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Pressure Dependence of Associative Substitution Reactions of $(\eta^5\text{-}C_5H_5)Rh(CO)_2$

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Summary: The substitution reactions of $(\eta^5\text{-}C_5H_5)Rh(CO)_2$ with PPh_3 and $P(n\text{-}Bu)_3$ were studied as a function of nucleophile concentration, temperature, and pressure up to 150 MPa in toluene as solvent. The pressure dependence of the substitution reactions results in volumes of activation between −14 and −17 $cm^3\ mol^{-1}$ at 40 °C. The results are interpreted in terms of a ring-slippage mechanism ($\eta^5 \rightarrow \eta^3 \rightarrow \eta^5$), which facilitates the associative attack at the metal center. The results are discussed in reference to available literature information.

It is generally accepted that substitution reactions of 18-electron metal complexes may proceed according to an associative reaction mode when the complex can delocalize a pair of electrons onto a ligand such as cyclopentadienyl (Cp) or nitrosyl and so make available a coordination site for the nucleophilic attack.[2–6] In other cases, such complexes usually undergo dissociative substitution via a 16-electron intermediate, although two-term rate laws in favor of parallel associative and dissociative substitution reactions have also been reported.[7–9]

Recent work in our laboratories on the substitution behavior of metal carbonyl complexes has clearly demonstrated that the assignment of a mechanism based on kinetic data at ambient pressure only is not unequivocal.[10–12] The volume of activation for such reactions, determined from the pressure dependence of the rate constant, exhibits a strong mechanistic discrimination ability and assists the assignment of the intimate mechanism.[12–20] Typical values for the rate-determining dissociation of CO are around +20 $cm^3\ mol^{-1}$.[12,17] No characteristic values are presently available for limiting associative substitution reactions of metal carbonyl complexes.[20] For this reason, we have studied the pressure dependence of the substitution of CO in $Rh(Cp)(CO)_2$ by PPh_3 and $P(n\text{-}Bu)_3$. We found indirect evidence for the participation of an intermediate species in the overall substitution process.

Experimental Section

$Rh(Cp)(CO)_2$ was prepared from $[Rh(CO)_2Cl]_2$[21] and $TlCp$[22] according to the method reported in the literature[23] and the cited modifications.[24,25] The yellow-orange oil was purified a few times via high vacuum freeze distillation, which resulted in a deep orange solution. The overall yield was 35% by weight after the third purification cycle. The IR spectrum recorded in a liquid cell (NaCl windows) was in good agreement with that in the literature.[2,23] Chemical analyses[26] resulted in (theoretically expected values) % C, 37.4 (37.5); % H, 2.0 (2.2); % O, 14.4 (14.3); and % Rh 46.1 (45.9). All reactions were performed in toluene (Merck, Uvasol), which was distilled over CaH_2 under N_2 atmosphere.

All test solutions were prepared under N_2 atmosphere using gas-tight syringes and Schlenk techniques. PPh_3 (Janssen) was freshly recrystallized out of ethanol, whereas $P(n\text{-}Bu)_3$ was distilled under N_2. Kinetic and spectral measuremnets were performed in a thermostated (±0.1 °C) cell compartment of a Shimadzu UV-250 spectrophotometer. Kinetic experiments at elevated pressure were performed in a thermostated (±0.1 °C) high-pressure cell[27] attached to a Zeiss spectrophotometer. Solutions were placed in a pillbox optical cell[28] with the aid of a special filling system.[29] IR spectra were recorded on a Nicolet 5 SX FT-IR instrument.

Results and Discussion

The IR spectrum of $(\eta^5\text{-}Cp)Rh(CO)_2$ in toluene exhibits strong absorption bands at 2049 and 1984 cm^{-1}, which are in excellent agreement with those reported elsewhere.[2,23] During reaction 1, these carbonyl bands decrease and a

$$(\eta^5\text{-}Cp)Rh(CO)_2 + P(n\text{-}Bu)_3 \rightarrow (\eta^5\text{-}Cp)Rh(CO)P(n\text{-}Bu)_3 + CO \quad (1)$$

new band occurs at 1944 cm^{-1}, which is in good agreement with a band at 1942 cm^{-1} reported in the literature.[4] Very similar spectral changes were recently reported for substitution reactions of $(\eta^5\text{-}C_5H_4X)Rh(CO)_2$.[6] The UV–vis spectrum of $(\eta^5\text{-}Cp)Rh(CO)_2$ in toluene exhibits a characteristic shoulder at 430 nm (ϵ = 262 $M^{-1}\ cm^{-1}$). Both spectroscopic methods indicated that such solutions are stable for a few days at 40 °C, in agreement with literature findings.[4] On addition of PPh_3, the UV–vis spectrum of the final product is characterized by an absorbance maximum at 445 nm. Repetitive scan spectra indicated two reaction steps; the first is accompanied by an absorbance decrease at 410 nm and the second by an absorbance increase at 370 and 445 nm, respectively. The rates of the two reactions differ significantly such that they can be

