Journal of Organometallic Chemistry, 287 (1985) 275–278
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

η^3-ALLYL COMPLEXES OF PALLADIUM WITH PHOSPHORUS–SULFUR HYBRID LIGANDS AND THEIR REDUCTION TO PALLADIUM(0) DERIVATIVES

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(Received November 5th, 1984)

Summary

The ^1H and ^{31}P NMR spectra of $[(\eta^3\text{-2-Me-allyl})Pd(PSR)]BF_4$ (PSR = $Ph_2PC_2H_4SR$, R = Ph, Et, Me) complexes have been investigated. Attempts to reduce the complexes to $[Pd(PSR)_2]$ complexes are described.

Introduction

Palladium(0) complexes, generally containing triphenylphosphine, are known to be active in the stoichiometric oxygen transfer of dioxygen to olefins to yield methyl ketones [1]. In line with our interest in O_2-oxidations promoted by cationic complexes of rhodium(I), containing, among others, the hybrid ligands PSR (PSR = $Ph_2PC_2H_4SR$) [2,3] we wished to synthetise palladium(0) derivatives of the type $[Pd(PSR)_2]$, with the aim of trying them out in the above reactions.

Phosphinepalladium(0) complexes are usually prepared from the corresponding palladium(II) complexes, by treatment with strong reducing agents such as hydrazine, alcoholic KOH [4], or alcoholic $NaBH_4$ [5]. In the case of palladium(II) complexes involving the phosphorus–sulfur ligands PSR [6], however, we found that reduction of the ligand always occurred on the ligand rather than at the metal, giving ill-characterized complexes and volatile, sulfur-containing products.

Thus, a milder route to palladium(0) was chosen, viz. one first suggested by Musco [7], who prepared $[Pd(PR_3)_n]$ complexes quantitatively by treating $[(\eta^3\text{-2-Me-allyl})Pd(PR_3)_2]Y$ derivatives with bases, such as primary amines, alkoxide ions, or even the phosphine ligand itself. In the present paper we describe the preparation and characterization of methallyl derivatives of palladium of composition $[(\eta^3\text{-2-Me-allyl})Pd(PSR)]BF_4$, and attempts to reduce them to palladium(0) derivatives.

Experimental

^1H NMR spectra were recorded with WP-60 or WH-300 Bruker instruments. ^{31}P NMR spectra were recorded on a WP-60 Bruker spectrometer at 24.28 MHz with

0022-328X/85/$03.30

complete ^1H decoupling using 85% H_3PO_4 as external standard. The PSR ligands were prepared by published procedures [8].

[(η^3-2-Me-allyl)Pd(PSR)]BF_4 (PSR = $Ph_2PC_2H_4SR$, R = Ph, Et, Me)

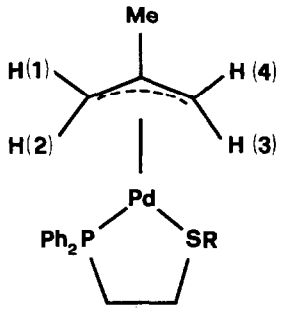
A solution of the stoichiometric amount of the appropriate ligand in methanol, was added dropwise to a stirred suspension of Pd(2-Me-allyl)Cl]$_2$ [9] in methanol. One equivalent of $NaBF_4$ was then added, and the solution was evaporated to dryness in vacuo. The solid residue was recrystallized from dichloromethane/2-propanol and washed with diethyl ether (yield: 70–80%). Anal. found: C, 44.86; H, 4.85; S, 6.05. Pd(C_4H_7) (PSMe)BF_4 calcd.: C, 44.87; H, 4.76; S, 6.30%. ^{31}P NMR: 49.55 ppm. Found: C, 46.63; H, 5.14; S, 6.22. Pd(C_4H_7) (PSEt)BF_4 calcd.: C, 45.96; H, 5.01; S, 6.13%. ^{31}P NMR: 49.62 ppm. Found: C, 49.90; H, 4.58; S, 5.62. Pd(C_4H_7) (PSPh)BF_4 calcd.: C, 50.51; H, 4.59; S, 5.62%. ^{31}P NMR: 49.32 ppm.

[Pd(PSPh)$_2$]

A saturated solution of [(η^3-2-Me-allyl)Pd(PSPh)]BF_4 (1 mmol) and PSPh (2 mmol) in methanol was stirred overnight under nitrogen. Red crystals slowly separated, and these were recrystallized from dichloromethane/methanol. Anal.: found: C, 64.63; H, 4.99; S, 8.24. $C_{12}H_{10}P_2PdS_2$ calcd.: C, 63.95; H, 5.10; S, 8.54%.

Results

The compounds [(η^3-2-Me-allyl)Pd(PSR)]BF_4 were prepared by the method used for the complexes [(η^3-2-Me-allyl)Pd(diphos)]BF_4 [10], involving treatment of [Pd(2-Me-allyl)Cl]$_2$ with the stoichiometric amount of PSR and $NaBF_4$ in methanol. All the complexes are colorless and behave as 1/1 electrolytes in nitromethane (Λ_M ca. 90 mol^{-1} cm^2 Ω^{-1}). ^{31}P NMR data confirm the chelate nature of the phosphorus–sulfur ligands PSR in $CDCl_3$ solutions, showing a single sharp signal at about 49 ppm.



It should be noted that the specific 5-membered chelate ring effect (Δ ring) has been always observed in the case of the palladium(II) complexes containing these PSR ligands [6], similar to that previously known for the more common diphosphino derivatives [11].

