_2Zn/TmZnBr system also have been investigated by variable-temperature NMR line-shape methods.

Experimental Section

Preparation of Compounds. Reagent grade THF and diethyl ether were dried over $LiAlH_4$, distilled into the vacuum line, and stored. Zinc bromide was obtained from Research Inorganic Chemicals, opened, and stored only in an argon-filled drybox. Reagent grade Bu_4NBr was dried under vacuum at 120 °C for several days and then transferred to the drybox.

The compounds Tm_2Zn,[1] TmZnBr,[1] and Tm_2Hg[6] were prepared as described in the literature.

Na^+Tm^- was prepared by reaction of excess sodium amalgum with either cyclopentadienyl(tricarbonyl)molybdenum dimer or Tm_2Hg. Typically 1.0 g of Tm_2Hg in THF was added to Na/Hg and sealed in a shaker tube. After shaking for 1 day the tube was opened in a drybox, the supernatant liquid filtered off giving a clear yellow solution. Removal of the solvent by vacuum distillation followed by gentle warming under high vacuum gave a quantitative yield of NaTm powder as indicated from spectral analysis.

A 1:1 mixture of Na^+Tm^- and Tm_2Zn in a THF/hexane solvent produced a yellow precipitate, $\{Na[\eta^5\text{-}C_5H_5(CO)_3Mo]_3Zn\}\cdot C_4H_8O$ (295–310 °C dec without melting). Anal. Calcd: C, 37.46; H, 2.56. Found: C, 36.74; H, 2.81.[13] The IR mull spectra show no presence of Na^+Tm^- or Tm_2Zn; however, redissolving $Na^+Tm_3Zn^-$ in THF at concentrations suitable for IR work yield solutions containing very small quantities of Tm_3Zn^- due to eq 5. Characteristic bands of Tm_3Zn^- are obscured by bands due to Tm_2Zn.

A 4:1 mixture of Bu_4NBr and Tm_2Zn in a THF/hexane solvent produced yellow crystals $[(C_4H_9)_4N^+][\eta^5\text{-}C_5H_5(CO)_3Mo^-]$ (mp 83 °C). Anal. Calcd: C, 59.16; H, 8.42; N, 2.87. Found: C, 57.08; H, 8.56; N, 4.32.[13]

Sample Preparation and Spectral Studies. Infrared samples were prepared in the argon-filled drybox using KBr cells for solutions or KBr plates and fluorokerosene for solid mulls. The spectra were recorded immediately on a Perkin-Elmer Model 267.

All NMR samples of air-sensitive materials were prepared in the drybox in NMR tubes equipped with stopcocks. Subsequently they were degassed on a high vacuum line and sealed. The light-sensitive but air-stable Tm_2Hg solutions were prepared under subdued light and the containers covered with aluminum foil to protect the solutions from light. The spectra were run as soon as possible following preparation.

NMR spectra were obtained using a Varian A60A spectrometer equipped with variable-temperature accessories. Temperature measurements were made using ethylene glycol or methanol samples after each spectrum was recorded during variable-temperature operation.[14] All chemical shifts were measured relative to internal Me_4Si.

Line-shape analysis was accomplished using the program KINFIT[15] with the line-shape equation given by Carlson.[16] The analysis was conducted assuming the nonexchange relaxation time, $1/T_2$, to be constant with temperature and equal to the natural line width of the

Table I. Infrared Frequencies for the Carbonyl Groups in a Series of Derivatives Containing the η^5-$C_5H_5(CO)_3Mo$ Moiety[b]

	Species in solution				
Sample[a]	Tm_2Zn	TmZnBr	Tm_3Zn^-	Tm_2ZnBr^-	Tm^-
Tm_2Zn	1978 s 1958 s 1870 b				
TmZnBr		1964 s 1879 s 1849 s			1900 w 1786 w 1746 w
NaTm					1901 s 1796 s 1746 s
NaTm and Bu_4NBr 1:4					1896 s (1786, 1764) b
Tm_2Zn in DMF					1895 s 1775 b
Tm_2Zn in Me_2SO					1894 s (1776, 1766) s
Tm_2Zn (0.0618 M) and Bu_4NBr (0.0394 M)		1965 s 1880 s 1850 s	1940 sh 1841 sh		1897 s (1785, 1765) b
NaTm (0.0478 M) and Tm_2Zn (0.0119 M)	1972 s 1955 s 1971 s		1941 s 1896 sh 1841 sh		1899 vs 1795 vs 1740 vs
NaTm (0.0358 M) and Tm_2Zn (0.0332 M)	1960 s 1876 s		1935 s 1850 s		1900 vs 1798 vs 1741 vs
Tm_2Zn (0.0389 M) and $ZnBr_2$ (0.0173 M)	1975 sh 1955 sh	1964 s (1870, 1850) b	1935 sh		1899 vw 1790 vw 1750 vw
Tm_2Zn (0.0499 M) and $ZnBr_2$ (0.0231 M)		1964 vs 1880 vs 1850 vs	1935 m		1800 vvw 1750 vvw
Tm_2Zn (0.0371 M) and Bu_4NBr (0.0578 M)		1965 s 1876 s 1849 s		1954 s 1866 sh	1899 s (1784, 1966) b
Tm_2Zn, mull	1964 s 1894 s 1861 b				
TmZnBr·THF, mull		1959 s 1879 s 1831 b			
$NaTm_3Zn$·THF, mull			1925 s 1860 sh 1840 sh 1825 b		

