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Synthesis of Novel σ-Allyl Platinum(II) Complexes

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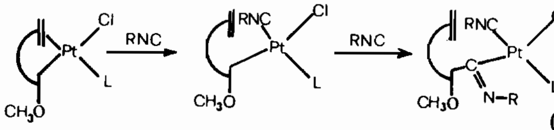
The reaction of [Pt(allyl)Cl]$_4$ with isocyanides gives dimeric allyl complexes of type [Pt(σ-allyl)-(CNR)Cl]$_2$ (R = CH_3, C_6H_{11}, and 2,6-dimethylphenyl) which dissolved in CH_2Cl_2 lead to [(η^3-allyl)Pt(CNR)Cl] derivatives. These latter react further with isocyanides to give the novel complexes [(σ-allyl)Pt-(CNR)$_2$Cl]. The mode of coordination of the allyl group has been studied by PMR and IR spectroscopy. The results obtained are compared with those related to the analogous palladium derivatives and methoxydienyl–Pt^{II} complexes.

Introduction

Compounds of the type [M(diene·OCH_3)LCl] (**1**) (L = PPh_3, isocyanides; diene = 1,5-cyclooctadiene, norbornadiene and dicyclopentadiene; M = Pt, Pd) react in two steps with carbon monoxide or isocyanides leading eventually to displacement of coordinated olefin and insertion of CO or CNR across the M–C σ bond [1–4]. In the case of the reaction of isocyanides with Pt^{II} complexes of type (**1**), the following mechanism was found:



(I)

wherein the first step involves substitution of the coordinated olefin [3]. We also showed that changes in the nature of the metal and of the σ + π ligand yielded different reaction products. This can be accounted for simply in terms of different steric and electronic properties of the chelating methoxydienyl moiety, as found for instance for the reaction of [Pd-(norbornadiene·OCH_3)Cl]$_2$ and [Pd-(dicyclopentadiene·OCH_3)Cl]$_2$ with 1,2-bis(diphenylphosphino)-etane [5]. The former norbornadiene complex and the platinum analog display a different behaviour also in the reaction with isocyanides [4], pyridine [6] and carbon monoxide [7] attributed to the peculiarity of the "pseudo-allyl" norbornadiene·-OCH_3 ligand. The allyl group, which has also been treated as a combination of σ M–C and π M–olefin bonding contributions, can be looked upon as a limiting example of the diene·OCH_3 ligands from both steric and electronic points of view, based also on structural data [8]. In this regard we deemed it worthwhile to study the reactivity of complexes [Pt-(allyl)Cl]$_4$ and [Pt(allyl)(CNR)Cl] with isocyanides, in order to shed some light on the course of reactions of type [I] as dictated by the nature of the σ + π allyl moiety and of the other ligands in the complex.

Results and Discussion

On reacting an ether suspension of [Pt(allyl)Cl]$_4$ (**2**) with a solution of isocyanides in the same solvent (Pt/CNR molar ratio 1) rapid changes of the nature and color of the solid were observed. The obtained ivory or pale yellow products have the elemental composition corresponding to adducts of one molecule of isocyanide for each platinum atom, [Pt-(allyl)(CNR)Cl]$_n$. The analytical and spectroscopic data for the compounds are listed in Tables I and II.

The infrared spectra of these complexes show strong bands in the $\nu_{C\equiv N}$ region according to the presence of coordinated isocyanides, a medium absorption at 1610 cm^{-1} attributable to the uncoordinated C=C stretching [9, 10] and two bands in the ν_{Pt-Cl} region. These latter absorptions support the dimeric formulation for these complexes with bridging chlorides [11, 12].

