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Mechanistic Information from the Effect of Pressure on Ligand Substitution and Chelate Ring-Closure Reactions of Photogenerated Chlorobenzene Solvates of Tungsten Tetracarbonyl Intermediates in Mixed Solvents

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Earlier studies on the effect of pressure on the displacement of coordinated solvent molecules in photogenerated metal carbonyl intermediates were mostly restricted to measurements in neat solvent. In this paper such measurements have been extended to include the variation of the solvent composition in order to be able to resolve the contribution and mechanism of parallel, reverse, and consecutive reaction steps. The systems investigated include substitution of chlorobenzene (CB) in *cis*-$(CB)(Ph_2MeP)W(CO)_4$ by 1-hexene in CB/hexene solvent mixtures, and chelate ring closure in *cis*-$(CB)(Ph_2P(CH_2)_nCH{=}CH_2)W(CO)_4$ (n = 1–4) in CB/n-heptane solvent mixtures. The ΔV^* data for the ligand substitution reaction enable the unequivocal assignment of a dissociative (D) mechanism. In addition, the results for the chelate ring closure indicate that the major reaction path for n = 1, 2 involves an interchange (I_d) mechanism in which the olefin moiety is preassociated with the metal center followed by the rate-determining loss of CB. Both reaction steps are suggested to involve the participation of agostically H-bonded intermediates. The results of this study are discussed in reference to all data available for the displacement of solvent molecules in group 6B metal carbonyl complexes and demonstrate the usefulness of combined solvent- and pressure-dependent kinetic studies.

Introduction

Mechanistic studies on the substitution behavior of coordinated solvent molecules in transition-metal complexes are of fundamental importance to the understanding of the general substitution behavior and reactivity patterns of metal complexes in solution. Even if such solvent-coordinated complexes are present at very low concentrations under normal experimental conditions, they may through their extreme lability represent the main reaction route for all ligand substitution processes. It is along these lines that Dobson and co-workers have performed systematic studies on the solvent displacement from group 6B metal carbonyl complexes (see refs 1–3 and earlier papers of that series).

Detailed mechanistic investigations of solvent exchange and substitution reactions of transition-metal complexes have demonstrated that important information on the intimate nature of such processes can be obtained from the effect of pressure on these reactions.[4-6] The fact that such solvent displacement reactions usually do not involve major changes in electrostriction, since they involve the exchange of neutral molecules, has made the interpretation of the observed volumes of activation in terms of intrinsic volume changes rather straightforward.[4,7] In this way a sensitive mechanistic parameter was developed to distinguish between associative (A), interchange (I_a, I_d), and dissociative (D) solvent displacement mechanisms.

Recent studies performed in our laboratories revealed that solvent displacement from group 6B metal carbonyl complexes may take place via competitive dissociative and interchange (or associative) paths.[1,8-10] If, for instance, we consider solvent displacement in $M(CO)_5S$ (M = Cr, Mo, W; S = solvent), parallel reaction paths as outlined in (1) result in the rate law (2) (L = entering nucleophile), from which the contributions of the separate paths can only be resolved via a systematic variation of [S].[8-10] In neat solvent where [S] remains constant, eq 2 results in a linear or nonlinear dependence of k_{obs} on [L] (depending on the competition ratio $k_{-1}[S]/k_2[L]$), from which the contributions from the parallel reaction paths cannot be separated. This means that the observed second-order rate constants and associated activation parameters are composite quantities and can only be interpreted in a qualitative way.[8-10] Also, the application of high-pressure techniques can reveal at most only specific trends in the ΔV^* values and no exact assignment of the mechanism under such conditions.

$$\begin{tikzcd}
M(CO)_5S \arrow[rr, shift left, "k_1"] \arrow[dr, "k_3\ {+}L,{-}S"'] & & M(CO)_5 + S \arrow[ll, shift left, "k_{-1}"] \arrow[dl, "{+}L\ k_2"] \\
& M(CO)_5L &
\end{tikzcd} \qquad (1)$$

$$k_{obs} = k_3[L] + \frac{k_1k_2[L]}{k_{-1}[S] + k_2[L]} \qquad (2)$$

To resolve this problem, a series of studies was recently undertaken in which the solvent concentration was varied over a wide range in order to resolve the contributions of