[a] Solutions in THF or 70:30 THF–Et_2O mixture unless otherwise noted. Mulls made with fluorokerosene; Tm = η^5-$C_5H_5(CO)_3Mo$. [b] IR wavelength in cm^{-1}.

internal Me_4Si. The curve fitting yields the parameters R and k_a for the equation

$$R = k_a/k_b = \frac{1/\tau_a}{1/\tau_b} = \frac{[B]}{[A]} \tag{3}$$

where [A] and [B] represent the mole fractions of the protons on the respective sites.

Results and Discussion

Identification of Species. In order to discuss the complex equilibria present in the solutions of Tm_2Zn, TmZnBr, and NaTm it is essential to establish suitable criteria for identification of each of the ionic or neutral species present in solution. This was accomplished by examination of both infrared frequencies associated with the carbonyl group and NMR chemical shifts of the cyclopentadienyl (Cp) group for pure compounds and for solutions in which the concentrations had been adjusted to force the equilibrium in a specific direction. The data from these studies are presented in Tables I and II.

The carbonyl frequencies occur at 1978, 1958, and 1870 cm^{-1} for Tm_2Zn (THF solution) and are shifted to 1964, 1879, and 1849 cm^{-1} for TmZnBr (THF solution). For the ionic species NaTm the bands are shifted further to lower energy occurring at 1901, 1796, and 1746 cm^{-1} in THF. In Me_2SO they are at 1894, 1776, and 1766 cm^{-1} while DMF solution gives rise to only two bands at 1895 and 1775 cm^{-1} showing not only a discernible shift on proceeding from the less ionic to the more ionic derivatives but also showing some moderate solvent effects. When the counterion was changed from Na^+ to $[(n\text{-}Bu)_4N]^+$, the observed bands shifted to 1900, 1786, and 1746 cm^{-1} (THF solution) indicating small effects resulting from ion pair interactions. Further small effects are shown in the infrared spectra of THF solutions of NaTm containing increasing amounts of Bu_4NBr in which the low-frequency bands at 1796 and 1746 cm^{-1} shift toward each other in a fashion similar to that observed for solutions of NaTm in Me_2SO and DMF. Spectra showing this change are available.[17]

The most important feature of these studies is that the highest energy band is relatively insensitive to solvent effects and normally lies in a region which allows it to be used for identification. The first result of this is seen on closer examination of the spectra of THF solutions of TmZnBr which show weak bands at 1900, 1786, and 1746 cm^{-1} indicating dissociation with formation of Tm^-, eq 4. Dissociation also

$$TmZnBr \rightleftarrows Tm^- + ZnBr^+ \tag{4}$$

is indicated for Tm_2Zn in DMF[5] and Me_2SO but not in THF.

Table II. Chemical Shifts for the C_5H_5 Group in a Series of Derivatives Containing the η^5-$C_5H_5(CO)_3Mo$ Moiety[b]

Sample[a]	Chemical shift at 35 °C	Variable-temperature spectra[c]				
		Tm_2Zn	TmZnBr	Tm_3Zn^-	Tm_2ZnBr^-	Tm^-
Tm_2Zn	5.457					
TmBr	5.312		5.38 (–45 °C)			
NaTm	4.985					
NaTm and Bu_4NBr, 4:1	4.970					
Tm_2Zn (0.0618 M) and Bu_4NBr (0.0394 M)	5.28	5.53 (–90 °C) 7%	5.43 37%	5.32 42%	5.15 1%	4.98 13%
Tm_2Zn (0.0371 M) and Bu_4NBr (0.0578 M)	5.12		5.38 (–90 °C) 31%		5.22 16%	4.97 51%
NaTm (0.0478 M) and Tm_2Zn (0.0119 M)	5.12	5.50 (–90 °C) 18%		5.30 67%		4.97 15%
Tm_2Zn (0.389 M) and $ZnBr_2$ (0.0173 M)	*d*	5.47 (20 °C) 58%	5.32 42%			
Tm_2Zn (0.0499 M) and $ZnBr_2$ (0.0231 M)	*d*	5.42 (35 °C) 23%	5.30 77%			

[a] Solution in THF or 70:30 THF–Et_2O mixture. Tm = η^5-$C_5H_5(CO)_3Mo$. [b] Chemical shifts in ppm from internal Me_4Si. [c] Percent peak intensity is indicated below chemical shift. [d] Two peaks are observed: Tm_2Zn downfield, TmZnBr upfield.