These spectral data could indicate a σ-allyl configuration in the products, according to the following reaction:

$$\underset{(2)}{[Pt(allyl)Cl]_4} + 4\,CNR \rightarrow 2\,\underset{(3)}{[Pt(\sigma\text{-allyl})(CNR)Cl]_2} \qquad [II]$$

(R = CH_3, C_6H_{11}, 2,6-dimethylphenyl)

Compounds of type (**3**) readily react with hydrogen chloride in dry ether or benzene to give the dimeric species [Pt(CNR)Cl_2]$_2$, identified on the basis of their spectroscopic properties [12]. This result may be considered as an evidence for the presence of a Pt–C σ bond since, it is known, HCl reacts with Pt^{II}–alkyl compounds to give the corresponding Pt^{II}–Cl complexes [13]. Compounds of type (**3**) are

TABLE I. Physical Properties and Analytical Data.

	M.p., °C	% C		% H		% N		% Cl	
		Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
Compounds of Type **3**									
[Pt(σ-allyl)(CH_3NC)Cl]$_2$	95	19.19	20.70	2.55	2.80	4.48	4.53	11.21	11.36
[Pt(σ-allyl)(C_6H_4NC)Cl]$_2$	110	31.56	31.60	4.20	4.18	3.67	3.81	9.31	9.42
[Pt(σ-allyl)(2,6-dimethylphenylisocyanide)Cl]$_2$	142	35.79	34.96	3.48	3.50	3.48	3.55	8.80	9.01
Compounds of Type **4**									
[Pt(η^3-allyl)(CH_3NC)Cl]^a	120	19.19	18.89	2.55	2.72	4.48	4.57	11.21	11.37
[Pt(η^3-allyl)($C_6H_{11}NC$)Cl]	134	31.56	30.96	4.20	4.10	3.67	3.54	9.31	9.20
[Pt(η^3-allyl)(2,6-dimethylphenylisocyanide)Cl]	175	35.79	36.21	3.48	3.54	3.48	3.29	8.80	8.70
Compounds of Type **5**									
[Pt(σ-allyl)(CH_3NC)$_2$Cl]	108	23.77	23.47	3.11	3.09	7.91	7.83	10.01	9.87
[Pt(σ-allyl)($C_6H_{11}NC$)$_2$Cl]	117	47.25	47.08	5.51	5.62	5.71	5.73	7.23	7.36
[Pt(σ-allyl)(2,6-dimethylphenylisocyanide)$_2$Cl]^b	220	41.69	41.64	4.30	4.15	5.24	5.05	6.64	6.60
[Pt(σ-allyl)(*p*-ClC_6H_4NC)$_2$Cl]	106	37.35	37.30	2.37	2.29	5.12	5.23	19.45	19.70

[a] M.wt. determined osmometrically in CH_2Cl_2 = 345, calcd. 312. [b] M.wt. in CH_2Cl_2 = 520, calcd. 533.

TABLE II. I.R. Spectral Data.[a]

	$\nu_{C\equiv N}$, cm^{-1}	$\nu_{C=C}$, cm^{-1}	ν_{Pt-Cl}, cm^{-1}
Compounds of Type **3**^{b}			
[Pt(σ-allyl)(CH_3NC)Cl]$_2$	2230	1613	320, 280
[Pt(σ-allyl)($C_6H_{11}NC$)Cl]$_2$	2200	1610	322. 278
[Pt(σ-allyl)(2,6-dimethylphenylisocyanide)Cl]$_2$	2180	1612	325, 280
Compounds of Type **5**			
[Pt(σ-allyl)(CH_3NC)$_2$Cl]	2250 2220	1620	325
[Pt(σ-allyl)($C_6H_{11}NC$)$_2$Cl]	2200 2165	1615	325
[Pt(σ-allyl)(2,6-dimethylphenylisocyanide)$_2$Cl]	2190 2160	1613	320
[Pt(σ-allyl)(*p*-ClC_6H_4NC)$_2$Cl]	2185 2160	1618	322

[a] Nujol mull. [b] The corresponding compounds of type **4** present the same $\nu_{C\equiv N}$ and one ν_{Pt-Cl} between 270–280 cm^{-1}.

moderately soluble in CH_2Cl_2 or $CHCl_3$ but insoluble in ethyl ether or petroleum ether, like the parent [Pt(allyl)Cl]$_4$. This latter presents in the solid state allyl bridges with each allyl group σ bonded to one platinum atom and π bonded to the other [14] so that, under the experimental conditions used, products of type (**3**) are somewhat expected. As a matter of fact, reaction [II] may be considered the replacement of a coordinated monoolefin by the entering isocyanide.

