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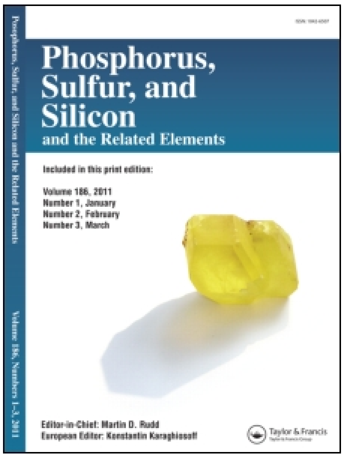

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CYANAMIDE SUBSTITUTED PHOSPHORUS COMPOUNDS

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Abstract Referring to the field of phosphorus chemistry the fragment N(CN) is discussed as pseudochalcogen.

INTRODUCTION

The general principle of element displacement [1], including the special case of the cyanogen displacement, allows the deduction of oxygen homologous functional groups. From this point of view the radicals N(CN) and $C(CN)_2$ can be considered as pseudochalcogens. Parallel to the well established pseudohalides a pseudochalconide concept was suggested by KÖHLER in 1970 [2,3] which is based on a multitude of formal identical reactions of (pseudo)chalcogen compounds like H_2Y, YH^- and Y^{2-} ($Y = O, NCN, C(CN)_2$ etc.).

The comparative investigation of water, formaldehyde and pseudochalcogen modified homologs H_2Y and $H_2C{=}Y$, respectively, by means of theoretical methods reveals similarities referring to electronic, thermochemical, and structural properties which allows a quantitative description of these relations [4].

NCN-MODIFICATION OF PHOSPHORUS COMPOUNDS

Phosphorus chemistry is a suitable field to demonstrate the pseudochalcogen character of the groups N(CN) and $C(CN)_2$. The ability to oxidize is one of the features of (pseudo)chalcogens. It is necessarry to emphasize that oxygen, ozone, nitrous oxide, amineoxides and sulfoxides and on the other hand the N(CN) and $C(CN)_2$ homologs are able to oxidize phosphines and to transfer these pseudoelements in place of oxygen [3].

These types of reactions can be used to synthesize very different phosphorus compounds. *We tried to prepare a homolog of P_4O_{10}. For that reason we oxidized P_4O_6 with cyanogen* azide and isolated a nearly unsoluble, colourless solid which together with sodium hydroxide produces quantitatively monocyanamido monophosphate.

$$P_4O_6 + 4\,NNN\text{-}CN \rightarrow P_4O_6(NCN)_4 + 4\,N_2 \quad (1)$$

The oxidation of diorganophosphides with cyanogen azide, yielding bis(cyanamido)phosphinates $[R_2P(NCN)_2]^-$, is an other example of this type of reactions.

$$[Ph_2P]^- + NNN\text{-}CN \rightarrow [Ph_2P(NCN)_2]^- + 2\,N_2 \quad (2)$$

A second group of reactions can be summerized under the headline pseudochalcogenolysis relating to the parallel behaviour of water, hydroxide, oxide and the homologous N(CN) or $C(CN)_2$ representatives toward most different species of phosphorus. In this connection we were concerned with the cyanamidolysis of phosphorus halides, for instance $PSCl_3$, under different conditions. The cyanamidolysis of phosphorus oxo- and thiochloride in the presence of $p\text{-}Me_2NC_5H_5N$ produces donor stabilized halides of modified derivatives of the monometaphosphorus acid.

$$PYCl_3 + NaNHCN + 2\,B \rightarrow B \rightarrow P(Y)(NCN)Cl + NaCl + [HB]Cl \quad (3)$$

$B = p\text{-}Me_2NC_5H_5N$; $Y = O, S$

On the other hand $PSCl_3$ reacts with a lye of cyanamide in water to a mixture of different cyanamido thiophosphates. The ability of the hydrogen cyanamide ion to compete in the system hydroxide water was rather surprizing.

$$PSCl_3 \xrightarrow[-Cl^-,\ H_2O]{NHCN^-,\ OH^-} \begin{array}{ll} [PO_2S(NCN)]^{3-} & 20\% \\ [POS(NCN)_2]^{3-} & 50\% \\ [PS(NCN)_3]^{3-} & 30\% \end{array} \quad (4)$$

Under comparable conditions the P-S-P sequences of P_4S_{10} are cleaved by hydrogen cyanamide in water, and mixed cyanamido thio-monophosphates are isolated.

P_4S_{10} + 12 NaNHCN -> 2 $Na_3[PS_3NCN]$ + 2 $Na_3[PS_2(NCN)_2]$ + 6 H_2NCN (5)

This kind of synthetic routes can be applied to gain any other phosphorus pseudochalconide derivatives as you like: phosphimates, phosphonates, phosphinates etc.