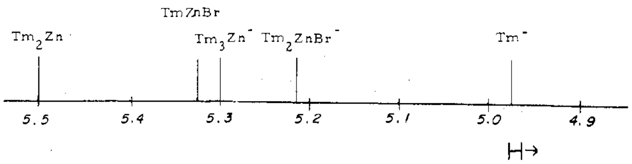


Figure 1. Relative chemical shifts of the Cp protons for a variety of TmZn species obtained at –90 °C in a mixed THF/ether solvent.

Study of the infrared spectra of mixtures of NaTm and Bu_4NBr with Tm_2Zn in THF solution leads to identification of the complexes Tm_3Zn^- and Tm_2ZnBr^- in their equilibrium mixtures. For the solutions of NaTm–Tm_2Zn new bands at 1940 and 1841 cm^{-1} and occasionally a band at 1860 cm^{-1} are ascribed to the Tm_3Zn^- complex. In the solutions containing bromide ions two bands at 1955 and 1866 cm^{-1} are observed which are assigned to the Tm_2ZnBr^- ion.

Examination of the low-temperature NMR spectra are consistent with these findings showing a variety of nonexchanging species present between –50 and –90 °C. The specific assignments of chemical shifts are given in Table II and are represented graphically in Figure 1. It should be noted that many of the species indicated undergo rapid exchange on the NMR time scale with increasing temperature and lead to exchange averaged chemical shifts at ambient temperature.

Equilibrium Studies. Mixtures of Tm_2Zn or TmZnBr with NaTm or with Bu_4NBr give rise to the exchange products. The most readily treated system is that of NaTm/Tm_2Zn solutions, which can be described by eq 5. The formation constant, K_5 = 124 (32), was determined under slow-exchange conditions by integration of the NMR signals at –80 to –90 °C.[17]

$$Tm^- + Tm_2Zn = Tm_3Zn^-;\ K_5 = 124\ (32)^{2b} \qquad (5)$$

Similarly, the NaTm/TmZnBr solutions may be discussed in terms of eq 6 in which the Tm^- group coordinates with the zinc atom forming the adduct Tm_2ZnBr^-. The formation constant, K_6, may be evaluated as 5.9 (16) for solutions of TmZnBr and NaTm from NMR measurements at –80 to –90 °C,[17] a value considerably lower than that for the formation constant of the complex Tm_3Zn^-.

$$Tm^- + TmZnBr = Tm_2ZnBr^-;\ K_6 = 5.9\ (16) \qquad (6)$$

Addition of Bu_4NBr to Tm_2Zn also results in a system with rapid exchange as indicated in Figure 2. The first step in this process involves production of TmZnBr by displacement as shown in eq 7, which goes essentially to completion. Molar ratios of Br^-/Tm_2Zn of 1.0 or greater produce solutions containing no Tm_2Zn.[17] The products, TmZnBr and Tm^-, undergo the acid–base reaction of eq 6 forming Tm_2ZnBr^-. The formation constant, K_6 = 11.3 (63), may also be determined in this system at –50 to –70 °C and is within experimental error of the value obtained using solutions of TmZnBr and Tm^-.[17]

$$Tm_2Zn + Br^- \rightarrow TmZnBr + Tm^- \qquad (7)$$

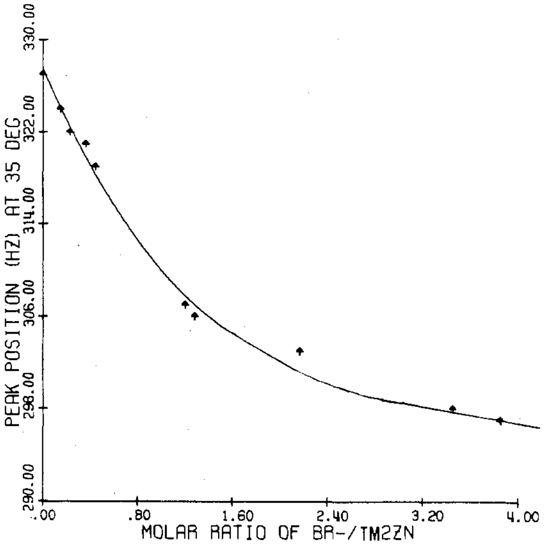


Figure 2. Concentration dependence of the Cp chemical shift as a function of the $(n\text{-}Bu)_4NBr/Tm_2Zn$ ratio obtained at ambient temperature (~35 °C) at 60 MHz.

