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Réplique: A New Concept for Bonding in Carbodiphosphoranes?

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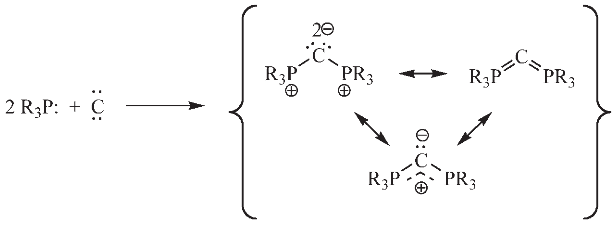
A recent publication by Tonner, Öxler, Neumüller, Petz, and Frenking[1] must leave the reader with the impression that in this Communication a novel and useful concept has been introduced describing carbodiphosphoranes [R_3PCPR_3] as 1:2 complexes of a carbon atom C with two tertiary phosphines R_3P. Moreover, it is claimed that evidence for the validity of this concept has now been obtained by considering and providing examples in which two lone pairs of electrons at the central carbon atom are engaged in dative bonding to various acceptors.[1] The impression clearly made by this Communication is reflected by the immediate appearance of a Note in another journal presenting the new concept as a sort of a highlight.[2]

Ironically, a look into somewhat distant back volumes of the same two periodicals shows, however, that this concept was considered quite explicitly in much of the earlier work on the coordination chemistry of carbodiphosphoranes, which had been initiated about a decade after the discovery of these diphosphonium ylides:[3] Scheme 1 has been presented in 1983 in a then comprehensive Review,[4] preceded by an Essay addressing a wider audience in 1979.[5] Later Reviews also have left no doubt that the coordination chemistry of carbodiphosphoranes clearly shows that the electronic structure with two lone pairs at the central carbon atoms "*predominates the ground state of these molecules.*"[6]



Scheme 1.

Recognizing the donor potential of carbodiphosphoranes with two lone pairs of electrons at the central carbon atom, the first 1:2 complex was synthesized in 1975 employing two acceptors CH_3Au to produce the dinuclear adduct $(Me_3P)_2C(AuMe)_2$ which was assigned a structure with a tetracoordinate carbon atom,[7] later confirmed in work by Vicente et al. for an analogous 2:1 complex of ClAu with Ph_3PCPPh_3.[8] Similar tetracoordination has appeared in related 2:2 complexes with zinc and cadmium dialkyls.[9] (It should be noted that in a seminal paper by Kaska et al. in 1973 the first 1:1 complexes of Ph_3PCPPh_3 with metal carbonyls were described, but attempts to obtain 1:2 complexes—or to protonate the 1:1 complexes—had remained unsuccessful.[10])

As a benchmark for their discussion of bonding in the title compounds, the authors of the Communication refer in their Table 2 to the basic geometry of carbodiphosphoranes in general, and to the P-C-P angle in particular, but rely only on a very early result[11] for Ph_3PCPPh_3, ignoring the fact that this angle is known to vary considerably with the substituent pattern, and even with the crystal packing in different polymorphs, and that the energy profile of bending is extremely flat.

To contribute to the discussion of the P-C-P valence angle as a probe for the nature of this linkage, as early as the mid-1970s, the species with the smallest possible set of organic substituents had been synthesized, Me_3PCPMe_3, and its structure and dynamics investigated by electron diffraction in the first and hitherto only gas-phase study,[12] complemented by determination of the crystal structure of $MePh_2PCPPh_2Me$.[13,14] The photoelectron spectra of Me_3PCPMe_3 have been recorded to obtain experimental information about the HOMO energies of this key compound,[15] and the dipole moment of Ph_3PCPPh_3 was determined in benzene solution by Bestmann et al.[16] All these results have provided a consistent picture of the bonding situation in carbodiphosphoranes[4,6] and its consequences for the donor properties.

The Communication by Tonner et al.[1] ends with the somewhat surprising conclusion, that the new results "*can be utilized for synthesizing compounds that exhibit unusual features, such as dication [$(Ph_3P)_2CH_2$]$^{2+}$ and trication [$\{(Ph_3P)_2CH\}_2Ag$]$^{3+}$*" (a bis(ylide) complex of silver(I)).

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From a traditional point of view, however, the synthesis of salts with the dication $[Ph_3PCH_2PPh_3]^{2+}$ and its homologues has never presented any problems to the experimentalists,[3,6,7,9,13,14] and the properties of the products have always been seen as expected and by no means unusual. Conventional diprotonation of carbodiphosphoranes to give, in two steps, diquaternary phosphonium salts and the reverse reactions were successfully carried out many times in the past, which naturally went without any far-reaching comments.[17]

Bis(ylide) silver complexes have been known since 1975 with unequivocal proof of covalent Ag–C bonding through one of the first observations of large ^{13}C–$^{107/109}Ag$ spin–spin couplings,[18,19] and there is precedent for complexes of other metals (in particular gold)[20] with ligands of the type $[(Ph_3P)_2CR]^+$.[4,6,21] It is true that formation of a *tri*cation—against Coulomb repulsion—is remarkable, but this just confirms the pronounced donor capacity of carbodiphosphoranes and the strength of the Ag–C bonds.

A simple BH_3 adduct of a carbodiphosphorane, now the subject of calculations and of unpublished experimental work quoted as ref. [15] in the Communication by Tonner et al.[1] was prepared in 1981.[9b]

Regarding the general formula EL_2 now proposed for further work,[1] there were first studies on carbodi*arsoranes* $R_3AsCAsR_3$ in 1985, and these compounds were again referred to as complexes of a carbon atom (E) with tertiary arsines (L).[22] For a further extension, announced in the Communication,[1] into the chemistry of phospha-cumulenes $R_3PC(CX)$ ($X = O$, S, Se, NH, etc.) with similar bonding characteristics, a Review by Bestmann of 1977 even today can serve as an introduction.[23]

The work by Tonner et al.[1] has been introduced as an extension of recent theoretical and experimental studies of carbenes and carbene adducts to include now ylides as related carbon-donor ligands. The heuristic concept of donor–acceptor complexes of carbon atoms is certainly valid, but not entirely new. Maybe this new round of advertising will be instrumental in attracting new attention, but more thought must be given to the formulae used in future presentations.[24]

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[24] The two formulae presented in the Communication (see below)[1] as a description of bonding in carbodiphosphoranes are very confusing. While formula **B** is a conventional resonance formula with a full and correct account of all valence electron pairs and formal charges,[4–6] formula **A** is not. By its two unidirectional arrows it simply indicates the way in which **B** is formed, and therefore it must not be connected with **B** by a bidirectional arrow suggesting resonance.

A **B**