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the parallel paths in (1). In these studies the displacement of chlorobenzene (CB) in photogenerated *cis*-(CB)(η^1-P-ol)W(CO)$_4$ (P-ol = $Ph_2P(CH_2)_nCH{=}CH_2$, n = 1–4) via chelate ring closure was studied in CB–hep solvent mixtures (hep = *n*-heptane).[1] The results revealed evidence for loss of CB via initial CB dissociation (D) and via displacement of CB upon chelate ring closure (I). The entropy of activation varied between +5.2 and +11.8 cal K^{-1} mol^{-1} for the former and between −2.1 and +2.9 cal K^{-1} mol^{-1} for the latter path, respectively.[1] These data indicate that displacement of CB upon chelate ring closure is a significantly more associative type of reaction, although the exact nature of the interchange process (I_d or I_a) cannot be concluded from these data.

We have, therefore, in the present study, performed a detailed combined pressure and solvent dependence study of the mentioned systems. In addition, we have also studied the displacement of CB from photogenerated *cis*-(CB)(Ph_2MeP)W(CO)$_4$ by 1-hexene in CB–hexene solvent mixtures. The results demonstrate the usefulness of such combined pressure and solvent dependence studies in order to resolve the intimate nature of the parallel solvent displacement mechanisms in such systems.

Experimental Section

Materials. Details on the solvents, ligands, and general chemicals used in this study are given elsewhere.[1] The *cis*-(pip)(P-ol)W(CO)$_4$ and *cis*-(pip)(Ph_2MeP)W(CO)$_4$ complexes (pip = piperidine; P-ol = $Ph_2PCH_2CH{=}CH_2$ (2-propenyldiphenylphosphine, prdpp), $Ph_2CH_2CH_2CH{=}CH_2$ (3-butenyldiphenylphosphine, bdpp), 4-pentenyldiphenylphosphine (pdpp), $Ph_2PCH_2CH_2CH_2CH{=}CH_2$ (5-hexenyldiphenylphosphine, hdpp)) were prepared and characterized as described before.[1,3,11]

Flash Photolysis Studies. These were carried out at the Center for Fast Kinetics Research, Austin, TX, using the flash photolysis system and variable-pressure equipment described previously.[12,13] Further experimental details are similar to those adopted for the ambient-pressure kinetic work.[1] Solutions were flashed in quartz pillbox cells[14] and stirred between experiments with the aid of a small Teflon-coated magnetic stirring bar and a magnetic stirrer placed below the high-pressure cell on the optical rail. The temperature of the high-pressure cell was controlled to within ±0.1 °C with the aid of an external thermostat. The pseudo-first-order rate constants, k_{obs}, were obtained as averages of 1–10 kinetic traces. Limits of error, given in parentheses as the uncertainties of the last digit(s) of the reported values, are 1 standard deviation.

Results and Discussion

Earlier high-pressure kinetic studies on the displacement of coordinated solvent molecules in metal carbonyl complexes almost all suffered from the shortcoming that the reactions were investigated in neat solvent; i.e., the concentration of the solvent could be treated as a constant factor in the rate law.[9,10,15] The result was that the ΔV^* data represented overall effects and could only be interpreted in a qualitative way. The data did exhibit specific trends that suggested possible mechanistic changeovers[9,10] along a series of complexes (see further discussion for a more detailed analysis of these data). In one recent study,[8] however, the solvent concentration was varied systematically over a wide range, viz., for the displacement of coordinated benzene (BZ) in Cr(CO)$_5$(η^2-BZ) by piperidine (pip). This reaction was found to follow the mechanism in (3), which is similar to the general one given in (1) except for the absence of the k_3 path. A systematic variation of [BZ]/[pip] and of pressure enabled through the rate expression in (4) the estimation of the volume of activation for the various steps in (3), viz. $\Delta V^*(k_1)$ = +12.3 ± 1.4 cm^3 mol^{-1} and $\Delta V^*(k_1k_2/k_{-1})$ = +4.0 ± 0.5 cm^3 mol^{-1}, which is close to the value of +4.2 ± 0.3 cm^3 mol^{-1} measured directly in neat BZ at low [pip].[8] From the difference in the quoted values, it followed that $\Delta V^*(k_2/k_{-1})$ = −8.3 ± 1.9 cm^3 mol^{-1}. Thus, the separation of the overall ΔV^* value into the two components for k_1 and k_2/k_{-1} demonstrates the validity of the suggested limiting D mechanism (large positive ΔV^* for k_1) and indicates less volume collapse upon Cr–BZ bond making than upon Cr–pip bond formation since $\Delta V^*(k_2/k_1) = \Delta V^*(k_2) - \Delta V^*(k_1)$.

