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Synthesis, Structure, and Reactivity of Carbene-Stabilized Phosphorus(III)-Centered Trications $[L_3P]^{3+}$

Jekaterina Petuškova, Mahendra Patil, Sigrid Holle, Christian W. Lehmann, Walter Thiel, and Manuel Alcarazo*

Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, D-45470 Mülheim an der Ruhr, Germany

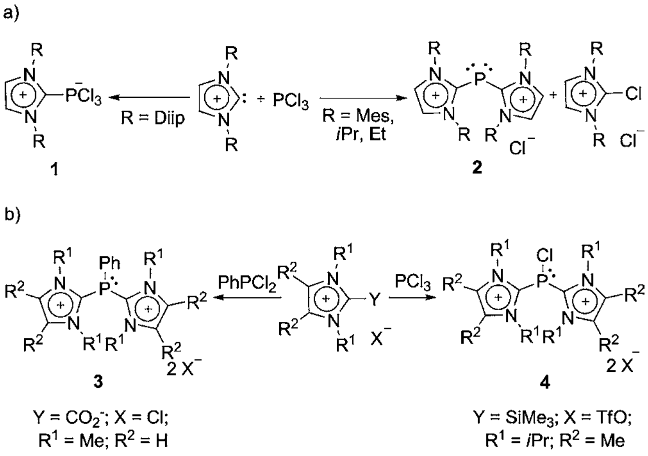
S Supporting Information

ABSTRACT: Carbene-stabilized $[L_3P]^{+3}$ cations have been synthesized for the first time by a reaction between 1-chloro-2,3-bis(dialkylamino)cyclopropenium salts and $P(SiMe_3)_3$. In addition, the first structural characterization of such an entity is reported. Consistent with the X-ray data, density functional calculations indicate that these P-centered cations, despite their high positive charge, still feature a nonbonding electron pair on the P-atom (HOMO) and a very low-lying LUMO depicting them as poor σ-donors and excellent π-acceptors.

Some of the most significant advances in p-block chemistry come from the recent realization that compounds derived from these elements can perform tasks previously restricted to transition metals, namely, the activation of inorganic molecules,[1] the splitting of enthalpically robust bonds,[2] or the stabilization of highly reactive species.[3] Specifically, highly charged cations centered at main group elements are promising reagents for the activation of small molecules.[4] Moreover, their geometries and unusual electronic environments make them interesting targets for theoretical studies as they often have intricate bonding situations not always free of controversy.[5] Concerning phosphorus, only three examples of $[L_3P]^{3+}$ cations have been described, all of which are stabilized by N-based ligands (L = 4-(dimethylamino)pyridine, quinuclidine, and 1,5-diazabicyclo[4.3.0]non-5-ene).[6] Up to now, no solid-state structural analysis involving these species has been reported and their connectivities were thus determined only on the basis of spectroscopic and chemical data.

The outstanding donor properties exhibited by N-heterocyclic carbenes (NHCs) have rendered them privileged ligands for the stabilization of metal complexes and highly electrophilic species.[7] However, in the case of P^{3+} centers no success has been achieved. Reactions of free N-heterocyclic carbenes with electrophilic phosphorus sources such as PCl_3 proved to be very sensitive to steric hindrance. While bulky carbenes afford hypervalent ($NHC\rightarrow PCl_3$) complexes **1** that do not react further,[8] less sterically demanding NHCs promote a reductive process probably initiated by preferential nucleophilic attack of the carbene at the highly activated Cl-atom, instead of the central P-atom, in intermediates of general formula **4**.[9] Thus, $[(NHC)_2P]^+$ derivatives **2** are the ultimate result of this transformation (Scheme 1a). Only recently, new synthetic approaches based on Bertrand's "onio-substituent transfer" methodology[10] have circumvented this reductive pathway by employing masked rather than free carbenes. In that manner, the synthesis of a few mono- and dicationic P(III) species **3** and **4** has been accomplished (Scheme 1b).[11] Triply charged carbene-stabilized phosphorus cations have not yet been reported.

