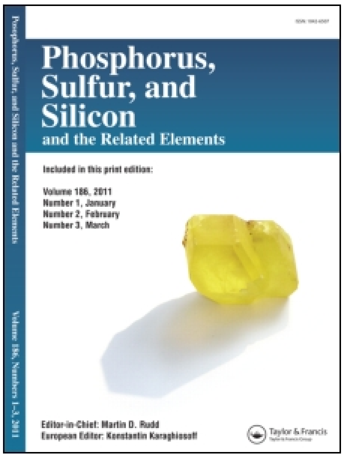

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Oxidation and Reduction of Bis-Phosphonio-Isophosphindolides : from Phosphorus Crown Ethers to Phosphine-Functionalized Phospholides

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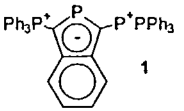
The ambiphilic redox behavior of bis-phosphonio-isophosphindolide ions is discussed. Oxidation occurs site-selectively at the endocyclic two coordinate phosphorus to give λ^5-isophosphindolide cations, while reduction proceeds, depending on the reducing agent, under conversion of phosphonium into phosphine or phosphanide centers.

Keywords: phosphorus heterocycles; oxidation; reduction; benzophospholide anions

In the frame of isolobal and isoelectronic analogies, the exocyclic tetracoordinate phosphorus atoms in bis-phosphonio-isophosphindolide cations such as **1** [1] can be compared with a tetravalent aliphatic carbon atom, while the two coordinate endocyclic phosphorus resembles a hybrid between a carbene and a CH-moiety in an aromatic ring.[2,3] The expected reactivity patterns for the endocyclic phosphorus are mirrored in the ligand properties of **1**,[2,3] but reactions involving the phosphonio groups have as yet not been reported. Starting from an introductory cyclovoltammetric study which revealed that **1** undergoes both electrochemical oxidation (irrev., E_{peak} +1.7 V vs. SCE) and reduction (decomp. at E < -1.6V), we explored chemically induced oxidation and reduction reactions, anticipating that participation of both types of phosphorus centers should lead to an ambiphilic redox behavior.

Figure1: Cyclovoltammogram of 1[OTf] (CH_2Cl_2, 0.1 m Bu_4NBF_4)



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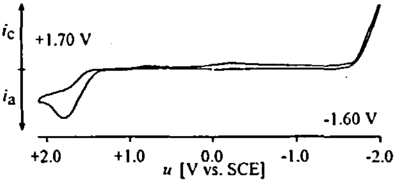
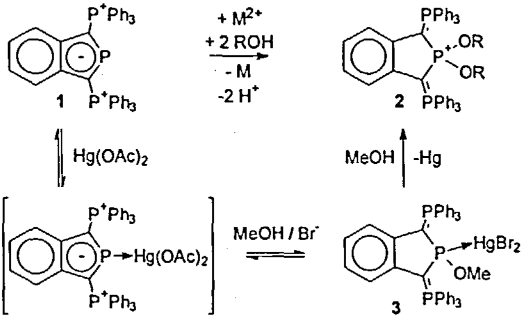


OXIDATION REACTIONS

In the course of the exploration of the coordination chemistry of bis-phosphonio-isophosphindolide ions, we found that ternary reactions of **1**, a divalent metal ion such as Pd(II), Hg(II), or Cu(II), and an alcohol proceed cleanly with reduction of the metal ion and formation of dialkoxy-λ^5-isophosphindolides **2**.[4,5] This reaction resembles closely the oxidation of λ^3- to λ^5-phosphabenzenes [6] which takes place under very similar conditions, and the parallels between both reactions emphasize the idea of an aromatic character of bis-phosphonio-isophosphindolide ions.

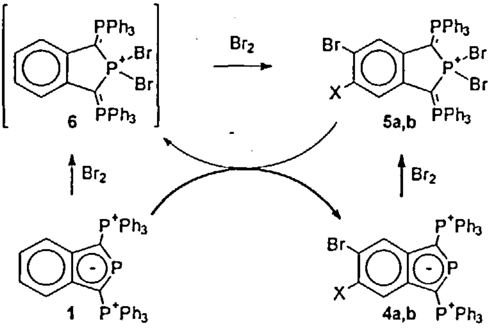


RO-...-OR = 2 OMe (**2a**), $-O(CH_2CH_2O)_n-$; n = 1(**2b**), 3(**2c**), 4(**2d**), 5(**2e**)

Mechanistic studies of the reaction of **1** with $Hg(OAc)_2$ / MeOH revealed that after initial formation of an instable Hg-complex, addition of MeOH followed by ligand exchange and deprotonation by OAc^- gave first the isolable neutral complex **3**.[5] Further reaction with excess MeOH finally produced elemental Hg and the λ^5-isophosphindolide **2a**. The formation of **3** is reversible, and **1** may be liberated e.g. by reductive cleavage with zink. A crystal structure analysis revealed **3** to be the first example of a monomeric 1:1 complex of the type $(R_3P)HgX_2$ with a 3-coordinate metal in a planar T-shaped coordination geometry; the usually observed formation of halide bridged dimers is here prevented by the extraordinary steric demand of the ligand.

