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NUCLEOPHILIC ATTACK OF IMIDATE ANIONS ON [Pt(DIENE)Cl_2] COMPLEXES

FORMATION OF COMPOUNDS WITH Pt—N σ-BONDS

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Summary

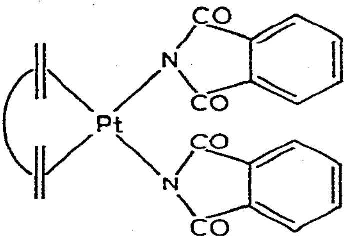
A basic aqueous solution of maleimide or phthalimide reacts with [Pt(diene)Cl_2] complexes to give complexes of the type [Pt(diene)(imidate)$_2$] (diene = 1,5-cyclooctadiene, dicyclopentadiene and norbornadiene). The spectra and the reactions of these complexes give information about the nature of the Pt—N σ-bond.

Introduction

There have been extensive studies on the reactions of nucleophiles (Y) such as ammonia and amines [1], methylate [2], acetylacetonate [3] or malonate [4] with diene complexes of the type [M(diene)Cl_2], (M = Pt or Pd; diene = dicyclopentadiene, 1,5-cyclooctadiene or norbornadiene) to give compounds of the type [M(Y—diene)Cl]$_2$. The reactions of the platinum and palladium enyl complexes and their bridge-splitting derivatives with a variety of small unsaturated molecules such as CO [5,6] or RNC [7,8] were also investigated. However, with benzylamine ($C_6H_5CH_2NH_2$) as the nucleophile, the product from the reaction with [Pd(1,5-cyclooctadiene)Cl_2] was reported to have a tetrameric structure with an uncoordinated double bond [9]. Moreover, the reactions with $LiCH_3$ [10], $NaSCF_3$ [11] or TlC_5H_5 [12] proceed differently to give replacement of the halide, but these reactions probably have a different mechanism. In order to clarify the factors favouring the alternative reaction paths, we have investigated the reactions of platinum complexes $[Pt(diene)Cl_2]$ (diene = 1,5-cyclooctadiene, norbornadiene or dicyclopentadiene) with the phthalimidate, $\overline{\mathrm{COC_6H_4CON}}^-$, and maleimidate, $\overline{\mathrm{COHC{=}CHCON}}^-$, anions, which because of the electron-withdrawing effect of the carbonyl groups can be considered to have a nucleophilic character intermediate between amines and CH_3^- or $^-SCF_3$.

Results and discussion

Treatment of a CH_2Cl_2 solution of $[Pt(diene)Cl_2]$ (diene = 1,5-cyclooctadiene, norbornadiene or dicyclopentadiene) with a basic aqueous solution of phthalimide gave white products which were shown by analysis and spectroscopic data to be compounds of type I.



(I)

Analogous compounds were obtained from $[Pt(C_8H_{12})Cl_2]$ and maleimide. The analytical and spectroscopic data for the compounds discussed are listed in Table 1 and 2.

TABLE 1

ANALYTICAL DATA

Compound	M.p. [a] (°C)	Analysis found (calcd.) (%)			Mol. wt. (in acetone)
		C	H	N	
$[Pt(C_8H_{12})(phthalimidate)_2]$	200	48.49 (48.40)	3.39 (3.38)	4.73 (4.70)	615 (595)
$[Pt(C_{10}H_{12})(phthalimidate)_2]$	190	49.56 (50.40)	3.21 (3.25)	4.61 (4.54)	—
$[Pt(C_7H_8)(phthalimidate)_2]$	210	47.20 (47.66)	2.75 (2.78)	4.88 (4.84)	—
$[Pt(C_8H_{12})(maleimidate)_2]$	205	38.76 (38.79)	3.30 (3.25)	5.63 (5.65)	—
$[Pt(CH_3NC)_2(maleimidate)_2]$	190	30.40 (30.57)	2.62 (2.55)	11.70 (11.89)	480 (471)
$[Pt(CH_3NC)_2(phthalimidate)_2]$	220	41.10 (42.33)	2.10 (2.12)	9.61 (9.87)	—
$[Pt(PPh_3)_2(phthalimidate)_2]$	240	60.30 (59.58)	7.11 (7.11)	2.70 (2.67)	—

[a] All compounds melting with decomposition.

