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Mechanistic study of the substitution behavior of complexes of the type metal carbonyltetrahydrofuran [M(CO)5(THF), M = chromium, molybdenum, tungsten]

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yellow crystals of 1, 30.5 mg (44%).

Reaction of 2 with Hydrogen. Hydrogen gas was bubbled into a toluene solution of **2** (80.5 mg, 0.1048 mmol) for 7 h at room temperature. After removal of toluene under vacuum, the residual solid, which was recrystallized from ether, was found to be $ReH_5(PMe_2Ph)_3$ by ^1H NMR. Yield: 0.0464 mmol, 44%. When the reaction was quenched after 4 h, a mixture of $ReH_3(PMe_2Ph)_4$[12] and $ReH_5(PMe_2Ph)_3$[11] was obtained in a ca. 1:1 ratio.

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Supplementary Material Available: Tables of atomic positional parameters, bond distances, bond angles, and anisotropic thermal parameters for complexes 1 and 2 (14 pages); listings of observed and calculated structure factors for 1 and 2 (21 pages). Ordering information is given on any current masthead page.

Mechanistic Study of the Substitution Behavior of Complexes of the Type $M(CO)_5(THF)$ (M = Cr, Mo, W)

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The kinetics and mechanism of the substitution of $M(CO)_5(THF)$ (M = Cr, Mo, W) by piperidine, triethyl phosphite, and triphenylphosphine in tetrahydrofuran (THF) were studied with use of conventional and high-pressure techniques. The reactions follow the reactivity order Mo > Cr > W and are characterized by ΔH^{*} values between 38 and 78 kJ mol^{-1}, ΔS^{*} values between 0 and −120 J K^{-1} mol^{-1}, and ΔV^{*} values between −2 and −15 cm^3 mol^{-1}. The latter values exhibit a specific trend toward more negative values along the series Cr, Mo, and W, which is interpreted as evidence for a gradual changeover in mechanism from a more dissociative to a more associative activation process along the series of complexes.

Introduction

Our general interest in the mechanistic behavior of solventometal carbonyl complexes and their possible role in homogeneous catalysis has led us to a series of studies dealing with such species.[1-3] In general, complexes of the type $M(CO)_5S$, where S = solvent and M = Cr, Mo, and W, can be prepared either as transient species by flash photolysis techniques or as stable intermediates by conventional photochemical techniques depending on the nature of S. For weak-coordinating solvents like *n*-alkanes, benzene, toluene, and their fluorinated analogues, the $M(CO)_5S$ species are short-lived and undergo rapid substitution with the offered nucleophile. In the case of a strong-coordinating solvent like THF, it is possible to prepare pure and stable complexes of the type $M(CO)_5THF$ in solution.

The subsequent substitution reactions of $M(CO)_5S$ exhibit interesting mechanistic aspects, which caught the attention of several investigators in recent years.[4-8] Such studies usually include systematic investigations of the effect of solvent, entering ligand concentration, and temperature on the substitution process. Our earlier experience has demonstrated the difficulties involved in the assignment of the intimate nature of the substitution process based on the observed rate law and thermal activation parameters (ΔH^{*} and ΔS^{*}). The value of ΔS^{*} especially does not seem to be a strong indicator for the underlying mechanism in such systems.[7,8] On the basis of our earlier experience with the application of high-pressure kinetic techniques in the study of substitution reactions of metal carbonyl complexes[1,9-15], we undertook a series of flash photolysis studies[2,3] in an effort to improve our understanding of the mechanistic behavior of complexes of the type $M(CO)_5S$. In this paper we report results for M = Cr, Mo, and W, S = tetrahydrofuran (THF), and L = piperidine, PPh_3, and $P(OEt)_3$.[16] The reported data allow a systematic analysis of the influence of M and L on the underlying substitution mechanism and demonstrate a gradual changeover from a dissociative to a more associative process along the series Cr, Mo, and W.

