Journal of Organometallic Chemistry, 187 (1980) C17—C21
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Preliminary communication

REACTIONS OF STABLE [$PtCl_2(\eta^2-C_2H_4)$(t-BuNCHCHNt-Bu)]. RETENTION OF THE PENTACOORDINATE STRUCTURE UPON HALOGEN EXCHANGE AND LIGAND SUBSTITUTION WITH OLEFINS, α-DIIMINES AND *N,N′*-DISUBSTITUTED 1,2-DIAMINOETHANES

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(Received November 19th, 1979)

Summary

The axial halogen atoms as well as the equatorial η^2-C_2H_4 and σ,σ'-*N,N′* chelate bonded t-BuNCHCHNt-Bu ligands in pentacoordinate [$PtCl_2(\eta^2-C_2H_4)$-(t-BuNCHCHNt-Bu)] can be displaced with retention of the trigonal bipyramidal structure. Halogen—halogen exchange is initiated by formation of an ionic intermediate [$PtCl(\eta^2-C_2H_4)$(t-BuNCHCHNt-Bu)]Cl. The reversible exchange of the equatorial ligands with olefins or bidentate diimine or diamine ligands (N—N) is proposed to proceed via pentacoordinate intermediates [$PtCl_2(\eta^2-C_2H_4)(\eta^2$-olefin)(t-BuNCHCHNt-Bu)] and [$PtCl_2(\eta^2-C_2H_4)$(t-BuNCH-CHNt-Bu)(N-N)], respectively in which the α-diimine is σ-*N* monodentate bonded. Selective coordination of *cis*-olefins (maleic anhydride, dimethylmalonate, methylacrylate or acrolein) has been observed. Some relevant ^1H and ^{13}C NMR data for the novel pentacoordinate Pt^{II}-olefin complexes are given.

Both pyridine (L) [1] and olefin (ol) exchange [2] in complexes *trans*-[$PtCl_2(\eta^2$-ol)L] have been demonstrated to proceed via pentacoordinate transition states [$PtCl_2(\eta^2$-ol)L_2] and [$PtCl_2(\eta^2$-ol$)_2$L], respectively. In the course of our investigations on the coordination behaviour of α-diimines, RN=CHCH=NR, (R-dim) towards Pd^{II}, Pt^{II} and Rh^I [3—7], we found that stable analogues of the [$PtCl_2(\eta^2$-ol)L_2] transition state can be prepared if L_2 is a bidentate R-dim ligand and the R group is connected to the nitrogen via a quarternary carbon atom. This enabled us to study separately the factors determining the stability and the molecular dynamics of Pt^{II}-olefin complexes possessing a pentacoordinate structure. For example, for the first time the occurrence of olefin rotation

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TABLE 1

^{1}H AND ^{13}C NMR DATA OF [PtCl$_2$(η^2-C$_2$H$_4$L] COMPLEXES

	^{1}NMR (δ, ppm) ^{a}				^{13}C NMR (δ, ppm) ^{b}				
	CH_3	CH_2	HC = N	C_2H_4	CH_3	CH_2	C—N	N = C	C_2H_4
[PtCl$_2$(η^2-C$_2$H$_4$)(t-Bu-dim)]	1.67(s)		8.68 (36.5)(s)	3.53 (71)	30.60 (4)		64.30 (25)	156.80	38.10 (292)
[PtBr$_2$(η^2-C$_2$H$_4$)(t-Bu-dim)]	1.68(s)		8.67 (37)(s)	3.63 (70)	31.28		64.35 (24)	157.56	35.59 (286)
[PtBrCl(η^2-C$_2$H$_4$)(t-Bu-dim)]	1.68(s)		8.67 (37)(s)	3.56 (70)	30.87		64.31 (24)	157.14	36.78 (287)
[PtI$_2$(η^2-C$_2$H$_4$)(t-Bu-dim)] ^{c}	1.77(s)		8.68 (38)(s)	3.68 (71)					
[PtCl$_2$(η^2-C$_2$H$_4$)(EtMe$_2$C-dim)]	0.91(t); 1.63(s)	2.05(q)	8.58 (36)(s)	3.55 (71)	8.76; 27.71	39.18	67.09 (25)	157.14	39.18 (293)
[PtCl$_2$(η^2-C$_2$H$_4$)(t-Bu-diam)]	1.43(s)	3.03(b)		3.37 (71)	29.25 (6)	43.87 (9)	56.11 (4)		35.71 (298)
[PtCl$_2$(η^2-C$_2$H$_4$)(NC$_5$H$_5$)] ^{d}				4.92 (61)					75.3 (164)
[PtCl$_2$(η^2-C$_2$H$_4$)(NC$_5$H$_5$)] ^{e}				3.9 (70)					