Attempted recrystallization from solvents in which compounds (**3**) are moderately soluble (such as anhydrous and HCl-free chloroform or dichloromethane) produces white compounds which show only one ν_{Pt-Cl} band and no absorption at 1610 cm^{-1}, while having the same elemental analysis of the parent σ-allyl species (**3**). These facts associated with the PMR results discussed below, indicate the following reaction scheme:

$$\begin{array}{ccc} [\mathrm{Pt(allyl)Cl}]_4 + 4\mathrm{CNR} \rightarrow & 2\ [(\sigma\text{-allyl})\mathrm{Pt(CNR)Cl}]_2 & \\ 2 & \downarrow 3\ \text{(dissolution)} & \text{(III)} \\ & 4\ [\mathrm{Pt(allyl)(CNR)Cl}] & \\ & 4 & \end{array}$$

(R = CH_3, C_6H_{11}, 2,6-dimethylphenyl)

Selected data for the PMR spectra of compounds of type (**4**) are listed in Table III, and Figure 1 reports the PMR spectrum of [Pt(allyl)(CH_3NC)Cl].

This spectrum shows at 6.55 τ the CH_3 resonance of the isocyanide group with J_{Pt-H} = 17 Hz [15]. Other signals are present at 7.65 τ (doublet; J = 12Hz), 7.28 τ (doublet; J = 13Hz), 6.15 τ (doublet;

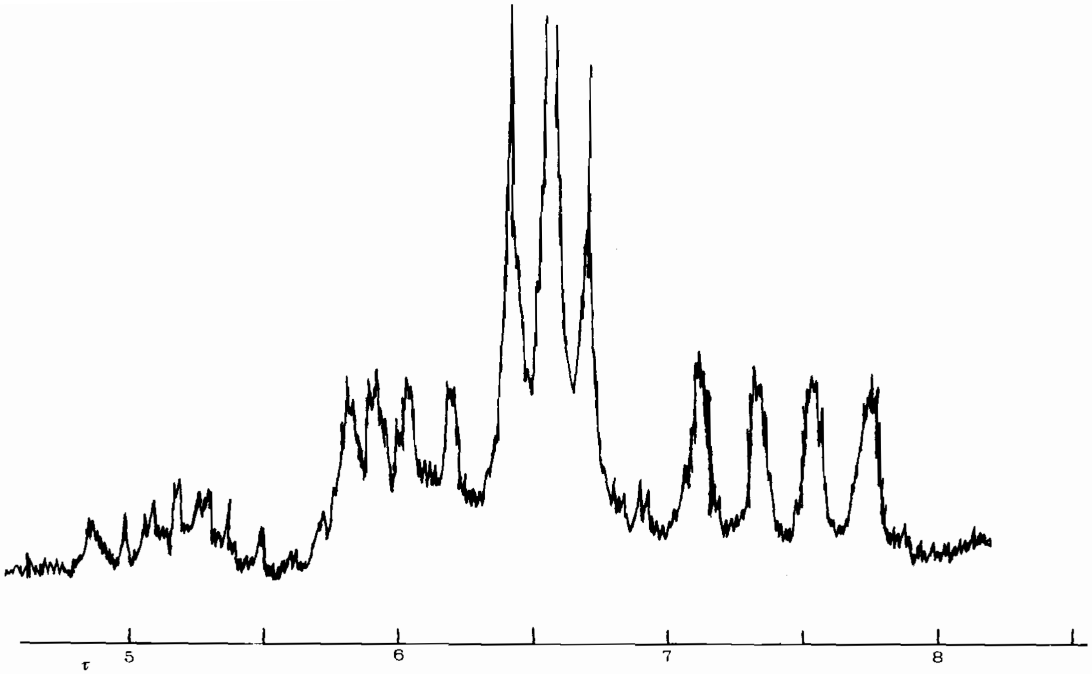


Figure 1. PMR spectrum at 60 MHz in $CDCl_3$ solution of $[Pt(\eta^3\text{-allyl})(CH_3NC)Cl]$.

