of inorganic complexes with molecular weights as high as 20000 amu undoubtedly will be obtained by this technique in the near future.

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Registry No. $(Bu_4N)_6[H_2Si_2W_{18}Nb_6O_{77}]$, 92844-06-9; $(Bu_4N)_7HSi_2W_{18}O_{68}(ZrOH_2)_3$, 99593-28-9; $(Bu_4N)_7HSi_2W_{18}O_{68}(Zr(OH_2)_2)_3$, 99593-27-8.

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Kinetics of the Reaction of Palladium(II) with Various Dienes and the Importance of the Diene Conformation

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The reactions of dienes with palladium(II) to give chelated diene complexes are of interest in three areas: first, the extent to which the conformation of the diene has to be changed after reaction of the first double bond before coordination of the second can occur, i.e. after reaction 1 and before reaction 2; second, whether the most favorable conformation the diene can adopt is particularly good for formation of $Pd(diene)Cl_2$ and vice versa; third, in obtaining quantitative data relevant to the Wacker process since in these reactions palladium is formed (as a result of hydroxypalladation) much less readily than in the corresponding monoene systems.

$$PdCl_3(OCMe_2)^- + \text{diene} \rightleftharpoons Pd(\eta^2\text{-diene})Cl_3^- + Me_2CO \qquad (1)$$

$$Pd(\eta^2\text{-diene})Cl_3^- \rightleftharpoons Pd(\eta^4\text{-diene})Cl_2 + Cl^- \qquad (2)$$

The reactions of $Na[PdCl_3(OCMe_2)]$[1] with 1,5-cyclooctadiene (1,5-COD), 1,5-cyclononadiene (1,5-CND), norbornadiene (NBD) and 1,5-hexadiene (1,5-HD) have been studied in 2% aqueous acetone (viz. 1:49 (v:v) water:acetone) by using changes in ultraviolet and ^1H NMR spectra. The processes follow reactions 1 and 2; complexes are formed in which the diene is bonded through one and then two C=C links. On the basis of the kinetic and equilibrium studies below, the speeds and completeness of the reactions of the four dienes can be summarized qualitatively as in Table I.

Kinetics

The positions of the CH=CH resonances in the $Pd(diene)Cl_2$ complexes and the parent dienes are quite distinct; see Table II. In solutions ca. 10^{-2} M in $PdCl_3(OCMe_2)^-$ and in the diene at ca. 25 °C, these $Pd(diene)Cl_2$ peaks become apparent on the order of minutes for NBD and 1,5-COD and of hours for 1,5-CND and 1,5-HD, suggesting very approximate rate constants of 0.05, 1, 10^{-4}, and 10^{-4} M^{-1} s^{-1}. No free diene can be detected at the end of the reactions of NBD and 1,5-COD, but in the case of 1,5-CND and 1,5-HD, completion is not reached even after some 2 days. After a few minutes of reaction by 1,5-CND and 1,5-HD, CH=CH peaks different from those of either free diene or $Pd(diene)Cl_2$ are formed, which we attribute to $Pd(diene)Cl_3^-$, see Table II.

Changes in absorbance at 380–410 nm between 15 and 30 °C on solutions ca. 4×10^{-4} M in $PdCl_3(OH_2)^-$ and 3.3×10^{-2} to 1.6×10^{-1} M in diene over time spans of 15 s to 24 h reveal the following. 1,5-CND and 1,5-HD show an initial fast reaction that fits eq 3,[6,7] followed by a slow step with a rate independent of diene concentration and with a rate constant at 25.0 °C approximately equal to those determined by NMR data. Thus the UV and NMR data are fully compatible with the occurrence of (reversible) reactions 1 and 2 ($k_a \equiv k_1$ and $k_b \equiv k_{-1}$). For 1,5-CND and 1,5-HD, equilibrium studies were also made to study reaction 1, aliquots of diene being added to the palladium ion. The customary Hill plots of $(A_0 - A_x)/(A_\infty - A_0)$ against [diene][8] were linear, thus also demonstrating that free Cl^- is not produced during reaction 1 and also giving values of K_1; see Table III.

$$k_{obsd} = k_a[\text{diene}] + k_b \qquad (3)$$

Analogous experiments on NBD show only one fast step, obeying eq 4. The failure to detect $Pd(diene)Cl_3^-$ with NMR suggests that (2) is now fast compared with (1). Thus k_a corresponds to K_1k_2 (see Table III), while the absence of a k_b term indicates that (2) proceeds to "completion".

$$k_{obsd} = k_a[\text{diene}] \qquad (4)$$

In the case of 1,5-COD, graphs of ln $|A_t - A_\infty|$ against time display a change from one apparent step to two steps as the concentration of the diene rises, so that data can be handled in two ways. Where two steps can be discerned, the second is independent of diene concentration and so corresponds to (2). After correction for the second step,[9] k_{obsd} for the first follows eq 3 and so is identified with (1) (k_a being equivalent to k_1 as before). Alternatively, if k_{obsd} for runs in which there is only one apparent reaction are combined with k_{obsd} for those second steps that can be detected, graphs conforming to eq 5 are obtained. This equation describes a fast initial equilibrium followed by a slower step, viz. (1) followed by (2) here ($k_c \equiv K_1k_2$ and $k_d \equiv k_2$; see Table III). The value of K_1k_2 at 25.0 °C found in this way corresponds reasonably with the rate constant estimated from the NMR runs.

$$1/k_{obsd} = 1/(k_c[\text{diene}]) + 1/k_d \qquad (5)$$

Discussion and Conclusions

Kinetic parameters are given in Table III, while a qualitative idea of relative rates and completeness of reactions is shown in

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(1) $Na[PdCl_3(OCMe_2)]$ is prepared in situ by mixing anhydrous Na_2PdCl_4 with dry acetone. After 1 h of stirring, there is quantitative precipitation of 1 equiv. of NaCl, which is removed by filtration. The required solutions are obtained by diluting the filtrate with acetone and adding 2% water. In analogous work using pure acetone, NaCl tends to be precipitated, but the kinetics are very similar.

