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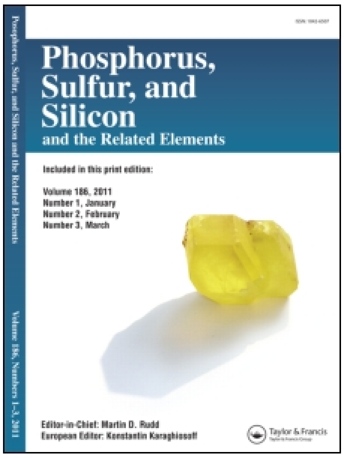

Phosphorus, Sulfur, and Silicon and the Related Elements

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Phosphorus-based Ligands in Coordination Chemistry and Catalysis

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PHOSPHORUS CONTAINING MACROCYCLIC MOLECULES. J.P. Dutasta , CENG-DRF/CH Laboratoire associé au CNRS 321, 85X , 38041 Grenoble Cedex FRANCE.

The huge development of macrocyclic molecules is indebted to the specific properties of such species.Among these compounds only few of them contain phosphorus moieties.
We will present new organic phosphorus compounds with a "coronand" like structure.Various compounds were obtained by reacting functionalized phosphanes with amino-ether derivatives. Synthesis from tris-(dimethylamino)phosphane leads to a bis-crown derivative with a dimeric structure.Two isomers are expected and such macrocyclic systems are able to complex two cationic species.Mass spectra and nmr data agree with these macrocyclic structures.Further experiments are yet in progress to improve the properties of these new ligands.Experimental results will be presented among with spectroscopic data.

STABILIZATION OF OLIGOPHOSPHANES AS LIGANDS IN METAL CARBONYL COMPLEXES

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The coordination of organobromophosphanes to metal carbonyl moieties followed by the reaction with reducing agents leads to several compounds, in which previously unknown resp. rapidly decomposing oligophosphanes are stabilized.

$(CO)_5M\text{-}Br_2PPBr_2\text{-}M(CO)_5$ (M=Cr,W), containing the yet unknown diphosphorus tetrabromide as bridging ligand, is synthesized by the reduction of $(CO)_5MPBr_3$ with stoichiometric amounts of magnesium as well as by the reaction of $M(CO)_5THF$ with PBr_3.

Several cyclotriphosphanes are stabilized in complexes $(CO)_5Cr(RP)_3$, which are prepared by the reaction of $(CO)_5Cr(RPBr_2)$ with an excess of magnesium. $(CO)_5Cr\text{-}Ph(Br)P\text{-}PPh\text{-}PPh\text{-}P(Br)Ph\text{-}Cr(CO)_5$, containing a linear tetraphosphane as bridging ligand, is formed by the same reaction using an equimolar amount of magnesium.

Compounds $(CO)_5M\text{-}R(Br)PP(Br)R\text{-}M(CO)_5$ (M=Cr,W) are prepared by the substitution of $M(CO)_5THF$ with R(Br)PP(Br)R. While the free ligands are found to undergo a disproportionation equilibrium in liquid phase, the complex is shown to be stable in most solvents. Ph(H)PP(H)Ph is stabilized as a bridging ligand by reducing $(CO)_5Cr\text{-}Ph(Br)PP(Br)Ph\text{-}Cr(CO)_5$ with $LiAlH_4$.

UNEXPECTED SYNTHESIS OF ALKOXYBICYCLOAMINOPHOSPHORANE VIA N-COORDINATED BICYCLOAMINOPHOSPHANE COMPLEXES. EVALUATION OF ITS DONOR PROPERTIES.

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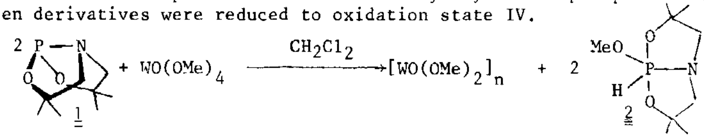
The bicycloaminophosphanes (bcap) of type 1 have been reported to act as a bidentate ligand towards diborane, giving P- and N-bonded stable BH_3 adducts. The constrained structure allowed the nitrogen to recover some of its donor character. However, with transition metal derivatives, bcap-type ligands have so far been found to coordinate through phosphorus only.

