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π-BENZYLBIS(TRIETHYLPHOSPHINE)PALLADIUM(II) TETRAFLUOROBORATE

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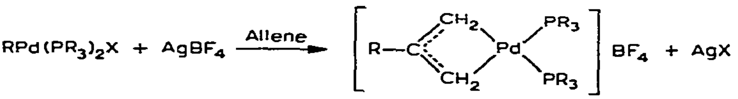
SUMMARY

Silver tetrafluoroborate has been found to react with bromo(benzyl)bis(triethylphosphine)palladium(II) to form silver bromide and π-benzylbis(triethylphosphine)palladium(II) tetrafluoroborate. This compound is fluxional in the π-benzyl ligand as shown by the temperature dependence of its NMR spectrum. The benzyl protons of the π-benzyl ligand appear as a doublet $J = 9$ Hz at $-50°$ and as a more complex feature at higher temperature.

INTRODUCTION

In 1966, King and Fronzaglia reported a compound which they identified as π-benzyl-π-cyclopentadienyldicarbonylmolybdenum(II) (I)[1]. Cotton[2-4] has recently published detailed studies on the structure and NMR spectra of closely analogous compounds, confirming the original structure proposed by King, and giving a detailed analysis of the temperature dependence of the NMR spectra of these unusual compounds.

We have recently studied the reaction of halo(organo)bis(phosphine)palladium(II) complexes with silver tetrafluoroborate in the presence of allene[5] and found that a π-allylpalladium complex is formed. This reaction proceeds satisfactorily



(1)

where R is methyl or phenyl, but the product of an attempted reaction with bromo(benzyl)bis(triethylphosphine)palladium(II) did not have the expected NMR spectrum of a π-(2-benzylallyl)palladium complex.

RESULTS AND DISCUSSION

The experiment described above was repeated without allene, and the room temperature NMR spectrum of the starting material and the product are shown in Fig. 1a and 1b. The most significant change is the disappearance of the triplet for the

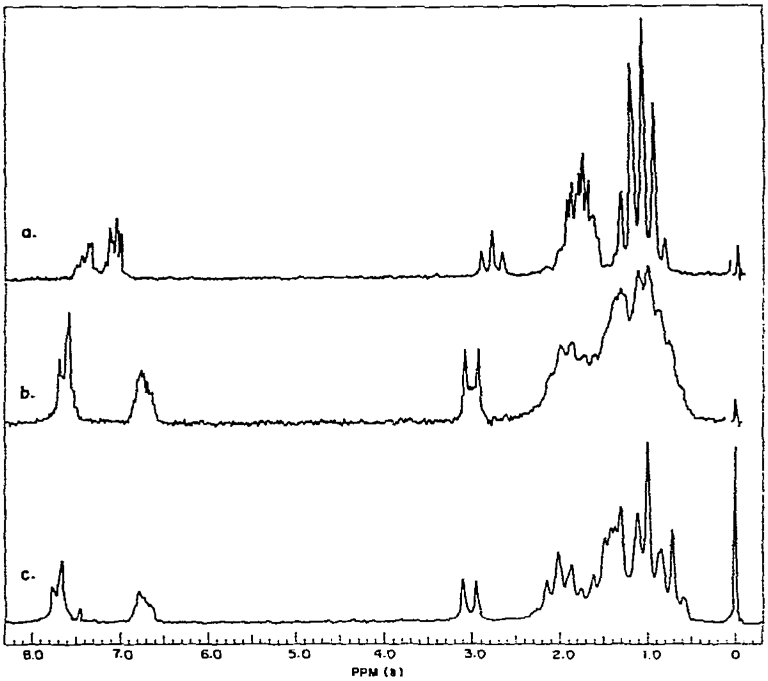
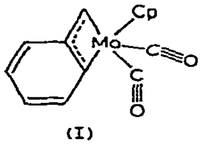


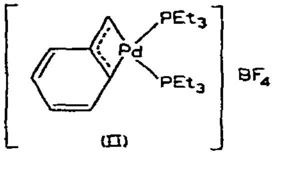
Fig. 1. (a) The NMR spectrum of bromo(benzyl)bis(triethylphosphine)palladium(II) in $CDCl_3$ at 60 MHz. (b) The NMR spectrum of (II) in $CDCl_3$ at 27° and 60 MHz. (c) The NMR spectrum of (II) in $CDCl_3$ at −50° and 60 MHz.

benzylic protons in Fig. 1a and the appearance of a feature at a slightly different chemical shift which integrates for two protons in Fig. 1b. The aliphatic region of the spectrum in Fig. 1a is quite well resolved, but in Fig. 1b it is significantly broadened. The aromatic region also shows significant differences between Fig. 1a and Fig. 1b, in which the aromatic protons are split into two features with a large separation. The feature at δ 6.6 ppm integrates for two protons, and the one at δ 7.6 ppm integrates for 3 protons. The low temperature spectrum shown in Fig. 1c differs from 1b only in the increased resolution of the aliphatic region and the appearance of the benzylic protons as a doublet, $J=9$ Hz.