^{a} In CDCl$_3$ relative to TMS $J(^{195}Pt—^1H)$ coupling (in Hz) between parenthesis; recorded on a Varian T 60 spectrometer. ^{b} In CDCl$_3$ relative to TMS inlined CDCl$_3$ reference, $J(^{195}Pt—^{13}C)$ coupling (in Hz) between parenthesis; recorded on a Varian CFt 20 spectrometer. ^{c} Recorded in acetone relative to TMS. ^{d} Taken from ref. 11. ^{e} Taken from ref. 1c.

at pentacoordinate Pt^{II} centers could be detected [6]. Furthermore, it appeared that the η^2-bonded olefins stabilized the σ,σ'-N,N' chelating coordination mode of the R-dim ligand. Replacement of the olefin by a phosphine ligand or a second R-dim ligand changes the coordination mode of R-dim into either a monodentate σ-N [3,4], bridging σ-N, σ'-N' [3,5,6,7] or fluxional σ-$N \leftrightarrow \sigma'$-$N'$ [4] type.

In the complexes containing fluxional bonded R-dim the N to N' site exchange occurs intramolecularly and involves a pentacoordinate transition state [$PtCl_2(PR_3)$(R-dim)] [4]. In particular, this observation, which indicates that the R-dim ligand can act both as a σ-N ($2e$) and σ,σ'-N,N' ($4e$) ligand, encouraged us to study ligand exchange reactions with the stable $18e$ Pt-R-dim complex [$PtCl_2(\eta^2$-$C_2H_4)$(t-Bu-dim)] (I). In this paper we report the results of a study of the exchange of a, the axial Cl atoms and b, the equatorial η^2-C_2H_4 and σ,σ'-N,N' chelate bonded t-BuN=CHCH=Nt-Bu ligands *.

Halogen exchange in I [ν_{as}(Pt—Cl) 332 cm^{-1}] was found to be very slow. Quantitative Cl/I exchange to give [$PtI_2(\eta^2$-$C_2H_4)$(t-Bu-dim)] (II: ν_{as}(Pt—I) 178 cm^{-1}) occurred during 24 h in the 1/3 molar reaction of I with NaI in acetone. The reaction of I with NaBr is much slower (>3 days) and a better route for obtaining [$PtBr_2(\eta^2$-(C_2H_4)(t-Bu-dim)] (III) (ν_{as}(Pt—Br) 256 cm^{-1}) is the reaction of K[$PtBr_3(\eta^2$-$C_2H_4)$] with t-Bu-dim. I—III are non-electrolytes in acetone and are monomeric in $CHCl_3$. ^1H and ^{13}C NMR spectrometry revealed that II and III have the same trigonal bipyramidal structure as was established for I [3b,6]. On going from square planar [$PtCl_2(\eta^2$-$C_2H_4)L$] to pentacoordinate [$PtCl_2(\eta^2$-$C_2H_4)$(R-dim)] the η^2-C_2H_4 ligand shows a diagnostic increase of $J(^{195}Pt$—$^{13}C)$ and $^2J(^{195}Pt$—$^1H)$ values as well as the upfield shift of δ(C) and δ(H) [1c,6,8—11]; in this respect the NMR data of II and III are clearly consistent with the trigonal bipyramidal formulation [cf. data in Table 1].