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Table I. k_{obs} as a Function of [PPh$_3$], Temperature, and Pressure for Reaction^a 1

temp, °C	[PPh$_3$], M	$10^5 k_{obs}$,^{b} s^{-1}	$10^4 k$,^{c} M^{-1} s^{-1}	$\Delta H^{\ddagger}$, kJ mol^{-1}	$\Delta S^{\ddagger}$ J K^{-1} mol^{-1}
35.0	0.10	1.6 ± 0.1	1.55 ± 0.09	75 ± 3	−73 ± 11
	0.15	2.2 ± 0.1			
	0.20	3.2 ± 0.2			
40.0	0.10	2.6 ± 0.1	2.8 ± 0.1		
	0.15	4.3 ± 0.2			
	0.20	5.6 ± 0.2			
45.0	0.10	4.3 ± 0.2	4.3 ± 0.1		
	0.15	6.3 ± 0.3			
	0.20	8.8 ± 0.3			
50.0	0.10	7.1 ± 0.3	7.2 ± 0.1		
	0.15	10.8 ± 0.4			
	0.20	14.6 ± 0.5			
55.0	0.10	9.7 ± 0.4	9.8 ± 0.1		
	0.15	14.8 ± 0.6			
	0.20	19.6 ± 0.8			

temp, °C	pressure, MPa	$10^5 k_{obs}$,^{d} s^{-1}	$\Delta V^{\ddagger}$, cm^3 mol^{-1}
40.0	5	4.9 ± 0.2	−14.3 ± 1.5
	50	5.6 ± 0.2	
	100	7.7 ± 0.2	
	150	10.7 ± 0.3	

^{a} [Rh] = 1.5×10^{-3} M; reaction was followed at 370 nm. ^{b} Mean value of at least three kinetic runs. ^{c} Second-order rate constant calculated as the mean value of k_{obs}/[PPh$_3$]. ^{d} Mean value of at least three kinetic runs; [PPh$_3$] = 0.15 M.

studied separately. We performed a detailed kinetic and spectroscopic study of both steps,[1] and our data for the second step are in good agreement with those reported in the literature.[4] Our IR measurements indicated only one reaction step. We also ran a series of ^{1}H spectra on a Bruker 400-MHz NMR instrument but could not find evidence for the formation of an intermediate species. Our inability to detect the first step by IR or NMR techniques led to the conclusion that we may be dealing with the reaction of a minor colored impurity that is unrelated to reaction 1. In addition, only one reaction step was observed when P(n-Bu)$_3$ was used as the entering ligand in reaction 1.

The investigated reactions exhibit excellent first-order behavior in the presence of an excess PPh$_3$ or P(n-Bu)$_3$. The observed rate constants as a function of entering ligand concentration, temperature, and pressure, along with the calculated activation parameters, are summarized in Tables I and II. Our rate constant of $(2.8 \pm 0.1) \times 10^{-4}$ M^{-1} s^{-1} for the reaction with PPh$_3$ at 40 °C is in excellent agreement with a literature value of 2.9×10^{-4} M^{-1} s^{-1} under these conditions.[4] A similar agreement exists for the reaction with P(n-Bu)$_3$, viz., 3.5×10^{-3} M^{-1} s^{-1} at 40 °C compared to 3.3×10^{-3} M^{-1} s^{-1} in the literature.[4] The higher basicity of P(n-Bu)$_3$ and its smaller cone angle and size in terms of steric hindrance should account for the higher substitution rate. Both reactions are significantly accelerated by pressure. Plots of ln k_{obs} versus pressure are linear within the experimental error limits, and the volumes of activation, $\Delta V^{\ddagger}$, were calculated from the slope of these plots ($= -\Delta V^{\ddagger}/RT$) in the usual way. The reported rate and activation parameters, especially the significantly negative $\Delta S^{\ddagger}$ and $\Delta V^{\ddagger}$ values, strongly support the operation of a limiting associative (A) mechanism for both reactions.[4] This suggestion is in line with the general tendency of cyclopentadienyl ligands to undergo ring slippage ($\eta^5 \rightarrow \eta^3 \rightarrow \eta^5$) in order to accept an electron pair from the metal center and to vacate a metal orbital for associative attack by the entering nucleophile.[3]