Experimental Section

Materials. $Cr(CO)_6$ (Ventron), $Mo(CO)_6$, and $W(CO)_6$ (Riedel-de-Haen) were vacuum-sublimed before use. All solvents used were distilled and dried over Na or P_2O_5 under N_2 or Ar. Piperidine (Aldrich) was distilled over KOH under N_2. Solutions

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[†] Work performed at the Institute for Physical and Theoretical Chemistry, University of Frankfurt, FRG.

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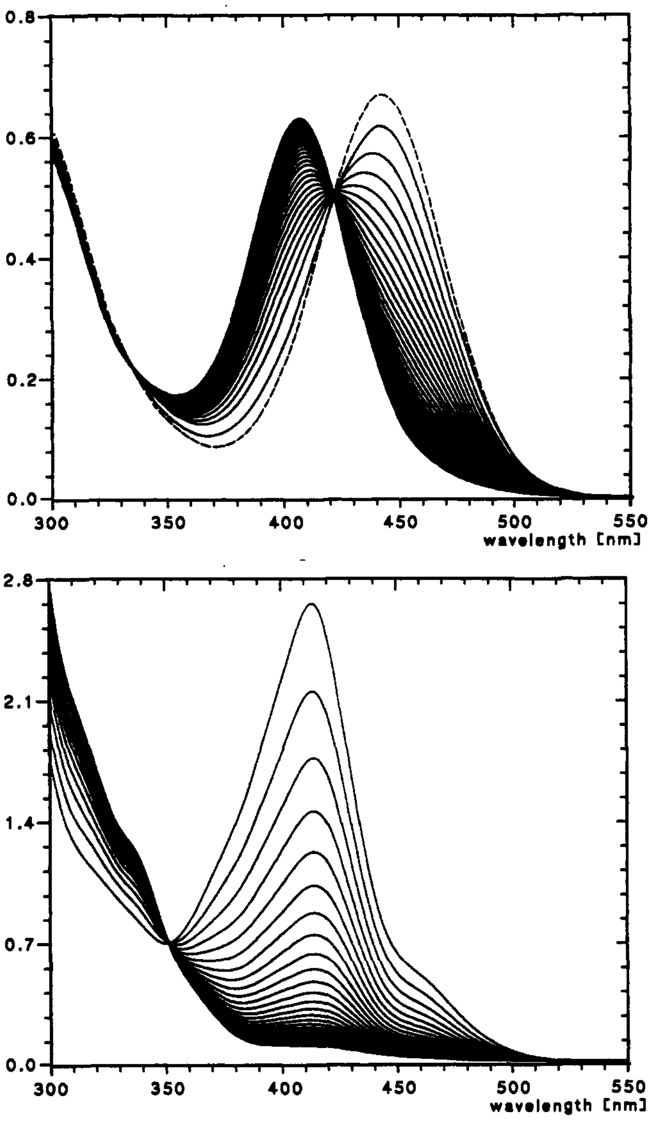

Figure 1. (a) (Top) UV-visible spectral changes observed during the reaction Cr(CO)$_5$THF + piperidine → Cr(CO)$_5$[piperidine] + THF. The reaction was conducted under an argon atmosphere, T = 288 K, [piperidine] ≈ 4.10^{-3} mol/L, Δt = 30 s (time interval between successive spectra). (---) initial spectrum of (Cr(CO)$_5$THF) before mixing of Cr(CO)$_5$THF and piperidine solutions. (b) (Bottom) UV-visible spectral changes observed during the reaction W(CO)$_5$THF + P(OC$_2$H$_5$)$_3$ → W(CO)$_5$[P(OC$_2$H$_5$)$_3$] + THF. The reaction was conducted under an argon atmosphere, T = 288 K, [P(OC$_2$H$_5$)$_3$] = 0.029 mol/L, Δt = 40 s (time interval between successive spectra).

containing M(CO)$_5$THF were prepared via UV irradiation of the M(CO)$_6$ complexes in THF under a constant stream of N$_2$ to remove the released CO and to prevent the back-reaction. All test solutions were handled with use of Schlenk techniques and gas-tight syringes.

