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The Mechanism of Facial–Meridional Isomerism in Octahedral Metal Carbonyl Complexes: *fac*-[1,2-bis(diphenylphosphino)ethane](triisopropyl phosphite)tricarbonylmolybdenum(0)*

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(Diphos)Mo(CO)$_4$ (diphos = 1,2-bis(diphenylphosphino)ethane) reacts with Lewis bases (L, phosphines, phosphites, amines) at *ca.* 125 °C in mesitylene solvent to afford, depending upon the identity of L, *fac-* and *mer*-(diphos)(L)Mo(CO)$_3$ products [1]. The reaction has been found to proceed *via* rate-determining fission of Mo–CO bonds [2], and recent ^{13}CO labeling studies have shown that initial loss of CO occurs *cis* to diphos, and that the five-coordinate [(diphos)Mo(CO)$_3$] intermediate formed through Mo–CO bond-breaking, probably square-pyramidal [3], is fluxional [4].

Reactions of (diphos)Mo(CO)$_4$ with P(OPr^i)$_3$ or PPh$_3$ at 125 °C in mesitylene afford exclusively the *mer* products. However, reactions of *fac*-(diphos)(cyclohexylamine)Mo(CO)$_3$ with these ligands at 25 °C afford only the *fac*-diphos)(L)Mo(CO)$_3$ products. Thus, under these milder reaction conditions, the five-coordinate intermediate formed through dissociation of cyclohexylamine is non-fluxional.

A qualitative study of the reaction of *fac*-(diphos)[P(OPr^i)$_3$]Mo(CO)$_3$ with L′ which form *mer*-(diphos)(L′)Mo(CO)$_3$ products in their reactions with (diphos)Mo(CO)$_4$ (L′ = PBu$^n{}_3$, P(OPh)$_3$) has revealed that ligand substitution also takes place rapidly compared to isomerization. Thus the kinetics of isomerization of that substrats, reported in this communication, study the isomerization of the five-coordinate intermediate formed through dissociation of P(OPr^i)$_3$.

Rate data for (1) were obtained by monitoring the disappearance of the A′(2) carbonyl stretching mode of the substrate (C$_s$ symmetry) [5] at 1950 cm^{-1} (xylene solvent) under pseudo first-order reaction conditions (at least a ten-fold excess of P(OPr^i)$_3$) employing techniques which have been described previously [2, 6]. The rate data (Table) support a rate law,

$$fac\text{-(diphos)[P(OPr}^i)_3]\text{Mo(CO)}_3 \longrightarrow mer\text{-(diphos)[P(OPr}^i)_3]\text{Mo(CO)}_3 \qquad (1)$$

$$-d[S]/dt = k[S] \qquad (2)$$

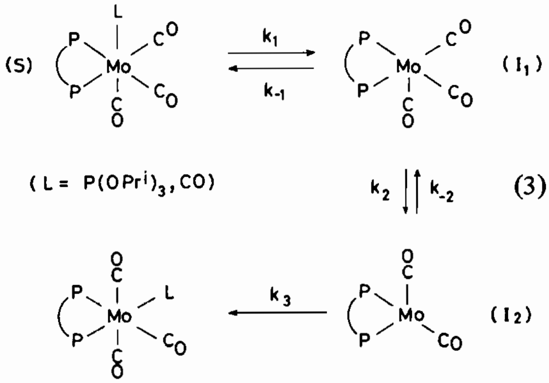
TABLE. Rates and Activation Parameters for Facial–Meridional Isomerization of (Diphos)[P(OPr^i)$_3$]Mo(CO)$_3$ in Mesitylene Solvent at Various Temperatures.^{a}

Temperature (°C)	[P(OPr^i)$_3$] (*M*)	$10^4 \cdot k_{obsd}$ (sec^{-1})	$10^4 \cdot \bar{k}$ (sec^{-1})
90.4	0.0803	0.94(1)	
	0.3809	0.89(1)	0.92(2)
94.7	0.0538	1.49(1)	
	0.1236	1.49(2)	
	0.2174	1.43(1)	
	0.3604	1.42(1)	
	0.5230	1.39(2)	1.44(4)
100.8	0.0518	2.90(3)	
	0.2007	2.73(3)	
	0.4649	2.86(1)	2.83(7)
105.4	0.0765	4.35(5)	
	0.0855	4.44(4)	
	0.0893	4.15(3)	
	0.0904	4.25(4)	
	0.2116	3.99(3)	
	0.4669	4.34(6)	
	0.9246	3.97(4)	4.21(17)

$\Delta H^* = 27.4(11)$ kcal/mol; $\Delta S^* = -4.1(30)$ cal/deg-mol

*Limits of error (shown in parentheses): one standard deviation.

Given the generalized mechanism



(3)

the rate law,

$$-d[S]/dt = k_1k_2k_3/\{(k_{-1}k_{-2} + k_2k_3) + k_{-1}k_3[L]\} \qquad (4)$$

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is applicable under the assumption of steady-state concentrations of intermediates ($3\text{-}I_1$) and ($3\text{-}I_2$).

Since the rate of isomerization is independent of the concentration of $P(OPr^i)_3$, the rate of ligand-substitution is fast relative to the rate of isomerization, the Eyring plot for rate data at four temperatures is linear and assuming, on the basis of steric requirements imposed in the reaction of L with the two intermediates that $k_3 \gtrsim k_{-1}$ [7], it can be demonstrated that the pseudo first order rate constant k_{obsd} (= k, Eq. 1) is $k_1k_2k_3/k_{-1}k_{-2}$ and that $k_{-2} \gg k_3 \gtrsim k_{-1} \gg k_2$.

A comparison of rates and activation parameters for (1) and for the reaction of $(diphos)Mo(CO)_4$ with L to afford *mer*-$(diphos)(L)Mo(CO)_3$ indicates that the $\Delta H^{\neq}$ values, which refer to unimolecular Mo–CO bond-breaking in $(diphos)Mo(CO)_4$, and include unimolecular Mo–L bond-breaking in *fac*-$(diphos)(L)Mo(CO)_3$, are significantly different (Table), although directly comparable; in both substrates a bond *cis* to the diphos P's is broken, and each process leads to the formation of the same intermediate. Thus, given that Mo–P bond-breaking is fast compared to isomerization, *i.e.*, $k_1 \gg k_1k_2/k_{-1}$, the Mo–CO (*fac*) bond is > 10 kcal/mol stronger than the Mo–P (*fac*) bond.

The conclusion that $k_{-2} \gg k_2$ provides the first direct kinetic evidence that an intermediate of the type ($3\text{-}I_2$), containing charge-releasing substituents in the equatorial plane of the five-coordinate, square-pyramidal [3] intermediate, is significantly more stable thermodynamically than the intermediate ($3\text{-}I_1$) containing such a substituent in the axial position. This observation is consistent with the Atwood–Brown "site preference" model of the influence of transition-state energies on reactivity in octahedral metal carbonyl systems [8], which predicts just such relative stabilities.

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7 There is evidence that five-coordinate intermediates derived from octahedral metal carbonyl complexes react with Lewis bases *via* highly exothermic processes of low free energy of activation; thus there is little ability of the intermediates to discriminate among nucleophiles. See, *e.g.*, W. D. Covey and T. L. Brown, *Inorg. Chem., 12,* 2820 (1973).

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