Solutions in which the ratio $[Br^-]/[Tm_2Zn]$ is less than 1.0 show appreciable concentrations of Tm_2Zn and the adduct Tm_3Zn^-, as well as TmZnBr, Tm_2ZnBr^-, and Tm^-.[17] When the $[Br^-]/[Tm_2Zn]$ is large, the adduct $TmZnBr_2^-$ which might be expected to form via eq 8 is not observed even in the low-temperature NMR spectra.[17]

$$TmZnBr + Br^- = TmZnBr_2^- \qquad (8)$$

Solutions in which the ratio $[Br^-]/[Tm_2Zn]$ is above 3.0, Figure 2, contain one molybdenum species, Tm^-, implying the formation of $ZnBr_3^-$ via eq 7, 9, and 10. If K_{10} is not large

$$Tm_2Zn + Br^- = TmZnBr + Tm^- \qquad (7)$$

$$TmZnBr + Br^- = ZnBr_2 + Tm^-;\ K_9 = 3.7\ (26) \qquad (9)$$

$$ZnBr_2 + Br^- = ZnBr_3^- \qquad (10)$$

an estimate of K_9 = 3.7 (26) is obtained,[17] assuming that the zinc not accounted for by concentrations of TmZnBr and Tm_2ZnBr^- is present as $ZnBr_2$. The yellow crystals of

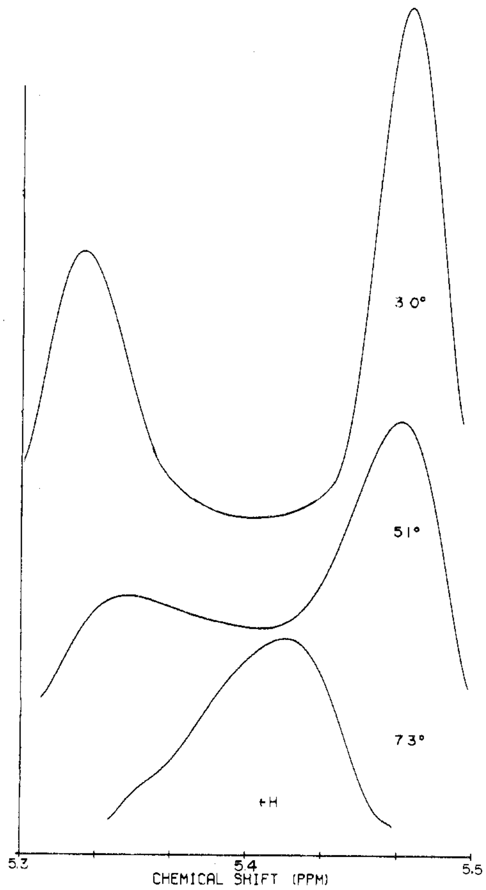


Figure 3. Calculated spectra for the slow exchange of a sample of $Tm_2Zn/TmZnBr$ as a function of temperature.

Bu_4NTm may be grown from the solutions in which a ratio of $[Br^-]/[Tm_2Zn]$ greater than 3.0 is used.

Making use of the relationship

$$\delta_{obsd} = X_a\delta_a + X_b\delta_b \ldots \qquad (11)$$

where X is the mole fraction of protons and δ is the chemical shift of the species in the absence of exchange, permits estimation of the equilibrium constant at higher temperatures where rapid exchange occurs. These studies indicate that the equilibrium constants, K_5 and K_6, do not change outside of the experimental error, over the temperature range of +35 to -90 °C. The small differences in chemical shifts as well as the accuracy of chemical shift measurement suggest caution in interpretation of this result, however.

The above observations might be contrasted with the results of Mays and Robb[6] who have reported formation of solid 1:1 and 1:2 complexes between Tm_2Cd or TmCdI and Me_4NI. The 1:2 complexes were formulated as $[Me_4N]_2[Tm_2CdI_2]$ and $[Me_4N]_2[TmCdI_3]$ while the composition of the 1:1 complexes was less certain. These results would suggest substantial differences in the stability of the complexes between the Tm–Cd–I system and the Tm–Zn–Br system. However, on examination of the IR spectra of the two systems some interesting questions may be raised. The 1:1 cadmium adduct $Me_4NI\cdot Tm_2Cd$ shows a broad absorption band in the region 1950–1800 cm^{-1} similar to that observed for some solutions of $Bu_4NBr\cdot Tm_2Zn$ mixtures, suggesting some similarities between these systems. Of even more interest is the appearance of bands at 1895 and 1776 cm^{-1}, characteristic of Tm^-, in the IR spectra of the 1:2 adduct $2(Me_4NI)\cdot Tm_2Cd$. In view of these similarities, it would appear that further investigation of the cadmium systems seems in order to clarify the nature of the species formed.