The ^1H NMR data for the above complexes are listed in Table 1. The 300 MHz spectrum of the complex [(η^3-2-Me-allyl)Pd(PSPh)]BF_4 (Fig. 1) exhibits, besides the signals due to the ligand, an approximately first-order pattern for the four allylic protons. The resonances at 3.64 and 4.68 ppm appear as doublets, and are assigned

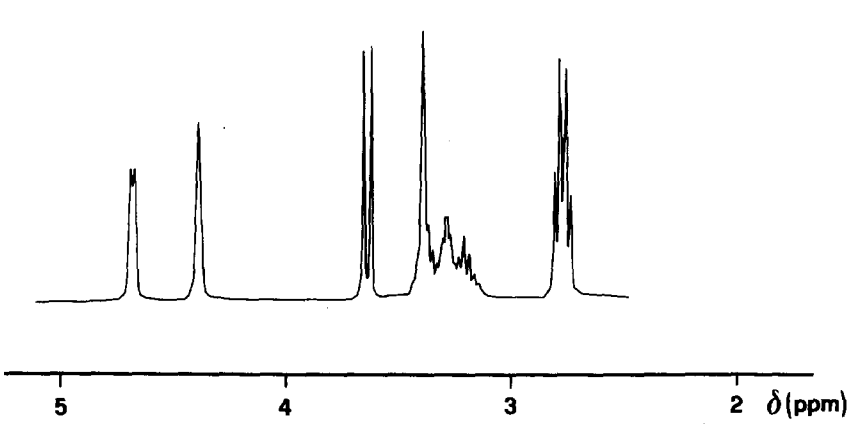


Fig. 1. 300 MHz ^{1}H NMR spectrum of [(η^3-2-Me-allyl)Pd(PSPh)]BF_4 in $CDCl_3$ (10^{-2} *M*) at 25°C.

to H(3) and H(4) on the basis of preferential coupling of the allylic protons with the "*trans*" phosphorus atom of the ligand [12]. Moreover, the magnitudes of *J*(H–P) allow assignement of H(3) and H(4) as the *anti* and *syn* protons, respectively [12]. The resonances at 4.38 and 3.39 ppm show no splitting and are attributed to the protons in "*cis*" position. However, a complete assignment could not be made because the spectrum remained unchanged at higher temperatures (50°C, in $CDCl_3$) [12]. The upper-field allylic signal partly overlaps with the complex multiplet of the P-CH_2 protons (at ca. 3.3 ppm), whereas the S-CH_2 protons resonate at higher fields (2.76 ppm), giving rise to a quasi AB system.

The ^{1}H NMR spectra of the other two complexes containing the PSMe and PSEt ligands are quite similar to that of the PSPh derivative described above, except that some larger overlap between the signals of the ligands and the allyl group is observed. The spectra were temperature independent in the range −60 to 50°C, indicating a static (and asymmetric) configuration for the allylic protons.

Treatment of the complexes [(η^3-2-Me-allyl)Pd(PSR)]BF_4 (R = Me, Et) with excess base (benzylamine, PSR, sodium methoxide) in methanol gives red solutions, from which red compounds were isolated by addition of $NaBPh_4$ or diethyl ether. Elemental analyses point to compositions close to the formula $Pd(Ph_2PC_2H_4S)Y$ (Y = BF_4, BPh_4), but the compounds are rather unstable in solution (acetone, dichloromethane), and this prevents complete ^{1}H NMR characterization.

It is likely that dealkylation of the thioethereal moieties occurs during the reduction, with formation of oligomeric thiolate derivatives of variable complexity.

TABLE 1

^{1}H NMR DATA (δ, ppm) FOR [(η^3-2-Me-allyl)Pd(PSR)]BF_4 COMPLEXES [a]

PSR	H(1), H(2)	H(3)	H(4)	Me	Ligand resonances
PSMe	4.22, (3.15) [b]	3.55 *J* 9.67 Hz	4.77 *J* 5.47 Hz	1.99	2.74(CH_3S), 2.90(CH_2S), 3.10 (CH_2P) 7.5 (Ph)
PSEt	4.22, (3.15) [b]	3.53 *J* 9.71 Hz	4.76 *J* 5.56 Hz	1.99	1.39 (CH_3CH_2,t), 2.90(CH_2S), 3.10 (CH_2P, CH_2CH_3), 7.5 (Ph)
PSPh	4.38, 3.39	3.64 *J* 10.0 Hz	4.68 *J* 5.51 Hz	2.02	2.76(CH_2S), 3.27 (CH_2P), 7.5 (Ph)

[a] $CDCl_3$ at 20°C. [b] Covered by ligand resonances.

Conversion of alkyl thioether complexes into thiolate metal compounds by the loss of an alkyl group has been extensively reported for a number of compounds. More recently, *o*-diphenylphosphinothioanisole derivatives of palladium(II) were found to be readily converted into thiolato complexes of palladium(II) in the presence of nucleophiles [13].

Only in the case of R = PSPh, treatment of $[(\eta^3\text{-2-allyl})Pd(PSPh)]BF_4$ with excess PSPh resulted in the formation of a palladium(0) derivative of composition $[Pd(PSPh)_2]$. The compound does not react detectably with dioxygen at ambient conditions in ethanol, nor does it promote the O_2-oxidation of 1-octene to 2-octanone in the presence of added $MeSO_3H$ even during several days at 50°C. Since $[Pd(PPh_3)_2O_2]$ has been reported to promote oxidation of 1-octene [1] we conclude that $[Pd(PSPh)_2]$ is rather stable in solution, and does not generate unsaturated, reactive species.

The authors wish to thank Mr. A. Ravazzolo for technical assistance.

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