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Activation Volume for Ligand Exchange in Labile Tetrahedral Complexes: Triphenylphosphine (TPP) Exchange with CoBr$_2$(TPP)$_2$ by High-Pressure ^{1}H NMR

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Studies of reaction rates at high pressures are being used increasingly to give more insight into reaction mechanisms.[1,2] We have recently reported high-pressure nuclear magnetic resonance studies of nonaqueous solvent exchange[3,4] and ligand exchange[5] on octahedral complexes of transition metals. Using this technique, we investigated the pressure dependence of the rate of triphenylphosphine (TPP) exchange with CoBr$_2$(TPP)$_2$ in deuterated chloroform and obtained a volume of activation of −12.1 cm^3 mol^{-1} at 303 K. This indicates an associative activation mode for this ligand-exchange reaction. To our knowledge, this is the first reported volume of activation for ligand exchange with a labile tetrahedral complex of a divalent transition-metal ion.

Pignolet and Horrocks[6] investigated the temperature dependence of triphenylphosphine exchange with pseudotetrahedral CoBr$_2$(TPP)$_2$ by ^{1}H NMR. Second-order kinetics and a strongly negative entropy of activation also suggest a bimolecular mechanism, proceeding through a pentacoordinate transition state.

The volume of activation ΔV^* expresses the change of volume on going from the reactants to the transition state. It is obtained from the change of the rate constant as a function of pressure through eq 1 given by transition-state theory. In

$$(\partial \ln k/\partial P)_T = -\Delta V^*/RT \qquad (1)$$

our case where no charges are formed or neutralized during the reaction, the electrostrictive contribution to the volume of activation is negligible,[1] and ΔV^* can be directly related to the partial formation, rupture, or stretching of a bond during the activation process. It is clear that in a simple dissociative reaction there is an increase in volume going from reactants to the activated complex ($\Delta V^* > 0$) and vice versa for an associative activation mode ($\Delta V^* < 0$). From the variable-temperature kinetic studies, one thus expects a negative ΔV^*, e.g., an increase of the exchange rate with pressure. The magnitude of the volume of activation is much more difficult to estimate since there is no data available for similar ligand-exchange reactions.[2] A model for dissociative ligand exchange on octahedral complexes has been used with success by Vanni.[7] Predicting values for associative reactions is much more difficult since there is appreciable lengthening of the complex bonds as the activated complex is formed.

CoBr$_2$(TPP)$_2$ was prepared as outlined by Chatt and Shaw.[8] The metal content of the crystalline product was obtained by EDTA titration. The NMR solution was prepared by weight, dissolving the salt and the triphenylphosphine in deuteriochloroform (99.9%, Ciba-Geigy). Me$_4$Si (1%) was added as line width standard. The broadening of the downfield-shifted meta proton resonance was used to obtain the rate data. The data treatment is similar to that of Pignolet and Horrocks.[6] The second-order rate constant k_2, at a given pressure, was obtained by subtracting the transverse relaxation rate in the absence of exchange T_{2m}^{-1} (50 s^{-1} at 303 K, obtained from variable-temperature study) from the observed T_2^{-1} and dividing by the concentration of excess ligand. This is assuming that T_{2m}^{-1} has a negligible pressure dependence, as observed for acetonitrile bound to Ni(II).[4] Concentrations were expressed as molalities, thus avoiding correcting for volume

Table I. Observed T_2^{-1} and Derived Second-Order Rate Constants for Deuteriochloroform Solutions of CoBr$_2$(TPP)$_2$ (0.05 m) with 0.065 Molal Excess TPP (TPP = Triphenylphosphine) at 303 K as a Function of Pressure

pressure, MPa	$1/T_2$, s^{-1}	k_2, s^{-1} kg mol^{-1}	pressure, MPa	$1/T_2$, s^{-1}	k_2, s^{-1} kg mol^{-1}
0.1	139.8	1375	187.0	223.0	2649
33.0	152.4	1568	235.0	243.5	2963
85.0	180.6	2000	265.0	256.0	3155
135.0	204.2	2361			

