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Preliminary communication

Steric and electronic effects in molybdenum(II) acetyl complexes

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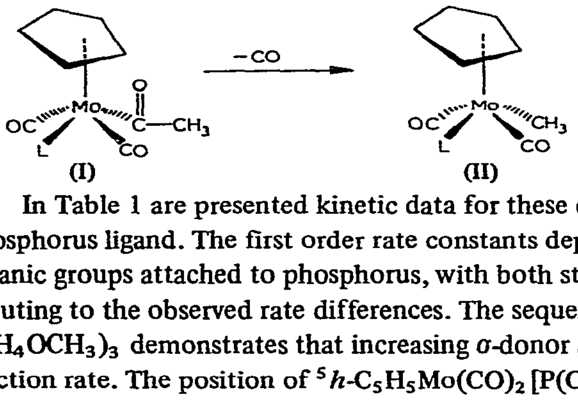
In a recent paper Tolman[1] has shown that ligand dissociations in NiL_4 complexes (L = a tertiary phosphine or phosphite) and the degree of substitution of L into $Ni(CO)_4$ to afford $Ni(CO)_nL_{4-n}$ are dominated by steric, rather than electronic considerations. It was suggested that steric interactions would be of even greater importance in complexes of higher coordination number. We have noted previously that the rates of the decarbonylations I → II depend qualitatively upon the phosphorus ligand L[2,3]. Herein are reported data which suggest that this ligand dependence is largely steric in origin, consistent with the predictions of Tolman*.



(I) (II)

In Table 1 are presented kinetic data for these decarbonylations as a function of the phosphorus ligand. The first order rate constants depend markedly on the nature of the organic groups attached to phosphorus, with both steric and electronic factors contributing to the observed rate differences. The sequence $P(C_6H_5)_3 > P(p\text{-}C_6H_4CH_3) > P(p\text{-}C_6H_4OCH_3)_3$ demonstrates that increasing σ-donor ability of the phosphine retards the reaction rate. The position of ^5h-$C_5H_5Mo(CO)_2[P(C_6H_{11})_3]COCH_3$ at the high end of the reactivity scale suggests, however, that steric considerations dominate the decarbonylation rates, with electronic effects playing only a minor role. That the bulk of the phosphorus ligand is of overriding importance is attested to by the relative decarbonylation rates of the tricyclohexyl- and tri-n-butylphosphine derivatives, which differ by more than an order of magnitude. The σ-donor and π-acceptor properties of these ligands should be virtually equal[6,7], but the $P(C_6H_{11})_3$ ligand is considerably more sterically demanding

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*For additional discussion of possible steric effects in complexes of the formula ^5h-$C_5H_5Mo(CO)_2(L)X$ see references 4 and 5.

TABLE 1

$C_5H_5Mo(CO)_2(L)COCH_3 \rightarrow C_5H_5Mo(CO)_2(L)CH_3 + CO^a$
(60°, CH_3CN solvent)

L	k(sec^{-1} (× 10^6))^{b,c}
$P(C_6H_5)_3$	13.2
$P(p\text{-}C_6H_4CH_3)_3$	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
$P(C_6H_{11})_3$	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 resonance 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] Rates in benzene are identical, precluding solvent assistance in the decarbonylations. [c] A five to ten molar excess of ligand was employed to inhibit dissociation (Table 2). Rate constants independent of [L] and [$^5h\text{-}C_5H_5Mo(CO)_3CH_3$].

Similarly, the decrease in decarbonylation rates of $^5h\text{-}C_5H_5Mo(CO)_2(L)COCH_3$ as L is varied from $P(C_6H_5)_3$ to $P(C_6H_5)_2CH_3$ to $P(C_6H_5)(CH_3)_2$ could be interpreted solely in terms of increasing basicity of L. That this interpretation is incorrect is shown by the fact that $^5h\text{-}C_5H_5Mo(CO)_2[P(C_6H_5)_2(i\text{-}C_3H_7)]COCH_3$ decarbonylates twice as fast as the triphenylphosphine complex and four times as fast as the diphenylmethylphosphine compound (Table 1). This observation is entirely inconsistent with electronic effects and can only be rationalized in terms of the greater size of the isopropyl group relative to phenyl or methyl.

