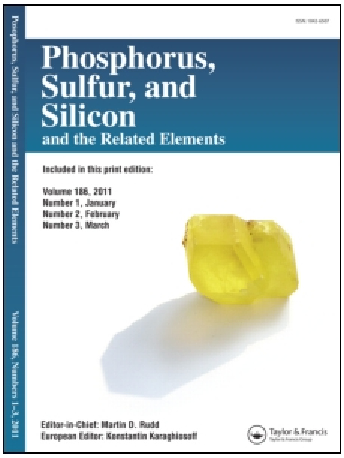

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BIS(PHOSPHONIO)-ISOPHOSPHINDOLIUM CATIONS AS LIGANDS IN COORDINATION CHEMISTRY: ANIONIC BEHAVIOUR OF CATIONIC SPECIES

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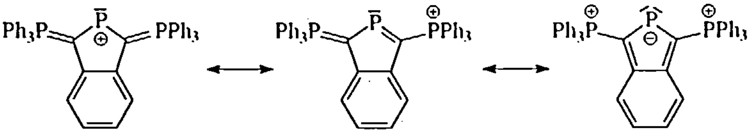
Abstract Crystal structures and spectroscopic properties of the title cations and their reactivity towards transition metal carbonylates and coinage metals are discussed.

INTRODUCTION

The bonding situation in the bis(phosphonio)-isophosphindolium cation 1 may be described by a set of mesomeric structures containing both formulas with a positive (1a) and a negative charge at the two coordinate phosphorus (1c).[1] Accordingly, 1 resembles both an electrophilic phosphenium ion and a nucleophilic 2-phospha-allylic ion and thus forms a bridge between the two principal categories[2] of cations with two coordinate phosphorus.

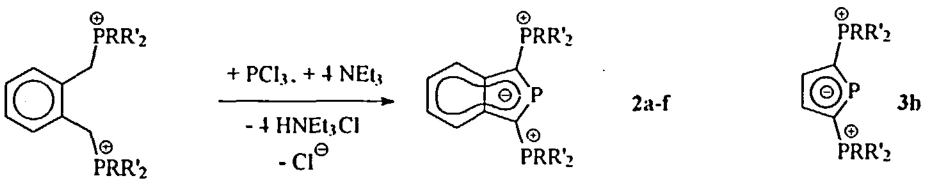


1a 1b 1c

Regarding that phosphenium ions form complexes[3] which can be considered as isoelectronic and isolobal to Fischer carbene complexes, the enhanced nucleophilicity of cations of type 1 as compared to a phosphenium ion[1] makes these species interesting ligands in coordination chemistry. Here, we report on a modification of the synthetic route to 1[1] giving a more general access to the title cations. Their characterisation by spectroscopic methods and x-ray diffractommetry provides a detailed understanding of the bonding situation. Finally, the reaction behaviour of these compounds towards both nucleophilic and electrophilic transition metal compounds will be explored.

PROPERTIES OF BIS(PHOSPHONIO)-ISOPHOSPHINDOLIUM CATIONS

The synthesis of 1 was achieved via a multistep condensation reaction starting from PCl_3 and a xylylene-bisphosphonium salt.[1] Examining this reaction in more detail we found that the cations 2a-g are easily accessible when one or two of the peripheral phenyl moieties in the bisphosphonium salt are formally replaced by heteroaryl (2a,b)[4], vinyl (2c)[5], alkyl (2d,e)[4,6] or functionalized alkyl residues (2f,g)[6].



R' = Ph, R = 2-C_4H_3S (a), 2-C_5H_4N (b), C_2H_3 (c), Me (d), -$(CH_2)_2PPh_2$ (f), -$(CH_2)_2PSPh_2$ (g)
R = Me, R' = Ph (e)

Limitations of this method are that no trialkylphosphonio substituted cations are accessible, and that alkyl groups in the phosphonio fragments may have no further activating functionalities ($SiMe_3$, CO_2R') on the α-carbon. The monocyclic bis(phosphonio)-phospholium cation 3b was obtained in low yield by analogy via condensation of a butenylidene-bis(phosphonium) salt with PCl_3.[4] The cations 2 are isolated as halides whose anions are easily metathetically exchanged against $CF_3SO_3^-$, $CF_3CO_2^-$, or BPh_4^- anions.

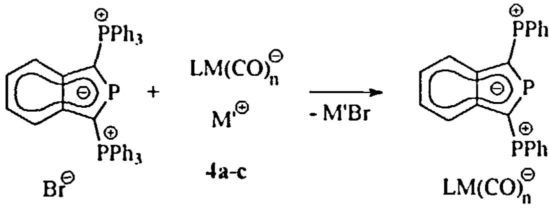
Characterisation of 2a-f by nmr spectroscopy revealed similar data as compared to 1. The x-ray crystal structures of the salts 1[CpW(CO)$_3$][7] and 2[Br][5] revealed the presence of discrete cations and anions. The isophosphindole rings are planar, and the bond distances in the different cations differ not significantly. As expected, the endocyclic P-C distances are equal (av. 1.735 Å) and lie halfway between a single and double bond. The exocyclic P-C distances are comparable (av. 1.746 Å) and suggest that the ylide character in these bonds is very low. The distribution of the C-C distances in the ring suggests the presence of a delocalized π-electron system extending over both rings. This is further confirmed by the results of spectroscopic and quantum chemical[5] studies. Of particular importance are the UV/VIS-spectra which display three bands at 353, 336, and 262 nm attributable to transitions of the isophosphindole chromophore. The first excitation energy is similar as in 2-phospha-naphthalenes, and the position of the bands remains unchanged for all cations 2a-f, indicating that electronic interaction of the π-system with the phosphonio fragments is unimportant.