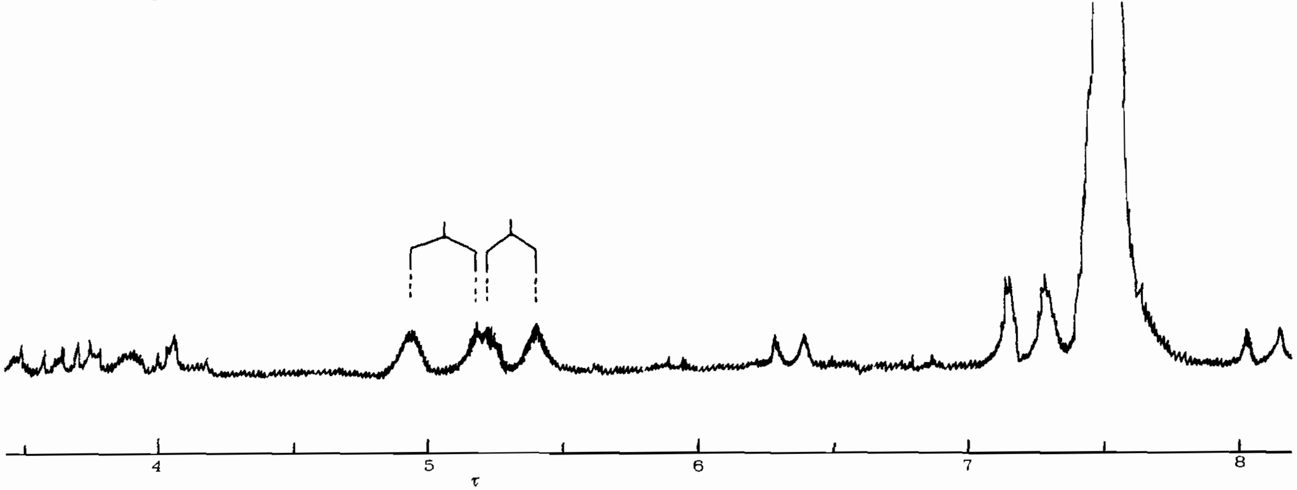
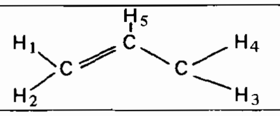


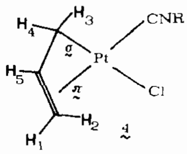
Figure 2. PMR spectrum at 60 MHz in $CDCl_3$ solution of $[Pt(\sigma\text{-allyl})(2,6\text{-dimethylphenylisocyanide})_2Cl]$.

TABLE III. Proton Magnetic Resonance Data.[a]