The use of polyethylene glycols as alcohol component allowed further to obtain macrocycles **2b-d** featuring a λ^5-isophosphindolide unit incorporated in a crown ether. As further modification of the reaction scheme, oxidation of **1** was also possible using molecular oxygen in the presence of a catalytic amount of a Cu(I) salt as oxidant.[7]

Like phosphinines, the cation **1** is as well oxidized by Br_2 or $PhICl_2$, but not by I_2. The reaction with Br_2 is peculiar, since treatment of **1** with a stoichiometric amount of Br_2 afforded first substitution products **4a,b** which were oxidized to **5a,b** only upon addition of excess oxidant. A detailed study revealed that **4a,b** are formed via an "indirect" mechanism which had been previously noted for phosphinines [6] and proceeds via initial oxidative bromination of **1** to give **6**, subsequent electrophilic substitution to **5a,b**, and a final transfer of Br_2 from **5a,b** to **1**, with formation of the products **4a,b** and regeneration of **6**.[8]

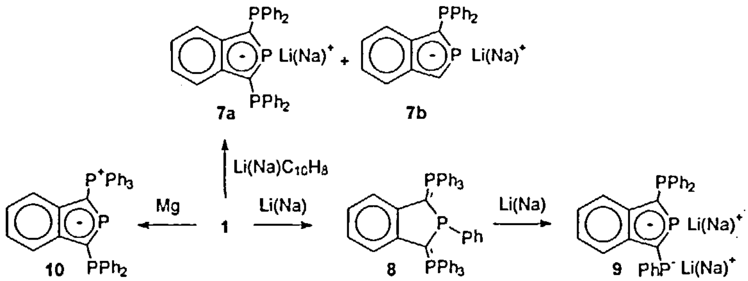


X = H (4a, 5a), Br (4b, 5b)

REDUCTION REACTIONS

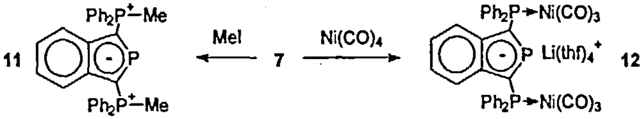
Reactions with reduction of bis-phosphonio-isophosphindolide cations were found to proceed as multi-step processes whose first stages are characterized by selective cleavage of P-C single bonds in the phosphonio-substituents, whereas the last stages involve unspecific decomposition of the ring system and formation of $MPPh_2$ (M = Na, Li) as the only identified products. Both the extent of the reduction and the reaction mechanism can be controlled by the choice of the reducing agent.[9]

For example, reaction of **1** with Li(Na)-naphthalenide proceeds very cleanly with selective cleavage of one P-C single bond in each phosphonio-moiety to give mixtures of the mono- and bis-phosphino-substituted benzophospholides **7a,b** (ratio approx. 3:1), together with PhLi(Na) and Ph_3P. All products were characterized *in situ* by multinuclear 1D and 2D NMR spectroscopy. The formation of **7a** can be explained by considering that reduction of a $PPh_3{}^+$-moiety may not only proceed via cleavage of a peripheral phenyl, but also by rupture of a skeletal P-C(ring) bond to give Ph_3P and an intermediate α-metallated phospholide dianion which is quenched by capture of a proton.



Reduction of **1** with alkaline metals instead of napthalenides yielded as initial products a mixture of **7a,b** together with the benzophosphole **8** whose formation via interception of the formed PhLi(Na) by excess **1** was verified by independent synthesis. Prolonged reaction times lead to a further reaction with P-Ph cleavage to give as the main product (80%) the phosphido-substituted phospholide dianion **9** which was characterized *in situ* by NMR spectroscopy. Finally, reduction of only one PPh_3^+-moiety to give the neutral phosphino-benzophospholide **10** was observed in the reaction of **1** with magnesium which is a weaker reductant than alkaline metals.[9]

Introductory investigations of the reactivity of the phosphine-functionalized benzophospholides **7**, **10** indicate that electrophilic attack of alkyl halides or metal carbonyls occurs preferably at the PPh_2-groups which must thus be considered stronger nucleophilic centers than the benzophospholide ring, to give cations such as **11** or metal complexes like **12**.[9] A crystal structure determination of this complex reveals the presence of isolated benzophospholide anions with a planar bicyclic ring system. While the endocyclic bond distances in **12**[9] and **1** are comparable, the exocyclic P-C bonds are slightly longer in **12**, indicating weaker hyperconjugation between the exocyclic substituents and the delocalized π-system.[10]



References

[1] A. Schmidpeter, M. Thiele, *Angew. Chem.* 103, 333 (1991); *Angew. Chem. Int. Ed. Engl.* 30, 308 (1991)

[2] D. Gudat, M. Schrott, V. Bajorat, M. Nieger, *Phosphorus Sulfur Silicon rel. El.*, **109**, 125 (1996)

[3] D. Gudat, *Coord. Chem. Rev.*, **162**, 71 (1997)

[4] D. Gudat, M. Schrott, M. Nieger, *J. Chem. Soc. Chem. Commun.*, 1541 (1995)

[5] D. Gudat, M. Nieger, M. Schrott, *Inorg. Chem.*, **36**, 1476 (1997)

[6] G. Märkl, in: *Multiple Bonds and Low Coordination in Phosphorus Chemistry*, edited by M. Regitz, O.J. Scherer (Georg Thieme Verlag, Stuttgart, 1990), p. 220ff

[7] D. Gudat; A.W. Holderberg, unpublished results

[8] D. Gudat, A.W. Holderberg, M. Nieger, M. Schrott, *Eur. J. Inorg. Chem.*, 101 (1998)

[9] D. Gudat, V. Bajorat, M. Nieger, submitted for publication

[10] D. Gudat, V. Bajorat, M. Nieger, *Bull. Soc. Chim. Fr.*, **132**, 280 (1995)