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MOLYBDENUM ACETYL COMPLEXES: A KINETIC STUDY OF THE DECARBONYLATION REACTION*

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Summary

The molybdenum acetyl complexes *trans*-(h^5-C_5H_5)Mo(CO)$_2$(L)COCH$_3$ (L = a tertiary phosphine) are thermally decarbonylated in a variety of solvents to the corresponding methyl derivatives (h^5-C_5H_5)Mo(CO)$_2$(L)CH$_3$. Reaction rates are independent of the solvent employed but depend markedly on the nature of the phosphorus ligand. At 60° in acetonitrile the observed order of relative rates is P(cyclo-C_6H_{11})$_3$ (fastest) $>$ P(C_6H_5)$_2$ (i-C_3H_7) $>$ P(C_6H_5)$_3$ $>$ P(*p*-$CH_3C_6H_4$)$_3$ $>$ P(*p*-$CH_3OC_6H_4$)$_3$ $>$ P(C_6H_5)$_2$CH$_3$ $>$ P(i-C_4H_9)$_3$ $>$ P(C_6H_5)-(CH$_3$)$_2$ $\gg$ P(n-C_4H_9)$_3$ (slowest). These data demonstrate that the rate of decarbonylation is dominated by the steric bulk of the phosphorus ligand, with σ-donor and π-acceptor properties playing only a minor role. A study of the temperature dependence of the reaction rates of the triphenyl- and tri-n-butylphosphine acetyls yielded activation parameters suggesting that dissociation of a terminal CO is the rate-limiting step.

Introduction

Complexes of the general formula CpMo(CO)$_3$R (Cp = h^5-C_5H_5, R = alkyl group) react with phosphines or phosphites to yield acyl derivatives of the general formula CpMo(CO)$_2$(L)COR [1—8] in which a coordinated carbon monoxide ligand has formally been "inserted" into the molybdenum—carbon σ-bond [9]. Kinetic studies [4—6, 8] of these reactions have shown them to be first order in the molybdenum alkyl and independent of the nature and concentration of the phosphorus ligand. Only in non-polar solvents with strongly basic phosphines does a second order term appear in the rate law [4, 5, 8].

The decarbonylation reactions of the CpMo(CO)$_2$(L)COCH$_3$ complexes to afford the corresponding σ-methyl derivatives CpMo(CO)$_2$(L)CH$_3$ are quite different, their relative rates showing a marked dependence on the nature of the

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*For a preliminary communication of portions of this work see ref. 1.

phosphorus ligand and virtually no effect of solvent [1, 7]. Herein we report details of our study of these reactions and discuss mechanisms consistent with the ligand effects and product stereochemistry observed.

Experimental

All operations were conducted under nitrogen or argon atmospheres, including admission of argon to evacuated flasks. Acetonitrile and benzene were distilled under argon from phosphorus pentoxide and sodium, respectively, and stored over Linde 3A Molecular Sieves. h^5-$C_5H_5Mo(CO)_3CH_3$ was prepared by the standard method [10]. Phosphorus ligands were purchased from Strem Chemical Company, Danvers, Massachusetts and used as received. The complexes *trans*-$CpMo(CO)_2(L)COCH_3$ were prepared by direct reaction of the appropriate phosphorus ligand and $CpMo(CO)_3CH_3$ in acetonitrile at room temperature for 2—3 h [5]. Recrystallization from chloroform/hexane routinely afforded 75—85% yields of the acetyl complexes, which were shown by infrared and proton NMR spectroscopy to be identical to the complexes previously prepared [3—5, 7]. The methyl complexes resulting from decarbonylation were similarly characterized after chromatography from alumina with chloroform/hexane (1/4) eluent. Proton NMR data for the complexes studied are collected in Table 1.

The kinetics of the decarbonylations were followed by observing the disappearance and appearance of the C_5H_5 proton resonances of the acetyl and methyl complexes, respectively. The reactions were carried out at 60 ± 0.5° under a slow flow of argon and aliquots were syringed from the reaction vessel at appropriate intervals. The rate constants obtained in this manner are shown in Table 2, the reported values being the average of two or more runs and accurate to ± 5.0%.