The spectra shown in Fig. 1 can be interpreted as arising from compound (II).

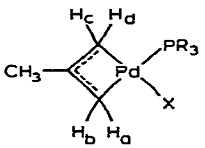


(I)



(III)

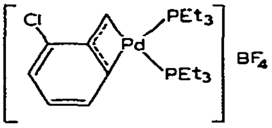
The spectral features are closely analogous to those observed for (I) at temperatures where time average equivalence makes the benzyl protons, the *ortho* protons, and the *meta* plus *para* protons of the π-benzyl ligand appear as three distinct peaks in the NMR spectrum. As in (I) the *ortho* protons of (II) are shifted upfield from the *meta* and *para* protons. It is well established[6] that phosphorus in complexes of type (III) shows substantial coupling constants with protons H_a and H_b in the *trans* position



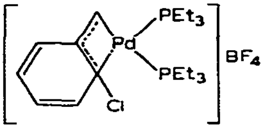
(III)

to the phosphine ligand, but no coupling is observed with H_c and H_d. The splitting of the benzylic protons of (II) is probably due to coupling with the *trans* phosphine ligand, and the magnitude of the splitting is reasonable. At higher temperature a broad feature is observed as in Fig. 1b at the same chemical shift as the benzyl protons and between the benzyl doublet. The appearance of this feature correlates with the loss of resolution in the aliphatic region of the spectrum, and this may indicate onset of intramolecular phosphine exchange. There is no change in the NMR spectrum of (II) from that shown in Fig. 1c at −70° in methylene chloride-d_2.

We made the *o*-chloro derivative of (II) on the assumption that either (IVa) or



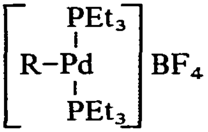
(IVa)



(IVb)

(IVb) should be more stable and that it might be possible to observe more resolution in the NMR spectrum. The 60 MHz spectrum of (IV) at −22° is shown in Fig. 2, and it is very similar to Fig. 1c. Nonequivalence of the benzylic protons is not resolved at this temperature, and the feature at δ 6.4 ppm in Fig. 2 integrates for one proton, showing that this is the *ortho* proton. At −56° the *ortho* proton has shifted 0.13 ppm to higher field and the feature for the benzylic protons has become very broad. At −69° the benzylic protons have split into two broad peaks symmetrically distributed about the original high temperature chemical shift of the benzylic protons at δ 3.10 ppm. One of these peaks is at δ 3.7 ppm and the other appears as a shoulder on the phosphine ethyl resonance. These peaks are sharper at −83°. At sufficiently low temperature it should be possible to observe phosphorus splitting of each of the benzylic protons and also the *ortho* proton of (IVa). We were not able to observe phosphorus splitting, but the shift of the *ortho* proton to higher field suggests that (IVa) is the low temperature form of the complex.

The NMR spectra show that (II) is a labile complex at temperatures much lower than (I). However, (II) has significant chemical stability. Compounds like (V) decompose very rapidly at room temperature where R is methyl or phenyl[5], but (II)



$$\left[\begin{array}{c} \mathrm{PEt_3} \\ | \\ \mathrm{R{-}Pd} \\ | \\ \mathrm{PEt_3} \end{array}\right] \mathrm{BF_4}$$

(V)

is easily isolable and stable indefinitely under refrigeration. Complex (V) also reacts nearly instantaneously with allene at room temperature to form π-allyl complexes,

