Mechanism of Electrophilic Cleavage of the Pt–C Bond in *trans*-[PtX(CH_2CMe_3)(PEt_3)$_2$] by HX (X = Cl, Br)

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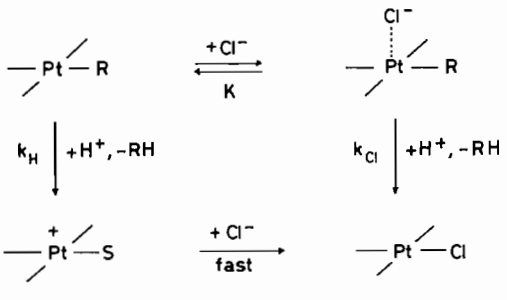
We have recently shown [1] that protonolysis of *trans*-[PtXR(PEt_3)$_2$] (X = Cl, Br; R = Me, Et, n-Pr, n-Bu, CH_2Ph) by HX in aqueous methanol to yield *trans*-[PtX$_2$(PEt_3)$_2$] and RH proceeds by fast pre-equilibrium formation of a Pt(II) anionic intermediate via interaction of the halide with the square-planar substrate, combined with slow parallel protonation of both the substrate and the intermediate, causing the cleavage of the metal–carbon σ bond:



The k_{obs} values were a linear function of $[H^+]$ and an increasing curvilinear function of $[X^-]$ which levelled off to a limiting value at high X^- concentrations, according to the general rate law

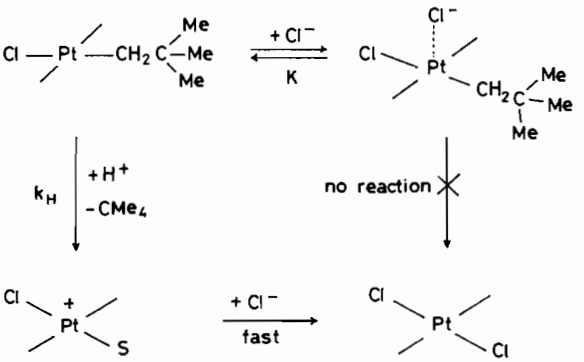
$$k_{obs} = [H^+]\frac{k_H + k_X K[X^-]}{1 + K[X^-]} \quad (1)$$

We have now found that the protonolysis of the neopentyl complex *trans*-[PtX(neopentyl)(PEt_3)$_2$] by HX in 9/1 v/v MeOH/H_2O (neopentyl = CH_2CMe_3*) proceeds by essentially the same mechanism, but with a rate law which is a particular case of the general expression of eqn. (1) where $k_X \approx .0$ for X = Cl^- and $K \approx 0$, $k_X \approx 0$ for X = Br^-.

Table I lists the k_{obs} values at 30 °C (I = 0.4 M, $LiClO_4$). For the reaction with X = Cl^- the rate decreases with increasing Cl^- concentration according to the rate law

$$k_{obs} = \frac{k_H[H^+]}{1 + K[Cl^-]} \quad (2)$$

The following parameters were computed by a non-linear least-squares fit of data in Table I to eqn. (2): $k_H = 0.090 \pm 0.001$ M^{-1} s^{-1}, $K = 2.5 \pm 0.1$ M^{-1}, $k_{Cl} \approx 0$. Accordingly, the mechanism again involves prior fast formation of the anionic intermediate which, however, appears to be inert toward attack by the proton, probably because of steric crowding by the bulky neopentyl group:



It is noteworthy that the k_H term is much higher than the corresponding parameter for the previously studied [1] *trans*-[PtXR(PEt_3)$_2$] substrates, as a consequence of the good donor properties of the neopentyl group which offset the adverse steric factor. An increased protonolysis rate with increasing electron density at the protonation site was previously observed for the cleavage of substituted phenyl derivatives *cis*-[Pt(C_6H_4Y)$_2$(PEt_3)$_2$] [2] and

trans-[PtBr(neopentyl)(PEt_3)$_2$] was prepared by reaction of neopentylMgBr with *cis*-[PtCl$_2$(PEt_3)$_2$] in Et_2O at 0 °C (50% excess) and recrystallization from methanol. *Anal.* Found (calc.): C, 34.88(35.05); H, 6.98(7.09)%. ^{31}P NMR (C_6D_6, H_3PO_4 external ref.): δ + 8.8 ppm(t), ^1J(Pt–P) 2995 Hz. *trans*-[PtCl(neopentyl)(PEt_3)$_2$] was prepared by metathesis from the bromide analog with $AgNO_3$/LiCl in aqueous acetone. *Anal.* Found (calc.): C, 38.40 (37.95); H, 7.38 (7.68)%. ^{31}P NMR: δ +11.1, ^1J(Pt–P) 3011 Hz.

