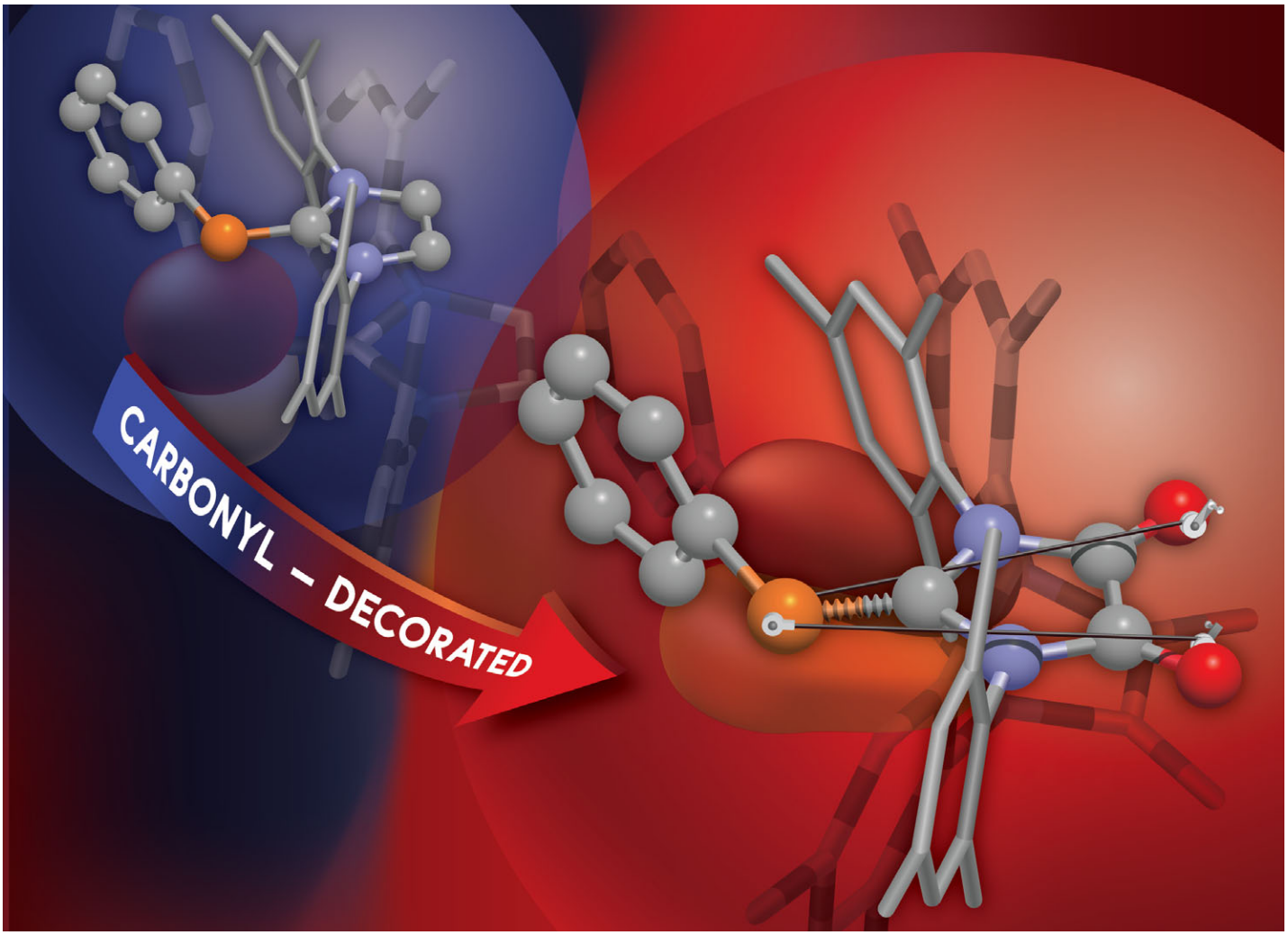

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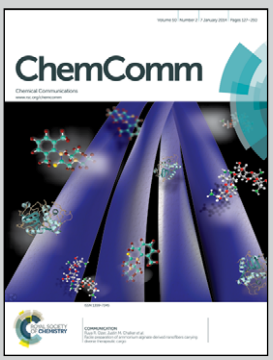
Phosphaalkene *vs*. phosphinidene: the nature of the P–C bond in carbonyl-decorated carbene→PPh adducts

Carbonyl-decorated carbenes afford phosphaalkenes: Carbonyl moieties can act as pulleys in carbene→PPh adducts by pulling electron density away from the phosphorus centre. This enhances π-bond character, and results in a shortening of the P–C interaction.