In order to exclude the possibility that these halogen exchange reactions occur via intermediate formation of Na[$PtX_3(\eta^2$-$C_2H_4)$], a solution of I and III (3/4 molar ratio) in $CDCl_3$ was stirred at room temperature and the reaction was monitored by ^1H and ^{13}C NMR spectrometry. After 10 days an equilibrium was reached, invoking a mixture of I, III and the mixed halide product [$PtClBr(\eta^2$-$C_2H_4)$(t-Bu-dim)] (IV), (see Table 1). This suggests that these exchange reactions are initiated by the formation of an ionic intermediate [$PtX(\eta^2$-$C_2H_4)$(t-Bu-dim)] Y (V) **. In this respect the recently established X-ray crystal structure of [$PtCl(\eta^2$-$C_2H_4)$(tmed)] ClO_4 is of interest [12].

The σ,σ'-N,N' bonded t-Bu-dim ligand of I can readily be replaced by reaction with excess of other nitrogen ligands e.g. pyridines, 1,2-diamines or other R-dim ligands. For example, the 1/5 molar reaction of I with $EtMe_2C$-dim in $CHCl_3$ or CH_2Cl_2 resulted in free t-Bu-dim and [$PtCl(\eta^2$-$C_2H_4)$($EtMe_2C$-dim)], which was isolated almost quantitatively. Furthermore, reaction of I with 2,4,6-trimethylpyridine in a 1/5 molar ratio afforded pure *trans*-

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* Satisfactory C, H, N and X analyses were obtained for all new compounds.

** In view of the specific formation of the *trans* products we assume, that the cation interacts with neutral I, thus forming a binuclear cationic species, e.g. [Cl(t-Bu-dim)(η^2-C_2H_4)PtCl—PtBr(η^2-C_2H_4)(t-Bu-dim)$]^+$ which upon dissociation produces either the starting species or the exchange products. Attempts to synthesize compounds V in which X = halogen and Y = BF_4^- or PF_6^- failed.

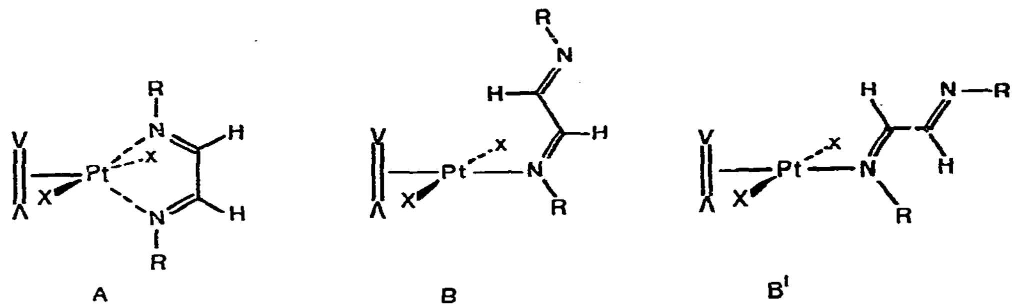

Fig. 1. A. Pentacoordinate structure containing σ,σ'-*N,N'* (4*e*) bonded R-dim. B. Two possible conformations of the intermediate, formed by Pt—N dissociation and concomitant rotation around the C—C bond, which contains σ-*N* (2*e*) bonded R-dim i.e. I, X = Cl; II, X = I; III, X = Br; IV, X = Br or Cl.

[$PtCl_2(\eta^2-C_2H_4)$(2,4,6-trimethylpyridine)]. The reverse reaction using excess t-Bu-dim appeared to be a convenient alternative route for the synthesis of [$PtCl_2(\eta^2$-ol)(R-dim)] complexes. Likewise, the novel complexes [$PtCl_2(\eta^2-C_2H_4)$\{σ,σ'-*N,N'*-R(H)NCH_2CH_2N(H)R\}] (VI, R = t-Bu, $EtMe_2C$-) (see Table I) * could be directly prepared by reacting R(H)NCH_2CH_2N(H)R (R-diam) with either tetracoordinate complexes [$PtCl_2(\eta^2-C_2H_4)$(2,4,6-trimethylpyridine)] or K[$PtCl_3(\eta^2-C_2H_4)$], or with pentacoordinate [$PtCl_2(\eta^2-C_2H_4)$(R-dim)] complexes.