Stopped-Flow Studies. The substitution reactions of THF could be followed by conventional stopped-flow techniques. The ambient-pressure work was performed on a modified Aminco stopped-flow system, whereas the reactions at elevated pressure were studied on a homemade high-pressure stopped-flow unit,[17] using a modified mixing chamber and glass syringes.[16] Both instruments were thermostated (±0.1 °C) and hooked up to an advanced data acquisition and handling system.[18] The pseudo-first-order observed rate constants were calculated by least-squares fits, after calculation of the infinity absorbance values by the Kezdy-Swinbourne method. The corresponding first-order plots were linear for at least 2-3 half-lives of the reaction.

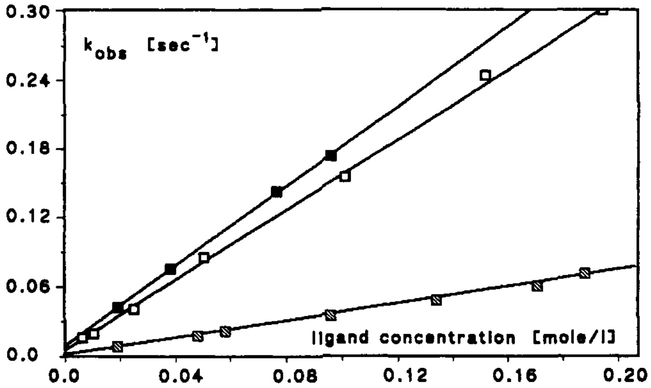

Figure 2. Plot of k_{obs} versus concentration of the entering ligand for the reaction M(CO)$_5$THF + L → M(CO)$_5$L + THF. Solvent = THF, T = 298 K: M = Mo, L = P(OC$_2$H$_5$)$_3$ (■); M = Cr, L = piperidine (□); M = Cr, L = P(OC$_2$H$_5$)$_3$ (▨).

Results and Discussion

Observations at Ambient Pressure. The general substitution reaction given in (1) is accompanied by characteristic spectral changes as illustrated for two typical examples in Figure 1. It can be seen that reaction 1 is accompanied by characteristic, clean isosbestic points and very significant spectral changes. These reactions can therefore be studied conveniently by selecting a wavelength in the visible or near-ultraviolet region that corresponds to a large spectral change during the reaction. In the presence of an at least a 10-fold excess of L, reaction 1 exhibits excellent pseudo-first-order behavior. For all the systems studied, k_{obs} depends linearly on the concentration of L (see Figure 2 and Table I), such that the observed rate law can be expressed as indicated in eq 2. No deviation from linearity was observed in such plots at higher [L], and no significant intercept was observed either. A summary of the observed rate constants as a function of M, L, and temperature is given in Table II.

$$\mathrm{M(CO)_5THF} + \mathrm{L} \xrightarrow{k} \mathrm{M(CO)_5L} + \mathrm{THF} \qquad (1)$$

$$k_{obs} = k[\mathrm{L}] \qquad (2)$$

The linear ligand concentration dependencies observed for these reactions (see Figure 2) can be interpreted in terms of the general dissociative mechanism given in (3), for which the rate expression is given in (4). The inclusion of an associative reaction path (k_3) leads to the mechanism shown in (5), and the rate law is now given in (6). The expressions in both (4) and (6) predict a nonlinear dependence of k_{obs} on [L], especially at higher [L], which

$$\begin{tikzcd}\mathrm{M(CO)_5THF} \arrow[r, shift left, "k_1"] & \mathrm{M(CO)_5} + \mathrm{THF} \arrow[l, shift left, "k_{-1}"] \arrow[d, "+\mathrm{L}"', "k_2"] \\ & \mathrm{M(CO)_5L}\end{tikzcd} \qquad (3)$$

$$k_{obs} = k_1k_2[\mathrm{L}]/\{k_{-1}[\mathrm{THF}] + k_2[\mathrm{L}]\} \qquad (4)$$