We considered that a comparison of the decarbonylation rates of the 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 attempts at synthesizing $^5h\text{-}C_5H_5Mo(CO)_2[P(o\text{-}C_6H_4CH_3)_3]COCH_3$ from $^5h\text{-}C_5H_5Mo(CO)_3CH_3$ and the ligand were unsuccessful, even under conditions considerably more vigorous than those required for producing the other acetyl complexes. This suggests that the complex is so crowded as to preclude its existence, consistent with the data of Tolman[1] which show $P(o\text{-}C_6H_4CH_3)_3$ to be the most sterically demanding of the ligands included in our study.

Values of K_{eq} at 60° in acetonitrile for the equilibrium below are shown in Table 2. Equilibrium is established within 15–20 minutes in all cases,

$$^5h\text{-}C_5H_5Mo(CO)_2(L)COCH_3 \rightleftharpoons {}^5h\text{-}C_5H_5Mo(CO)_3CH_3 + L$$

with no evidence of decomposition. All measurements were made before the onset of decarbonylation. The largest values of K_{eq} (highest degree of dissociation) are exhibited

TABLE 2

$C_5H_5Mo(CO)_2(L)COCH_3 \rightleftarrows C_5H_5Mo(CO)_3 + L$

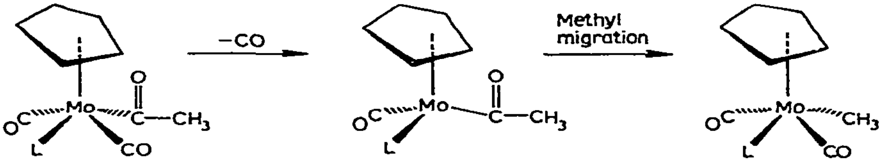
L	K_{eq} (60°) (× 10^4)[a]	
$P(C_6H_5)_3$	8.3	(25% dissoc.)
$P(p\text{-}C_6H_4CH_3)_3$	6.1	(20% dissoc.)
$P(p\text{-}C_6H_4OCH_3)_3$	5.3	(20% dissoc.)
$P(o\text{-}C_6H_4CH_3)_3$		100% dissoc.
$P(C_6H_{11})_3$	50	(50% dissoc.)
$P(n\text{-}C_4H_9)_3$	0.3	(5% dissoc.)
$P(C_6H_5)_2CH_3$	1.3	(10% dissoc.)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

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

by the more crowded acetyl complexes (containing the bulkiest ligands), and the overall trend correlates well with the observed decarbonylation rates. Although the close agreement between the trends in K_{eq} and k_{decarb} may in part be fortuitous, we consider nonetheless that the former provide a valid measure of the crowding in the acetyl complexes[1] and that this is the dominant force at work in causing the observed rate differences.

The decarbonylation reactions are first order in acetyl complex concentration for at least four half lives and rate constants for disappearance of ^5h-$C_5H_5Mo(CO)_2(L)$-$COCH_3$ and appearance of ^5h-$C_5H_5Mo(CO)_2(L)CH_3$ are identical within experimental error. Rate constants for the formation of (II) are unaffected by the concentrations of phosphorus ligand or ^5h-$C_5H_5Mo(CO)_3CH_3$, precluding a significant role for the latter complex in product formation.

In light of these results we propose the dissociative mechanism below, which is consistent with both the steric and electronic effects observed. Increasing size of L should favor dissociation of carbon monoxide to afford the postulated coordinatively



unsaturated intermediate. Increasing basicity of the phosphine could inhibit dissociation of CO by forcing greater Mo→CO back-bonding. The observation of purely *trans*-^5h-C_5H_5-$Mo(CO)_2(L)CH_3$* products could reasonably result from preferential migration of CH_3

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*The assignments of *trans* stereochemistry to all the complexes in this study are based upon and consistent with the criteria set forth by Faller[4] and Mawby[8].

away from the phosphorus ligand, toward the smaller carbon monoxide.

Labeling studies to test the validity of the suggested mechanism and investigations of related chromium and tungsten systems are in progress and will be reported shortly.

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