	Allylic Protons[b,c,d],					Isocyanide Protons, τ[c,d]
	τ_1	τ_2	τ_3	τ_4	τ_5	
Compounds of Type **4**						
[Pt(η^3-allyl)(CH_3NC)Cl]	5.85d (1) $J_{1-5} = 6$	6.15d(1) $J_{2-5} = 10$	7.65d(1) $J_{3-5} = 12$	7.28d(1) $J_{4-5} = 13$	5.26bm (1) –	6.55s (3) $^3J_{Pt-H} = 17$
[Pt(η^3-allyl)($C_6H_{11}NC$)Cl]	5.7–6.4[e] –	5.7–6.4[e] –	7.68d (1) $J_{3-5} = 13$	7.25d (1) $J_{4-5} = 14$	5.30bm (1) –	8.3bs (10) and 5.7–6.4 (1 + 2 of allyl group)[b]
[Pt(η^3-allyl)(2,6-dimethyl-phenylisocyanide)Cl]	5.74d (1) $J_{1-5} = 6–7$	6.03d (1) $J_{2-5} = 9$	7.41[e] –	7.10d (1) $J_{4-5} = 12$	5.18bm (1) –	7.50s (6); 2.85s (3)
	$\tau_{3,4}$	τ_1	τ_2	τ_5		
Compounds of Type **5**						
[Pt(σ-allyl)(2,6-dimethyl-phenylisocyanide)$_2$Cl]	7.23d (2) $J_{3,4-5} = 8$ $^2J_{Pt-H} = 108$	5.32d (1) $J_{1-5} = 10$ –	5.05d (1) $J_{2-5} = 15$ –	3.66bm (1) – –		7.51s (12), 2.83bs (6)
[Pt(σ-allyl)(p-ClC_6H_4NC)$_2$Cl]	7.55d (2) $J_{3,4-5} = 8$ $^2J_{Pt-H} = 106$	5.58d (1) $J_{1-5} = 10$ –	5.30d (1) $J_{2-5} = 14$ –	4.15bm (1) – –		2.80bm (8)
[Pt(σ-allyl)($C_6H_{11}NC$)$_2$Cl]	7.35d (2) $J_{3,4-5} = 8$ $^2J_{Pt-H} = 107$[e]	5.46d (1) $J_{1-5} = 9$ –	5.05d (1) $J_{2-5} = 15$ –	3.95bm (1) – –		8.3bs (20), 6.2bm (2)[b]
[Pt(σ-allyl)(CH_3NC)$_2$Cl]	7.40d (2) $J_{3,4-5} = 9$ $^2J_{Pt-H} = 109$[e]	5.51d (1) $J_{1-5} = 10$ –	5.10d (1) $J_{2-5} = 16$ –	3.9bm (1) – –		6.55s (6), $^3J_{Pt-H} = 18$

[a] In $CDCl_3$ or CD_2Cl_2 solution with TMS as internal standard. [b] J_{Pt-H} cannot be observed. [c] Coupling constants are reported in Hz. [d] Values in parenthesis refer to number of protons. [e] Partially masked by the isocyanide proton resonances.

J = 10Hz), 5.85 τ (doublet; J = 6Hz), 5.26 τ (multiplet), having intensity ratios 1:1:1:1:1. This spectrum is closely related to those of some unsymmetric allyl derivatives such as [(π-C_4H_7) and (π-C_3H_5)M(L)Cl] (M = Pd, L = PPh_3 [16] or PPh_2Me [17]; M = Pt, L = PPh_3, $AsPh_3$, pyridine and isoquinoline [18] which exhibit an ABCDX pattern for the allylic protons. The differences in the J coupling constant values of the doublets at 6.15 τ and 5.85 τ may be justified assuming that these signals are attributable to protons respectively *anti* and *syn* to the central proton. On the other hand, the almost similar coupling constant values for the two high field signals can difficultly be attributed to different *cis* and *trans* coupling constants, which are usually quite different. This anomaly was also present in the complex [(allyl)Pt($AsPh_3$)Cl] [18] and may be related to a strongly unsymmetric structure, so that compounds (**4**) could be formally represented by the $\sigma + \pi$ symbolic formulation [IV].

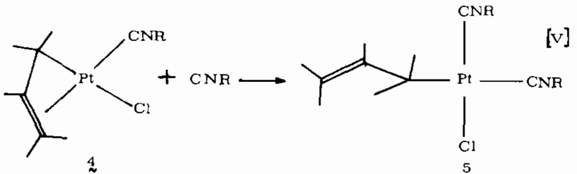


(IV)

In fact a structure of type [IV] may be considered as a limiting case of the unsymmetrically bonded allylic ligand, in relation to the large difference in *trans* influences between isocyanides and the chloride ligand.