$$\begin{tikzcd}\mathrm{M(CO)_5THF} \arrow[r, shift left, "k_1"] \arrow[dr, "+\mathrm{L},\ -\mathrm{THF}"', "k_3"] & \mathrm{M(CO)_5} + \mathrm{THF} \arrow[l, shift left, "k_{-1}"] \arrow[d, "+\mathrm{L}"', "k_2"] \\ & \mathrm{M(CO)_5L}\end{tikzcd} \qquad (5)$$

$$k_{obs} = k_3[\mathrm{L}] + k_1k_2[\mathrm{L}]/\{k_{-1}[\mathrm{THF}] + k_2[\mathrm{L}]\} \qquad (6)$$

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Table I. Rate Constants k_{obs} as a Function of Ligand Concentration [L] for the Reaction[a] $M(CO)_5THF + L \xrightarrow{k} M(CO)_5L + THF$

ligand	$[L] \times 10^2$, M	$k_{obs} \times 10^2$,[b] s^{-1} Cr(CO)$_5$THF	Mo(CO)$_5$THF	W(CO)$_5$THF
piperidine	0.705	1.38 ± 0.11		
	1.01	1.70 ± 0.11	13.4 ± 0.5	
	2.53	4.00 ± 0.08	33.1 ± 0.5	1.21 ± 0.07
	5.05	8.75 ± 0.09	68 ± 3	2.60 ± 0.10
	10.1	15.6 ± 0.8	138 ± 10	5.69 ± 0.04
	15.2	24.4 ± 0.4	231 ± 5	
	20.2	30.9 ± 0.1		15.6 ± 0.5
	30.3	46.7 ± 0.8		21.2 ± 0.4
$P(OC_2H_5)_3$	1.94	0.753 ± 0.005	4.12 ± 0.08	0.696 ± 0.006
	3.86		7.50 ± 0.10	1.42 ± 0.02
	4.82	1.85 ± 0.02		
	5.77	2.27 ± 0.02		2.07 ± 0.03
m	7.67		14.3 ± 0.1	
	9.56	3.69 ± 0.13	17.2 ± 0.2	3.45 ± 0.08
	13.3	4.85 ± 0.07		4.45 ± 0.10
	17.0	5.92 ± 0.10		
	18.8	7.42 ± 0.17		5.94 ± 0.08
$P(C_6H_5)_3$	0.229		0.51 ± 0.05	
	0.462		1.03 ± 0.01	
	0.480		1.24 ± 0.01	
	0.833		1.94 ± 0.02	
	0.987		2.44 ± 0.05	
	1.2	0.454 ± 0.009		0.0997 ± 0.0003
	4.86			0.383 ± 0.001
	5.2	2.03 ± 0.02		
	7.84			0.627 ± 0.003
	11.5	3.69 ± 0.07		
	11.8			0.944 ± 0.004
	15.8			1.18 ± 0.01
	16.4	6.22 ± 0.17		
	20.1			1.42 ± 0.01

[a] T = 298 K, performed at different M(CO)$_5$THF concentratons selected in the range from 0.28 to 0.61 mmol/L. [b] Mean value of at least five kinetic experiments.

could in principle be used to distinguish between the significance of the various reaction steps. However, under our conditions with THF as solvent, no such deviation from linearity was observed for all investigated reactions, from which we conclude that $k_{-1}[THF] \gg k_2[L]$. Equation 6 can then be simplified to (7), from which it follows that the observed second-order substitution rate constant could be a composite of the parallel associative (k_3) and dissociative (k_1) reaction paths.