Table I. k_{obs} as a Function of Pressure for the Reaction Taking Place after Flash Photolysis of *cis*-(pip)(Ph_2MeP)W(CO)$_4$ in CB–hex Mixtures[a]

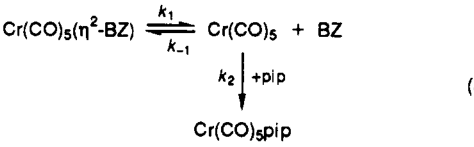
pressure, MPa	[CB], M	[hex], M	$10^{-3}k_{obs}$, s^{-1}
5	6.147	2.992	22.6 (10)
	5.377	3.644	30.2 (10)
	4.347	4.457	37.9 (11)
	2.778	5.738	58.4 (11)
	1.361	6.815	79.0 (27)
50	6.147	2.992	18.2 (6)
	5.377	3.644	23.6 (11)
	4.347	4.457	31.3 (24)
	2.778	5.738	48.1 (14)
	1.361	6.815	62.0 (68)
100	6.147	2.992	15.1 (8)
	5.377	3.644	19.6 (2)
	4.347	4.457	26.3 (15)
	2.778	5.738	38.3 (11)
	1.361	6.815	51.8 (7)
150	6.147	2.992	13.9 (2)
	5.377	3.644	16.6 (4)
	4.347	4.457	21.6 (16)
	2.778	5.738	32.7 (17)
	1.361	6.815	43.8 (19)

[a] Temperature 35.3 °C.

Table II. Rate Constants as a Function of Pressure and ΔV^* Data for the Reaction of *cis*-(CB)(Ph_2MeP)W(CO)$_4$ with 1-Hexene[a]

pressure, MPa	$10^{-4}k_1k_2/k_{-1}$, s^{-1}	$10^{-4}k_1$, s^{-1}	k_2/k_{-1}
5	5.9 (2)	10.8 (7)	0.55 (5)
50	4.7 (1)	8.9 (5)	0.53 (4)
100	3.95 (5)	7.2 (2)	0.55 (2)
150	3.41 (4)	5.9 (2)	0.58 (3)
ΔV^*, cm^3 mol^{-1}	+9.7 ± 0.8	+10.7 ± 0.2	−1.0 ± 1.0

[a] Temperature 35.3 °C.



(3)

$$k_{obs} = k_1k_2[pip]/(k_{-1}[BZ] + k_2[pip]) \qquad (4)$$

Substitution Reactions of *cis*-(CB)(Ph_2MeP)W(CO)$_4$. By way of comparison, and in order to serve as a reference system for the more complex ring-closure reactions of the corresponding P-olefin complexes,[1] a similar study was undertaken for the displacement of chlorobenzene (CB) in *cis*-(CB)(Ph_2MeP)W(CO)$_4$ by 1-hexene (hex). The detailed ambient-pressure kinetic study[1] revealed that a mechanism and rate law similar to (3) and (4), i.e. (5) and (6), respectively, can account for the ex-

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$$\begin{tikzcd}
cis\text{-(CB)(Ph}_2\text{MeP)W(CO)}_4 \arrow[r, shift left, "k_1"] & \text{(Ph}_2\text{MeP)W(CO)}_4 \arrow[l, shift left, "k_{-1}"] \arrow[d, "k_2"', "+\text{hex}"] + \text{CB} \\
 & cis\text{-(hex)(Ph}_2\text{MeP)W(CO)}_4
\end{tikzcd} \qquad (5)$$

$$k_{obs} = k_1k_2[\text{hex}]/(k_{-1}[\text{CB}] + k_2[\text{hex}]) \qquad (6)$$