Table II. Activation Parameters for Triphenylphosphine (TPP) Exchange in Deuteriochloroform Solutions of CoBr$_2$(TPP)$_2$

$$\Delta H^* = 7.7 \pm 0.5 \text{ kcal mol}^{-1} \, {}^a$$
$$\Delta S^* = -19 \pm 3 \text{ cal mol}^{-1} \text{ K}^{-1} \, {}^a$$
$$\Delta V_0^* = -12.1 \pm 0.6 \text{ cm}^3 \text{ mol}^{-1} \, {}^b$$
$$\Delta \beta^* = -(3.3 \pm 0.5) \times 10^{-2} \text{ cm}^3 \text{ mol}^{-1} \text{ MPa}^{-1} \, {}^b$$

^{a} From ref 6. ^{b} Errors are standard deviations.

changes with pressure. The high-pressure NMR probe head used and the "in situ" temperature measurement technique have been described elsewhere.[9,10]

The pressure dependence of the exchange rate was studied at 303 K with a solution containing CoBr$_2$(TPP)$_2$ (0.05 m) and TPP (0.0653 m) in excess in deuteriochloroform. The observed transverse relaxation rates as a function of pressure are given in Table I together with the derived second-order rate constants. The volume of activation at zero pressure ΔV_0^* and the compressibility of activation $\Delta \beta^*$ $(=-\partial \Delta V^*/\partial P)$ obtained by use of a quadratic least-squares fitting of ln k vs. P are given in Table II.

The negative ΔV^* observed is in good agreement with a bimolecular mechanism, although it is small with respect to the molar volume of the reactants. Kohnstam[11] predicts a ΔV^* between −5 and −12 cm^3 mol for the formation of a partial C–C bond. A related reaction in organic chemistry is the Mentschutkin reaction (tertiary amine + RX), and volumes of activation (structural contribution only) between −8 and −16 cm^3 are reported.[12]

A pentacoordinate transition state is quite reasonable for tetracoordinate complexes. Stable pentacoordinate tertiary phosphine complexes of the type M(R$_3$P)$_2$X$_2$ are known with Ni(II).[13] There is no evidence here for an associative A mechanism, and thus an I$_a$ mechanism can be assigned to this exchange reaction. The significant value of $\Delta \beta^*$, e.g., the difference in compressibility between the transition state and the reactants, suggests that the I$_a$ mechanism must have considerable associative character. The proportionally small value of ΔV^* may be due to the fact that loosening of the complex must occur in order to accommodate the bulky incoming triphenylphosphine, thus canceling out some of the volume decrease due to the bond formation. For substitution by triethylphosphine at the 18-electron system Ni(CO)$_4$, a dissociative mechanism would be expected, and a positive ΔV^* value (8 cm^3 mol^{-1}) has been reported by Brower.[14] However, for electronically unsaturated tetrahedral complexes, an associative activation mode is most likely.

Registry No. CoBr$_2$(TPP)$_2$, 14126-32-0; TPP, 603-35-0.

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Table I. Mass Spectral Data for $(\eta^5\text{-RC}_5\text{H}_4)\text{Mn(CO)(NO)I}$ Complexes[a]

R = H			R = CH₃	
m/e	rel abund	assignment[b]	rel abund	*m/e*
305	57	(RC₅H₄)Mn(CO)(NO)I⁺	31	319
277	69	(RC₅H₄)Mn(NO)I⁺	58	291
275	12	(RC₅H₄)Mn(CO)I⁺	8	289
247	80	(RC₅H₄)MnI⁺	100	261
186	0	H(RC₅H₄)₂Mn⁺	33	214
185	0	(RC₅H₄)₂Mn⁺	29	213
192	45	RC₅H₄I⁺	29	206
182	60	MnI⁺	63	182
130	34	(RC₅H₄)₂⁺	38	158
120	100	(RC₅H₄)Mn⁺	71	134
65	(150)	RC₅H₄⁺	(158)	79
55	29	Mn⁺	50	55

[a] Probe temperature ~70 °C. Reference 14. [b] Reference 15.