$$k_{obs} = k_3[L] + k_1k_2[L]/k_{-1}[THF] \qquad (7)$$

The rate and activation parameters ($\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$) in Table III exhibit the following tendencies. The second-order rate constant follows the sequence Mo > Cr > W as observed for many such substitution processes.[19] Throughout the series of THF complexes the substitution by piperidine is significantly faster than that by $P(C_6H_5)_3$ and $P(OC_2H_5)_3$, although this effect is not so significant in the case of the W complex. This trend is not in agreement with that expected on the basis of the usual nucleophilicity for associative substitution reactions. Similar results were reported for the substitution reactions of *cis*-$W(CO)_4(CB)P(C_6H_5)_3$ (CB = chlorobenzene).[20] This trend can partly be interpreted in terms of steric hindrance due to the size of the entering ligand, since for instance the Tolmann cone angle is 145° for $P(C_6H_5)_3$ but only 109° for $P(OC_2H_5)_3$. On the other hand, electronic effects cannot be ignored in determining the reactivity pattern since phosphines are in general better σ-donors, whereas phosphites are better π-acceptors. Furthermore, the composite nature of k as indicated in eq 7 may result in various contributions from k_2 and k_3 depending on the nature of L and thus complicate the discussion of k. The values of $\Delta S^{\ddagger}$ show a general trend to more negative values for the W complexes than for the Cr and Mo complexes. The majority of data for the THF substitution reactions are significantly negative, which would favor an associative (k_2) reaction path. More precise mechanistic information can be obtained from the pressure dependence data.

The results for the pressure dependence of all the investigated reactions are included in Table III. Plots of ln k_{obs} versus pressure were linear within the experimental error limits (see Figure 3), and the volumes of activation $\Delta V^{\ddagger}$ were calculated from the slope ($=-\Delta V^{\ddagger}/RT$) of such plots in the usual way. For the dissociative reaction path outlined in (3), $\Delta V^{\ddagger} = \Delta V^{\ddagger}(k_1) - \Delta V^{\ddagger}(k_{-1}) + \Delta V^{\ddagger}(k_2) = \Delta\bar{V}(K_1) + \Delta V^{\ddagger}(k_2)$. $\Delta\bar{V}(K_1)$ is expected to be positive since we are dealing with the release of a solvent molecule. However, its value may depend on the coordination ability (nucleophilicity) of the solvent (S), since that will determine the effectiveness of M–S bond formation, i.e., the value of $\Delta V^{\ddagger}(k_{-1})$. In a similar way, $\Delta V^{\ddagger}(k_2)$ is expected to be negative, and its absolute value should correlate with the size of the entering ligand, i.e., the magnitude of the overlap of the van der Waals radii during bond formation. A very similar trend is expected for the associative reaction path, $\Delta V^{\ddagger}(k_3)$. In the case of eq 5 the observed $\Delta V^{\ddagger}$ value for the overall second-order rate constant is a complicated composite since it represents the sum of different reaction steps and not simply a product of rate constants.

All the reported $\Delta V^{\ddagger}$ values for the reactions in THF are slightly or significantly negative. The reactions in THF are orders of magnitude slower than in the other investigated solvents,[2,3] indicating that THF is significantly

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Table II. Temperature Dependence of the Second-Order Rate Constant k (M^{-1} s^{-1}) for the Reaction[a] $M(CO)_5THF + L \xrightarrow{k} M(CO)_5L + THF$

$Cr(CO)_5THF + L$

temp, °C	piperidine (0.202 M)	$P(OC_2H_5)_3$ (0.0956 M)	$P(C_6H_5)_3$ (0.0254 M)
15	0.85 ± 0.04	0.166 ± 0.008	0.116 ± 0.006
20	1.17 ± 0.02	0.247 ± 0.007	0.194 ± 0.005
25	1.53 ± 0.02	0.37 ± 0.02	0.36 ± 0.03
30	2.19 ± 0.08	0.53 ± 0.02	0.60 ± 0.01
35	3.35 ± 0.03	0.75 ± 0.03	
40	3.84 ± 0.10		