As featured in:



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Phosphaalkene *vs.* phosphinidene: the nature of the P–C bond in carbonyl-decorated carbene → PPh adducts†

Roberta R. Rodrigues, Christopher L. Dorsey, Chelsee A. Arceneaux and Todd W. Hudnall*

Treatment of dichlorophenylphosphine with two equivalents of carbonyl-decorated carbenes results in a two-electron reduction of the phosphorus centre concomitant with carbene oxidation to afford novel phosphaalkenes as confirmed *via* crystallographic, spectroscopic, and DFT analyses.

The preparation of isolable phosphaalkenes ($R_2C{=}PR'$) bearing a variety of substituents continues to be a contemporary research area due to the growing interest of utilizing P=C bonds in applications ranging from materials science[1–3] to ligands in catalysis.[4,5] There are currently several synthetic routes for preparing P=C bonds[6] including: Becker condensation/1,3-silatropic rearrangement;[7] 1,2-elimination;[8] and phospha-Peterson[9–13] methods as well as others.[14] However, these methods require large bulky phosphorus substituents, limiting their utility.

Alternatively, Arduengo showed that carbene → phosphinidene (PR) adducts such as **I** can be regarded as two canonical forms **A** and **B** (Fig. 1).[15] Crystallographic and ^{31}P NMR spectroscopic data (Table 1) however, determined that phosphinidene form **A** dominated. Bertrand recently described that the nature of the P–C bond in these adducts lies on a continuum between the forms **A** and **B**, respectively.[16] Moreover, the π-accepting properties of carbenes can be quantified by evaluating the ^{31}P NMR of these carbene → PPh adducts. Indeed, for strongly π-acidic carbenes, the phosphaalkene form dominates in compounds such as **II** as revealed through a short P–C bond and low-field ^{31}P resonance (Table 1).[16]

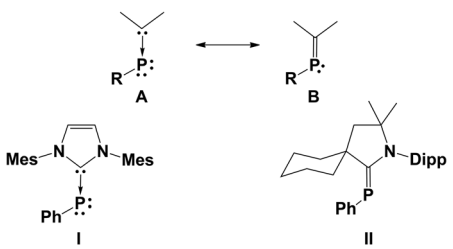

Fig. 1 Two extreme representations and representative examples of carbene → PPh adducts. Mes = 2,4,6-$(CH_3)_3$–C_6H_2; Dipp = 2,6-$(iPr)_2$-C_6H_3.

We and others have recently been exploring the ability to modulate carbene reactivity *via* decoration with carbonyl-containing functional groups.[17,18] We recently disseminated our results which demonstrate that these electrophilic carbenes readily activate white phosphorus (P_4) to afford novel meta stable P_4 and P_8 allotropes that feature P=C bonds.[19] Given that carbenes are well-suited to stabilizing P(I) species,[16,20,21] we sought to investigate the utility of carbonyl-decorated carbenes (CDCs) as phosphaalkene precursors.

We initially attempted Bertrand's two-step synthesis[16,20] by treating carbenes **1–3** with dichlorophenylphosphine ($PhPCl_2$, 1 eq.) followed by reduction with magnesium (2 eq.) to afford the desired phosphaalkenes. However, treatment of a diamidocarbene (DAC) **1** or **2** with $PhPCl_2$ in C_6D_6 was sluggish and did not afford the phosphonylated salt required for the Mg reduction.‡ Addition of trimethylsilyl triflate (TMSOTf) greatly increased the reaction rates; however, ^{1}H NMR ($CDCl_3$) of the product revealed two carbene-containing compounds in a 1:1 molar ratio. We found that the phosphorus-containing product could be extracted from the crude reaction mixture using hexanes, suggesting the formation of a neutral phosphorus compound. Multinuclear NMR of the second carbene-containing species revealed the formation of a triflate salt (^{19}F: δ = −79 ppm, $CDCl_3$) that did not exhibit a signal in the ^{31}P spectrum.

These results suggested that a redox process occurred in which a sacrificial equivalent of carbene was oxidized concomitant with phosphorus reduction. Optimization found that treating $PhPCl_2$ with two equivalents of carbenes **1–3** in the presence of TMSOTf (1.0 eq.) afforded the desired phosphaalkenes **1·PPh–3·PPh**§ along with their 2-chloropyrimidinum (iminium) triflate salts¶ in modest yields (Scheme 1).