Scheme 1. (a) Reaction of PCl_3 with Free Carbenes; (b) Synthetic Routes for the Preparation of Dicationic P(III) Species via "Onio-Substituent Transfer" Methodology



Herein, we describe an alternative synthetic approach, based on the use of an unprecedented "reverse electron demand" onio-substituent transfer strategy, which for the first time allows the isolation and structural characterization of the elusive $[(carbene)_3P]^{+3}$ species. Instead of using PCl_3 and silylated bases as starting materials, we envisaged that the alternative conceivable reaction partners, silyl-substituted phosphines and chloroiminium salts, might also participate in this transformation by sequential nucleophilic attack of the phosphine to the electron-deficient chlorinated carbon and concomitant release of TMSCl. To put this concept into practice, 1-chlorocyclopropenium cations were deliberately chosen as carbene precursors instead of the more common chloroimidazolium salts due to the simultaneous confluence of three beneficial factors: (a) an enhanced tendency to undergo nucleophilic attack at the chlorinated carbon;[12] (b) the smaller steric demand derived from a carbene embedded in a three-membered ring that facilitates the coordination of several of

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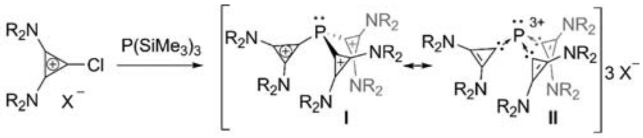
these ligands to the same central atom,[13] and (c) the stronger σ-donor and weaker π-acceptor properties of cyclopropenylidenes as compared with NHCs. Note that the net donation from the carbene ligand must compensate for the continuous increase of formal positive charge on the phosphorus atom in order to allow the consecutive nucleophilic substitution process to take place.[14] Thus, by gentle heating of a mixture of 1-chloro-2,3-bis(dialkylamino)cyclopropenium salts with P(SiMe$_3$)$_3$, the desired P(III)-centered trications were isolated as white or light orange solids in moderate to good yields (Scheme 2).[15]

Scheme 2. Synthesis of [L$_3$P]$^{+3}$ Cations by Reaction of 1-Chlorocyclopropenium Salts with Silylated Phosphines



5, R = *i*Pr; X = BF$_4$
6, R = *i*Pr; X = TfO
7, R = Me; X = ClO$_4$

8, R = *i*Pr; X = BF$_4$; 22%
9, R = *i*Pr; X = TfO; 45 %
10, R = Me; X = ClO$_4$; 68%

The tricationic character of **8**−**10** was suggested by the increased shielding of the P center (^{31}P NMR resonances at δ = −76.5, −76.4, and −93.5 ppm, respectively) when compared with the data reported for dicationic bisimidazolylidene substituted sister compounds **3** (δ = −50.8 ppm).[11b] Subsequently, single crystal X-ray diffraction analysis unambiguously confirmed the proposed connectivity for the cationic part of **8** (Figure 1).

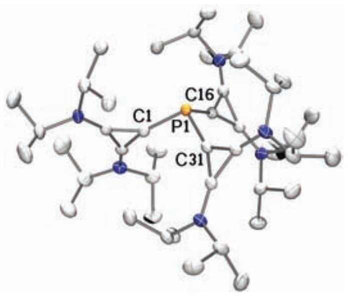


Figure 1. Molecular structures of compound **8** in the solid state. Thermal ellipsoids at 50% probability; tetrafluoroborate counterions, solvent molecules, and hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): C(1)−P(1) 1.7870(18), C(16)−P(1) 1.7901(18), C(31)−P(1) 1.7964(18), C(1)−P(1)−C(16) 104.93(8), C(16)−P(1)−C(31) 103.31(8), C(1)−P(1)−C(31) 103.31(8).

Two structural parameters are crucial for understanding the electron environment around phosphorus in **8**. The P−C(carbene) bond distances are only slightly shorter than those observed in neutral aromatic phosphines but significantly longer than typical P−C double bonds.[16] In addition, the degree of pyramidalization at phosphorus (65.2%) is even higher than that observed for neutral aromatic phosphines (56.7% for PPh$_3$).[17] Both parameters reveal that back-donation from the phosphorus to the cyclopropenyl rings must be marginal, if any, and suggest retention of a nonbonding electron pair on this atom.

In an attempt to gain insight into the electronic structure in these compounds, density functional calculations at the B3LYP/6-31G* level were performed. The optimized structures closely match the experimental data (see the Supporting Information). According to natural population analysis, the phosphorus atom in **8** bears a positive charge of +0.88*e*. This indicates that although the real nature of **8** is in between Lewis structures **I** and **II**, it is closer to **I** (Scheme 2). Moreover, in line with our analysis of the crystal structure, the Wiberg bond index values (0.91 for each C−P bond) support the absence of back-donation from phosphorus to the carbene moieties.