TABLE 1

PROTON NMR DATA FOR $C_5H_5Mo(CO)_2(L)R$ COMPLEXES[a]

L	R	$\delta(C_5H_5)^b$	$\delta(CH_3)^c$
$P(C_6H_5)_3$	$COCH_3$	5.03	2.62
$P(C_6H_5)_3$	CH_3	4.74	0.50 (d, J(PH) 4)
$P(p\text{-}CH_3C_6H_4)_3$	$COCH_3$	5.16	2.75
$P(p\text{-}CH_3C_6H_4)_3$	CH_3	4.70	0.31 (d, J(PH) 6)
$P(p\text{-}CH_3OC_6H_4)_3$	$COCH_3$	5.07	2.63
$P(p\text{-}CH_3OC_6H_4)_3$	CH_3	4.73	0.40 (d, J(PH) 4)
$P(n\text{-}C_4H_9)_3$	$COCH_3$	5.13	2.60
$P(n\text{-}C_4H_9)_3$	CH_3	4.90[d]	0.28 (d, J(PH) 3)[d]
$P(C_6H_{11})_3$	$COCH_3$	5.20	2.55
$P(C_6H_{11})_3$	CH_3	4.87	0.14 (d, J(PH) 5)
$P(i\text{-}C_4H_9)_3$	$COCH_3$	5.11	2.58
$P(i\text{-}C_4H_9)_3$	CH_3	4.92	0.29 (d, J(PH) 4)
$P(C_6H_5)_2CH_3$	$COCH_3$	5.00	2.70
$P(C_6H_5)_2CH_3$	CH_3	4.71	0.35 (d, J(PH) 5)
$P(C_6H_5)(CH_3)_2$	$COCH_3$	4.98	2.58
$P(C_6H_5)(CH_3)_2$	CH_3	4.72[e]	0.23 (d, J(PH) 4)[e]
$P(C_6H_5)_2(i\text{-}C_3H_7)$	$COCH_3$	4.83	2.63
$P(C_6H_5)_2(i\text{-}C_3H_7)$	CH_3	4.52	0.40 (d, J(PH) 4)

[a] All spectra determined in $CDCl_3$ solvent. Chemical shifts in ppm downfield from internal TMS. *J* in Hz. [b] C_5H_5 resonances all appear as doublets, *J(PH)* 1.5—2.0 Hz, unless otherwise noted. [c] Acetyl protons are sharp singlets. For methyl complexes doublets are observed. [d] *Cis* isomer, $\delta(C_5H_5)$ 5.20, singlet; $\delta(CH_3)$ 0.05, *J*(PH) 9.0 Hz. [e] *Cis* isomer, $\delta(C_5H_5)$ 5.10, singlet; $\delta(CH_3)$ —0.20, *J*(PH) 12.0 Hz.

Within experimental error, identical values were obtained using benzene or tetrahydrofuran solvents and control experiments indicated no effect of normal laboratory light on the rate constants. The rate of escape of carbon monoxide from the reaction solvent does not affect the value of k_{obs}, as identical values were obtained whether the reactions were conducted under an argon atmosphere or with argon being bubbled through the reaction mixture. Non-weighted least-squares plots of log[$CpMo(CO)_2(L)COCH_3$] vs. time were linear for at least two half-lives in all cases, correlation coefficients ranging from −0.987 to −0.998. To inhibit dissociation of the acetyl complexes to $CpMo(CO)_3CH_3$ and L (Table 3) kinetic runs were conducted in the presence of a 10-fold molar excess of the ligand. Control experiments with varying amounts of added ligand demonstrated that the rate constants for disappearance of $CpMo(CO)_2(L)COCH_3$ and appearance of $CpMo(CO)_2(L)CH_3$ were identical within experimental error and independent of [$CpMo(CO)_3CH_3$] and [L].

Values of K_{eq} and percent dissociation pertaining to eq. 3 are given in Table 3. These data were determined by heating $CpMo(CO)_2(L)COCH_3$ (0.01*M*) in acetonitrile for 1—2 h at 60° and measuring the areas of the C_5H_5 resonances of starting material and $CpMo(CO)_3CH_3$. Equilibrium is established within 10—20 min in all cases. Measurements were made before the onset of decarbonylation and are accurate to within ± 10%.

Activation parameters (Table 4) were obtained for the decarbonylation of the triphenyl- and tri-n-butylphosphine acetyls by measuring k at three temperatures and plotting log k vs. $1/T$. Least-squares lines for the resultant data (average of three determinations at each temp.) gave correlation coefficients of −0.9997 in both cases. Error analyses on $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were performed by the methods of Benson [11] using one standard deviation. Rate constants are accurate to ± 5.0% and temp. to ± 0.1°.