1·PPh–3·PPh were fully characterized by multinuclear NMR spectroscopy, as well as single crystal X-ray diffraction for **1·PPh** and **2·PPh** (Fig. 2). Most notably, the phosphorus atoms in **1·PPh** and **2·PPh** resonate down-field (+85.4 and +78.6 ppm, respectively)

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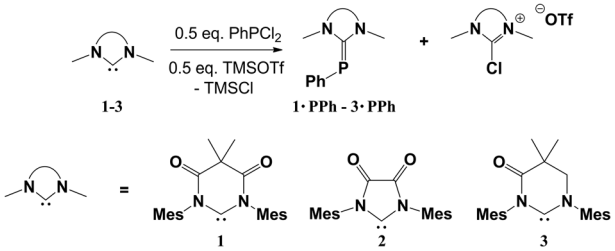
† Electronic supplementary information (ESI) available: General experimental information, synthetic procedures, computational data, and additional figures. CCDC 946638–946640. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3cc45134h

Table 1 Pertinent metrical and spectroscopic data associated with phosphaalkenes derived from singlet carbenes

Compound	P═C (Å) (X-ray)	C–P–C < (°) (X-ray)	P═C (Å) (calculated)	C–P–C < (°) (calculated)	Torsion angle (X-ray)	Torsion angle (calculated)	^{31}P NMR (ppm)	^{13}C NMR[b] (ppm)
1·PPh	1.726(3)	108.22(13)	1.738	110.59	9.83	10.78	+83.0[a]	172.0 (75.1)[c]
2·PPh	1.691(4)	106.65(17)	1.721	108.10	0.77	0.93	+78.6[a]	169.9 (66.6)
3·PPh	—	—	1.755	110.45	—	19.11	+37.7[a]	180.1 (78.8)
I[d]	1.763(6)	99.9(3)	1.768	105.88	26.5	14.22	−23.0[a]	170.0 (49.7)
II[e]	1.7336(15)	104.94(6)	1.737	108.07	4.25	0.43	+68.9[a]	208.1 (66.0)
III	—	—	1.685	105.99	—	2.31	—	—

[a] NMR data obtained in C_6D_6. [b] P–C coupling constants *J* (in parenthesis) are given in Hz. [c] NMR data obtained in $CDCl_3$. [d] Experimental data obtained from ref. 15. [e] Experimental data obtained from ref. 16.



Scheme 1 Synthesis of phosphaalkenes **1·PPh–3·PPh**. Yields: **1·PPh** (47.4%), **2·PPh** (31.9%), **3·PPh** (55.4%).

from **3·PPh** (+39.7 ppm) due to the greater π-acidity of DACs **1** and **2** when compared **3**.[18] The ^{31}P signals of **1·PPh–3·PPh** were observed at high-field in comparison to the chemical shift of non-polarized phosphaalkenes (δ = +230–420 ppm),[6,22] but are considerably downfield with respect to **I** (^{31}P for = −23.0 ppm)[15] indicating a more electron-deficient phosphorus centre. Moreover, the ^{31}P chemical shift of compounds **1·PPh** and **2·PPh** is approximately 10 ppm downfield relative to **II**, indicating that DACs are stronger π acceptors than cyclic alkyl amino carbenes (CAAC).

To further substantiate the presence of a P═C bond in **1·PPh–3·PPh**, we note a barrier of rotation about the P–C bond as indicated by the ^{1}H NMR of each phosphaalkene. Indeed, the ^{1}H NMR of **1·PPh–3·PPh** exhibited inequivalent mesityl substituents in solution, consistent with considerable multiple bond character. In contrast, the ^{1}H NMR of **I** exhibited equivalent mesityl groups, thus illustrating a poorly developed multiple bond between the carbene and phosphorus centres.[15]

The X-ray structures of phosphaalkenes **1·PPh** and **2·PPh** also corroborated the existence of multiple bond character between the $C_{carbene}$ and the P centres. Indeed the short P–C distances (1.726(3) and 1.691(4) Å for **1·PPh** and **2·PPh**, respectively) coupled with the C–P–C angles (108.22(33) and 106.65(17)°) are comparable with what has been observed for nonconjugated phosphaalkenes (1.65–1.68 Å; 105–111°).[6,22,23] Additionally, the C_{Ph}–P1–C2–N2 (see Fig. 2 for numbering) torsion angles for **1·PPh** and **2·PPh** were 9.83 and 0.77°, respectively. These values compare well with **II** (4.25°),[16] indicating increased planarity at the phosphorus centre when compared to **I** (torsion angle = 26.5°).[15]

