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NUCLEOPHILIC ATTACK ON OLEFINS COORDINATED TO PLATINUM

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SUMMARY

NMR at 220 MHz is used to demonstrate nucleophilic addition of amines to olefins coordinated to platinum, and to identify products; bonding occurs at the β position, and attack is limited to unhindered secondary amines of high basicity.

INTRODUCTION

Nucleophilic attack by amines on olefins coordinated to platinum and the concomitant $\pi \rightarrow \sigma$ rearrangement has been identified either by NMR[1] or by chemical analysis of products[2]. We report some examples where both techniques have been used simultaneously and the reaction shown to be rapid and reversible, leading to moderately stable σ-bonded products. NMR at 220 MHz has proved to be particularly definitive in assigning structures.

EXPERIMENTAL AND DISCUSSION

Evaporation under vacuum of a solution of a-(π-C_2H_4)-c-(Et_2NH)$PtCl_2$, or (I), and diethylamine (in approximate molar ratio, 1/1.1) in acetone gives a yellow solid to which we have assigned structure (II) on the following evidence. Found: C, 27.50; H, 5.34; N, 6.20; res. 43.5%. (II) requires: C, 27.26; H, 5.95; N, 6.36; Pt, 44.4%. In acetone the compound is a non-conductor, and has an approximate molecular weight of 430 [mol. wt. of (II) is 440.2]. τ-Values (measured at 220 MHz) for the compound together with those of the parent compounds are given in Table 1. A spectrum identical to that of the new compound is produced by adding diethylamine gradually to (I) in acetone-d_6 at 33°; moreover the areas of the peaks at τ 5.48, 8.59, 6.60, 7.15 and 8.20 grow in the approximate ratio, $-4/6/4/2/2$. The peaks at τ 7.15 and 8.20 are 1/2/1 triplets; satellite bands attributable to ^{195}Pt are shown by the latter, but any exhibited by the former are obscured by other resonances (*cf.* the analogous dimethylamine complex). The NMR spectra provide no evidence in any of the examples studied of coordination of amine to an α-carbon as in (III). Reaction (1)

TABLE 1

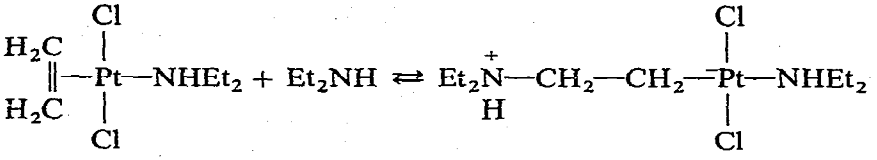
NMR DATA[a]

Compound	$C\underline{H}_3CH_2N$	$PtNCH_2C\underline{H}_3$	$CH_3C\underline{H}_2N$	$PtNC\underline{H}_2CH_3$	$NC\underline{H}_2CH_2Pt$	$NCH_2C\underline{H}_2Pt$	π-$C_2\underline{H}_4$
Et_2NH	8.97		7.42				
$(C_2H_4)PtCl_2(NHEt_2)$		8.45		6.75, 7.03			5.48
$Et_2NHCH_2CH_2PtCl_2(NHEt_2)$	8.59(t)	8.8–8.9(b)	6.60(q)	6.9–7.1(b), 7.2–7.4(b)	7.15(t)	8.20(t) J(Pt–H) 89 Hz	
	$C\underline{H}_3N$	$PtNC\underline{H}_3$			$NC\underline{H}_2CH_2Pt$	$NCH_2C\underline{H}_2Pt$	π-$C_2\underline{H}_4$
Me_2NH	7.80						
$(C_2H_4)PtCl_2NHMe_2$		7.48					5.54
$Me_2NHCH_2CH_2PtCl_2(NHMe_2)$	6.95(s)	7.48(s)			7.09(t) J(Pt–H) 36 Hz	8.25(t) J(Pt–H) 88 Hz	
	$C\underline{H}_3CH_2N$	$C\underline{H}_3CO$	$CH_3C\underline{H}_2N$	$\underline{H}C(COCH_3)_2$	$NC\underline{H}_2CH_2Pt$	$NCH_2C\underline{H}_2Pt$	π-$C_2\underline{H}_4$
Et_2NH	8.97		7.42				
$(C_2H_4)PtCl(Acac)$		8.00, 7.89		4.22			5.60
$Et_2NHCH_2CH_2PtCl(Acac)$	8.61(t)	8.38(s), 8.35(s)	6.60(q)	4.75(s)	7.21(t) J(Pt–H) 48 Hz	8.00(t) J(Pt–H) 98 Hz	

[a] b = broad, q = quartet, s = singlet, t = triplet.