The coupling constants between the allylic protons and the ^{195}Pt were not observed, since the corresponding resonances are likely to be lost in the background of the spectrum or masked by other proton resonances of the coordinated ligands. Structure [IV] shows the chloride ligand in *trans* position to the σ Pt–C bond as confirmed by the values of ν_{Pt-Cl} and the PMR resonances of the allylic protons [16, 18] (*cfr.* Tables II and III). It is noteworthy that the analogous Pd^{II} derivatives [Pd(allyl)(CNR)Cl] have a "dynamic allyl" structure [19], probably in connection with the different strengths of Pt–allyl bond relative to the Pd–allyl counterparts.

The reactions of products of type (**3**) or (**4**) in benzene solution with stoichiometric amounts of isocyanides underline the different behaviour of the allyl–Pt^{II} derivatives (**4**) relative to the corresponding Pd^{II} complexes. The palladium(II) compounds react with isocyanides to give insertion products of CNR across the Pd–allyl bond, with formation of dimeric $\{PdCl[C(=NR)C_3H_5](CNR)\}_2$ species with bridging chlorides [19]. In our case, at variance, a σ-allyl structure is proposed on the basis of spectroscopic properties and chemical reactivity:



[v]

4 5

The PMR spectrum of [Pt(σ-allyl) (2,6-dimethylphenylisocyanide)$_2$Cl] is reported in Figure 2. It shows the allyl group proton resonances at 7.23 τ (doublet, J = 8 Hz), 5.32 τ, 5.05 τ (doublets, J = 15 Hz, J = 10 Hz), 3.66 τ (multiplet) with integration ratios 2:2:1. The resonances at 7.23 τ are attributable to the protons on the carbon σ bonded to the metal. In fact they present two satellite peaks due to ^{195}Pt-coupling (J_{Pt-H} = 108 Hz) which is fairly large as expected for a $^2J_{Pt-H}$ coupling constant [20]. The position and multiplicity of the other resonances are comparable with those reported for other σ-allyl derivatives [9, 10, 21] and the σ-allyl structure of compounds (**5**) is also confirmed by the presence in the IR spectrum of the $\nu_{C=C}$ at 1615 cm^{-1} and of one single ν_{Pt-Cl} at 320 cm^{-1}. The analytical and spectral data of products of type (**5**) are reported in Tables I, II and III. Conductivity measurements in CH_2Cl_2 solution of complexes (**5**) indicate that they are non-electrolytes.

The presence of two $\nu_{C\equiv N}$ absorptions indicates a *cis* structure, and from the reaction with HCl in anhydrous benzene *cis*-$[Pt(CNR)_2Cl_2]$ complexes were obtained. This confirms the σ-allylic formulation of compounds (**5**). Products of type (**5**) constitute one of the few examples of stable σ-allyl derivatives of Pt^{II} [18], although σ-allyl derivatives were often proposed in order to explain some features of the PMR spectra of Pt–allyl complexes [22, 23].

The isolation of products (**5**) was favoured in our case (**i**) by the bonding mode of the allyl moiety in the starting [Pt(allyl)(CNR)Cl] (**4**) complexes and (**ii**) by the strong coordination ability of isocyanides. As for point (**i**) it has to be noted that reaction [V] parallels, at variance with the Pd^{II} case [19], the first step of the reaction of $[Pt(diene\cdot OCH_3)(CNR)Cl]$ with isocyanides, suggesting that for these types of reactions the factors favouring insertion across the Pt–C σ bond *versus* olefin displacement must be essentially electronic in nature. As for point (**ii**), in the case of reactions of [Pd(allyl)Cl]$_2$ with nucleophiles [24] or carbon monoxide [16] the weak coordinating ability of reactants employed prevented isolation of σ-allyl species analogous to (**5**), which nevertheless were shown to be present in solution.

Experimental

^{1}H NMR spectra were recorded in $CDCl_3$ (DCl free) or CD_2Cl_2 solutions with a VARIAN NV-14 60 MHz Spectrometer using TMS as internal standard.

IR spectra were registered on a Perkin–Elmer 457 Spectrophotometer in Nujol mulls.

