Preliminary communication

OCTAHEDRAL METAL CARBONYLS

IL*. RATES OF COMBINATION OF PYRIDINE WITH FIVE-COORDINATE SPECIES PRODUCED FROM SUBSTITUTED OCTAHEDRAL METAL CARBONYLS VIA M—CO BOND FISSION

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Summary

Rates of combination of pyridine (py) with five-coordinate species formed via laser flash photolytic M—CO bond fission in (diphos)Mo(CO)$_4$ (diphos = 1,2-bis-(diphenylphosphino)ethane) and (P-en)W(CO)$_4$ (P-en = ethylenediphosphine) in cyclohexane have been determined at room temperature. Free energies of activation for these processes and for those involving Cr(CO)$_6$, previously reported, are ca. 2—5 kcal/mol. The results indicate that transition states leading to formation of combination products closely resemble the intermediates, as has been inferred through ligand-competition studies in related systems.

Ligand-exchange reactions of octahedral metal carbonyls which involve carbonyl replacement, e.g.,

$$L_x M(CO)_{6-x} + L' \rightarrow L_x L'M(CO)_{5-x} + CO \tag{1}$$
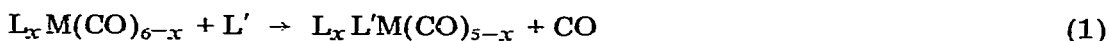
($x = 1, 2$; L, L' = Lewis base)

usually proceed via unimolecular fission of a M—CO bond [2]. Consequently, a five-coordinate intermediate, probably square-pyramidal, is produced. Evidence thus far accumulated supports fission of a M—CO bond *trans* to another CO in the substrates [1, 3—6]. The ligand-exchange product thus is formed through combination of the intermediate with L' (eq. 1).

The determination of the rates of combination of such five-coordinate species with Lewis bases is of great importance, since, through use of Hammond's postulate [7], they permit an evaluation of the nature of transition states leading

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*For part XXXXVIiI see ref. 1.
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TABLE 1

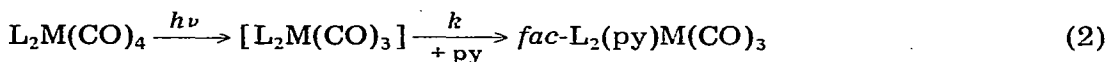RATES OF COMBINATION OF FIVE-COORDINATE INTERMEDIATES WITH NUCLEOPHILES (L)

Intermediate	L	10^{-6} k (M^{-1} sec^{-1}) (vacuum-degassed)	10^{-6} k (M^{-1} sec^{-1}) (Ar-bubbling)
[Cr(CO)$_5$] [a]	C$_6$H$_6$	7.0	
	Et$_2$O	11.0	
	MeOH	31	
	EtOCOEt	92	
	Me$_2$CO	130	
	CH$_3$CN	160	
[(P-en)W(CO)$_3$]	py	2.60 ± 0.10	2.79 ± 0.20
[(diphos)Mo(CO)$_3$]	py	9.47 ± 0.06	12.0 ± 0.4

[a] Data taken from ref. 10.

to product formation. The properties of the intermediates and transition states are of prime importance to the development of a detailed understanding of homogeneous catalytic processes for which the active species is coordinatively-unsaturated.

While there has been reported significant indirect evidence, in the form of the ratios of combination of various nucleophiles with such intermediates, "competition ratios" [8,9], only one investigation, of [Cr(CO)$_5$] [10], has reported bimolecular rate constants for such recombination processes.

Herein are presented bimolecular rate constants, k (eq. 2) for the combination

$$L_2M(CO)_4 \xrightarrow{h\nu} [L_2M(CO)_3] \xrightarrow[+\ py]{k} fac\text{-}L_2(py)M(CO)_3 \qquad (2)$$

of [L$_2$M(CO)$_3$] intermediates (L$_2$ = P-en; M = W; L$_2$ = diphos; M = Mo) with py. These data constitute the first direct measurements of the rates of combination of five-coordinate intermediates derived through M—CO bond fission (eq. 1) for substituted complexes, which can afford stereochemically-distinct reaction products [3].

Substrates, the cyclohexane solvent, and py were rigorously purified. Laser flash photolysis was carried out at 337 nm (N$_2$ laser, 8 ns FWHM) in 1 cm cells utilizing substrate concentrations ca. 5×10^{-4} M and varying concentrations of py (large excess). Spectral changes were monitored at 425 nm (the absorption of the fac-L$_2$(py)M(CO)$_3$ reaction products). Bimolecular rate constants, obtained from plots of the pseudo first-order rate constants, k_{obsd}, vs. [py] were obtained both for vacuum-degassed and Ar-bubbled samples, and are presented in Table 1. Also reported are the bimolecular rate constants for the Cr(CO)$_6$ system, as reported by Koerner von Gustorf and associates [10].

The data, taken among complexes of the three Group VIB metals for substrates exhibiting widely-varying steric and electronic properties, and for differing incoming nucleophiles show bimolecular rate constants varying over less than two orders of magnitude, which correspond to free energies of activation in the range 2.2 to 4.6 kcal/mol*. The results indicate that for these systems, the transition states leading to product formation closely resemble the intermediates from which they are produced regardless of the identity of the metal, or of steric or electronic considerations.

*The diffusion-controlled rate constant in cyclohexane is 6.6×10^9 M^{-1} sec^{-1} [11].

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Acknowledgments

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