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DISPLACEMENT OF DIENES FROM PLANAR COMPLEXES

REACTION OF (1,2-BISDIPHENYLPHOSPHINOETHANE)(3a,4,7,7a-TETRAHYDRO-*exo*-6-METHOXY-*endo*-4,7-METHANOINDENE-*endo*-$5\tau,2\pi$)-PALLADIUM(II) AND -PLATINUM(II) CATIONS WITH ACIDS

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Summary

A kinetic study of the reaction of $[M(C_{10}H_{12} \cdot OCH_3)(P—P)]^+$ complexes (M = Pd, Pt; P—P = 1,2-bisdiphenylphosphinoethane; $C_{10}H_{12}$ = *endo*-dicyclopentadiene) with hydrogen halides, HX (X = Cl, Br) in aqueous methanol at 35°C is described. The proposed mechanism involves slow formation of the solvato species $[M(C_{10}H_{12})(solv.)(P—P)]^{2+}$ followed by fast reaction with X^- to give $M(P—P)X_2$.

Introduction

The displacement of polydentate ligands from d^8 transition metal complexes generally involves opening of the chelated ring followed by competition between ring closure and diplacement of the ligand [1]. In a previous paper [2] the kinetics of the reaction between $[Pd(C_8H_{12} \cdot OCH_3)(2,2'\text{-bipyridyl})]^+$ and hydrogen halides in aqueous methanol were described. Now we report a kinetic investigation of the reaction of $[M(C_{10}H_{12} \cdot OCH_3)(P—P)]^+$ complexes (M = Pd, Pt; $C_{10}H_{12} \cdot OCH_3$ = 3a,4,7,7a-tetrahydro-*exo*-6-methoxy-*endo*-4,7-methanoindene-*endo*-$5\sigma,2\pi$; P—P = 1,2-bisdiphenylphosphinoethane) with hydrogen halides in aqueous methanol at 35°C. Our aim is to determine the influence of the central metal on the diene substitution mechanism in such complexes.

Experimental

$[Pd(C_{10}H_{12} \cdot OCH_3)(P—P)]PF_6$ [3], $[Pt(C_{10}H_{12} \cdot OCH_3)(P—P)]Cl$ [4] and $M(P—P)Cl_2$ [5] complexes were made by published procedures. $M(P—P)Cl_2$ compounds were prepared by treating $[M(C_{10}H_{12} \cdot OCH_3)(P—P)]^+$ with HCl in methanol.

Kinetics

The reactions were carried out in aqueous methanol at 35° C and 0.5 *M* ionic strength. The concentrations of halides and acid were determined by titration. A freshly made solution of the complex $[M(C_{10}H_{12} \cdot OCH_3)(P—P)]^+$ (ca. 10^{-4} *M*) and a solution of the acid HX (X = Cl, Br), containing lithium perchlorate, were placed in a thermostat. The reactions were started by mixing known volumes of the two solutions in a 1-cm quartz cell placed in the thermostated compartment of an Optica CF4R double-beam recording spectrophotometer. The progress of the reaction was monitored by recording the UV spectral change. A large excess of lithium chloride and acid was used in order to give pseudo-first-order conditions. Pseudo-first-order rate constants, k_{obs} (s^{-1}) were determined from slopes of plots of $\log(A_t - A_\infty)$ vs. time (A_t and A_∞ are the optical densities after time *t* and 10 half lives respectively at a chosen wavelength).

The identification of dicyclopentadiene as the only organic reaction product was accomplished as follows. Concentrated methanol solutions of $[M(C_{10}H_{12} \cdot OCH_3)(P—P)]^+$ complexes were allowed to react with a slight excess of HCl, and the organic material was extracted with n-hexane. The $C_{10}H_{12}$ was identified in the extract by GC analysis using a Dexil column (column temperature 70° C; injector and detector temperature 150° C).