The complex $CpMo(CO)_2[P(C_6H_5)(CH_3)_2]COCH_3$ specifically labled in the acetyl CO was prepared from $Na^+[CpMo(CO)_2[P(C_6H_5)(CH_3)_2]^-$ and 1-^{14}C-acetyl chloride (Mallinckrodt), in an attempt to determine unequivocally whether a terminal or an acyl CO is lost on decarbonylation. This experiment was unsuccessful, however, owing to rapid scrambling of the label among the terminal and acetyl groups at 60°.

Results and discussion

The kinetics of the carbon monoxide insertions given by eq. 1 (L = a trivalent phosphine) have been studied by several groups of workers [4—6, 8], using infrared spectroscopy. As we have previously noted [1, 7] the decarbonyl-

$$CpMo(CO)_3CH_3 + L \rightarrow CpMo(CO)_2(L)COCH_3 \qquad (1)$$

$$CpMo(CO)_2(L)COCH_3 \rightarrow CpMo(CO)_2(L)CH_3 + CO \qquad (2)$$

ation reactions (eq. 2) cannot be followed accurately by this method due to the near coincidence of the terminal CO stretching frequencies of reactants and products. However, the C_5H_5 proton NMR resonances of the *trans*-acetyl and -methyl complexes differ uniformly by 0.3—0.4 ppm (Table 1) and integration of spectra of aliquots taken from reaction mixtures at appropriate time intervals

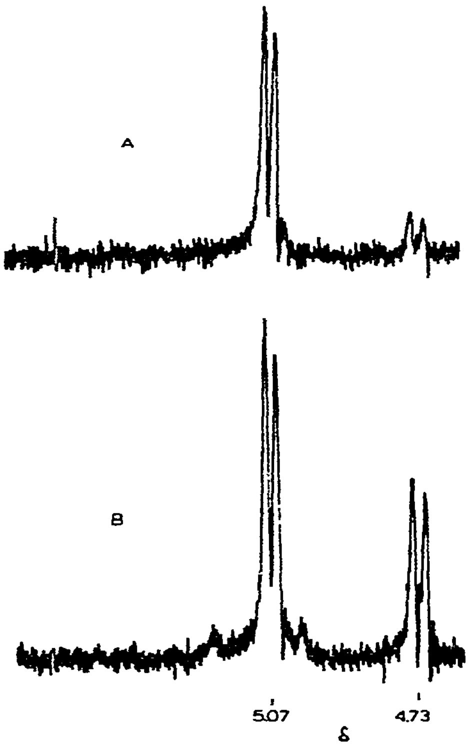

Fig. 1. Proton NMR spectrum of the C_5H_5 region of the $CpMo(CO)_2[P(p\text{-}C_6H_4OCH_3)_3]COCH_3$ reaction mixture as a function of time: A = 3 h, B = 12 h. The resonances at δ 5.07 and 4.73 ppm correspond to starting material and product, respectively (see Table 1).

yields directly the extent of reaction. For the complexes containing $P(n\text{-}C_4H_9)_3$ and $P(C_6H_5)(CH_3)_2$ ligands, small quantities of the *cis*-methyl complexes were observed, but the C_5H_5 chemical shifts were sufficiently different from the *trans*-acetyl and -methyl complexes to allow integration (Table 1). Spectra of the C_5H_5 region for the $CpMo(CO)_2[P(p\text{-}C_6H_4OCH_3)_3]COCH_3$ system as a function of time are shown in Fig. 1.

In Table 2 are presented kinetic data for these decarbonylations as a function of the phosphorus ligand. The observed first order rate constants depend markedly on the nature of the organic groups attached to phosphorus, the rate constants decreasing in the order $P(cyclo\text{-}C_6H_{11})_3 > P(C_6H_5)_2(i\text{-}C_3H_7) > P(C_6H_5)_3 > P(p\text{-}CH_3C_6H_4)_3 > P(p\text{-}CH_3OC_6H_4)_3 > P(C_6H_5)_2CH_3 > P(i\text{-}C_4H_9)_3 > P(C_6H_5)(CH_3)_2 \geqslant P(n\text{-}C_4H_9)_3$.