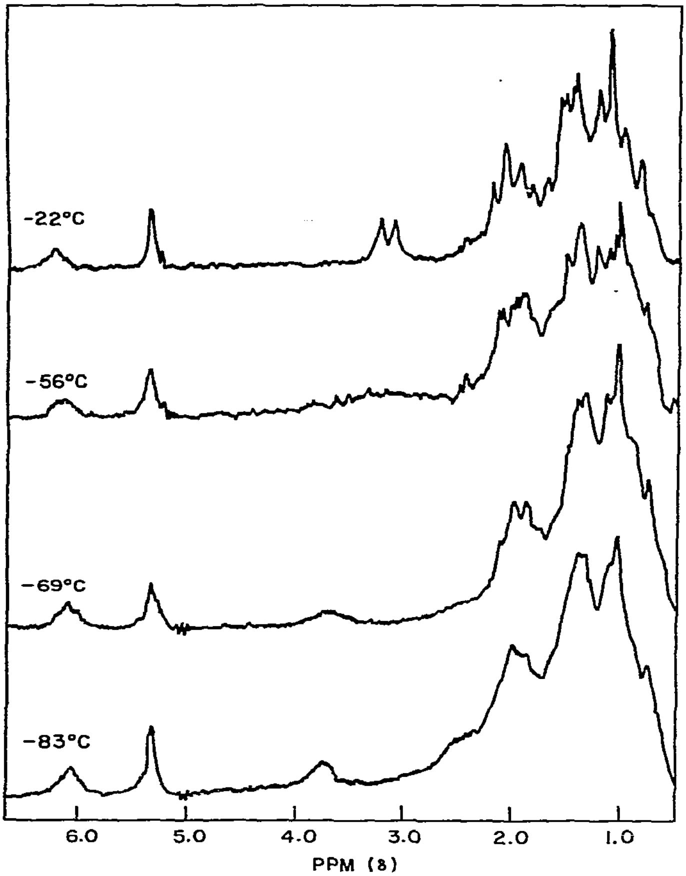


Fig. 2. The temperature dependence of the 60 MHz NMR spectrum of (IV) in CD_2Cl_2.

but (II) does not insert allene under these conditions. The compound crystallizes from tetrahydrofuran without solvent of crystallization, again indicating significant stability for the π-benzyl structure. However, when 2 moles of pyridine are added to a sample of (II) in an NMR tube the spectrum changes to that for a σ-bonded benzyl complex with a triplet for the benzylic protons at δ 2.56 ppm. This shows that strongly coordinating ligands can cause conversion of the π-benzyl ligand to a σ-benzyl ligand. The temperature dependence of the NMR spectrum of (II) and (IV) is probably due to intramolecular phosphine exchange and fluxional behavior of the π-benzyl ligand, but the precise nature of these processes is not clear.

EXPERIMENTAL

The bromo(benzyl)bis(triethylphosphine)palladium compounds were prepared by a literature method[7], and silver tetrafluoroborate was purchased from Alpha Inorganics. Reactions were run with exclusion of air, and products were stored at −20° under nitrogen. The crystalline compounds are not very air sensitive, but all solutions were made up under nitrogen. The tempearature dependence of the NMR spectrum of both samples was reversible so long as temperatures were not allowed to exceed room temperature for (II) and 0° for (IV). The compounds were poorly soluble, particularly at low temperatures. Complex (II) was more soluble than (IV). The probe temperature was found from the chemical shift difference of methanol.

π-Benzylbis(triethylphosphine)palladium(II) tetrafluoroborate

Bromo(benzyl)bis(triethylphosphine)palladium(II) 0.22 g was weighed into a flask equipped with a side arm sealed by a rubber septum, and 5 ml tetrahydrofuran was added. The solution was cooled to 0° and stirred magnetically. A solution of 0.082 g silver tetrafluoroborate in 3 ml tetrahydrofuran was added causing the precipitation of silver bromide. After coming to room temperature the solution was stirred for 1 h and filtered to give a clear yellow solution which was reduced to 2 ml under vacuum. Addition of 3 ml ethyl ether and scratching at 0° caused formation of a light yellow crystalline product. The IR spectrum (KBr) showed tetrafluoroborate bands and P–C bands at about 1100 cm^{-1} and bands assignable to the benzyl ligand at 1490 cm^{-1} and 1600 cm^{-1}. Other bands at 2970, 2940, 2880, 1460, 1420, 1380, 770 and 730 cm^{-1} were assignable to the triethylphosphine ligand. (Found: C, 44.1; H, 7.1. $C_{19}H_{37}BF_4P_2Pd$ calcd.: C, 43.8; H, 7.12%.)

π-(2-Chlorobenzyl)bis(triethylphosphine)palladium(II) tetrafluoroborate

This product was obtained as yellow-orange crystals by the above procedure and was significantly less stable than the unsubstituted product. (Found: C, 42.3, 42.0; H, 6.70, 6.69. $C_{19}H_{36}BClF_4P_2Pd$ calcd.: C, 43.6; H, 6.88%.)

REFERENCES

1 R. B. King and A. Fronzaglia, *J. Amer. Chem. Soc.*, 88 (1966) 709.
2 F. A. Cotton and M. D. LaPrade, *J. Amer. Chem. Soc.*, 90 (1968) 5418.
3 F. A. Cotton and T. J. Marks, *J. Amer. Chem. Soc.*, 91 (1969) 1339
4 F. A. Cotton, *Accounts Chem. Res.*, 1 (1968) 257.
5 G. D. Shier, J. Brewbaker and R. R. Stevens, manuscript in preparation.
6 J. Powell and B. L. Shaw, *J. Chem. Soc., A*, (1967) 1839.
7 G. Calvin and G. E. Coates, *J. Chem. Soc.*, (1960) 2008.