We now show the N-donor behavior of bcap with respect to transition metal derivatives; but this requires very hard metallic derivatives such as W(VI) alkoxides. However, the adducts are generally unstable, giving rise to oxido-reduction reactions. Thus smooth alkoxo group transfer reactions between the metal and the phosphorus atom led to a quantitative conversion of bcap to uncoordinated alkoxybicycloaminophosphorane (2), while the tungsten derivatives were reduced to oxidation state IV.



The isolation of the alkoxybicycloaminophosphorane was achieved in its P^V tautomeric form. Preliminary results on its dinuclear rhodium(I) complexes are also reported.

STEREOCHEMISTRY OF PF_5 COMPLEXES WITH TETRAPHENYLALKYLENDIPHOSPHINES DIOXIDES AND DIPHENYLCARBAMOILMETHYLPHOSPHINE OXIDES.

E.G. Ilyin*, M.N. Tsherbakova*, Yu.A. Buslaev*, T.Ya. Medved**, N.P. Nesterova** and M.I. Kabachnik**

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NMR ^{19}F and ^{31}P investigations are presented by composition and structure of reaction products between PF_5 and $Ph_2P(O)CHXP(O)Ph_2$ (X = H, Cl, Bu) L^{I-III}, $Ph_2P(O)(CH_2)_2P(O)Ph_2$ L^{IV} and $Ph_2P(O)CHYC(O)NEt_2$ (Y = H, Cl, Me) L^{V-VII} in non-aqueous solutions. L^{I-III} are shown to coordinate one or two PF_5 molecules as well as substitute F^- ion in PF_5 to close the chelate ring and form octahedral cations. If the hydrocarbon bridge between P=O groups is made longer (by passing from L^I to L^{IV}) the closing of the chelate ring is not observed. Monodentate coordination of L^{V-VII} to PF_5 occurs only through P=O groups whereas bidentate coordination is accompanied by closing of the chelate cycle, substitution for F^- ion and formation of cation complexes. Basic differences are observed in stabilities of the octahedral complexes with mono- and bi-dentate ligands towards exchange of F atoms.

THE COORDINATION CHEMISTRY OF PHOSPHONIO-ALKANEDITHIOCARBOXYLATES - PHOSPHONIUM BETAINES AS PHOTOSENSITIVE COMPLEX LIGANDS

U. Kunze, R. Merkel and W. Winter, Universität Tübingen (F.R.G.)

Zwitterionic phosphonium betaines, $Ph_3\overset{+}{P}-CR^1R^2-CS_2^-$, are obtained by nucleophilic addition of phosphorus ylides to carbon disulfide. Dialkylated betaines decompose under formation of 1,2,4-trithiolanes probably by a [2+3] cycloaddition of the intermediate thioketene and the substrate. With carbonylmetal halides, $(CO)_5MX$ (M = Mn,Re; X = Cl,Br,I), light-sensitive, facial tricarbonyl complexes are formed which tend to fission of the P-C bond when irradiated. The complexation of the betaine causes a thermal stabilisation but renders a photochemical sensitisation. Such complexes could be useful for the study of controlled photochemical activation by metal coordination. The molecule structures of the dimethyl betaine, trithiolane, bromomanganese and -rhenium complexes have been determined by X-ray analysis.

SYNTHESIS AND COORDINATION PROPERTIES OF CARBAMYLMETHYLENE PHOSPHONATE LIGANDS.

R. T. Paine, S. M. Bowen, L. J. Caudle and E. N. Duesler, Department of Chemistry, University of New Mexico, Albuquerque, NM 87131 USA.