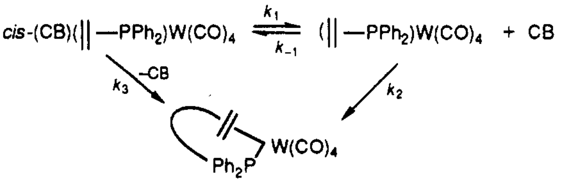
perimental data obtained over a wide range of [hex]/[CB], from 0.17 to 2.0, in which *cis*-(CB)(Ph$_2$MeP)W(CO)$_4$ was generated via flash photolysis of *cis*-(pip)(Ph$_2$MeP)W(CO)$_4$. Such experiments were now repeated at pressures up to 150 MPa, and the results are summarized in Table I. According to the rate expression (6), plots of k_{obs}^{-1} versus [CB]/[hex] should be linear and allow the estimation of k_1 and k_1k_2/k_{-1}. This is indeed the case, and the corresponding results are summarized in Table II along with the estimated $\Delta V^{\ddagger}$ values. The results indicate the validity of the suggested mechanism, since k_1 is characterized by a significantly positive $\Delta V^{\ddagger}$ value, compared to an almost zero $\Delta S^{\ddagger}$ value (+3.8 ± 2.6 cal K^{-1} mol^{-1}).[1] The detailed ambient-pressure work[1] suggested that CB displacement from the solvated species involves the formation of a C–H–W agostic bond with Ph$_2$MeP, such that the reaction intermediate may not be a five-coordinate species. Furthermore, the almost zero value of $\Delta V^{\ddagger}(k_2/k_{-1})$ demonstrates that bond formation of (Ph$_2$MeP)W(CO)$_4$ with CB and hex is accompanied by a similar volume collapse. This could indicate that similar bond formation modes are at hand for W–CB and W–hex, compared to different modes for Cr–BZ and Cr–pip as reported earlier.[8]

Table III. k_{obs} as a Function of Pressure for the Reaction Taking Place after Flash Photolysis of *cis*-(pip)(η^1-P-ol)W(CO)$_4$ in CB and CB/hep Mixtures[a]

P-ol	pressure, MPa	[CB], M	$10^{-3}k_{obs}$, s^{-1}
hdpp	5	9.73	7.47 (4)
		8.40	8.13 (12)
		7.35	8.67 (16)
		6.54	9.61 (20)
		5.09	11.46 (29)
	50	9.73	6.13 (1)
		8.40	6.69 (20)
		7.35	7.33 (9)
		6.54	7.77 (11)
		5.09	9.31 (14)
	100	9.73	5.00 (10)
		8.40	5.60 (13)
		7.35	5.85 (11)
		6.54	6.23 (8)
		5.09	7.56 (14)
	150	9.73	4.13 (9)
		8.40	4.34 (15)
		7.35	4.91 (12)
		6.54	5.24 (8)
		5.09	5.94 (12)
pdpp	5	9.73	5.33 (14)
	50		4.15 (20)
	100		3.51 (6)
	150		2.87 (2)
bdpp	5	9.73	15.1 (7)
	50		13.8 (5)
	100		12.5 (5)
	150		11.3 (9)
prdpp	5	9.73	38.4 (6)
		8.52	39.7 (7)
		7.42	43.0 (11)
		6.38	47.5 (7)
		5.07	50.4 (13)
	50	9.73	31.6 (10)
		8.52	34.5 (4)
		7.42	34.6 (8)
		6.38	37.9 (22)
		5.07	41.5 (21)
	100	9.73	27.9 (8)
		8.52	29.8 (11)
		7.42	32.0 (14)
		6.38	32.6 (5)
		5.07	35.5 (15)
	150	9.73	24.6 (6)
		8.52	25.4 (19)
		7.42	25.8 (9)
		6.38	27.0 (11)
		5.07	29.7 (32)

[a] Temperature 35.3 °C.