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(6) The rate is taken as $-d[PtCl_4^{2-}]/dt$, and customary pseudo-first-order conditions are used, so that a plot of ln $[A_t - A_\infty]$ against times gives k_{obsd} in the usual way.

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Table I. Speed and Completeness of Reactions[a]

diene	reaction 1		reaction 2		overall process	
1,5-COD	fast	incomplete	fast—comparable with (1)	complete	fast	complete
1,5-CND	fast	incomplete	slow	incomplete	slow	incomplete
NBD	moderate–slower than (2)[b]	?	too fast for Pd(diene)Cl_3^- to be detected[b]	complete	moderate	complete
1,5-HD	fast	incomplete	slow	incomplete	slow	incomplete

[a] On the basis of rate constants in Table III and NMR observations recorded in the text. [b] Alternatively, Pd(η^4-NBD)Cl_2 is formed directly from NBD in a one-step process.

Table II. Olefinic ^{1}H NMR δ Values in Acetone-d_6 at Ca. 25 °C[a]

	δ		
diene	free diene	Pd(diene)Cl_3^-	Pd(diene)Cl_2[b]
1,5-COD	5.51	*c*	6.2
1,5-CND	5.57–5.25	5.9–5.62	6.54
NBD	6.73	*c*	6.23
1,5-HD	6.0–5.65	5.43 (5.13–4.85)?	6.7–6.4, 5.4–5.1

[a] Addition of 2% D_2O has little effect other than to broaden the spectra slightly. [b] Preparations of Pd(diene)Cl_2 compounds are by published methods: 1,5-COD,[2] 1,5-CND,[3] NBD,[4] 1,5-HD.[5] [c] Not detected.

Table III. Rate Constants at 25.0 °C in 2% Aqueous Acetone[a]

diene	$k_1/M^{-1}\ s^{-1}$	k_{-1}/s^{-1}	K_1/M^{-1}	$K_1k_2/M^{-1}\ s^{-1}$	k_2/s^{-1}	$k_{-2}[Cl^-]/s^{-1}$
1,5-CND	1.5	1.3×10^{-2}	84[b]		4.5×10^{-5}	[ca. 5×10^{-5}]
1,5-HD	0.85	9.3×10^{-3}	31[b]		8.3×10^{-4}	[ca. 10^{-4}]
NBD				0.077		ca. 0
1,5-COD	ca. 1.0	(ca. 4.8×10^{-2})	(26)	0.85	0.038	[ca. 0]

[a] Unbracketed data are based on gradients and intercepts as indicated in the text. Brackets and parentheses signify data inferred from NMR and calculated from other data, respectively. [b] From Hill plots, not k_1/k_{-1}.

Table I. The rate constant for the reaction of an unhindered C═C bond with $PdCl_3(OCMe_2)^-$, a parameter which does not seem to have been determined, is about 1 $M^{-1}\ s^{-1}$ at 25.0 °C. Pd(η^2-NBD)Cl_3^- was not detected. Thus the η^4-species is formed either directly from NBD in a one-step process, or by a rapid reaction of the η^2-complex. Comparison of what we have called K_1k_2 for NBD with that for COD suggests that if there is a two-step process for the former, (1) is slower than for the other dienes.

The rate of formation and stability of the Pd(η^4-diene)Cl_2 species depends very much on the diene. Of the four species, only Pd(COD)Cl_2 and Pd(NBD)Cl_2 are stable (thermodynamically), the latter being formed less quickly than the former. Neither Pd(CND)Cl_2 nor Pd(HD)Cl_2 are stable; both are produced very slowly. Our results support enthalpy studies that indicate a fall in stability: COD > NBD > HD.[10,11] The stability of the η^4-complex seems to depend on the conformation of the diene. Very little change in the geometry of NBD can or does occur in NBD when it coordinates.[12] The most stable conformer of 1,5-COD is the twist-boat,[13] and this shape is retained in Pd(1,5-COD)Cl_2.[11] However, in Pd(1,5-HD)Cl_2 the diene has the conformation of a twist-boat but with a side missing[5] (that is, like 1,5-COD without the C^7–C^8 link). Simple modeling shows that in this conformer there is considerable van der Waals repulsion between the endo-H^1 and -H^6 atoms. One can be quantitative about 1,5-CND. It has to change from its natural C_2 conformer[14] to a twist-boat chair shape in Pd(1,5-CND)Cl_2,[11] which requires a free energy change[14] of 9.7 kJ mol^{-1}. The largest value of K_1 in Table III is about $10^2\ M^{-1}$, which corresponds to a free energy change of −5 kJ mol^{-1} at 298 K to replace an acetone ligand by the alkene. As Cl^- has a higher affinity for Pd^{II} than acetone has, the free energy change in (2) is probably larger and hence less favorable for the forward reaction. The implication is that in going from Pd(η^2-1,5-CND)Cl_3^- to Pd(η^4-1,5-CND)Cl_2, the replacement of Cl^- by C═C will not provide sufficient free energy to bring the ligand to the right conformation for bonding of the second alkene group.

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Registry No. 1,5-COD, 111-78-4; 1,5-CND, 57357-81-0; NBD, 121-46-0; 1,5-HD, 592-42-7; Na[$PdCl_3(OCMe_2)$], 98838-66-5; Na_2PdCl_4, 13820-55-8.

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