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Organometallic Nitrosyl Chemistry. 7.[1] Evidence for the Existence of $(\eta^5\text{-RC}_5\text{H}_4)\text{Mn(CO)(NO)I}$ (R = H, CH₃)

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In a recent paper,[2] Efraty and co-workers report that the complexes RC₅H₄Mn(CS)(NO)I (R = H, CH₃) are air stable in the solid state as well as in solution. Furthermore, they state: "This feature is of considerable interest, since it contrasts with the failure to synthesize the related carbonyl derivative C₅H₅Mn(CO)(NO)I by the ... reaction between [C₅H₅Mn-(CO)₂(NO)]⁺PF₆⁻ and KI or by the direct iodination of the dimer [C₅H₅Mn(CO)(NO)]₂.[3] Evidently, both of the attempted syntheses of the carbonyl analogue ... resulted in the formation of carbonyl- and nitrosyl-free decomposition products of an unknown nature." We take exception to these statements and now present evidence that $(\eta^5\text{-C}_5\text{H}_5)\text{Mn-(CO)(NO)I}$ and its methylcyclopentadienyl congener can indeed be synthesized by these types of reactions.

Experimental Section

All reactions and subsequent manipulations were performed under anaerobic and anhydrous conditions, and all reactants were of reagent grade purity.

Preparation of $(\eta^5\text{-RC}_5\text{H}_4)\text{Mn(CO)(NO)I}$ (R = H or CH₃). **Method A.** To a stirred solution of [(η⁵-C₅H₅)Mn(CO)(NO)]₂ (0.36 g, 1.0 mmol) in dichloromethane (50 mL) at room temperature was added solid I₂ (0.26 g, 1.0 mmol). The original red-violet solution rapidly turned green-brown and a dark green solid precipitated. After 3 min the reaction mixture was filtered and the filtrate was taken to dryness in vacuo to obtain ~0.5 g of a green-brown solid. This solid was formulated as slightly impure (η⁵-C₅H₅)Mn(CO)(NO)I by virtue of its IR spectrum in CH₂Cl₂ which exhibited strong absorptions at 2030 and 1776 cm⁻¹, its ¹H NMR spectrum in CDCl₃ which showed a strong, sharp peak at δ 5.30, and its ambient temperature mass spectrum which is summarized in Table I. Analytically pure samples of this compound could not be obtained because of its proclivity to decompose both in solution and in the solid state. For instance, a stirred dichloromethane solution (20 mL) containing 0.2 g of (η⁵-C₅H₅)Mn(CO)(NO)I slowly deposited a green solid which was insoluble in all common organic solvents; after 72 h complete decomposition had occurred. As a solid, the complex decomposed similarly but over a longer period of time (~8 days).

The reaction between [(η⁵-CH₃C₅H₄)Mn(CO)(NO)]₂[4] and I₂ in dichloromethane afforded impure (η⁵-CH₃C₅H₄)Mn(CO)(NO)I in an identical manner as evidenced by the IR spectrum of the product in CH₂Cl₂ which showed strong absorptions at 2050 and 1772 cm⁻¹. Furthermore, the elemental composition of this product was confirmed

by a molecular weight determination using an A.E.I. MS50 high-resolution mass spectrometer (calcd 318.8902, found 318.8908). Benzene could also be employed as the solvent for both transformations.

Method B. Solid KI (2.20 g, 13.3 mmol) was added to a stirred yellow solution of [(η⁵-C₅H₅)Mn(CO)₂(NO)]PF₆[3] (4.50 g, 12.8 mmol) in acetone (100 mL) at room temperature. A reaction occurred immediately as evidenced by a change in color to gray-brown, evolution of a gas, and formation of an off-white precipitate. The reaction mixture was stirred for 5 min during which time gas evolution ceased. The solvent was removed under reduced pressure, the resulting gray residue was extracted with three 25-mL portions of CH₂Cl₂, and the extracts were taken to dryness in vacuo to obtain a green-brown solid which exhibited the spectroscopic characteristics of (η⁵-C₅H₅)Mn-(CO)(NO)I (vide supra).