Ring-Closure Reactions of *cis*-(CB)(η^1-P-ol)W(CO)$_4$. Displacement of coordinated CB via the ring closure of a P-olefin ligand in *cis*-(CB)(η^1-P-ol)W(CO)$_4$ intermediates, generated by flash photolysis of *cis*-(pip)(η^1-P-ol)W(CO)$_4$, was demonstrated to involve parallel reaction paths as indicated in (7) by performing a detailed [CB] dependence



(7)

$$k_{obs} = k_3 + k_1k_2/(k_{-1}[\text{CB}] + k_2) \qquad (8)$$

study.[1] Values of k_3 for the ring closure of the six-coordinate species were obtained in two different ways. It was shown that, for high [CB], the rate law (8) can be simplified to (9),[1] according to which k_{obs} should exhibit a

$$k_{obs} = k_3 + k_1k_2/k_{-1}[\text{CB}] \qquad (9)$$

linear dependence on [CB]$^{-1}$. Such conditions were selected to study the pressure dependence of the process in CB/hep mixtures, for which the experimental results are summarized in Table III. It is known that the displacement of hep from photogenerated transients is much faster than the displacement of CB such that *cis*-(hep)(η^1-P-ol)W(CO)$_4$ intermediates will have largely decayed on the time scale of CB displacement and cause no complication in the present study.[1,9,16] A complete solvent dependence study could be performed for two of the investigated complexes, viz. P-ol = hdpp and prdpp. For P-ol = bdpp almost no [CB] dependence of k_{obs} was observed[1] such that $k_{obs} \approx k_3$, whereas for P-ol = pdpp, almost no intercept (k_3) was observed[1] such that $k_{obs} \approx k_1k_2/k_{-1}$[CB]. Application of (9) to the data in Table III results in the k_3 and k_1k_2/k_{-1} values and corresponding $\Delta V^{\ddagger}$ data summarized in Table IV. The results are in good agreement with the suggested mechansim in (7), since $\Delta V^{\ddagger}$ for the k_1k_2/k_{-1} path is significantly positive, in line with a dissociative (D) mechanism. On the other hand, $\Delta V^{\ddagger}(k_3)$ is small and positive for three of the four investigated systems and underlines the operation of a dissociative-interchange (I$_d$) mechanism. The latter values are significantly more conclusive than the $\Delta S^{\ddagger}(k_3)$ values of between −2.1 and +2.9 cal K^{-1} mol^{-1} referred to before.[1] From the rate constants at ambient pressure[1] it was estimated that the contribution of the D path decreases along the series of P-olefins, viz. hdpp (55%), pdpp (56%), bdpp (14%), and prdpp (27%). When we take a linear combination of the $\Delta V^{\ddagger}$ data for the parallel I$_d$ and D reaction paths according to the given distribution, $\Delta V^{\ddagger}$ in neat CB turns out to be +10.3 and +7.6 cm^3 mol^{-1} for P-ol = hdpp and prdpp, respectively, in excellent agreement with those values calculated from

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Table IV. Rate Constants as a Function of Pressure and $\Delta V^{\ddagger}$ Data for the Ring-Closure Reactions of *cis*-(CB)(η^1-P-ol)$W(CO)_4$[a]

P-ol	pressure, MPa	$10^{-3}k_3$, s^{-1}	$10^{-4}k_1k_2/k_{-1}$, s^{-1}
hdpp	5	2.99 (22)	4.30 (15)
	50	2.68 (11)	3.37 (7)
	100	2.31 (24)	2.64 (16)
	150	2.09 (24)	1.99 (16)
prdpp	5	24.6 (24)	13.5 (16)
	50	21.7 (15)	10.1 (10)
	100	20.8 (14)	7.6 (1)
	150	19.0 (6)	5.3 (4)

P-ol	$\Delta V^{\ddagger}$, cm^3 mol^{-1}	
hdpp	+6.5 ± 0.3	+13.5 ± 0.2
pdpp		+10.7 ± 0.8[b]
bdpp	+5.13 ± 0.01[b]	
prdpp	+4.4 ± 0.6	+16.2 ± 0.6

