Carbodiphosphoranes

DOI: 10.1002/ange.200700327

Reply to Réplique: A New Concept for Bonding in Carbodiphosphoranes?

Gernot Frenking, Bernhard Neumüller,* Wolfgang Petz,* Ralf Tonner, and Florian Öxler*

Stichwörter:
bonding analysis · carbodiphosphoranes · carbon · cations · donor–acceptor systems

We are puzzled by the réplique of Professor Schmidbaur[1] to our Communication[2] where we report a quantum chemical analysis of the electronic structure in carbodiphosphoranes (CDPs) which gives evidence for a bonding situation where the four valence electrons of carbon are not engaged in chemical bonding but remain as electron lone pairs. In our Communication we explicitly point out that in *some* previous experimental work the bonding in CDP compounds was described in terms of two electron pairs while in most papers it is delineated using two double bonds $R_3P{=}C{=}PR_3$. We actually cited the very first suggestion from 1973 where a bonding situation for carbodiphosphoranes with two donor–acceptor bonds to a carbon atom was suggested by Kaska et al.[3] which preceded work of Professor Schmidbaur cited in his Réplique.[1]

Perhaps the author of the preceding Réplique[1] does not realize that there is a significant difference between *suggesting* a chemical formula and a *quantum chemical investigation* of a bonding situation. The difference between the two may be compared with the difference between predicting the existence of a new molecule by a theoretical calculation and the first synthesis of the compound. Even when an unknown molecule has been calculated and when its properties are accurately predicted by quantum chemical calculations, it still takes much creativity and experimental skill to prepare it with experimental methods. If such a molecule has properties which are in agreement with previous calculations it would nevertheless be considered by most chemists as an achievement in its own right which deserves to become published. The same holds true when it comes to a theoretical study of an experimentally known compound. Chemists who are familiar with quantum chemical investigations[4] know that it also takes much effort and competence to carry out such work which then may become published if it leads to new important insights. The information which is gained in such studies goes far beyond writing a bonding line. This situation may not be cognizable by chemists who were never engaged in quantum chemical research. It is our conviction that experimental and theoretical work should be done with mutual respect for each other. Neither is the synthesis of a molecule a mere technical conformation of a theoretical prediction, nor is a quantum chemical investigation a mere supplement to experimental work. The two sides rather complement each other in a way which most chemists nowadays find stimulating and very useful.

Concerning the experimental part in our paper, we are pleased that Professor Schmidbaur calls the synthesis of a trication remarkable. In contrast to his opinion, however, we think that the synthesis is more than just a confirmation of the pronounced donor capacity of CDPs and the strength of the Ag–C bonds. It greatly extends the scope of CDP complexes towards multiply charged cations which hitherto were not known. Moreover, the calculated *negative* partial charge of −1.34 e (!) at the central carbon atom indicates a highly unusual electron-density distribution which will be interesting for many chemists. Our experimental work of a BH_3 adduct of a CDP was briefly mentioned because it was carried out in conjunction with the theoretical prediction that CDPs should be capable of binding *two* BH_3 molecules. Unlike previous studies, we were able to isolate a suitable crystal which could be used for the first X-ray structure analysis of a CDP–BH_3 adduct.[5] Furthermore, we found experimental evidence for the intermediate formation of a CDP–$(BH_3)_2$ complex. Details will be published in a forthcoming publication.

We share with Professor Schmidbaur the hope that our publication may become instrumental in attracting attention to the class of CDPs and related compounds to which he has made significant experimental contributions. Our theoretical study has shown that more compounds with the general formula EL_2 with donor–acceptor bonds E←L may exist which await synthesis. We already pointed out that carbon suboxide C_3O_2 and its complexes should be reinvestigated because they may exhibit properties which are in line with a bonding situation $C(CO)_2$. Insight into the electronic structure of CDPs gave us

[*] Prof. Dr. G. Frenking, Prof. Dr. B. Neumüller, Prof. Dr. W. Petz, Dipl. Chem. R. Tonner, Dipl. Chem. F. Öxler
Fachbereich Chemie
Philipps-Universität Marburg
Hans-Meerwein-Strasse, 35032 Marburg (Germany)
Fax: (+49) 6421-282-5566
E-mail: frenking@chemie.uni-marburg.de
neumuell@chemie.uni-marburg.de
petz@staff.uni-marburg.de

a hint to connect its reactivity to the recently synthesized carbon complexes $[Cl_2(PR_3)_2Ru(C)]$[6] where again a single carbon atom is engaged in donor–acceptor interactions.[7]

Finally, we are grateful to Professor Schmidbaur for pointing out that the bidirectional arrow in our Scheme 1 which is shown in ref. [24] in his rèplique[1] should be omitted.

Online veröffentlicht am 1. März 2007

[1] H. Schmidbaur, *Angew. Chem.* **2007**, *119*, 3042; *Angew. Chem. Int. Ed.* **2007**, *46*, 2984.

[2] R. Tonner, F. Öxler, B. Neumüller, W. Petz, G. Frenking, *Angew. Chem.* **2006**, *118*, 8206; *Angew. Chem. Int. Ed.* **2006**, *45*, 8038.

[3] W. C. Kaska, D. K. Mitchell, R. F. Reichelderfer, *J. Organomet. Chem.* **1973**, *47*, 391.

[4] Here we mean chemists who have a true insight into quantum chemical methods which goes beyond knowing the names of key words in popular program packages.

[5] F. Öxler, Diplomarbeit, Marburg, **2006**.

[6] a) R. G. Carlson, M. A. Gile, J. A. Heppert, M. H. Mason, D. R. Powell, D. V. Velde, J. M. Vilain, *J. Am. Chem. Soc.* **2002**, *124*, 1580; b) A. Hejl, T. M. Trnka, M. W. Day, R. H. Grubbs, *Chem. Commun.* **2002**, 2524.

[7] A. Krapp, K. K. Pandey, G. Frenking, *J. Am. Chem. Soc.*, submitted.