TABLE 2

SPECTRAL DATA

Compound	NMR[a] τ (ppm)									IR[b]
	Vinylic protons			Imidate protons			Other			ν(C=O) (cm^{-1})
	B	*N*	*J*	B	*N*	*J*	B	*N*	*J*	
[Pt(C_8H_{12})(phthalimidate)$_2$]	3.5	4	65	2.3–2.6	8	—	7.00–8.10	8	—	1665
[Pt($C_{10}H_{12}$)(phthalimidate)$_2$]	3.53–3.70	2 + 2	60	2.2–2.6	8	—	6.8–8.2	8	—	1668
[Pt(C_7H_8)(phthalimidate)$_2$]	3.68	4	62	2.3–2.6	8	—	5.70–8.20	2 + 2	—	1663
[Pt(C_8H_{12})(maleimidate)$_2$]	3.91	4	64	3.52	4	9	7.00–8.10	8	—	1670
[Pt(CH_3NC)$_2$(maleimidate)$_2$]	—	—	—	3.50	4	8	6.48	6	18	1674
[Pt(CH_3NC)(phthalimidate)$_2$]	—	—	—	2.3–2.6	8	—	6.50	6	19	1670

[a] $CDCl_3$ solution (TMS as internal standard); B = band centre; *N* = number of protons; *J* = *J*(Pt—H) in Hz. [b] Nujol mull, band centre.

The products of type I do not show the N—H absorption in the IR spectrum, and they react with hydrogen chloride in anhydrous benzene to give [Pt(diene)Cl_2] and the parent imide.

The NMR spectra of these complexes are consistent with a structure having two N-coordinated imidate anions. The vinylic absorption is shifted with respect to the uncoordinated olefin, for example, free norbornadiene has the olefinic protons absorptions at τ 3.25 and these are shifted to τ 3.68 ppm in the complex [Pt(C_7H_8)(phthalimidate)$_2$]. This result can be interpreted by assuming that the presence of two strongly σ-donor imidate anions makes the metal atom more effective in backbonding to the olefin, or less able to accept electrons from the olefin. The IR spectra of the uncoordinated imides show two bands attributable to ν(C=O) at 1781 and 1747 cm^{-1} for phthalimide, and at 1770 and 1737 cm^{-1} for maleimide [13]. Indeed, only one absorption attributed to ν(C=O) was observed in the IR spectra of compounds of type I, and the position of this band is lowered with respect to the lower frequency band of the free imide. This is in agreement with results for other N-bonded imide complexes of platinum(II) [14] of the type *trans*-[Pt(PPh_3)$_2$(imidate)H], for which the lowering of ν(C=O) was attributed to electron drift from the carbonyl groups to the central metal atom. The NMR spectrum of [Pt(C_8H_{12})(maleimidate)$_2$] supports this assumption, in that the olefinic protons absorptions of the anionic imidate ligand are coupled to platinum [J(Pt—H) = 8 Hz] indicating some interaction of the organic moiety with the metal. This conclusion may reasonably be extended to the phthalimide derivatives, although the phenyl ring protons appear in the NMR spectrum as unresolvable multiplets.

Nucleophilic attack of imidate anions to the [Pt(diene)Cl_2] complexes caused chloride displacement and, in the cases examined, no addition to the coordinated double bond was observed.

Addition reaction of amines to complexes of type [Pt(C_8H_{12})Cl_2] are thought to proceed by initial nucleophilic attack on the metal [15] and on this basis one would expect imidate also to give the same type of product. However, a complex rate law has been found for the attack of ROH on the double bond of [Pd(norbornadiene)Cl_2], and direct addition of methanol was shown to occur in the case of [Pd(dipyridyl)(C_8H_{12})]$^+$, where two *cis* positions are blocked by chelation [16]. On the other hand, migration of a $^-OCH_3$ group from the organic moiety to the coordinated carbonyl group has been reported [17] (eq. 1).

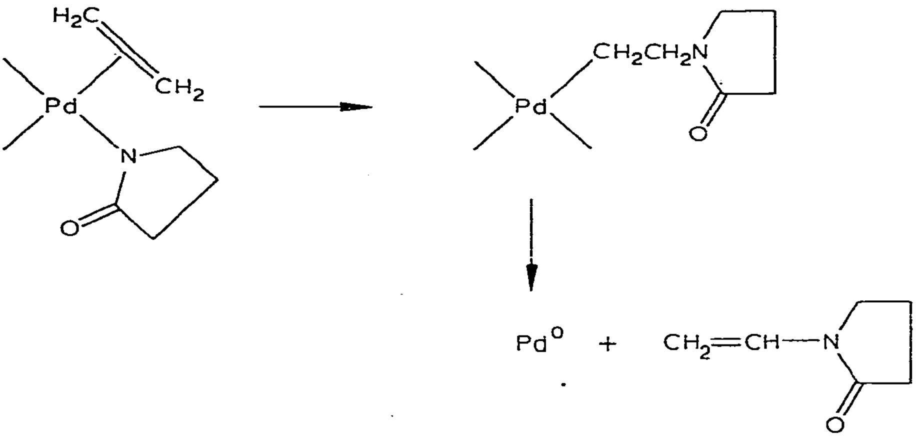
$$[\mathrm{Pt(COD{-}OR)COCl}] \rightleftharpoons [\mathrm{Pt(COD)COCl}]^+\mathrm{RO}^- \rightleftharpoons [\mathrm{Pt(COD)COORCl}] \qquad (1)$$

Analogously the imidate anions might migrate from the organic group to the metal (the equilibrium being shifted towards this latter product) giving halide displacement. The migration, if operative, probably depends on the experimental conditions and on the metal, since there has been recently reported [18] the synthesis of [Pd(diene—phthalimidate)Cl]$_2$, in which the amide has added to the coordinated double bond.