[a] Temperature 35.3 °C. [b] Calculated from the data in Table III for neat CB (see Results and Discussion).

the experimental data reported in Table III, viz. +10.5 ± 0.2 and +7.7 ± 0.8 cm^3 mol^{-1}, respectively. Finally, a comparison of the $\Delta V^{\ddagger}(k_1k_2/k_{-1})$ data in Table IV with $\Delta V^{\ddagger}(k_1)$ = +10.7 ± 0.2 cm^3 mol^{-1}, reported in Table II for the dissociation of CB, reveals that the volume collapse during ring closure (k_2) may vary with P-ol and is in two cases significantly smaller than for bond formation with CB (k_{-1}).

Comparison with Available Data. A summary of the available $\Delta V^{\ddagger}$ data for the displacement of solvent molecules in metal carbonyl complexes is given in Table V. It should be emphasized that the quoted numbers are for the reactions in neat solvent, which means that these represent composite quantities from various parallel and/or reversible reaction steps as outlined above. Nevertheless, the overall $\Delta V^{\ddagger}$ data exhibit interesting trends that call for further interpretation. It is safe to assume that the observed $\Delta V^{\ddagger}$ values mainly represent intrinsic volume changes, since the investigated reactions all involve neutral complexes and neutral ligands; i.e., no major solvational changes due to changes in electrostriction are expected to affect the interpretation. Data for the displacement of solvent from $M(CO)_5S$ indicate an overall trend to smaller, i.e. more negative, values in moving along the series Cr, Mo, and W. This has been interpreted in terms of bond formation of $M(CO)_5$ with L and/or of $M(CO)_5S$ with L becoming more important for the larger metal center.[9,10] Thus, Mo and W seem to be more capable of undergoing associative bond formation than Cr. The data for $Cr(CO)_5S$ demonstrate that bond formation with piperidine is, throughout the series of investigated solvents, more effective than with 1-hexene. This could be related to a difference in the bonding mode of these two ligands. The significantly more negative $\Delta V^{\ddagger}$ values reported for the THF complexes must be ascribed to the more important role of bond formation processes in these systems. By way of contrast, all the data for the solvent displacement reactions of the *cis*-tetracarbonyltungsten complexes are significantly more positive than for the pentacarbonyl systems. This means that the presence of a bulky phosphine ligand in the cis position may hinder associative attack by the entering nucleophile and at most allow the operation of an interchange (I_d) process as a parallel reaction path, in which some bond formation with the entering nucleophile is at hand.

It is also appropriate to comment on the participation of an I_d reaction path during the ring closure of the P-olefin complexes. As mentioned above, this reaction path is the more important one for the shorter olefin groups (bdpp and prdpp). The fundamental aspect of an interchange mechanism involves the participation of a precursor complex, i.e. a species in which the entering ligand is closely associated with the metal complex. This may well be the case for the bdpp and prdpp complexes, since through their shorter carbon chain lengths the olefin moiety may be in the vicinity of the departing solvent molecule. In the case of the longer carbon chain olefins (hdpp and pdpp), the precursor complex will be less structured, the olefin moiety being further removed from the metal–solvent center, and the I_d mechanism contributes only 50%. The observations that $\Delta V^{\ddagger}(k_3)$ in Table IV is almost constant for three different P-olefin complexes and that the ring-closure rate constant is virtually independent of chain length[1] are in excellent agreement with those expected for an I_d mechanism,[4-6] since CB is the common leaving group in all three systems. It is quite likely that agostic bonding involving

Table V. Summary of Overall $\Delta V^{\ddagger}$ Data Reported for the Displacement of Solvent Molecules in Group 6B Metal Carbonyl Complexes by the Nucleophile L