Table III. Line-Shape Parameters and Lifetimes Obtained for the Two-Site Intermolecular Exchange of $[\eta^5\text{-}C_5H_5(CO)_3Mo]_2Zn$ with $\eta^5\text{-}C_5H_5(CO)_3ZnBr$ in THF Solution as a Function of Concentration and Temperature

$10^2 \times [Mo_2Zn]_i$, M	$10^2 \times [ZnBr_2]_i$, M	Temp, °C	Line-shape parameters		
			R	$1/\tau_a$, Hz	$1/\tau_b$,[a] Hz
3.37	1.29	70.0	1.412	31.6	23.5
		49.6	1.342	20.5	15.2
		32.2	1.338	8.60	6.37
		21.9	1.301	6.47	4.80
3.08	0.888	73.4	1.471	25.4	18.0
		60.0	1.394	17.5	12.4
		50.9	1.371	14.3	10.1
		30.2	1.358	7.29	5.16
		23.3	1.951	6.29	4.45
2.48	1.47	66.2	0.7217	18.5	29.6
		41.9	0.5909	8.42	13.5
		34.8	0.5764	5.83	9.33
		21.5	0.6099	4.05	6.49
3.79	1.50	65.2	1.917	29.2	18.5
		36.4	1.643	12.9	8.18
		25.2	1.517	8.99	5.71
3.88	1.73	65.2	1.104	37.2	27.6
		49.3	1.348	25.2	18.7
		35.8	1.408	14.7	10.9
		26.8	1.489	11.4	8.47

[a] See eq 3 and 12.

Table IV. Initial and Equilibrium Concentration Data for THF Solutions of $[\eta^5\text{-}C_5H_5(CO)_3Mo]_2Zn$ and $ZnBr_2$ Used in Line-Shape Analysis

Initial concn (×10²), M			Calcd concn (×10²), M	
$[Tm_2Zn]_i$	$[ZnBr_2]_i$	R[a]	$[Tm_2Zn]_e$[b]	$[TmZnBr]_e$[b]
3.37	1.29	1.348	1.54	2.58
2.90	1.64	0.5108	0.838	3.28
3.04	0.888	1.399	1.24	1.78
2.48	1.47	0.6247	0.918	2.94
3.80	1.51	1.692	2.55	3.02
3.89	1.73	1.337	2.37	3.46

[a] Average R obtained from line-shape analysis eq 3. [b] Assuming $ZnBr_2$ is consumed and $[Tm_2Zn]_e = R[TmZnBr]_e/2$. See text.

Slow Exchange in $Tm_2Zn/ZnBr_2$ Solutions. Solutions of Tm_2Zn with $ZnBr_2$ as the source of halide show striking differences from solutions using Bu_4NBr. The NMR spectra of $Tm_2Zn/ZnBr_2$ solutions consist of two broad resonance lines, Figure 3, at 35 °C, which on cooling to 20 °C sharpen to two lines centered at 5.45 and 5.30 ppm downfield from internal Me_4Si. Cooling to -50 °C affects no further change in the spectra. The two lines correspond to those expected for Tm_2Zn and TmZnBr, respectively. This evidence of slow exchange on the NMR time scale is in sharp contrast to the rapid exchange evident in all solutions previously discussed.

IR spectra of these solutions indicate the presence of very small quantities of Tm^- as well as a shoulder at 1935 cm^{-1} representing small concentrations of Tm_3Zn^-, compared to the large concentrations of these species usually found in solutions made by addition of the 1:1 electrolyte, Bu_4NBr to Tm_2Zn.

Line-shape analysis of the variable-temperature NMR spectra of several solutions of $Tm_2Zn/TmZnBr$ yielded values of $1/\tau_a$ and $1/\tau_b$, the reciprocal lifetimes of TmZnBr and Tm_2Zn, respectively, given in Table III with the equilibrium concentrations given in Table IV. It is apparent from the values of R obtained from the analysis (eq 3) that $ZnBr_2$ is consumed completely by reaction (eq 12) with Tm_2Zn, but

$$Tm_2Zn + ZnBr_2 = 2TmZnBr \qquad (12)$$

impurities observable in the NMR spectra make the calculation of concentrations difficult. These impurities are