On the whole, the results of structural and spectroscopic studies indicate that the bonding in the cations 1, 2 is adequately described as a delocalized 10π-electron system which extends over both condensed rings. The exocyclic P-C-bonds have essentially single bond character. The bonding situation at the two coordinate phosphorus atom constitutes a hybrid between an electrophilic phosphenium and a nucleophilic phospholide environment, in accord with a superposition of mesomeric formulas 1a and 1c.

REACTIONS WITH TRANSITION METAL COMPOUNDS

Regarding the ambident nature of the two coordinate phosphorus in 1, 2, we expected that these cations should react with transition metal nucleophiles with formation of neutral metallophosphenium compounds featuring a phosphorus metal bond. However, investigating the reactions of 1 and 2d,e with the metal carbonylates 4 we found that not of the expected substitution products, but rather the ionic carbonyl metalates 5 were formed *via* metathetical anion exchange.[7] Inspection of the x-ray crystal structure of 5c[7] suggested that the unexpected behaviour is related to the steric protection of the two coordinate phosphorus rather than its poor electrophilicity.

1

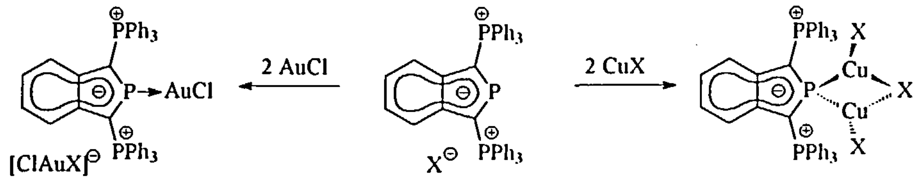


5a-c

$LM(CO)_n = Co(CO)_4$ (a), $CpMo(CO)_3$(b), $CpW(CO)_3$ (c)

In order to minimise any steric perturbations in reactions of bis(phosphonio)-isophosphindolium cations with electrophilic metal substrates, we investigated the reactivities of **1** towards compounds of the coinage metals.

Treatment of 1[Cl] and 1[CF_3SO_3] with AuCl yielded the phosphenium analogue complexes 6. The end-on coordination of the cationic ligand to a two coordinate gold atom was derived from nmr data as well as an x-ray crystal structure analysis.[7] Reactions of 6 with Lewis-bases and with water, respectively, indicate that the cationic ligand is readily displaced from the metal, and that the π-electron system in the coordinated ligand is activated towards addition reactions.[7]



6a,b **1** (X = Cl (a), Br (b)) **7a,b**

Reactions of 1[Cl] and 1[Br] with CuCl or CuBr, respectively, furnish the binuclear copper complexes 7a[8],b. According to crystal structure determinations, the two metal atoms in each complex exhibit significant differences in their coordination spheres (Fig. 1) which can be related with the asymmetric bridging mode of the μ^2(P)-coordinated isophosphindolium ligand. The observed effects suggest that the Cu-P interactions do not constitute electron precise 2-centre-2-electron (2c-2e) bonds as encountered in μ^2(P)-phospholide complexes[9], but should be rather described as electron deficient 3c-2e bonds in analogy to the bonding situation in μ^2-aryl copper compounds.[10] The differences in the P-Cu bond distances are in accord with the assumption that the Lewis basicity of the isophosphindole π-electron system is distinctly lower than that of the phosphorus lone pair.

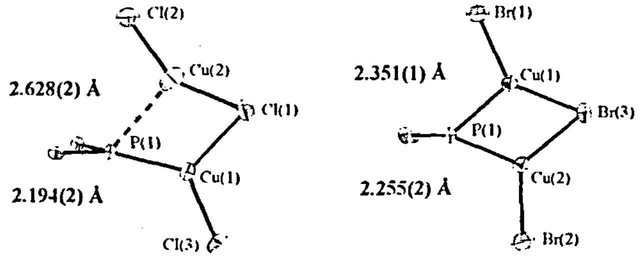
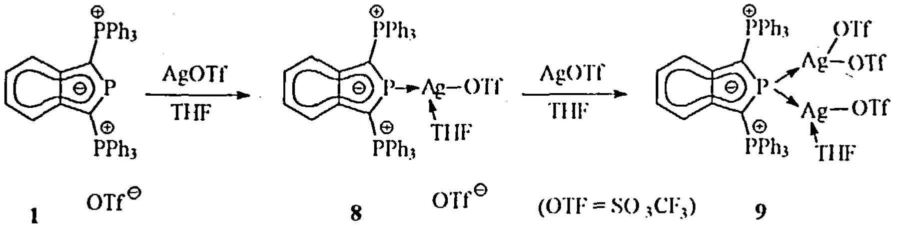


Figure 1:
ORTEP-plots of the metal coordination spheres in the copper complexes 7a,b.

Whereas 1 forms no complexes with silver halides due to their low solubility, both mononuclear (8) and binuclear (9) bis(phosphonio)-isophosphindolium silver complexes were obtained upon treatment of 1[CF_3SO_3] with CF_3SO_3Ag, depending on the reaction conditions. Both products were isolated and characterised by spectroscopic methods and x-ray crystallography. In contrast to the situation in 7a,b, the μ^2P-coordinated ligand in 9 forms a symmetric bridge, and the observed values for the P-Ag bond distances (2.41±0.02 Å) are more consistent with the presence of electron precise 2c-2e bonds.



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