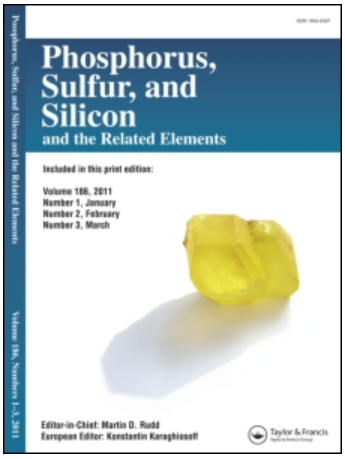

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Multiple Bonding Involving Phosphorus; Some Recent Developments

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MULTIPLE BONDING INVOLVING PHOSPHORUS; SOME RECENT DEVELOPMENTS

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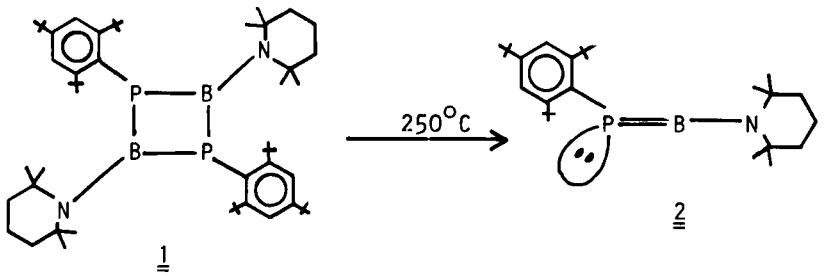
Abstract The first boraphosphene, (tmp)B=P(Ar) (tmp = 2,2,6,6-tetramethylpiperidino; Ar = 2,4,6-t-$Bu_3C_6H_2$) has been prepared by thermolysis of the corresponding dimer, $[(tmp)BP(Ar)]_2$ at 250°C. Mass spectral data are reported for (tmp)B=P(Ar) and ab initio MO calculations have been performed on the parent boraphosphene, HB=PH. The nature of the phosphorus-phosphorus bond in ArP=PAr has been investigated by solid state ^{31}P NMR. The reactivity of the phosphavinylidene, $[Mo(CO)_2(\eta^1\text{-}P{=}C(SiMe_3)_2(\eta\text{-}C_5H_5)]$ has been explored. The reaction of $ArPCl_2$ with $Na_2[(\eta\text{-}C_5H_5)\text{-}V(CO)_3]$ affords $[V_2(CO)_4(\eta\text{-}C_5H_5)_2\{\mu\text{-}PAr\}]$, the first example of a group 5 phosphinidene complex.

Iminoboranes, RN≡Br', are well-recognized species.[1] However, thus far no heavier congeners of the iminoboranes have been prepared. We report the production of a boraphosphene, the first compound featuring a phosphorus-boron double bond.[2]

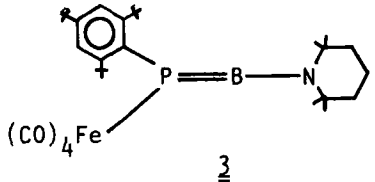
The diphosphadiboretane, 1, was prepared by treatment of $(tmp)BCl_2$ (tmp = 2,2,6,6-tetramethylpiperidino) with $ArP(Li)(SiMe_3)$ (Ar = 2,4,6-t-$Bu_3C_6H_2$). An X-ray crystallographic study of 1 revealed



1 2

the presence of considerable steric strain. For instance, the P_2B_2 moiety of 1 is rhombic (B-P-B = 93.1(8)°, P-B-P = 86.9(8)°)

while that of e.g. $[(tmp)BP(mesityl)]_2$ is square.[3] Moreover, the P-B bond distances in 1 are ~0.05Å longer than in the analogous mesityl compound. Thermolysis of 1 in the gas phase at 250°C results in the clean production of the boraphosphene, 2. Of particular significance is the fact that the EI-MS fragmentation pattern for boraphosphene 2 is completely different than that for e.g. $[(tmp)BP(mesityl)]_2$. The HRMS parent peak for 2 occurs at 427.3551(calculated, 427.3539). From the chemical standpoint, it has been found that 2 (but not 1) reacts with $Fe_2(CO)_9$ to produce what we believe to be 3. Ab initio MO calculations on the parent



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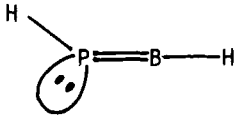
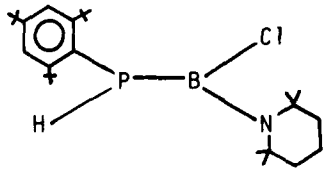


4

boraphosphene, HPBH, using the 6-31 G basis set, indicate that the minimum energy geometry corresponds to 4 with P-B = 1.649 Å, H-P-B = 94.5, and P-B-H = 175.0°.

The reaction of ArPHLi with $(tmp)BCl_2$ affords 5. In turn, treatment of 5 with RLi (R = Me, t-Bu) results in the novel anions, 6.