An acetone solution of [(η⁵-CH₃C₅H₄)Mn(CO)₂(NO)]PF₆[4] reacted with KI completely analogously.

This method of preparing the (η⁵-RC₅H₄)Mn(CO)(NO)I complexes could also be effected in tetrahydrofuran as both conversions went to completion within 10 min. However, IR monitoring of the final reaction mixtures indicated that both of the desired products decomposed more rapidly in this solvent. This decomposition was complete after 6 h.

Preparation of $(\eta^5\text{-C}_5\text{H}_5)\text{Mn(NO)[P(C}_6\text{H}_5)_3]\text{I}$. A solution of (η⁵-C₅H₅)Mn(CO)(NO)I was prepared by method B using 1.05 g (3.00 mmol) of [(η⁵-C₅H₅)Mn(CO)₂(NO)]PF₆ and 0.50 g (3.3 mmol) of NaI in acetone. The reaction mixture was filtered to remove the NaPF₆ byproduct, and the stirred green-brown filtrate was treated with 0.80 g (3.0 mmol) of solid P(C₆H₅)₃. Vigorous gas evolution occurred immediately and the solution developed a brown coloration. After 5 min a brown, crystalline solid began to precipitate, and crystallization was complete after 15 min. The solid was collected, washed with acetone (2 × 10 mL), and dried in vacuo to obtain 0.93 g (58% yield) of pure (η⁵-C₅H₅)Mn(NO)[P(C₆H₅)₃]I.

Anal. Calcd for C₂₃H₂₀MnNOPI: C, 51.23; H, 3.74; N, 2.60. Found:[5] C, 51.33; H, 3.50; N, 2.65. ν_{NO}[6] (CH₂Cl₂) 1720 cm⁻¹. ¹H NMR[7] (CDCl₃) δ 7.38 (15 H, m), 4.72 (5 H, s). Mp[8] (under N₂) 156 °C dec.

Preparation of $(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{Mn(NO)[P(C}_6\text{H}_5)_3]\text{I}$. A stirred CH₂Cl₂ solution (50 mL) of (η⁵-CH₃C₅H₄)Mn(CO)(NO)I prepared by method A from 0.77 g (2.0 mmol) of [(η⁵-CH₃C₅H₄)Mn(CO)-(NO)]₂ and 0.51 g (2.0 mmol) of I₂ was treated with 0.90 g (3.5 mmol) of solid P(C₆H₅)₃ at room temperature. The solution became brown and vigorous gas evolution occurred. After 15 min, hexanes (20 mL) were added, and the final reaction mixture was filtered. Slow concentration of the filtrate under reduced pressure afforded 1.64 g (74% yield) of (η⁵-CH₃C₅H₄)Mn(NO)[P(C₆H₅)₃]I as a brown, microcrystalline solid.

Anal. Calcd for C₂₄H₂₂MnNOPI: C, 52.10; H, 4.01; N, 2.53. Found:[5] C, 51.77; H, 3.81; N, 2.63. ν_{NO}[6] (CH₂Cl₂) 1720 cm⁻¹. ¹H NMR[7] (CDCl₃) δ 7.33 (15 H, m), 4.93 (2 H, b), 4.40 (1 H, b), 3.84 (1 H, b), 1.90 (3 H, s). Mp[8] (under N₂) 132–133 °C.

Isolation of $(\eta^5\text{-RC}_5\text{H}_4)_2\text{Mn}_2(\text{NO})_3\text{I}$ (R = H or CH₃). If benzene was used as the solvent for method A or if the impure gray solid from method B was extracted with benzene, a second nitrosyl-containing product remained in the solid residue. Extraction of either residue with dichloromethane produced a red-black solution. The addition