The observed order of rates demonstrates that steric rather than electronic effects are dominant in these reactions. This fact is most evident from the positions of the tricyclohexyl- and tri-n-butylphosphine acetyls at opposite ends of the reactivity series. While the donor-acceptor properties of these two ligands should be virtually identical [12, 13], the $P(cyclo\text{-}C_6H_{11})_3$ ligand is considerably more sterically demanding [14]. The decrease in decarbonylation rates of $CpMo(CO)_2(L)COCH_3$ as L is varied from $P(C_6H_5)_3$ to $P(C_6H_5)_2CH_3$ to

TABLE 2

RATE CONSTANTS FOR THE DECARBONYLATION REACTION
$C_5H_5Mo(CO)_2(L)COCH_3 \rightarrow C_5H_5Mo(CO)_2(L)CH_3 + CO$[a]
(60°, CH_3CN solvent)

L	$k(\times 10^6)$[b] (sec^{-1})
$P(C_6H_5)_3$	13.2[c]
$P(p\text{-}C_6H_4CH_3)_3$	10.9
$P(p\text{-}C_6H_4OCH_3)_3$	9.6
$P(C_6H_5)_2CH_3$	6.8
$P(C_6H_5)(CH_3)_2$	3.6
$P(n\text{-}C_4H_9)_3$	3.9
$P(i\text{-}C_4H_9)_3$	5.6
$P(C_6H_{11})_3$	46.4
$P(C_6H_5)_2(i\text{-}C_3H_7)$	23.9

[a] Rate constants determined by monitoring disappearance and appearance of C_5H_5 resonances of starting material and product, respectively: Varian Associates T-60 Spectrometer. Reported values are averages of two or more runs, with a reproducibility of ± 5%. [b] A five to ten molar excess of ligand was employed to inhibit dissociation (Table 3). Rate constants independent of [L] and [h^5-$C_5H_5Mo(CO)_3CH_3$]. [c] Under the same conditions but with benzene solvent, a value of 14.0 is obtained. Essentially identical values are obtained with hexane and THF solvents.

$P(C_6H_5)(CH_3)_2$ is also a result of decreasing bulk of the organic substituents on phosphorus. This is shown clearly by the much faster decarbonylation of $P(C_6H_5)_2(i\text{-}C_3H_7)$ relative to any of the above ligands. This result is entirely inconsistent with a major role for electronic effects. The latter cannot be dismissed entirely, however, as shown by the differing rates of the *para*-substituted triaryl phosphines (Table 1). Both $P(p\text{-}CH_3C_6H_4)_3$ and $P(p\text{-}CH_3OC_6H_4)_3$ [13, 15] are considerably more basic than $P(C_6H_5)_3$ and this is reflected to a slight extent in the slower decarbonylations of the *p*-tolyl and *p*-anisyl complexes. In this light it seems likely that there is some small contribution from ligand basicity to the observed rate differences in the mixed phenyl/methyl phosphines discussed above.

We considered that a comparison of the decarbonylation rates of acetyl complexes containing $P(p\text{-}C_6H_4CH_3)_3$ and $P(o\text{-}C_6H_4CH_3)_3$ ligands would prove conclusively our postulate of steric control, as these ligands should be identical with respect to electronic properties. Such a comparison is not possible, however, as all attempts at synthesizing $CpMo(CO)_2[P(o\text{-}C_6H_4CH_3)_3]COCH_3$ have failed. Likewise, $CH_3Mn(CO)_5$ [17], $CpMo(CO)_3Cl$ [18] and $CpMo(CO)_3Br$ [18] fail to react with tri(*o*-tolyl)phosphine, suggesting that the great steric bulk of the ligand precludes the existence of complexes of relatively high coordination number. This is consistent with the data of Tolman which show $P(o\text{-}C_6H_4CH_3)_3$ to be the most sterically demanding of the ligands included in our study [14].

Figure 2 shows a plot of k_{obs} for the decarbonylation rates vs. ligand cone angle [14], defined as the minimun angle swept at the metal by the freely rotating ligand. Cone angles for the mixed phenyl/alkyl phosphines were calculated by using the weighted sum of the corresponding angles for the symmetrically trisubstituted phosphines, e.g. $\theta\ P(C_6H_5)_2CH_3 = 2/3\theta\ P(C_6H_5)_3 + 1/3\theta\ P(CH_3)_3$*

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* The angles calculated by this method agree quite well with the angles measured by the method of ref. 14. See ref. 16.