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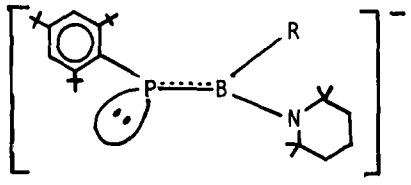


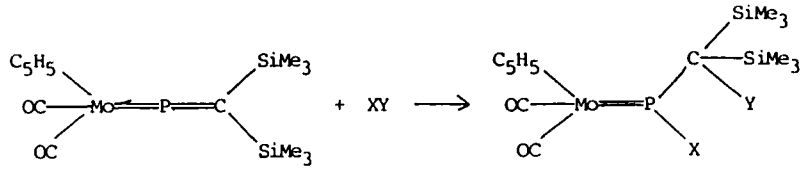
6

The ^{31}P chemical shifts of these anions are unusual (+72 for the Me compound and +85, +87 for the t-Bu analogue) and suggestive of multiple bonding between phosphorus and boron.

The nature of the phosphorus-phosphorus bond in ArP=PAr has been studied by static and magic angle spinning ^{31}P solid state NMR.[4] Static powder spectra show an exceptionally large shift anisotropy with σ_{11} = 1236, σ_{22} = 249, and σ_{33} = -3 ppm. These results

have been compared to the solid state ^{31}P spectra for Ar(H)PP(H)-Ar and $ArPH_2$. Comparison with previous work on olefins and disilenes shows that the P=P double bond is similar in many respects to the double bond in group 14 elements.

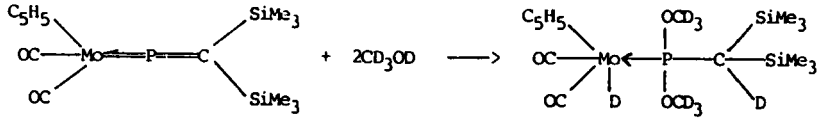
In previous work we have established synthetic roots to phosphavinylidene complexes of the type, $[M(CO)_2(\eta^1\text{-}P{=}C(SiMe_3)_2(\eta\text{-}C_5R_5)]$ (M = Mo, W; R = H, Me).[5] We have now found that $[(Mo(CO)_2(\eta^1\text{-}P{=}C(SiMe_3)_2(\eta\text{-}C_5H_5)]$ (7) (i) reacts readily with both electrophiles and nucleophiles, and (ii) undergo sequential reactions at the P=C and P=M functionalities.[6] In turn, the reaction of phosphavinylidenes with electrophiles represents a new approach to the synthesis of 3e⁻ donor phosphido complexes as summarized below.



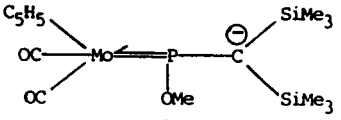
X	EtO	CD_3O	$i\text{-}Pr_2N$	C_6F_5S
Y	H	D	H	H
δ_P	367.9	369.1	344.2	297.7

The usefulness of the approach is illustrated by the facile introduction duterium labels and by the preparation of the first thio-substituted complex of this type. X-ray structural studies of all four compounds reveal a trigonal planar phosphorus geometry and relatively short phosphorus-molybdenum distances.

Treatment of 7 with an excess of CD_3OD results in reaction at both the Mo=P and P=C bonds. Compound 7 is also reactive toward CH_2N_2, CS_2, $Fe_2(CO)_9$, and several nucleophiles. For example, the reaction



of 7 with NaOMe affords the novel anion, 8 (δ_p = -20.1).



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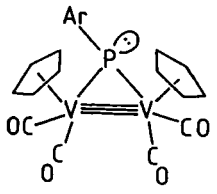
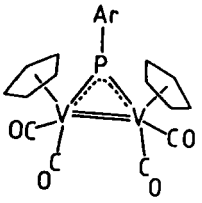
Several bimetallic phosphinidene complexes of the type $RP(ML_n)_2$ have been prepared for both sixteen-electron[7] and fifteen-electron[8] organometallic fragments. We have recently prepared the first example of a phosphinidene moiety bonded to a fourteen-electron ML_n fragment.[9] Treatment of $ArPCl_2$ with $Na_2[(\eta\text{-}C_5H_5)V(CO)_3]$ afforded $[V_2(CO)_4(\eta\text{-}C_5H_5)_2(\mu\text{-}PAr)]$ (9). Complex 9 is diamagnetic and the ^{31}P NMR spectrum comprises a broad singlet at +670 ppm which is in the region characteristic of μ_2-phosphinidene complexes. However, if each vanadium is to achieve an eighteen-electron configuration, two valence isomers, A and B, are possible. An X-ray crystallographic study revealed that the phosphorus is trigonal



A



B

planar. Together with the short vanadium-phosphorus distances (average 2.255 Å) these observations imply vanadium-phosphorus multiple bonding, thus favoring structure B. Extended Hückel MO calculations on the bonding in the V_2P ring show that the V-V bond

order is slightly greater than unity. The V-V bonding is strongly mediated by the bridging phosphinidene.

ACKNOWLEDGEMENT

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