$Ph_2P(Y)Cl$ + NaNHCN + NaOH -> $Na[Ph_2P(Y)NCN]$ + NaCl (6)
Y = O, S

Furthermore, the idea to build a group of pseudochalconide homologs parallel to any element chalcogenides can be transferred to other elements. Corresponding modified carbonates, nitrites, nitrates, sulfites, sulfates and related compounds are well known [3].

COORDINATION BEHAVIOUR OF CYANAMIDO ANIONS

In connection with the coordination behaviour we were interested in the charge distribution in these ambidentate ionic species. Both, structural and spectroscopical data reveal that the NCN group takes over a greater part of the ionic charge than each one of the oxygen or sulfur atoms. We assume that within the NCN group the ionic charge is concentrated on the nitrile N-atom. The charge on the amide N-atom and the angles NC=N-E (E = O_2N-, $R_2P(O)$-, $R_2P(S)$-, RSO_2-, NC-) seem to be a function of the character of the substituent E. However, the bonding angles within this row vary between 110 and 130° which has got consequences with regard to their coordination modes.

$>P(S)\text{-}NCN]^-$ $>P(O)\text{-}NCN]^-$ $\text{-}SO_2\text{-}NCN]^-$ $O_2N\text{-}NCN]^-$ $NC\text{-}NCN]^-$

For diphenyl-cyanamidothiophosphinate we obtained exclusively compounds with this ligand in a monodentate function. In agreement with the discussed relations the coordination is preferentially held on via the terminal N-position.

$$
[Ph_2P(S)NCN]^- \quad
\begin{array}{lll}
+ R_3ECl & \rightarrow Ph_2P(S)\text{-}NCN\text{-}ER_3 & (7) \\
+ Ni^{2+} + 4\,py & \rightarrow [Ni\{NCNP(S)Ph_2\}_2py_4] & (8) \\
+ Cu^{2+} + 2\,py & \rightarrow [Cu\{NCNP(S)Ph_2\}_2py_2] & (9)
\end{array}
$$

$[Ph_2P(S)NCN]^- + Au^+ + PPh_3 \rightarrow [AuSP(NCN)Ph_2(PPh_3)]$ (10)

Exclusively toward selected soft central atoms, like gold(I), cyanamido thiophosphinate is coordinated through the sulfur atom [5-7]. Parallel to these observations cyanamidosulfonate coordinates monodentately through the nitrile N-atom. Additionally, coordination polymers with this ligand in a bidentate bridging position and with bonds to the terminal N- (equatorial) and to one of the O-atoms (axial) of a neighbouring sulfonyl group are also known [8,9]. Dicyanoamide almost preferentially functions bidentately. In each case, for the mono- or bidentate bridging ligand exclusively bonds through the terminal N-atoms are observed [10,11]. On the other hand cyanamidonitrate coordinates through the nitrile and the amide nitrogen atoms [12].

REFERENCES

1. A. HAAS, Adv. Inorg. Chem. Radiochem., 28, 167 (1984).
2. H. KÖHLER, B. EICHLER, R. SALEWSKI, Z. Anorg. Allg. Chem., 379, 183 (1970).
3. L. JÄGER, H. KÖHLER, Sulfur Reports, 12, 159 (1992).
4. H.-D. SCHÄDLER, L. JÄGER, I. SENF, Z. Anorg. Allg. Chem., 619, 1115 (1993).
5. L. JÄGER, K. POLBORN, W. BECK, Z. Anorg. Allg. Chem., 618, 158 (1992).
6. L. JÄGER, A. KOLBE, K. POLBORN, W. BECK, Z. Anorg. Allg. Chem., 617, 117 (1992).
7. E. FRITSCH, K. POLBORN, K. SÜNKEL, W. BECK, H. KÖHLER, L. JÄGER, Z. Anorg. Allg. Chem., 617, 110 (1992).
8. L. JÄGER, B. FREUDE, A. KRUG, H. HARTUNG, J. Organomet. Chem., 467, 163 (1994).
9. J. KOZISEK, H. KÖHLER, B. FREUDE, Acta Cryst., C48, 368 (1992).
10. I. POTOCNAK, M. DUNAJ-JURCO, D. MIKLOS, M. KABESOVA, L. JÄGER, Acta Cryst., C51, 600 (1995).
11. M. HVASTIJOVA, J. KOZISEK, J. KOHOUT, L. JÄGER, H. FUESS, Tras. Met. Chem., 20 (1995), in press.
12. C. TRETNER, L. JÄGER, J. KOZISEK, M. HVASTIJOVA, K. SÜNKEL, Current Trends in Coordination Chemistry, 15th Conf. Coord. Chem. (Smolenice) 347 (1995).