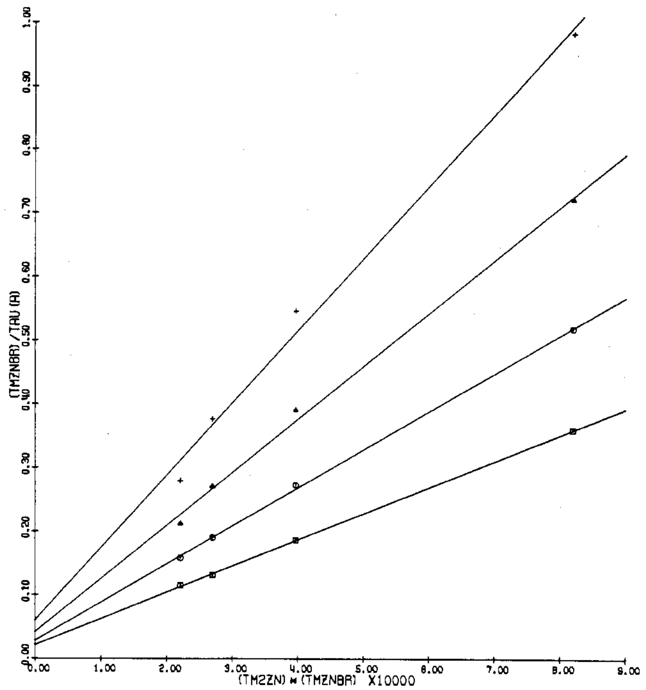


Figure 4. Plots of $[TmZnBr]/\tau_a$ vs. $[Tm_2Zn][TmZnBr]$: 25 °C, □; 35 °C, ○; 45 °C, △; 55 °C, +.

Table V. Specific Rate Constants and Activation Parameters for the Intermolecular Exchange of $[\eta^5\text{-}C_5H_5(CO)_3Mo]_2Zn$ with $\eta^5\text{-}C_5H_5(CO)_3ZnBr$ in THF Solutions

Specific rate constants T, °C	k_{av}, L/(mol s)	Activation parameters	
25	473 (77)	E_a	6.59 (25) kcal/mol
35	693 (150)	$\Delta H^{\ddagger}{}_{25°}$	6.00 (25) kcal/mol
45	996 (366)	$\Delta S^{\ddagger}{}_{25°}$	−26.2 (11) cal/(deg mol)
55	1300 (496)		

probably the result of the extreme air and moisture sensitivity of the solutions despite the precautions taken in their preparation. Plots of the concentration dependence (Figure 4) of the reaction yield the specific rate constants presented in Table V. Figure 5 shows the temperature dependence of the lifetimes for several samples from which the Arrhenius activation energy, $E_a = 6.59$ (25) kcal/mol, the enthalpy, $\Delta H^{\ddagger} = 6.00$ (25) kcal/mol, and the entropy, $\Delta S^{\ddagger} = -26.2$ (11) cal/(deg mol), can be obtained.

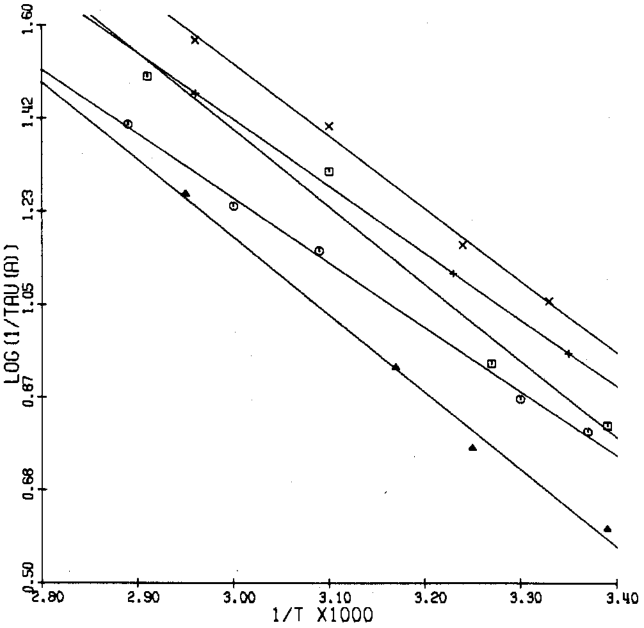
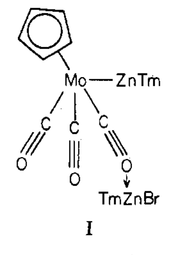


Figure 5. Plots of log $(1/\tau_a)$ vs. $1/T$ for a series of samples having different concentration ratios. The average $E_a = 6.59$ (25) kcal/mol.