Carbamylmethylenephosphonate ligands, $(RO)_2P(O)CH_2C(O)NR'_2$ are excellent extractants for a variety of metal ions, and the chemical and structural properties of the resulting complexes of interest. We have prepared a series of complexes including $Hg_2L_2(NO_3)_2$, $Cd_2L_2(NO_3)_2$, $Ln(L)_2(NO_3)_3$, $Ln(L)_2(NO_3)_3 \cdot H_2O$, $UO_2L(NO_3)_2$ and $Th(L)_2(NO_3)_4$ where R = EtO, i-PrO, n-BuO, as well as complexes where L = $Ph_2P(O)CH_2C(O)NEt_2$ and $(Ph)(EtO)P(O)CH_2C(O)NEt_2$. These complexes have been fully characterized and single crystal X-ray structures of representative complexes will be presented. The ligand cleavage chemistry induced by NCS^- will be described as well as the preparation of $(RO)_2P(O)CH(R'')C(O)NR'_2$ ligands where R = Me, Et, CH_2Ph, $SiMe_3$, P(O)(OR) and $CH_2C(O)NR_2$. The coordination chemistry of these ligands will be outlined.

COORDINATING PROPERTIES OF DIPHOSPHINE OXIDES IN ORGANOTIN(IV) ADDUCTS

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Istituto di Chimica Generale ed Inorganica, Università degli Studi, Parma, Italy.

Whereas considerable structural work has been devoted to the chemistry of diphosphines as ligands in metal complexes, very few publications have appeared in the literature giving X-ray structural information about complexes formed by diphosphine oxides.

The coordinating properties of diphosphine oxides of formula $Ph_2P(O)$-R-$P(O)Ph_2$ (R = CH_2, CH_2-CH_2, CH=CH) are being investigated in our laboratory in a series of adducts with triorgano- and diorganotin(IV) chlorides and nitrates.

The present contribution deals with the synthesis and the structural characterization by X-ray diffraction and i.r. spectroscopy of the following adducts: $SnBu_2Cl_2$(dppoe); $SnPh_3Cl$(*cis*-dppoet); $SnPh_2(NO_3)_2$(*cis*-dppoet); SnR_2Cl_2(*cis*-dppoet) (R = Et, Pr, Bu, Ph) and $\{SnPh_2(NO_3)_2\}_2$(*trans*-dppoet),where dppoe = 1,2-bis(diphenylphosphoryl)ethane and dppoet = 1,2-bis(diphenylphosphoryl)ethylene.

The different behaviour upon coordination deriving from the nature and the steric effects of the substituents on P as well as the number and nature of the organic and inorganic groups bonded to the tin atom give rise to five-, six- or seven-membered stereochemistries and produce different stoicheiometries involving mono-, di- or polynuclear systems.

CONFORMATIONS ET MODES DE COORDINATION DE DITHIOXODI-λ5-PHOSPHANES.

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et G.P.McQUILLAN, Department of Chemistry, University of Aberdeen, Meston Walk, OLD ABERDEEN, AB9 2UE, GREAT-BRITAIN.

Les propriétés basiques des atomes de soufre des dithioxodi-λ^5-phosphanes (disulfures de diphosphines) se manifestent par la formation de complexes avec des métaux variés. Les résultats présentés résument l'étude - par IR, Raman et diffraction X - des conformations et structures moléculaires de tels ligands : $R_2P(S)$-$P(S)R_2$ (R = Me, Et, Pr, Bu, C_3H_5, C_6H_5 NEt_2) et RR'P(S)-P(S)R'R (R = NEt_2, R'= C_6H_5, C_6H_{11}) et d'une cinquantaine de leurs complexes métalliques.