			$\Delta V^{\ddagger}$, cm^3 mol^{-1}			
complex	S[a]	L	M = Cr	M = Mo	M = W	ref
$M(CO)_5S$	FB	1-hexene	+9.4 ± 0.7	+5.8 ± 0.8	+2.5 ± 0.2	9
	tol		+10.8 ± 0.7	+3.2 ± 0.3	...	9
	BZ		+10.9 ± 1.0	...	...	9
	CB		+5.4 ± 0.4	+3.2 ± 0.3	+0.4 ± 0.3	9
	hep		+6.2 ± 0.2	+2.2 ± 0.3	+2.7 ± 0.4	9
	FB	piperidine	+6.1 ± 0.3			9
	tol		+4.8 ± 1.4			9
	BZ		+4.2 ± 0.3			8, 9
	CB		+0.2 ± 0.2			9
	hep		+1.4 ± 0.4			9
	THF	piperidine	−2.2 ± 0.6	−3.6 ± 1.2	−4.4 ± 0.5	10
	THF	$P(C_6H_5)_3$	−1.9 ± 1.0	−8.3 ± 1.0	−12.2 ± 0.4	10
	THF	$P(OC_2H_5)_3$	−3.6 ± 0.7	−5.8 ± 0.9	−14.9 ± 1.0	10
cis-(S)(PPh_3)$M(CO)_4$	CB	piperidine			+11.3 ± 0.4	15
cis-(S)(PPh_2Me)$M(CO)_4$	CB	1-hexene			+9.7 ± 0.8	*b*
cis-(S)($PPh_2(CH_2)_nCH{=}CH_2$)$M(CO)_4$	CB	*c*			+7.7 ± 0.8 (*n* = 1)	*b*
					+5.12 ± 0.01 (*n* = 2)	*b*
					+10.7 ± 0.8 (*n* = 3)	*b*
					+10.5 ± 0.3 (*n* = 4)	15
					+10.5 ± 0.2 (*n* = 4)	*b*

[a] Abbreviations: FB = fluorobenzene, tol = toluene; BZ = benzene; CB = chlorobenzene; hep = *n*-heptane, THF = tetrahydrofuran. [b] This work. [c] P-olefin ring closure measured in neat solvent.

the Ph_2MeP and P-ol hydrogens may play an important role in stabilizing the precursor complex in order to account for the operation of an I_d mechanism. The idea of preassociation of the olefin moiety with the metal center in the precursor complex is also in agreement with the trend to more associative types of ligand substitution reactions for the larger W center as found for the displacement of solvent in $M(CO)_5S$ (Table V) and the displacement of CO during ring closure of $M(CO)_5(N\text{-}N)$, where N-N = 1,10-phenanthroline, 1,4-diisopropyl-1,4-diazabutadiene, and ethylenediamine.[17,18]

Conclusions. The results of this and earlier studies[1-3,8,9,15,17,18] have clearly demonstrated that there are quite a number of factors that can influence the intimate nature of ligand substitution reactions in general and solvent replacement reactions in particular. It is in the latter case, especially the size of the metal center, the nucleophilicity of the entering and departing ligands, the degree of bond formation and bond cleavage in the transition state, and the actual molecular packing around the metal center that will all contribute in determining the nature of the mechanism. This means that we are dealing with a very fine tuning effect between the the various contributions of the mentioned factors. The observed activation parameters, especially ΔV^*, will be a composite of the various contributions and only allow an overall mechanistic assignment. Larger metal centers tend to favor bond formation processes, stronger nucleophiles tend to exhibit more negative ΔV^* values during bond formation, and close-packed ring-opened species may facilitate interchange types of ring-closure reactions, as demonstrated by the results reported in this study. Some separation of the different contributions is possible when mixtures of solvents of different nucleophilicity are employed. We therefore conclude that combined pressure and solvent dependence studies as performed in this investigation can assist the elucidation of the intimate ligand substitution mechanism.