Two observations indicate that the olefin—Pt^{II} bond remains intact during the exchange reaction which is at the slow exchange limit on the NMR time scale. Firstly, ^{13}C and ^1H NMR data of [$PtCl_2(\eta^2$-ol)(R-dim)] (where R and ol are prochiral) revealed that in solution no olefin—Pt^{II} bond dissociation occurs [6]. Secondly, cleavage of the olefin—Pt bond in [$PtCl_2(\eta^2$-ol)(R-dim)] or [$PtCl_2(\eta^2$-ol)(R-diam)] complexes which occurs at higher temperatures, is irreversible both in solution and in the solid. The resulting *cis*-[$PtCl_2$(R-dim)] or *cis*-[$PtCl_2$(R-diam)] (VII) complexes, in which the bidentate ligands are σ,σ'-*N,N'* bonded, are sparingly soluble in $CHCl_3$ and acetone. This excludes the formation of a *cis*-dichloroplatinum complex VII as an intermediate in the substitution reactions.

In view of our previous results [4] it seems likely, therefore, that in the first step of the substitution reaction the R-dim ligand becomes a σ-*N* (2*e*) donor by Pt—N dissociation. This occurs with concomitant rotation around the central C—C bond, which moves the non-coordinated C=Nt-Bu part of the t-Bu-dim ligand from the Pt coordination sphere (see Fig. 1). This is followed by coordination of the attacking R-dim, R-diam or pyridine ligand. It is interesting to note that R-dim/R'-dim or R-diam exchange implies formation of a pentacoordinate transition state containing two σ-*N* (2*e*) monodentate bonded R-dim ligands.

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* These results point to a trigonal bipyramidal structure, with the Cl atoms in axial position and the η^2-bonded olefin and σ,σ'-*N,N'* bonded R(H)NCH_2CH_2N(H)R ligands in the equatorial plane. The fact that only one resonance pattern is observed indicates that either only one diastereomer (the coordinated N atoms are stable chiral centers) is present in solution or rapid inversion of configuration at the N atoms takes place.

The same type of mechanism might operate for the observed specific olefin exchange of I with mono- and *cis*-di-substituted olefins. For example pure [$PtCl_2(\eta^2$-ol)(t-Bu-dim)] in which ol represents methylacrylate (VIII), dimethylmalonate (IX) or maleic anhydride (X) * was synthesized by treating a solution of I in CH_2Cl_2 or acetone with a 3—5 fold excess of the olefin for 3—48 h. In contrast, no reaction was observed when I was treated with dimethylfumarate, not even with a 5-fold excess of the olefin and reaction times exceeding 7 days. No exchange occurs between I and crotonaldehyde, metacrolein, *trans*-stilbene and tetracyanoethene.

This surprising selectivity for the exchange of *cis*-olefins is further demonstrated by the reaction of an 1/1 mixture of *cis*- and *trans*-$C_2H_2(COOCH_3)_2$ with a 2—3 fold excess of the Pt^{II} complex I in CH_2Cl_2. After 48 h a solution containing IX, unreacted I, and the *trans*-olefin was observed. This result is of synthetic interest because the *cis*-olefin $C_2H_2(COOCH_3)_2$ can be recovered from isolated IX by treatment with C_2H_4 (50 atm) in $CHCl_3$ solution.

Acknowledgement

Stimulating discussions with Prof. K. Vrieze are gratefully acknowledged.

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* $PtCl_2(\eta^2$-ol)(t-Bu-dim): ol = maleic anhydride, ^1H NMR δ(—CH=CH—) 4.58 ppm [$^2J(^{195}Pt^1H)$ 74 Hz]; ol = di-methylmalonate, ^1H NMR δ(—CH=CH—) 4.53 ppm [77 Hz] ^{13}C NMR δ(—C=C—) 37.55 ppm [$^1J(^{195}Pt^{13}C)$ 340 Hz]; ol = methylacrylate, ^{13}C NMR (C=C—) 39.40 ppm [321 Hz], 34.63 ppm [290 Hz].