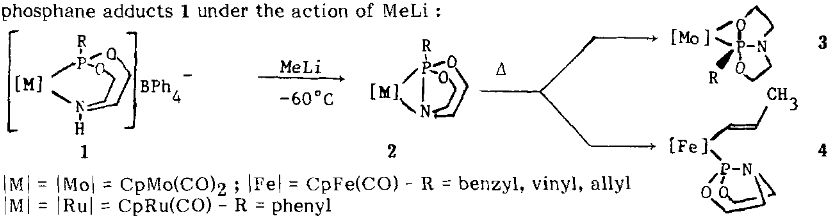
Les ligands libres (à l'état solide ou en solution) présentent toujours la conformation *trans*. Au contraire les complexes offrent une grande variété de géomètries tant par la conformation des ligands (*cis*, *gauche* ou *trans*) que par l'environnement du métal (tétraédrique, plan carré ou octaédrique) ou le degré d'association (complexes généralement monomères mais parfois dimères ou polymères).

Les longueurs de liaison P-P se répartissent en deux groupes centrés sur 2,21 et 2,25 Å dans les ligands libres (vraisemblablement en raison de contraintes stériques) et paraissent peu modifiées après complexation. De même les fréquences ν(P-P) des ligands libres sont en général peu affectées par la coordination. La diversité des complexes obtenus met en évidence l'influence des substituants R et R' sur la basicité du soufre.

SYNTHESIS AND REACTIVITY OF NEW TRANSITION METAL PHOSPHORANIDES. EVIDENCE FOR THE MIGRATION FROM PHOSPHORUS TO IRON AND REARRANGEMENT OF AN ALLYL GROUP INTO A PROPENYL GROUP σ-BONDED TO IRON.

J, Hartgerink, A. Sivade, P. Vierling and J.G. Riess, Laboratoire de Chimie Minérale Moléculaire, ERA-CNRS, Université de Nice, Parc Valrose, 06034 NICE Cedex, France.

Mo(II), Fe(II) and Ru(II) phosphoranides such as **2** have been obtained from the cationic cycloaminophosphane adducts **1** under the action of MeLi :



|M| = |Mo| = $CpMo(CO)_2$; |Fe| = CpFe(CO) - R = benzyl, vinyl, allyl
|M| = |Ru| = CpRu(CO) - R = phenyl

While under heating, **2** Mo isomerizes into **3**, with **2** Fe, Fe-vinylic compound **4** is obtained as a result of the migration plus rearrangement of the allyl group from P to Fe. This original rearrangement implies insertion of Fe into a vinylic or allylic CH bond followed by 1,3 proton shift to an allylic or vinylic C respectively. The migration of benzyl and vinyl groups are only detected as minor reactions. The reactivity of 2 with donor molecules such as CO, and other routes to phosphoranides will also be discussed.

THE ANIONIC LIGAND BIS(DIALKOXYPHOSPHINOYL)PHOSPHIDE AND ITS COMPLEXES

D.Weber, K. Peters, H.G.v.Schnering and E. Fluck*, Max-Planck-Institut für Festkörperforschung, Heisenbergstr. 1, D-7000 Stuttgart 80, FRG, *Gmelin-Institut der Max-Planck-Gesellschaft, Varrentrappstr. 40/42, D-6000 Frankfurt, FRG

The anionic ligand bis(dialkoxyphosphinoyl)phosphide(1) contains bicoordinated phosphorus which can form one and two nuclear metal complexes. Examples are bis(diethoxyphosphinoyl)phosphido pentacarbonyltungstate (2) and μ-bis(diethoxyphosphinoyl)phosphido bis(pentacarbonylomolybdate)(3). The reaction with AgI result the tetramere complex anion $\{IAg\ P[P(O)(Oet)_2]_2\}_4^{4-}$ (4) with tetrahydral and trigonal planar coordinated Ag(I). The P-P bond length (212 pm) of the free ligand (1) is about 10 pm shorten than a single P-P bond. It is enlarged in the complexes (2) and (3) to 215 and 219 pm. Bonding of the SnCl unit to the oxygen atom of the phosphinoyl part in (2) reduces the P-P bond length to 213 pm. The variation of the P-P bond length can be explained by additional p_π-d_π bonding.The coupling constant J_{P-P} of the ^{31}P nucleus has a maximum (412 Hz) in (1) with the shortest P-P bond in a minimum (158 Hz) in (3) with the longest P-P bond in the series.