The products we isolated may be regarded as a type of stable intermediate in these addition reactions. In fact, the scheme propesed for the reaction of ethylenepalladium(II) chloride with pyrrolidone involves the formation of a complex having a Pd—N σ-bond [19], which decomposes via migration of the amido group followed by hydride abstraction to produce palladium metal and *N*-vinylpyrrolidone (Scheme 1).

In the hope of observing attack of imidate anions on the coordinated olefins we studied the reactions of complexes of type I with neutral ligands which are known to promote migration from the metal to the coordinated double bond [3,11,20]. However, the reaction 2 occurs with displacement of the diene; this

SCHEME 1



$$[Pt(C_8H_{12})(imidate)_2] + 2\ L \rightarrow [PtL_2(imidate)_2] + C_8H_{12} \qquad (2)$$

(imidate = $C_8H_4NO_2^-$, L = CH_3NC, PPh_3; imidate = $C_4H_2NO_2^-$, L = CH_3NC)

behaviour is analogous to that of $[Pt(C_8H_{12})(CH_3)_2]$ [10] and $[Pt(C_7H_8)(SCF_3)_2]$ [11] complexes, suggesting a similarity between the σ Pt—N bonds in these compounds. The complexes of the type $[Pt(CH_3NC)_2(imidate)_2]$ prepared by this method show two absorption in the IR spectrum at 2200 and 2220 cm^{-1} attributed to $\nu(C{\equiv}N)$, indicative of a *cis* configuration for the coordinated isocyanides.

Experimental

IR spectra were recorded on a Perkin—Elmer 457 spectrophotometer and NMR spectra were obtained on a Varian NV14 spectrometer with $CDCl_3$ as solvent and TMS as internal standard. The compounds $[Pt(C_{10}H_{12})Cl_2]$ [2], $[Pt(C_8H_{12})Cl_2]$ [2] and $[Pt(C_7H_8)Cl_2]$ [21] were prepared by published methods.

Preparation of [Pt(diene)(imidate)$_2$]

$[Pt(C_8H_{12})Cl_2]$ (278 mg, 1.0 mmol) was dissolved in chloroform and treated, whilst stirring, with 100 ml of an aqueous solution containing 2.1 mmol of phthalimide (300 mg) and 9 mmol of Na_2CO_3 (1.044 mg). After 24 h the organic layer was separated and dried over anhydrous Na_2SO_4. The $CHCl_3$ solution was concentrated to a small volume under reduced pressure and ether was slowly added to give a white crystalline product identified as [Pt(C_8H_{12})($C_8H_4NO_2$)$_2$]. The compounds [Pt($C_{10}H_{12}$)($C_8H_4NO_2$)$_2$], [Pt(C_7H_8)($C_8H_4NO_2$)$_2$] and [Pt(C_8H_{12})($C_4H_2NO_2$)$_2$] were prepared similarly.

Reactions of [Pt(C_8H_{12})(imidate)$_2$] with neutral ligands

(a). Methyl isocyanide (82.1 mg, 2.0 mmol) in CH_2Cl_2 was added dropwise, with stirring, under nitrogen, to a dichloromethane solution of [Pt(C_8H_{12})($C_8H_4NO_2$)$_2$] (595.5 mg, 1.0 mmol) at room temperature. After 2 h the solution was evaporated, diluted with hexane, and the ivory-white precipitate filtered off and dried in vacuo. Recrystallization from chloroform/ether gave *cis*-[Pt(CH_3NC)$_2$($C_8H_4NO_2$)$_2$]. Under similar conditions the off-white complex [Pt(CH_3NC)$_2$($C_4H_2NO_2$)$_2$] was obtained from [Pt(C_8H_{12})($C_4H_2NO_2$)$_2$].

(b). Triphenylphosphine (263 mg, 1.0 mmol) in ether was added dropwise to a $CHCl_3$ solution of [Pt(C_8H_{12})($C_8H_4NO_2$)$_2$] (297.7 mg, 0.5 mmol) and the mixture was shaken for 2 h under nitrogen. After evaporation of the solvent and addition of hexane, the white compound [Pt(PPh_3)$_2$($C_8H_4NO_2$)$_2$] was isolated.

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