Results and discussion

The reaction:

$$[M(C_{10}H_{12} \cdot OCH_3)\ (P—P)]^+ + H^+ + 2\ X^- \rightarrow M(P—P)X_2 + C_{10}H_{12} + CH_3OH \qquad (1)$$

proceeds to completion in aqueous methanol at 35° C in a single observable stage *.

Kinetic runs were carried out at different halide, acid and water concentrations. In each set of runs one concentration was changed while the others were kept constant.

Table 1 lists rate data for reaction 1. The results can be summarized as follows:

(i) in the concentration range of X^- investigated, at constant proton and water concentrations, the rate is virtually independent of the nature and concentration of halide;

(ii) at constant water and halide concentrations values of k_{obs} (s^{-1}) depend linearly on $[H^+]$ (Fig. 1);

(iii) the rate decreases as the water content increases.

The kinetic results do not exclude the possibility that the rate determining step of reaction (1) is proton attack on the M—C σ bond of $[M(C_{10}H_{12} \cdot OCH_3)(P—P)]^+$ complexes. However, in this case, we expect the release of *exo*-6-methoxy-3a,4,5,6,7,7a-hexahydro-4,7-methanoindene instead of dicyclopen-

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* No significant UV spectral variation occurs on adding an excess of Cl^- to methanol solutions of $[M(C_{10}H_{12} \cdot OCH_3)(P—P)]^+$ complexes.

TABLE 1

VALUES OF KINETIC CONSTANTS FOR THE REACTION OF $[M(C_{10}H_{12}\cdot OCH_3)(P—P)]^+$ COMPLEXES WITH HYDROGEN HALIDES IN AQUEOUS METHANOL AT VARIOUS OXONIUM ION AND HALIDE CONCENTRATIONS (T 35°C)

M/X	$10^2[H^+]$ (mol/l)	$10^2[X^-]$ (mol/l)	$10[ClO_4^-]$ (mol/l)	H_2O (%)	$10^3\ k_{obs}$ (s^{-1})
Pd/Cl	2.00	2.00	4.80	5.00	21.00
	2.00	6.76	4.32	5.00	21.00
	2.00	16.20	3.38	5.00	19.50
	1.85	0.97	4.90	20.00	10.00
	1.85	1.85	4.815	20.00	10.00
	1.85	7.15	4.285	20.00	10.00
	1.85	9.70	4.03	20.00	9.70
	0.925	9.70	4.03	20.00	4.54
	4.62	9.70	4.03	20.00	22.70
Pd/Br	1.85	1.70	4.83	20.00	10.00
	1.85	8.50	4.15	20.00	10.00
	1.85	12.10	3.79	20.00	9.60
Pt/Cl	1.93	1.93	4.81	5.00	10.00
	1.93	6.83	4.317	5.00	10.00
	1.93	10.7	3.93	5.00	9.40
	1.85	0.97	4.903	20.00	3.70
	1.85	1.85	4.815	20.00	3.80
	1.85	7.15	4.285	20.00	4.00
	1.85	9.70	4.03	20.00	3.80
	0.50	9.70	4.03	20.00	0.97
	0.975	9.70	4.03	20.00	1.80
	4.62	9.70	4.03	20.00	9.70
Pt/Br	1.85	1.70	4.83	20.00	4.00
	1.85	8.50	4.15	20.00	4.00
	1.85	13.6	3.64	20.00	3.60