$Mo(CO)_5THF + L$

temp, °C	piperidine (0.06 M)	$P(OC_2H_5)_3$ (0.0386 M)	$P(C_6H_5)_3$ (0.0048 M)
15	5.8 ± 0.1	0.80 ± 0.05	0.93 ± 0.01
20	10.9 ± 0.1	1.13 ± 0.03	1.87 ± 0.08
25	15.2 ± 0.6	1.73 ± 0.03	2.5 ± 0.1
30	23 ± 1	2.40 ± 0.06	3.94 ± 0.07
35	34 ± 3	3.89 ± 0.11	7.27 ± 0.05
40	50 ± 3		8.9 ± 0.1

$W(CO)_5THF + L$

temp, °C	piperidine (0.202 M)	$P(OC_2H_5)_3$ (0.0956 M)	$P(C_6H_5)_3$ (0.152 M)[b]
15	0.36 ± 0.01	0.17 ± 0.01	0.301 ± 0.002
20	0.59 ± 0.01	0.25 ± 0.01	0.384 ± 0.003
25	0.75 ± 0.05	0.31 ± 0.01	0.71 ± 0.01
30	0.92 ± 0.01	0.50 ± 0.01	0.92 ± 0.01
35	1.11 ± 0.02	0.69 ± 0.02	1.25 ± 0.02
40			1.64 ± 0.04

[a] Experimental conditions: ligand concentrations as indicated, carbonyl complex concentrations in the range 0.28–0.61 mmol/L. [b] Values ×10.

stronger coordinated than the other solvent molecules. Since THF is the strongest ligand among the investigated solvents and has the smallest partial molar volume of all the investigated solvents, we expect $\Delta\bar{V}(K_1)$ to be significantly smaller than for the other solvents.[2,3] In the case of the $Cr(CO)_5THF$ substitution reactions, $|\Delta V^{*}(k_2)| > |\Delta\bar{V}(K_1)|$ such that the overall ΔV^{*} is slightly negative. There is no correlation with the size of the entering groups in this reaction, which further underlines the operation of the dissociative mechanism outlined in (3). In the case of the Mo and W analogues, the observed values are significantly more negative and become even more negative for the larger entering ligands. It follows that the associative components seem to contribute more strongly and to overrule the overall volume effects in these cases. A comparison of the ΔS^{*} and ΔV^{*} data reveals that significantly different ΔS^{*} values for a particular complex and different L are accompanied by very similar ΔV^{*} values, and vice versa. This lack of correlation between these activation parameters has been observed in many studies[13,15] and indicates that ΔS^{*} and ΔV^{*} can reveal different aspects of the activation process. It is important to note that although it is the natural expectation of kineticists that these parameters should exhibit some correlation, there is no thermodynamic relationship that links these parameters in a direct way.[15]