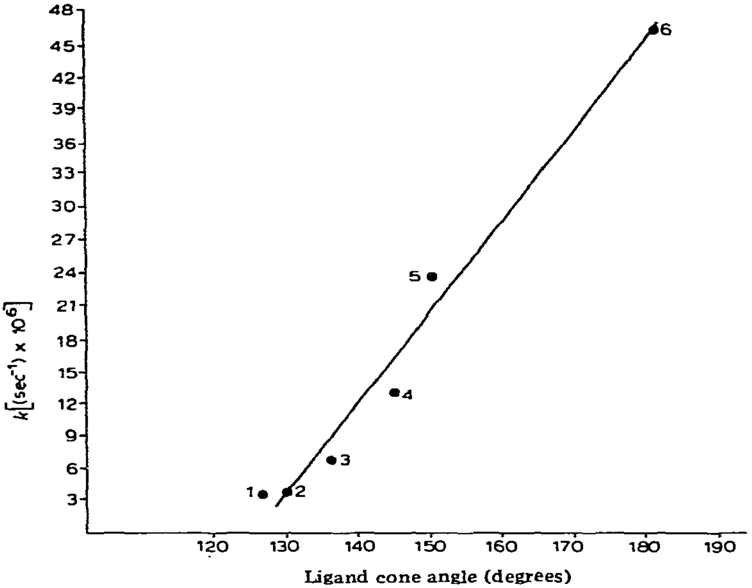


Fig. 2. Correlation of decarbonylation rate constants (Table 2) with ligand cone angles [14, 16]: 1, $P(C_6H_5)(CH_3)_2$; 2, $P(n\text{-}C_4H_9)_3$; 3, $P(C_6H_5)_2CH_3$; 4, $P(C_6H_5)_3$; 5, $P(C_6H_5)_2(i\text{-}C_3H_7)$; 6, $P(C_6H_{11})_3$.

It is readily apparent from Fig. 2 that a good correlation exists between the observed decarbonylation rate and the steric bulk of the ligand as measured by its cone angle. No such correlation with ligand basicity is found.

A potentially complicating feature of the decarbonylation kinetics is the tendency of the complexes to dissociate at 60° according to eq. (3).

$$CpMo(CO)_2(L)COCH_3 \rightleftharpoons CpMo(CO)_3CH_3 + L \qquad (3)$$

The percent dissociation and equilibrium constants for these reactions are shown in Table 3. As with the decarbonylation kinetics, these data are consistent with phosphine bulk being the determining factor. That there is no significant production of $CpMo(CO)_2(L)CH_3$ directly from $CpMo(CO)_3CH_3$ and the phosphorus ligand is shown by the fact that the rate constants for disappearance of $CpMo(CO)_2(L)COCH_3$ and appearance of $CpMo(CO)_2(L)CH_3$ are identical in all cases. These rate constants are also independent of the concentrations of $CpMo(CO)_3CH_3$ and L (See Experimental).

There is considerable mechanistic precedent [9] for loss of terminal rather than acyl carbon monoxide in the decarbonylation of acyl complexes of iron [19], manganese [20] and cobalt [21]. We have synthesized $CpMo(CO)_2$-$[P(C_6H_5)(CH_3)_2]$—$^{14}COCH_3$ and investigated the fate of the label in an attempt to further substantiate this seemingly general reaction pathway. Unfortunately the equilibrium given by eq. (3) is established extremely rapidly relative to the described decarbonylation and complete randomization of label in both the starting acyl complex and the product was observed.

The activation enthalpies obtained from the decarbonylations of the triphen-

TABLE 3

PERCENTAGE DISSOCIATION AND EQUILIBRIUM CONSTANTS FOR THE REACTION:
$C_5H_5Mo(CO)_2(L)COCH_3 \rightleftharpoons C_5H_5Mo(CO)_3CH_3 + L$

L	k_{eq}(60°)(X 10^4)[a]	Dissociation (%)
$P(C_6H_5)_3$	8.3	25
$P(p\text{-}C_6H_4CH_3)_3$	6.1	20
$P(p\text{-}C_6H_4OCH_3)_3$	5.3	20
$P(o\text{-}C_6H_4CH_3)_3$		100
$P(C_6H_{11})_3$	50	50
$P(n\text{-}C_4H_9)_3$	0.3	5
$P(C_6H_5)_2CH_3$	1.3	10
$P(C_6H_5)(CH_3)_2$	0.1	3
$P(C_6H_5)_2(i\text{-}C_3H_7)$	90	60

[a] Determined by heating h^5-$C_5H_5Mo(CO)_2(L)COCH_3$ (0.01*M*) in acetonitrile for 1—2 hours and measuring the areas of the C_5H_5 resonances of starting material and h^5-$C_5H_5Mo(CO)_3CH_3$. Values are accurate to within ± 10%.

yl- and tributylphosphine complexes (Table 4) are consistent with values obtained for dissociative reactions of a variety of similar metal carbonyl complexes [22—24] and suggest that loss of a terminal CO is the rate limiting step in the present systems. The positive activation entropies obtained are also consistent with a dissociative process, but their small absolute values discourage us from drawing firm conclusions on this basis. It should be pointed out that the absence of solvent polarity effects observed in the present study is strongly indicative of a dissociative mechanism [22, 24, 25].