Materials

[Pt(Allyl)Cl]$_4$ was prepared as previously described [25]. $C_6H_{11}NC$ and 2,6-dimethylphenylisocyanide were Fluka reagents and were used without further purification. Methylisocyanide and *p*-chlorophenylisocyanide were prepared according to literature methods [26].

Compounds of Type (3)

Preparation of [Pt(σ-allyl)(CH$_3$NC)Cl]$_2$.

A solution of methyl isocyanide (82 mg, 2 mmol) in 10 ml of dry ether was added dropwise under nitrogen to a stirred ether suspension of [Pt(allyl)-Cl]$_4$ (522 mg, 0.5 mmol) kept at –40 °C. The reacting mixture was allowed to react for 2 hr and then for further 4 hr at room temperature. The pale yellow product was separated by filtration and dried under vacuum (yield 546 mg: ≈90%).

Under similar experimental conditions, the analogous compound [Pt(σ-allyl)(2,6-dimethylphenylisocyanide)Cl]$_2$ was obtained in high yield (≈80%).

Similarly, but using petroleum ether as solvent, the complex [Pt(σ-allyl)($C_6H_{11}NC$)Cl]$_2$ was prepared.

The product obtained on reacting [Pt(allyl)Cl]$_4$ with *p*-Cl-phenylisocyanide was an untractable oil which prevented a complete characterization.

Compounds of Type (4)

Preparation of [Pt(allyl)(CH$_3$NC)Cl]

[Pt(σ-allyl)(CH$_3$NC)Cl]$_2$ (375 mg, 0.6 mmol) was dissolved in CH_2Cl_2 (35 ml) under nitrogen. It was then concentrated to small volume under reduced pressure and ether was added with stirring. The off-white product was obtained in almost quantitative yield.

The complexes [Pt(allyl)($C_6H_{11}NC$)Cl] and [Pt(allyl)(2,6-dimethylphenylisocyanide)Cl] were prepared under the same experimental conditions.

Compounds of Type (5)

Preparation of [Pt(σ-allyl)(CH_3NC)$_2$Cl]

To a suspension of 313 mg (1 mmol) of [Pt(allyl)(CH_3NC)Cl] in 50 ml of benzene (a solvent in which the complex is partially dissolved were added 20 ml of benzene solution of methylisocyanide (41 mg, 1 mmol) under nitrogen with stirring. After 1 hour an orange–yellow solid compound was formed and the precipitation was completed on diluting with petroleum ether. The yellow complex was then filtered and dried under vacuum (yield 306 mg, 86%).

The compounds [Pt(σ-allyl)($C_6H_{11}NC$)$_2$Cl] and [Pt(σ-allyl)(2,6-dimethylphenylisocyanide)$_2$Cl] were prepared in a similar way to the corresponding CH_3-CN complex. The complex [Pt(σ-allyl)(*p*-ClC_6H_4-NC)$_2$Cl] was obtained analogously by treatment of [Pt(allyl)Cl]$_4$ with a stoichiometric amount of the isocyanide.

Reactions of [Pt(allyl)(CH_3NC)Cl]$_2$ and [Pt(allyl')($C_6H_{11}NC$)$_2$Cl] with Hydrogen Chloride

A solution of [Pt(allyl)(CH_3NC)Cl]$_2$ in benzene was saturated with anhydrous HCl. Immediate precipitation of a white product occurred, which was identified as [Pt(CH_3NC)Cl_2]$_2$. *Infrared data:* $\nu_{C\equiv N}$ 2260 cm^{-1}; ν_{Pt-Cl} 350, 328, 308 cm^{-1}. *PMR data:* τ_{CH_3} at 6.25, J_{Pt-H} = 18 Hz. *Anal.:* Found: C 11.96, H 1.66, Cl 35.10. Calcd: C 11.60, H 1.46, Cl 34.29%.

Similarly was obtained the compound *cis*-[Pt($C_6H_{11}NC$)Cl_2] characterized by spectral comparison with an authentic sample [27].

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