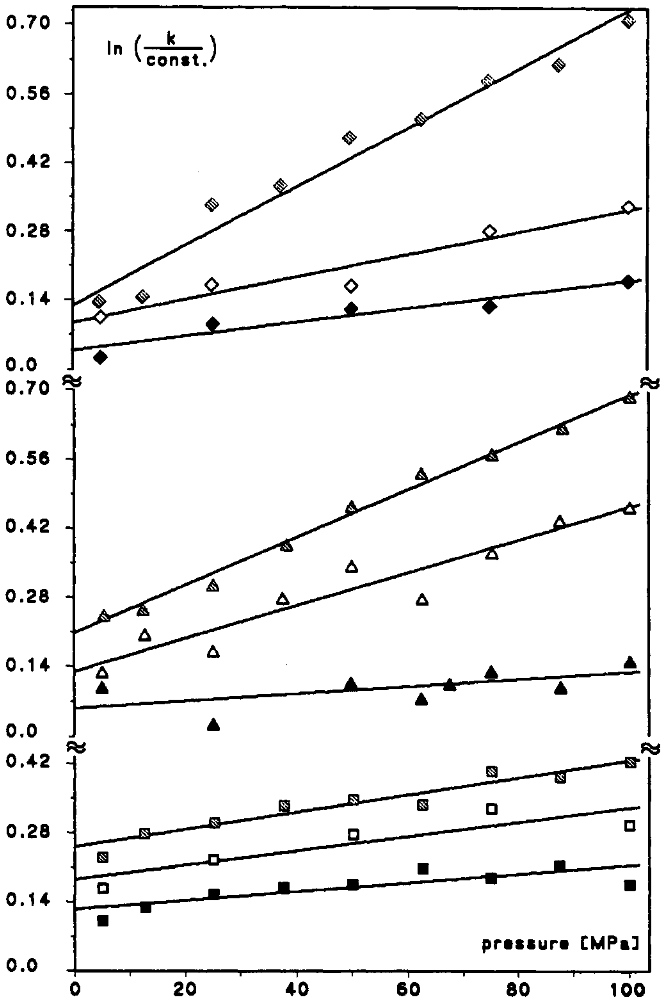

Figure 3. Pressure dependence of the rate constants for the substitution reaction $M(CO)_5THF + L \rightarrow M(CO)_5L + THF$. M = Cr (■, ▲, ◆), Mo (□, △, ◇), W (▨, ▲, ◈); L = piperidine (■, □, ▨), $P(C_6H_5)_3$ (▲, △, ▲), $P(OC_2H_5)_3$ (◆, ◇, ◈); solvent = THF, T = 298 K.

We conclude that the data in Table III suggest a gradual changeover from more dissociative to more associative activation for the substitution reactions of $M(CO)_5(THF)$ along the series Cr, Mo, and W. This trend is in good agreement with that reported for similar substitution reactions in aliphatic and aromatic hydrocarbon solvents.[2,3] It was generally found that the ΔV^{*} values tend to decrease (i.e., become more negative) in the series Cr, Mo, and W, which indicates that bond formation (k_2 and k_3) must be more important for the larger metal centers. The coordination ability of the solvent and the entering nucleophile may further account for smaller deviations observed in the reported data. Further insight into the intimate mechanism of reaction 1 should be obtained from solvent-exchange studies on $M(CO)_5THF$, especially via the appli-

Table III. Summary of the Rate Constants and Activation Parameters for the Reaction $M(CO)_5THF + L \xrightarrow{k} M(CO)_5L + THF$

M	ligand	k(298 K), M^{-1} s^{-1}	ΔG^{*}_{298}, kJ/mol	ΔH^{*}, kJ/mol	ΔS^{*}, J mol^{-1} K^{-1}	ΔV^{*}, cm^3 mol^{-1}
Cr	piperidine	1.53 ± 0.02	72 ± 4	45 ± 2	-90 ± 8	-2.2 ± 0.6
	$P(C_6H_5)_3$	0.36 ± 0.03	76 ± 4	78 ± 2	8 ± 8	-1.9 ± 1.0
	$P(OC_2H_5)_3$	0.37 ± 0.02	76 ± 2	53 ± 1	-74 ± 2	-3.6 ± 0.7
Mo	piperidine	15.2 ± 0.6	66 ± 4	60 ± 2	-21 ± 8	-3.6 ± 1.2
	$P(C_6H_5)_3$	2.5 ± 0.1	71 ± 8	65 ± 4	-17 ± 14	-8.3 ± 1.0
	$P(OC_2H_5)_3$	1.73 ± 0.03	72 ± 4	55 ± 2	-55 ± 8	-5.8 ± 0.9
W	piperidine	0.75 ± 0.05	74 ± 6	38 ± 5	-122 ± 2	-4.4 ± 0.5
	$P(C_6H_5)_3$	0.071 ± 0.003	80 ± 7	50 ± 3	-100 ± 11	-12.2 ± 0.4
	$P(OC_2H_5)_3$	0.31 ± 0.01	76 ± 6	49 ± 3	-89 ± 10	-14.9 ± 1.0

cation of high-pressure NMR techniques.[21,22] In addition, the significance of the various reaction routes in (5) could be resolved by performing a [THF] dependence study in which the solutions are diluted with a noncoordinating solvent.[22] In the investigated systems we are dealing with a fine balance of molecular size, steric hindrance, and nucleophilicity in determining the nature of the substitution process. Such mechanistic details could not be resolved on the basis of the thermal activation parameters only.