The mechanism shown in Scheme 1 is consistent with the observed steric and electronic effects as a function of the phosphorus ligand, with the activation parameters obtained, and the absence of solvent effects. Increasing bulk of the phosphorus ligand should favor dissociation of CO to afford the postulated coordinatively unsaturated intermediate. Increasing basicity of the phosphine could inhibit CO dissociation by forcing greater Mo→CO backbonding. Migration of the methyl group away from the bulky phosphine (path a) affords the *trans*-methyl complex which is the dominant product of all the reactions studied. Small quantities (8—12%) of the *cis*-methyls are observed in the cases where L = $P(n\text{-}C_4H_9)_3$ and $P(C_6H_5)(CH_3)_2$, indicating that path b may be important when L is sterically nondemanding. In the latter systems the *cis*- and *trans*-methyl complexes are formed at the same rate, indicative of a common

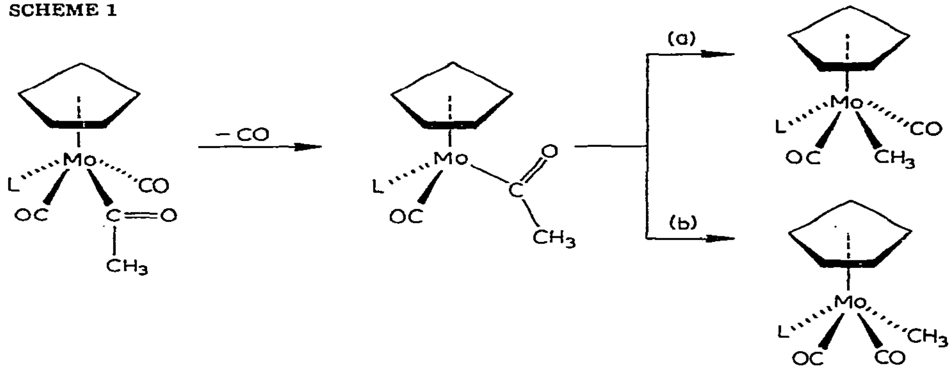
TABLE 4

DECARBONYLATION ACTIVATION PARAMETERS
$CpMo(CO)_2(L)COCH_3 \rightarrow CpMo(CO)_2(L)CH_3 + CO$

L	Temp. (°C)	k(X 10^6) (sec^{-1})	$\Delta H^{\ddagger}$ (Kcal/mole)	$\Delta S^{\ddagger}$ (cal/deg.mole)
$P(C_6H_5)_3$	50.2	2.8	29.3 ± 1.0	4.2 ± 3.0
$P(C_6H_5)_3$	60.4	13.5		
$P(C_6H_5)_3$	70.0	34.1		
$P(n\text{-}C_4H_9)_3$	50.0	0.90	30.3 ± 1.0	7.4 ± 3.0
$P(n\text{-}C_4H_9)_3$	60.2	3.80		
$P(n\text{-}C_4H_9)_3$	70.2	14.4		

intermediate or extremely rapid *cis*—*trans* equilibration if one of the isomers is formed preferentially.

SCHEME 1



While the above mechanism is consistent with our observations, we are unable to rigorously exclude other possible pathways. Expulsion of a terminal CO with concomitant methyl migration remains a distinct possibility. We consider less likely the intermediacy of *cis*-acetyl complexes although they could be present in concentrations below the detection limits of our techniques. Thus while the $[CpMo(CO)_2P(C_6H_5)(CH_3)_2]^-$ anion affords a 10/90 mixture of *cis*- and *trans*-methyl complexes when treated with methyl iodide, no *cis*-acetyl complex was observed in the corresponding reaction with acetyl chloride. It should be borne in mind, however, that Cotton and Lukehart [26] have observed unstable *cis*-acyls of the type $CpMo(CO)_2[P(C_6H_5)_3]CO(CH_2)_nBr$ which subsequently isomerize to the thermodynamically favored *trans*-isomer or cyclize to cationic carbene complexes having *cis*-stereochemistry.

Acknowledgements

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