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$(R_2PC_2H_4PR_2)Pd^0$ Alkene and Ethyne Complexes

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The palladium η^3-allyl complex $Pd(\eta^3\text{-}C_3H_5)_2$ reacts with bidentate phosphanes $^iPr_2PC_2H_4P^iPr_2$ and $^tBu_2PC_2H_4P^tBu_2$ below −30 °C to yield the light yellow, microcrystalline palladium(II) η^1-allyl compounds $(R_2PC_2H_4PR_2)Pd(\eta^1\text{-}C_3H_5)_2$ (R = ^{i}Pr (1), ^{t}Bu (2)), which are stable to about −30 °C. Above −30 °C, the allyl substituents of 1 and 2 couple with reduction of palladium to form a mixture of $(R_2PC_2H_4PR_2)Pd^0$ 1,5-hexadiene complexes. When this reaction is carried out in 1,5-hexadiene, the complexes $(R_2PC_2H_4PR_2)Pd(\eta^2\text{-}C_6H_{10})$ (R = ^{i}Pr (3), ^{t}Bu (4)) are obtained in pure form. According to IR and NMR spectral data, the palladium atoms in 3 and 4 are coordinated at low temperature by the chelating diphosphane and (statically) by one of the two diene double bonds in a trigonal-planar geometry. At higher temperatures, a rapid exchange of the coordinated and uncoordinated double bonds occurs, passing through an intermediate with C_2 symmetry. When suspensions of 1 in pentane and 2 in THF are warmed to 20 °C, dinuclear diastereomers *rac-/meso-*$\{(R_2PC_2H_4PR_2)Pd\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}C_6H_{10})$ (R = ^{i}Pr (**5a,b**), ^{t}Bu (**6a,b**)) are obtained, which upon treatment with 1,5-hexadiene furnish mononuclear derivatives 3 and 4. Similarly, when 1 is reacted with 1,5-cyclooctadiene at 20 °C, the mono- and dinuclear interconvertible complexes $(^iPr_2PC_2H_4P^iPr_2)Pd(\eta^2\text{-}C_8H_{12})$ (7) and $\{(^iPr_2PC_2H_4P^iPr_2)Pd\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}C_8H_{12})$ (8) are produced. From the reaction of 1 and 2 with ethene, stable complexes $(R_2PC_2H_4PR_2)Pd(C_2H_4)$ (R = ^{i}Pr (9), colorless; R = ^{t}Bu (10), tan) result. The colorless mononuclear palladium(0) ethyne complexes $(R_2PC_2H_4PR_2)Pd(C_2H_2)$ (R = ^{i}Pr (11), ^{t}Bu (12)) may be prepared (a) by a displacement reaction of one of the isolated alkene complexes with ethyne, (b) by a reductive elimination and concomitant displacement reaction of the η^1-allyl complexes 1 and 2 with ethyne, or (c) in a one-pot synthesis from either $Pd(\eta^3\text{-}C_3H_5)_2$ or $Pd(\eta^3\text{-}2\text{-}MeC_3H_4)_2$ with $^iPr_2PC_2H_4P^iPr_2$ or $^tBu_2PC_2H_4P^tBu_2$, respectively, and ethyne in excess. When the mononuclear ethyne complexes 11 and 12 are combined with an equimolar amount of the corresponding η^1-allyl complex 1 or 2, or the alkene complexes (especially the mononuclear 1,5-hexadiene (3, 4) or ethene (9, 10) derivatives), yellow dinuclear palladium(0) complexes $\{(R_2PC_2H_4PR_2)Pd\}_2(\mu\text{-}C_2H_2)$ (R = ^{i}Pr (13), ^{t}Bu (14)) are produced, in which the ethyne ligand bridges two palladium atoms. All the (diphosphane)palladium(0) alkene (3–10) and ethyne complexes (11–14) exhibit a trigonal-planar coordination geometry about the palladium atom. Most of the compounds have been isolated in high yield.

Introduction

In the context of our studies on the complexes of nickel(0) with ethyne, we have reported in detail the synthesis and characterization of monodentate ligand complexes, e.g. $(Ph_3P)_2Ni(C_2H_2)$,[1] as well as bidentate ligand complexes, e.g. $(^iPr_2PC_2H_4P^iPr_2)Ni(C_2H_2)$, $\{(^iPr_2PC_2H_4P^iPr_2)Ni\}_2(\mu\text{-}C_2H_2)$,[2] and $(^tBu_2PC_2H_4P^tBu_2)Ni(C_2H_2)$.[3] A similar

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