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Registry No. $Cr(CO)_5THF$, 15038-41-2; $Mo(CO)_5THF$, 53248-43-4; $W(CO)_5THF$, 36477-75-5; $P(OC_2H_5)_3$, 122-52-1; $P(C_6H_5)_3$, 603-35-0; piperidine, 110-89-4.

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Synthesis and Properties of the Novel η^4-Trimethylenemethane Compounds $\{\eta^4\text{-}C(CH_2)_3\}Fe(CO)_2L$ (L = Tertiary Phosphines, *tert*-Butyl Isocyanide)

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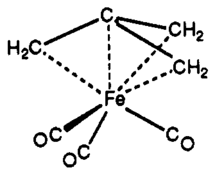
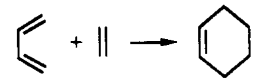
The new compounds $\{\eta^4\text{-}C(CH_2)_3\}Fe(CO)_2L$ ($(TMM)Fe(CO)_2L$; L = PPh_3, $PMePh_2$, PMe_2Ph, $PCyPh_2$, PCy_2Ph, PCy_3, $P(m\text{-xylyl})_3$, PBz_3, t-BuNC) have been synthesized by substitution of CO on $\{\eta^4\text{-}C(CH_2)_3\}Fe(CO)_3$ and are found to be surprisingly stable with respect to thermolysis and air oxidation. All have been characterized by IR and ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ spectroscopy, and some electrochemically; fluxional behavior involving TMM rotation is observed for several of the compounds. The X-ray crystal structure of $(TMM)Fe(CO)_2PCy_2Ph$ shows that the TMM ligand assumes a typical "umbrella-like" mode of coordination; the internal TMM ligand bond angles and distances differ little from those of other TMM–iron compounds, although the Fe–C distance of the methylene group "trans" to phosphorus is marginally longer than the other two iron–methylene distances.

Introduction

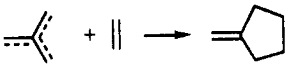
The short-lived, highly reactive biradical trimethylenemethane (TMM) was first stabilized by coordination to an $Fe(CO)_3$ fragment in 1966, yielding the novel compound $\{\eta^4\text{-}C(CH_2)_3\}Fe(CO)_3$ (I, $TMMFe(CO)_3$).[1] Since then, a large number of derivatives in which one or more hydrogen atoms of the TMM are substituted have also been reported,[2] and the chemistry of these compounds has been extensively reviewed.[3] Much of the interest in coordinated TMM stems from its potential use in [3 + 2] cycloadditions resembling Diels–Alder processes, an analogy prompted by the close topological similarities in the frontier orbitals of TMM and a cis-conjugated diene[4] and accentuated in eqs 1 and 2. Thus, although all attempts to react $(TMM)Fe(CO)_3$ with dienophiles have proven unsuccessful,[5] a number of η^3-TMM complexes of palladium have been found to participate in a variety of [3 + 2] cycloaddition reactions.[6] The low reactivity of $(TMM)Fe(CO)_3$ may be understood in terms of overlap arguments,[7] but may also, if the above-mentioned analogy with the Diels–Alder reaction is valid, be a result of the compound being too electron poor. Gas-phase valence-electron photoelectron data for this compound show that the first ionization potential is 8.32 eV,[8] and the reported values of $\nu(CO)$ are relatively high (2061, 1995 cm^{-1} in hexane[1]).



I



(1)



(2)

It follows that reactivity might be introduced into the system by substituting one or more of the carbonyl groups by tertiary phosphines, and we have investigated briefly the chemistry of the electron-rich compound $(\eta^4\text{-TMM})Fe(PMe_3)_3$.[9] Unfortunately, attempts to react this compound with a variety of reagents utilized previously[6] resulted in the formation only of 1,4-dimethylenecyclohexane, formally a dimer of the TMM diradical.[10]

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