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TABLE I. Rate Parameters for the Reaction *trans*-[PtX(neopentyl)$(PEt_3)_2$] + H^+ + X^- → *trans*-[$PtX_2(PEt_3)_2$] + neopentane in 9/1 v/v MeOH/H_2O at 30 °C. I = 0.4 M ($LiClO_4$)

X	$[H^+]$ (M)	$[X^-]$ (M)	$10^3 k_{obs}$ (s^{-1})
Cl	0.2	0.006	17.25
	0.2	0.012	17.55
	0.2	0.020	16.83
	0.05	0.025	4.14
	0.2	0.04	16.70
	0.2	0.08	15.10
	0.2	0.12	13.93
	0.05	0.15	3.25
	0.2	0.16	12.39
	0.2	0.20	12.01
	0.05	0.25	2.82
	0.05	0.30	2.56
	0.05	0.35	2.19
	0.2	0.40	8.25
	0.02	0.10	1.48
	0.04	0.10	2.93
	0.08	0.10	5.96
	0.12	0.10	8.88
	0.16	0.10	12.00
	0.20	0.10	14.93
	0.25	0.10	18.72
	0.30	0.10	22.13
Br	0.05	0.005	5.27
	0.05	0.012	5.53
	0.05	0.018	5.13
	0.05	0.05	5.28
	0.05	0.10	5.64
	0.05	0.15	5.49
	0.05	0.20	5.35
	0.05	0.25	5.32
	0.05	0.30	5.11
	0.05	0.35	5.27
	0.02	0.10	2.20
	0.04	0.10	4.58
	0.08	0.10	9.15
	0.12	0.10	12.96
	0.16	0.10	17.41
	0.20	0.10	22.61

for the cleavage of the Pt–Me bond in *trans*-[PtMe(Ar)$(PEt_3)_2$] [3]. The equilibrium constant K is virtually the same as that observed for *trans*-[PtXR$(PEt_3)_2$].

For the reaction of *trans*-[PtBr(neopentyl)$(PEt_3)_2$] with HBr, the rate is independent of Br^- concentration and is a linear function of $[H^+]$:

$$k_{obs} = k_H[H^+] \quad (3)$$

($k_H = 0.122 \pm 0.004$ M^{-1} s^{-1}). Rate law 3 was also observed for the protonolysis of *cis*-[$PtAr_2(PEt_3)_2$]

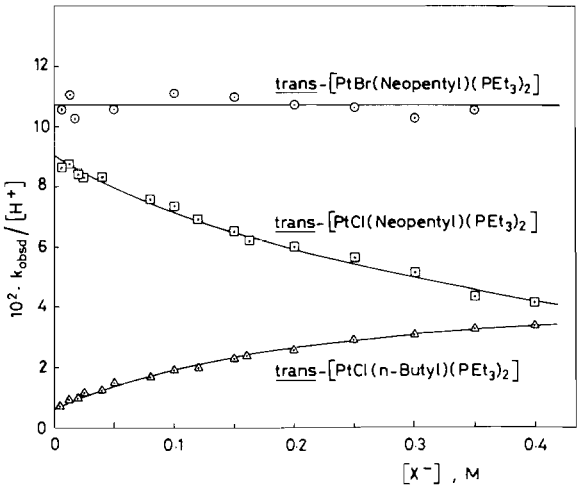
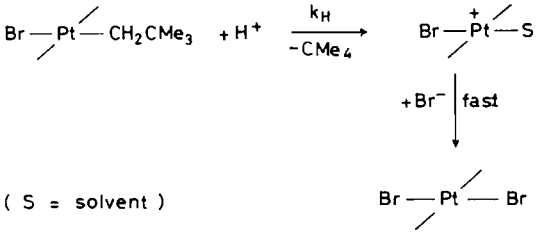


Fig. 1. Dependence of $k_{obs}/[H^+]$ on halide concentration for the systems *trans*-[PtX(R)$(PEt_3)_2$/HX (R = neopentyl, X = Cl, Br; R = n-Butyl, X = Cl).

and *trans*-[PtMe(Ar)$(PEt_3)_2$] [2, 3], and corresponds to simple electrophilic attack of the proton on the substrate, without formation of any intermediate:



Here the bulkiness of both the bromide and the neopentyl group militates against the interaction of the anion with the substrate.

Figure 1 shows the dependence of $k_{obs}/[H^+]$ on halide concentration for the systems *trans*-[PtX(R)$(PEt_3)_2$]/HX (R = neopentyl, X = Cl, Br; R = n-Butyl, X = Cl [1]). The present and previous results indicate that the particular mechanism observed depends on a delicate interplay of electronic and steric factors.

References

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