A more detailed analysis of the $\Delta V^{\ddagger}$ data is appropriate. In the type of substitution reactions investigated, no major change in solvation is expected to affect the value of $\Delta V^{\ddagger}$, and the observed effects must result from intrinsic volume changes, i.e., changes associated with changes in bond lengths and angles.[13,15] The values of −14 and −17 cm^3 mol^{-1} reported for the volume of activation indicate that significant bond formation (i.e., volume collapse) occurs on forming the transition state. The overall observed effect may be partially offset by the volume increase expected for the η^5 to η^3 ring slippage of the Cp ligand. We conclude that this study has provided evidence for the general reaction sequence ($\eta^5 \rightarrow \eta^3 \rightarrow \eta^5$) postulated before[5] and outlined in (2). It furthermore supports the general concept of a ring-slippage mechanism and the associative nature of the substitution process. The $\Delta V^{\ddagger}$ values of between −14 and −17 cm^3 mol^{-1} found in this study demonstrate the order of magnitude that this parameter can have for such processes. In this respect, it is interesting to note that $\Delta V^{\ddagger}$ values of between −6 and −20 cm^3 mol^{-1} were recently reported for associative substitution reactions of octahedral carbonyl complexes of Mo and W.[18,20,30] In general, a $\Delta V^{\ddagger}$ value of −15 cm^3 mol^{-1} will result in doubling the observed rate constant on increasing the pressure from ambient to 100 MPa. Such effects can be measured with great accuracy by using relatively unsophisticated equipment.[14]

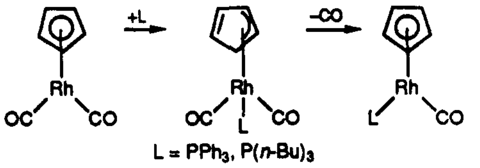
Table II. k_{obs} as a Function of [P(n-Bu)$_3$], Temperature, and Pressure for the Reaction^a

$$(\eta^5\text{-Cp})\text{Rh(CO)}_2 + \text{P}(n\text{-Bu})_3 \rightarrow (\eta^5\text{-Cp})\text{Rh(CO)P}(n\text{-Bu})_3 + \text{CO}$$

temp, °C	[P(n-Bu)$_3$], M	$10^4 k_{obs}$,^{b} s^{-1}	$10^3 k$,^{c} M^{-1} s^{-1}	$\Delta H^{\ddagger}$, kJ mol^{-1}	$\Delta S^{\ddagger}$, J K^{-1} mol^{-1}
30.0	0.10	1.45 ± 0.04	1.50 ± 0.05	71 ± 3	−64 ± 10
	0.15	2.25 ± 0.06			
	0.20	3.1 ± 0.1			
35.0	0.10	2.0 ± 0.1	2.1 ± 0.1		
	0.15	3.3 ± 0.1			
	0.20	4.2 ± 0.1			
40.0	0.10	3.4 ± 0.1	3.5 ± 0.1		
	0.15	5.2 ± 0.1			
	0.20	7.0 ± 0.2			
45.0	0.10	5.5 ± 0.2	5.5 ± 0.1		
	0.15	8.4 ± 0.2			
	0.20	11.0 ± 0.3			
50.0	0.10	8.9 ± 0.3	9.0 ± 0.1		
	0.15	13.5 ± 0.4			
	0.20	17.9 ± 0.5			

temp, °C	pressure, MPa	$10^4 k_{obs}$,^{d} s^{-1}	$\Delta V^{\ddagger}$, cm^3 mol^{-1}
40.0	5	6.6 ± 0.3	−17.0 ± 0.7
	50	9.2 ± 0.3	
	100	12.1 ± 0.3	
	150	17.3 ± 0.4	

^{a} [Rh] = 1.5×10^{-3} M; wavelength = 365 nm. ^{b} Mean value of at least three kinetic runs. ^{c} Second-order rate constant calculated as the mean value of k_{obs}/[P(n-Bu)$_3$]. ^{d} Mean value of at least three kinetic runs; [P(n-Bu)$_3$] = 0.18 M.



(2)

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