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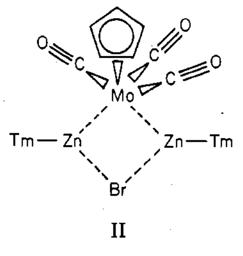

II

Several possible mechanisms were considered which appeared to be consistent with the kinetic data. Formation of a complex such as that indicated in I with Zn–O–C–Mo bridges seems probable but was not considered likely to lead to the observed exchange since it would require extensive rearrangement after formation of the complex. An alternate path involves the formation of a bridged transition state such as that indicated in II with Zn–Br–Zn and Zn–Mo–Zn bridge bonds. This structure is consistent with the known structures of these derivatives which are dimeric with halide bridges under some conditions.[1,3] Further, this transition state would lead directly to exchange without additional rearrangement and is consistent with the known exchange paths for many organometallic compounds.[18] Therefore it appears likely that the path for transfer of the transition metal moiety involves formation of a species containing a Zn–Mo–Zn bridge bond under the conditions described.

It should be emphasized that other routes for exchange are possible when ionic species such as Bu_4NBr or NaTm are added to Tm_2Zn. In these cases either free Tm^- is generated or complexes of the type Tm_2ZnBr^- are formed which undergo rapid exchange with Tm_2Zn as indicated earlier. In the system involving only TmZnBr and Tm_2Zn, no appreciable concentrations of Tm^- or other ionic species are present. This allows observation of the slower bimolecular process which appears to proceed through a bridged transition state.

Reactions similar to those described above might be expected for analogous mercury and cadmium compounds. Preliminary work with THF solutions of mercury compounds shows this to be the case. Tm_2Hg in THF exhibits an NMR chemical shift at 5.52 ppm below internal Me_4Si. Addition of $HgBr_2$ causes the peak to broaden and shift downfield toward 5.65 ppm. It seems likely that this exchange represents the transfer of the Tm moiety in a process similar to that indicated in eq 12. It seems probable that studies of the analogous cadmium and mercury reactions will show these systems to behave similar to the zinc systems described above.

In summary, the activity of the bases Tm^- and Br^- toward Tm_2Zn and TmZnBr has been investigated. These studies indicate that Br^- is the stronger base, displacing the Tm^- moiety from the zinc site whenever it is present in appreciable concentrations. Tm^- will bind to the acidic zinc site forming the three-coordinate species Tm_3Zn^- and Tm_2ZnBr^-. It is shown that TmZnBr is a poorer acid toward Tm^- than Tm_2Zn as evidenced by the much smaller formation constant of Tm_2ZnBr^-. It is known[1,3] that ethers bind readily to TmZnX but do not appear to bind to Tm_2Zn. Thus the observed order may result from this difference which requires displacement of ether from the halide derivative but not the Tm_2Zn molecule to form the complex with Tm^-. In the absence of appreciable concentrations of Br^- or Tm^-, solutions of Tm_2Zn and TmZnBr exhibit a slow exchange on the NMR time scale involving exchange of the Tm moiety through a bridged transition state.

Registry No. Tm_2Zn, 54244-98-3; TmZnBr, 63511-76-2; NaTm, 12107-35-6; Tm_2ZnBr^-, 63588-50-1; TmZnBr·THF, 63511-75-1; $NaTm_3Zn$·THF, 63511-74-0; TmBr, 12079-79-7; $[Bu_4N]Tm$, 61618-13-1; Tm_3Zn^-, 63588-53-4; Bu_4NBr, 1643-19-2; $ZnBr_2$, 7699-45-8.

Supplementary Material Available: Infrared spectra of THF solutions of NaTm with varying amounts of $(n\text{-Bu})_4NBr$ added are presented in Figure 1S; tables listing equilibrium concentrations determined from NMR spectral measurements in THF/Et_2O solutions of (a) $[\eta^5\text{-}C_5H_5(CO)_3Mo]$, (b) $\eta^5\text{-}C_5H_5(CO)_3MoZnBr$ and $Na[\eta^5\text{-}C_5H_5(CO)_3Mo]$, and (c) $[\eta^5\text{-}C_5H_5(CO)_3Mo]_2Zn$ and $n\text{-}Bu_4Br$ are given in Tables S-I, S-II, S-III, and S-IV (6 pages). Ordering information is given on any current masthead page.

References and Notes

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(2) (a) Abbreviations used in this paper: Tm = $\pi\text{-}C_5H_5(CO)_3Mo$; Bu = C_4H_9–; Et = C_2H_5–; Me = CH_3–; THF = tetrahydrofuran; DMF = dimethylformamide; Me_2SO = dimethyl sulfoxide. (b) Standard errors for the last digits are given in parentheses.