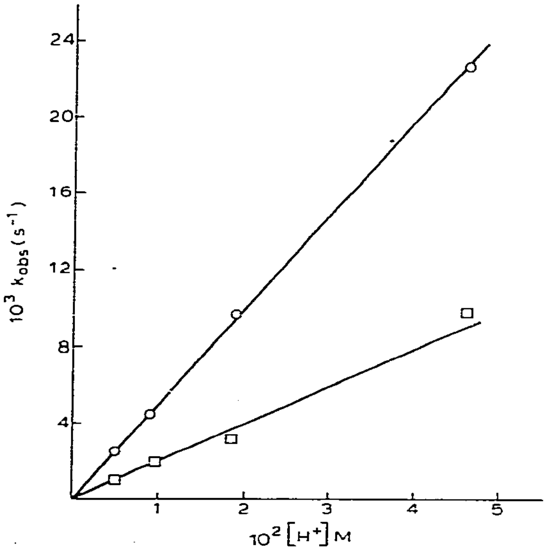
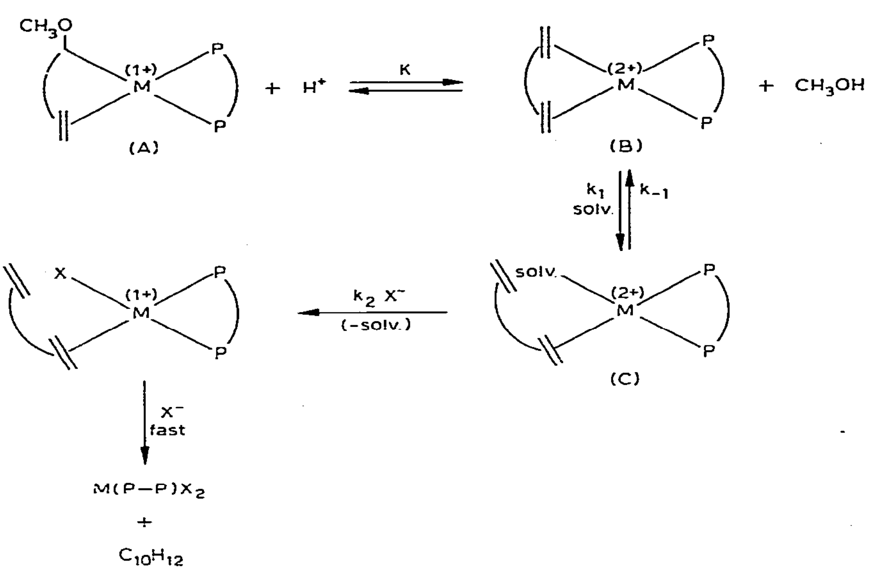


Fig. 1. Plots of k_{obs} (s^{-1}) versus $[H^+]$ at $[Cl^-] = 9.7 \times 10^{-2}$ M and $\mu = 0.5$ M for the reaction of $[M(C_{10}H_{12}\cdot OCH_3)(P—P)]^+$ complexes with HCl in methanol containing 20% water. ○, M = Pd; □, M = Pt.

tadiene. A mechanism consistent with our findings is shown in Scheme 1.

Scheme 1



Since no intermediate was detected the steady step approximation can be applied to species (C). If $K[\mathrm{H}^+] << 1$ the resultant rate law takes the form:

$$k_{\mathrm{obs}} = \frac{Kk_1k_2[\mathrm{H}^+][\mathrm{X}^-]}{k_2[\mathrm{X}^-] + k_{-1}} \tag{2}$$

If $k_2[\mathrm{X}^-] >> k_{-1}$ eq. 2 reduces to:

$$k_{\mathrm{obs}} = Kk_1[\mathrm{H}^+] \tag{3}$$

Eq. 3 accounts for the linear dependence of kinetic values on $[\mathrm{H}^+]$ (Fig. 1) and for their independence of $[\mathrm{X}^-]$.

The proposed mechanism involves the cleavage of the carbon bonded —OCH_3 group of A in an initial fast pre-equilibrium. The ensuing diene complex B undergoes a bimolecular attack by a molecule of solvent in the rate-determining step. The labile intermediate C then rapidly decomposes to the final product by release of the coordinated olefin. The decrease of the rate observed as the content of water increases can be attributed to increasing solvation of H^+.

It is well known that substitution reactions of palladium(II) complexes are generally faster than those of platinum(II) [6]. Therefore we expect that the values of k_1 should be higher for the palladium derivate [7]. Thus it is likely that the slight increase of the rate observed in reaction 1 when the central metal changes from platinum to palladium is the result of a balance of thermodynamic (K) and kinetic (k_1) factors.

Acknowledgements

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