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ALLYLPLATINUM AND PLATINUM(0) COMPLEXES WITH PHOSPHORUS-SULFUR MIXED LIGANDS

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Summary

Monomeric η^1-allyl complexes $[PtCl(C_3H_5)(PSR)]$, ($PSR = Ph_2P(CH_2)_2SR$, R = Me, Ph) are rapidly converted in polar media into the η^3-allyl derivatives $[Pt(C_3H_5)(PSR)]BF_4$. The NMR characteristics of both types of complex are discussed.

We recently described allylpalladium complexes containing mixed phosphorus-sulfur ligands of the type $R_2P(CH_2)_2SR$, which we prepared with the aim of providing new palladium(0) derivatives for testing in oxygenation reactions [1]. We now report the results of a parallel investigation on allylplatinum complexes containing the same hybrid ligands.

Both η^1- and η^3-allyl derivatives of platinum were prepared by treating $[PtCl(C_3H_5)]_4$ [2] with the bidentate ligands PSR ($PSR = Ph_2P(CH_2)_2SR$, R = Me, Ph) [3].

The neutral $[PtCl(\eta^1\text{-}C_3H_5)(PSPh)]$ is stable in benzene and its ^1H NMR spectrum exhibits resonances from σ-allyl protons in three distinct frequency regions (Table 1). The shifts and coupling constants and particularly the coupling between CH_2 protons and ^{195}Pt, are characteristic of a rigid η^1-allyl grouping [4–6]. The ^{31}P NMR spectrum shows a ^{31}P–^{195}Pt coupling constant of J 4500 Hz, large enough to indicate a mutual *trans*-position of η^1-allyl and phosphorous groupings [7].

In polar solvents, such as chlorinated compounds and alcohols, $[PtCl(\eta^1\text{-}C_3H_5)(PSPh)]$, slowly isomerizes, and eventually gives rise to limiting ^1H and ^{31}P NMR spectra characteristic of the ionic η^3-allyl derivative $[Pt(\eta^3\text{-}C_3H_5)(PSPh)]^+$ (eq. 1), which was independently prepared as its tetrafluoroborate salt.

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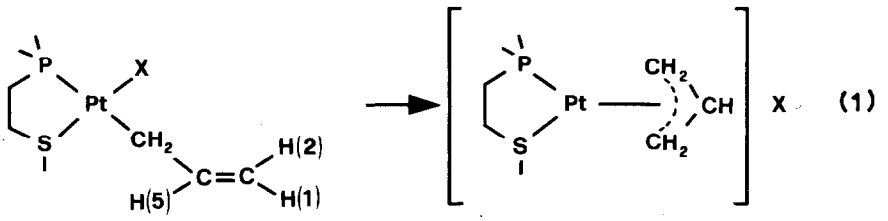
TABLE 1

NMR DATA FOR ALLYLPLATINUM COMPLEXES [a]

Complex	^1H	^{31}P
$[PtCl(\eta^1\text{-}C_3H_5)(PSPh)]$ [b]	H(1): 4.73 dd (J_5 10, J_2 2.5, J(Pt) 32) H(2): 4.46 dd (J_5 18, J_1 2.5, J(Pt) 36) CH_2: 3.08 dd (J_5 5, J(P) 8, J(Pt) 87) H(5): 5.78 m	37.9 (J(Pt) 4600)
$[Pt(\eta^3\text{-}C_3H_5)(PSPh)]BF_4$ [c]	2.75 m, 3.1 m	39.4 (J(Pt) 3590)

[a] δ in ppm, downfield from TMS and 85% H_3PO_4 respectively; J values in Hz; J_x: coupling constants with proton numbered x, J_P: with ^{31}P, J_{Pt}: with ^{195}Pt. [b] C_6D_6 solution. [c] CD_2Cl_2 solution.



The proton NMR spectrum of the cation $[Pt(\eta^3\text{-}C_3H_5)(PSPh)]^+$ shows allyl protons as broad multiplets in the 3.0 and 2.7 ppm regions, the latter being partly obscured by resonances from the methylene groups of the ligand, making it difficult to detect the ^{195}Pt satellites. The broad multiplets do not change significantly on lowering the temperature to $-60°C$, indicating a dynamic π-allyl bonding of platinum, probably via the conventional *syn,anti* exchange. The compound behaves differently from the analogous $[Pt(\eta^3\text{-allyl})L_2]^+$ species ($L = (PPh_3)_2$ or diars), which are fluxional only in the presence of coordinating counteranions, such as halides [8]. On the other hand, other related cations such as $[Pt(\eta^3\text{-allyl})COD]^+$ are strongly fluxional [7], even if in these cases the simple isomerization mechanism cationic π-allyl $\rightarrow$ neutral σ-allyl should not be obviously favored.

The NMR spectra of $[PtCl(C_3H_5)(PSMe)]$ and $[Pt(C_3H_5)(PSMe)]^+$ have little significance, since in solution both compounds rapidly undergo extensive decomposition to unknown products, probably via demethylation of the thioether moiety, as was observed in the case of the related allylpalladium derivatives [1].

As expected on the basis of the general behavior of the π-allylplatinum complexes [9], the treatment of $[Pt(\eta^3\text{-}C_3H_5)(PSPh)]BF_4$ with an excess of PSPh yields the platinum(0) derivative $[Pt(PSPh)_2]$ and the corresponding allylphosphonium salt. The platinum(0) derivative is unreactive towards oxygen, like the corresponding $[Pd(PSPh)_2]$ derivative [1], and it does not promote oxygen-transfer to olefins such as 1-octene.

Experimental

[PtCl(C$_3$H$_5$)(PSR)]

The ligand (1 mmol) was added to $[PtCl(C_3H_5)]_4$ (0.25 mmol) in methanol and the mixture stirred at room temperature. The colorless precipitate was recrystallized from CH_2Cl_2/ether (yield 65%). Anal. Found: C, 46.45; H, 4.03. $Pt(C_3H_5)(PSPh)Cl$

calcd.: C, 46.50; H, 3.73%. Found: C, 40.20; H, 4.27. $Pt(C_3H_5)(PSMe)Cl$ calcd.: C, 40.65; H, 4.17%.

$[Pt(C_3H_5)(PSR)]BF_4$

The procedure described above was repeated but in the presence of excess $NaBF_4$. Recrystallization from CH_2Cl_2/ether gave the pure product (yield 35%). Anal. Found: C, 42.47; H, 3.19. $Pt(C_3H_5)(PSPh)BF_4$ calcd.: C, 42.81; H, 3.44%. Found: C, 36.48; H, 3.50. $Pt(C_3H_5)(PSMe)BF_4$ calcd.: C, 37.08; H, 3.80%.

$[Pt(PSPh)_2]$

A saturated solution of $[Pt(C_3H_5)(PSPh)]BF_4$ and PSPh (2 ×) in methanol was stirred under N_2. Yellow crystals slowly separated (yield 50%). Anal. Found: C, 56.73; H, 4.56. $Pt(PSPh)_2$ calcd.: C, 57.19; H, 4.56%.

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