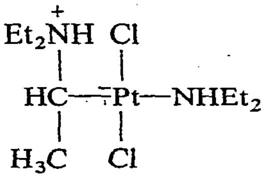
occurs within mixing time and is reversible. Similar results to those above are observed in $CHCl_3$-*d*.

The peaks at τ 6.75, 7.03 and 8.45 of (I) and those centred around τ 7.0, 7.3 and 8.85 of (II) do not coexist but collapse to form three broad peaks, whose positions depend on relative concentrations. Presumably the σ-bonded CH_2CH_2 group, like the π-C_2H_4[3], exerts a strong kinetic *trans* effect, so that the Pt-bonded $NHEt_2$ groups exchange very rapidly.



$$\begin{array}{c}H_2C\\ \|\\ H_2C\end{array}\!\!-\!\underset{\underset{Cl}{|}}{\overset{\overset{Cl}{|}}{Pt}}\!-NHEt_2 + Et_2NH \rightleftharpoons Et_2\underset{H}{\overset{+}{N}}-CH_2-CH_2-\underset{\underset{Cl}{|}}{\overset{\overset{Cl}{|}}{\bar{P}t}}-NHEt_2 \qquad (1)$$

(I) (II)



$$\begin{array}{cc}Et_2\overset{+}{N}H & Cl\\ | & |\\ HC- & \bar{P}t-NHEt_2\\ | & |\\ H_3C & Cl\end{array}$$

(III)

TABLE 2

EVIDENCE FOR NUCLEOPHILIC ADDITION AT 33° BY BASE, B, TO OLEFIN COORDINATED TO THE PLATINUM COMPLEXES $(C_2H_4)PtBCl_2$ AND $(C_2H_4)Pt(Acac)Cl$

B	pK_a[a]	*Evidence (–), or no evidence (×)*
Me_2NH	10.7	—
Et_2NH	11.0	—
Pr_2NH	10.9	—
i-Pr_2NH	11.0	×
Bu_2NH	11.3	—
i-Bu_2NH	11.0	×
t-Bu_2NH		×
cyclo-HexMeNH	10.5	—
Pyrrolidine	11.1	—
Piperidine	11.1	—
$PhCH_2MeNH$	9.5	—
PhMeNH	4.8	×
Pyridine	5.2	×
Pyrrole	ca. −3.8	×
$BuNH_2$	10.7	×[b]
n-$OctNH_2$	10.6	×
cyclo-$HexNH_2$	10.7	×
$PhNH_2$	4.6	×
Et_3N	10.7	×[b]

[a] Ref. 4, ±0.1 except for pyrrole. [b] Only $(C_2H_4)PtBCl_2$ tested.

Compounds analogous to (II) are formed by addition of dimethylamine to a-(π-C_2H_4)-c-(Me_2NH)$PtCl_2$ and of diethylamine to (π-C_2H_4)PtCl(Acac) in acetone-d_6 (see Table 1) (Acac≡acetylacetonato). In both of these new compounds coupling between ^{195}Pt and α- as well as β-CH_2 protons can be seen.

High basicity and relative freedom from steric hindrance are both important for the production of a σ-bonded compound from a secondary amine around room temperature. This was shown by following changes in NMR spectra in acetone-d_6 and in $CHCl_3$-d at 33°, evidence for rapid nucleophilic attack by other amines and $\pi \rightarrow \sigma$ rearrangements was sought (see Table 2). (The first solvent gives better spectra, but is liable to condense with primary amines to give enamines.) It is notable that a-(π-C_2H_4)-c-$BPtCl_2$ (where B is a base) and (π-C_2H_4)PtCl(Acac) are not attacked by primary amines (even strongly basic ones), unlike *cis*-(diene)$PtCl_2$ and a-C_2H_4-b-(phosphine)$PtCl_2$ complexes[2]. Moreover triethylamine does not attack a-(π-C_2H_4)-c-Et_3NPtCl_2.

The relative proportions of π-bonded starting material and σ-bonded product depend on amine concentration and temperature. Thus in reaction (1) at 33°, (I) only ceases to be detectable when a 10% excess of diethylamine is present, and $PyCH_2$-CH_2PtCl_2Py is only observed at reduced temperatures[1].

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