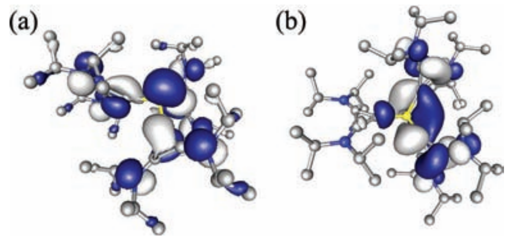
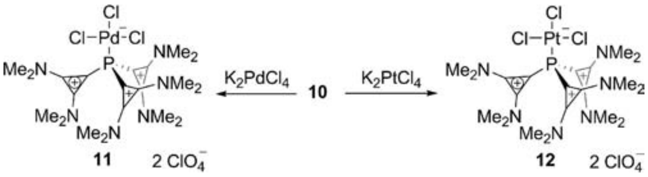


Figure 2. Representation of the calculated HOMO (left) and LUMO (right) for **8**.

Inspection of the frontier orbitals shows that the HOMO has substantial lone pair character at phosphorus, with a natural orbital occupancy of 1.84e (Figure 2). This might provide some Lewis base reactivity to this cation in spite of the global +3 charge that it bears. More importantly, the very low-lying LUMO is expected to confer remarkably strong π-acceptor properties (see the Supporting Information).

Encouraged by these distinctive electronic properties, electron-rich metal-containing moieties able to engage in gentle back-donation were chosen in an attempt to ascertain whether these trications could actually be employed as π-acid ligands. Thus, when **10** was reacted with K$_2$PdCl$_4$ and K$_2$PtCl$_4$, complexes **11** and **12** were efficiently obtained (Scheme 3).[18]

Scheme 3. Formation of Pd and Pt Complexes



The coordination of phosphorus to Pd and Pt in **11** and **12** was primarily suggested by the appearance of new resonances in the ^{31}P NMR spectra (δ = −46.1 and −62.4 ppm, respectively). Especially informative are the satellite signals in **12** ($^1J_{\mathrm{P-Pt}}$= 2033 Hz) that are indicative of Pt−P bond formation. Ultimately the structure of **12** was confirmed by X-ray diffraction analysis (Figure 3). The nature of this metal−ligand bonding has been further examined by quantum-chemical calculations. Charge decomposition analysis reveals that the total L→M σ-donation (0.31*e*) is lower than the M→L π-back-donation (0.43*e*) which should hence be regarded as the main interaction in **12** and thus as the principal source of its stability. Very often ligands are anionic or neutral species; monocationic ligands are already rare,[19] but compounds of this type, formally constituted by a tricationic ligand with no spacer

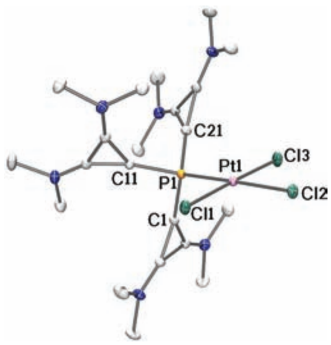


Figure 3. Molecular structure of compound **12** in the solid state. Thermal ellipsoids at 50% probability; perchlorate counterions, solvent molecules, and hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): C(1)−P(1) 1.781(2), C(11)−P(1) 1.777(3), C(21)−P(1) 1.781(2), P(1)−Pt(1) 2.1758(7), Pt(1)−Cl(1) 2.2979(7), Pt(1)−Cl(2) 2.3307(7), Pt(1)−Cl(3) 2.3022(7), C(21)−P(1)−C(11) 102.9(1), C(11)−P(1)−C(1) 103.9(1), C(1)−P(1)−C(21) 101.2(1).

between the donor atom and the positive charged groups, seem to be unknown.[20]

In summary, we have reported for the first time the synthesis and structure of tricationic P(III)-carbene stabilized centers obtained by modification of the "onio-substituent transfer" protocol. Unexpectedly, despite the presence of three positive charges, coordination of **10** to electron-rich transition metals has been demonstrated to be possible in both the solid state and in solution. Additionally, the nature of the metal−ligand interaction has been analyzed by DFT calculations. Whether this and related compounds could have application in catalysis is currently under investigation.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures including characterization data for all new compounds, CIF files for **8** and **12** as well as additional computational data. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

alcarazo@mpi-muelheim.mpg.de

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