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Stereochemistry of the Cycloaddition Reaction of 1,2-Dicyano-1,2-bis(trifluoromethyl)ethylene with Transition-Metal Complexes Containing σ-Bonded, Unsaturated Hydrocarbon Ligands[1]

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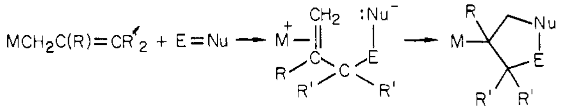
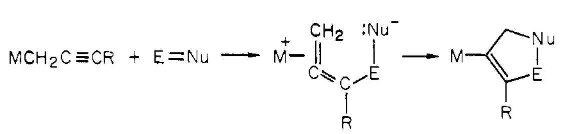
Several new transition-metal–cyclopentenyl and –cyclopentyl complexes were prepared by reactions of appropriate propargyl, allenyl, and η^1-allyl complexes of $\eta^5\text{-}C_5H_5Fe(CO)_2$, $Mn(CO)_5$, and $Re(CO)_5$ with *cis-* and *trans*-1,2-dicyano-1,2-bis(trifluoromethyl)ethylene ($C_6F_6N_2$). Each cycloaddition reaction affords a mixture of diastereomers, some of which were separated. The ratio of diastereomers was determined by ^{19}F NMR spectroscopy, and the data were used to calculate percent stereoselectivities of these cycloadditions. The reaction of $\eta^5\text{-}C_5H_5Fe(CO)_2CH_2C{\equiv}CC_6H_5$ with *trans*-$C_6F_6N_2$ in benzene at room temperature proceeds with ca. 75% stereoselectivity whereas that of $M(CO)_5CH_2C{\equiv}CC_6H_5$ (M = Mn or Re) with *trans*-$C_6F_6N_2$ in benzene and acetonitrile, also at ca. 25 °C, occurs with a lower, 32–40%, stereoselectivity. Similar reactions with *cis*-$C_6F_6N_2$ appear to proceed substantially, if not completely, via *cis*-$C_6F_6N_2$ to *trans*-$C_6F_6N_2$ isomerization to give comparable stereoselectivities. The cycloadditions of the metal–allenyl and –η^1-allyl complexes did not furnish any reliable or readily interpretable stereochemical data. The results obtained herein rule out the possibility of a concerted mechanism for the reaction of transition-metal–propargyl complexes with $C_6F_6N_2$ and are consistent with the previously proposed two-step pathway.

Introduction

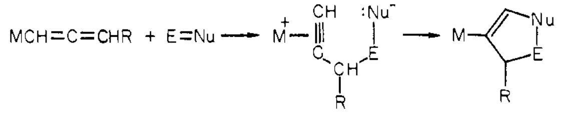
The addition of electrophilic reagents, E=Nu (E = electrophilic part, Nu = nucleophilic part), to η^1-allyl, propargyl, and allenyl ligands coordinated to transition metals has received considerable attention.[2,3] The reactions of the propargyl and allenyl fragments yield five-membered rings by (3 + 2) cycloaddition accompanied by 1,2 metal migration, whereas the reactions of the η^1-allyl moieties usually afford either analogous cycloadducts or insertion products. Support has been demonstrated[3-5] for similar, two-step paths (eq 1–3) of such cycloadditions.



(1)



(2)



(3)

Only in reaction 1 has there been any direct evidence for the proposed path: when E=Nu is SO_2, a dipolar metal–η^2-olefin species has been recently detected and intercepted.[3,4] Reaction 2 has been simulated by protonation and treatment of the resultant cationic η^2-allene derivatives with nucleophiles to give iron–vinyl complexes.[5,6]

To elucidate further the mechanism of these reactions we undertook an investigation of stereochemistry at the E–Nu bond of the formation of the cycloadducts. For that purpose an ideal electrophile is an isomeric olefin for which a physical measurement can differentiate the stereochemistry of the reactant as well as that of the product. Such stereochemical investigations have been conducted by ^{19}F NMR spectroscopy for several cycloaddition reactions of 1,2-dicyano-1,2-bis(trifluoromethyl)ethylene ($C_6F_6N_2$),[7-9] whose reactivity was shown to be similar to that of tetracyanoethylene (TCNE).

In this paper are reported the details of our study of the cycloaddition reactions of *cis-* and *trans*-$C_6F_6N_2$ with transition-metal–η^1-allyl, –propargyl, and –allenyl complexes conducted with a view to determining the stereoselectivity of these processes. Part of our work has been described in a preliminary communication.[10]

Results and Discussion

Characterization and Properties of Metal–Cyclopentenyl Complexes. Transition-metal–propargyl complexes react with $C_6F_6N_2$ at room temperature to yield 1:1 adducts as indicated by elemental analyses and mass spectrometry. These products