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Preliminary communication

SYNTHESIS OF ORGANOMETALLIC SOLVENTO COMPLEXES

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Summary

The isolation and characterization of solvento complexes obtained from cyclic complexes of palladium are reported; the solvents coordinated to palladium are acetone, diethyl ketone, ethanol and tetrahydrofuran, and an order of the strengths of the Pd←O bonds is proposed

A recent report of solvento complexes of palladium [1], and the increasing interest in such compounds** [2—4], prompt us to describe preliminary results of our studies on the reaction of silver hexafluorophosphate with cyclic complexes of palladium. We find that solvents containing an oxygen as donor atom, can be coordinated to palladium according to eq. 1 and 2.

A stoechiometric amount of $AgPF_6$ is allowed to react with complexes I or III [5] in 20 ml of CH_2Cl_2*** containing 1 ml of solvent S. Immediate precipitation of AgCl occurs and, after filtration, addition of pentane to the solution leads to precipitation of II. These compounds are recrystallized from a mixture CH_2Cl_2/pentane containing a few drops of the appropriate S. The manipulation were carried out at −10°C for IIc.

All compounds have satisfactory C, H, and N elemental analysis, IR and ^{1}H NMR data confirm the stereochemistry suggested for II and IV (Table 1). All ν(N—H) frequencies are characteristic of cationic cyclic complexes of palladium with this C—N ligand [5]. The ν(C=O) frequencies are similar to those observed by Clark et al. [4] for *trans*-$[Pt(PR_3)_2acX]^+$ (R = alkyl; X = H, CH_3) and confirm coordination through the oxygen atom. Furthermore, ^{1}H NMR signals integration indicates one S per complex II molecule.

We have noticed that THF and acetone are coordinated to the metal even in presence of C_2H_5OH whereas diethyl ketone is not and that acetone displaces THF from complex IId. Therefore we suggest the following order of relative stabilities for the Pd←O bond: acetone > THF > ethanol > diethyl ketone.

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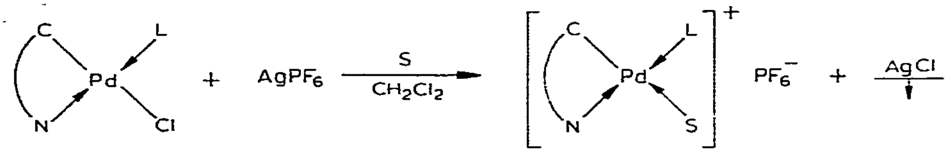
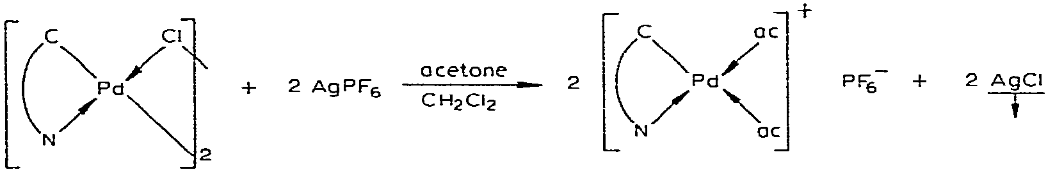
[**] They are often used as starting materials

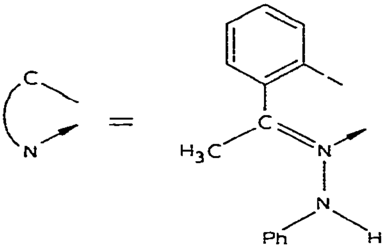
[***] We recommend the use of very pure CH_2Cl_2 (Aldrich Gold Label).



(I) (II) (1)



(III) (IV) (2)



(IIa) L = py, S = ac
(IIb) L = PPh_3, S = ac
(IIc) L = py, S = diethyl ketone
(IId) L = py, S = THF
(IIe) L = py, S = ethanol

py = pyridine
ac = acetone

TABLE 1

SPECTROSCOPIC PROPERTIES OF THE COMPLEXES

	Infrared[a] (cm^{-1})			Proton NMR data[d] δ(ppm)	
Compounds	ν(N—H)[b]	ν(C=O)[c]	ν(O—H)	CH_3[b]	S[e]
IIa	3328	1682	—	2.47	2.0(s)
IIb	3330	1650	—	2.56	1.67(s)
IIc	3352	1666	—	—	
IId	3370	—	—	2.46	1.72(m) 3.38(m)
IIe	3346	—	3448	2.53	0.83(t) CH_3 3.70(q) CH_2
IV	3339	1680 1666	—	—	

[a] In Nujol mull. Beckman IR-12. [b] (Typical) values of the chelating C—N ligand [5]. [c] ν(C=O) for the non-coordinated ketones [6]: $Me_2C=O$ 1710 cm^{-1}; $Et_2C=O$ 1721 cm^{-1}. [d] In CD_2Cl_2, $Si(CH_3)_4$ as internal reference, Perkin—Elmer R12B. The compounds (IIc) and IV decompose rapidly in solution. [e] Chemical shifts of the non-coordinated solvents [7] Me_2CO: 1.93s; THF: 1.79m, 3.60m; EtOH: 1.22t CH_3, 3.70q CH_2, 2.58s OH. (s, singulet; t, triplet; q, quadruplet; m, multiplet).

Although quite stable, all these solvento complexes are decomposed by halides: KBr pellets of II for example show a ν(N—H) at 3200 cm^{-1} (characteristic of compounds I [5]) instead of 3340 cm^{-1}.

Further studies of reactions 1 and 2 with a range of chelating C—N ligands are in progress.

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Erratum

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The ^{11}B chemical shift values for $Cl_2BC_2F_3$ and $BrB(C_2F_3)_2$ should read −49.4.