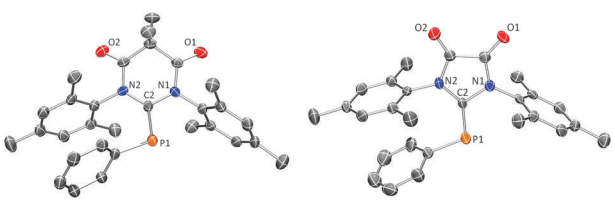


Fig. 2 ORTEP diagrams of **1·PPh** (left) and **2·PPh** (right). Ellipsoids are drawn at 50% probability and H-atoms have been omitted for clarity. Pertinent metrical parameters are provided in the text.

Remarkably, the short P–C distance of 1.691(4) Å observed in **2·PPh** is the shortest P–C bond reported to date for a carbene → PPh adduct, and attests to the high π-acidity of DACs. To further interrogate the nature of the P–C bond, compounds **1·PPh–3·PPh**, **I**, **II**, and a model complex **III** (Me_2C═PPh) were investigated computationally using density functional theory.

Geometry optimizations† of all compounds were performed, and the computed structures compared to the respective X-ray structures (when available, see Table 1). Though there are some slight variations in the overall structure, the geometry about the $C_{carbene}$ and P centres appears to be well modelled in all cases.

Importantly, the computed P–C distances follow the trend observed in the X-ray structures, and decrease on going from **I** (1.768 Å) to **2·PPh** (1.721 Å), with the model phosphaalkene **III** having shortest calculated P═C distance of 1.685 Å. The calculated data echoed the experimental data and revealed that compounds **III**, **1·PPh**, and **2·PPh** lie more toward the phosphaalkene form **B** on the continuum of structures, whereas compounds **II** and **3·PPh** lie in the middle between **A** and **B**, and compound **I** lies at the phosphinidene form **A** as previously described.[15] The nature of the bonding in **1·PPh–3·PPh** was further examined by subjecting the X-ray structures for all compounds to a natural bonding orbital (NBO) analysis.† ‖[24] The NBO analysis showed that for all carbene → PPh adducts, with the exception of **I**, the P–C bond was comprised of both σ and π bonds. The %C and %P localization of the π bond orbital was also determined from the NBO analyses (see Fig. 3 and Table S2).†

The NBO data concluded that model compound **III** has the most developed π bond, with equal localization on the C and P centres (50.19 and 49.81%, respectively), followed by **2·PPh** and **1·PPh** (%C = 47.11% and 46.30%, respectively). Moreover, it was observed that both **3·PPh** and **II** feature π bonds that are more polarized toward the phosphorus centre (%C = 39.95% and 39.71%, respectively). The NBO analyses also showed that the Wiberg bond indices (WBI) for the phosphorus atom in each compound ranged from 2.912–2.822, which indicated that the phosphorus centres form three bonds (two σ and one π) in all of the complexes with the exception of **I** for which no π bond could be located in the output file. Instead, the phosphorus centre in **I** formed one σ bond to the $C_{carbene}$ atom, one σ bond to the

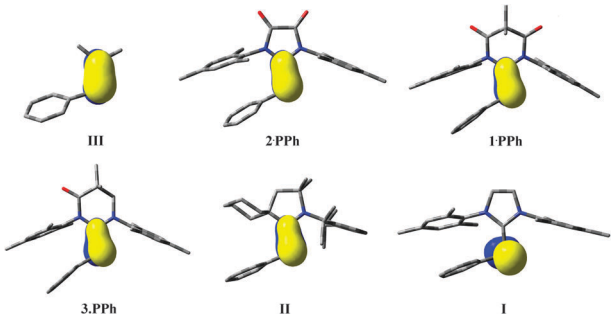


Fig. 3 NBOs of **1·PPh–3·PPh** and **I–III** depicting π bond (P_{LP} for **I**).

C_{Ph} atom and featured two lone-pairs in nonbonding orbitals of primarily s- (67.46% s-, 32.51% p-, and 0.04% d-) and p- (0.67% s-, 99.11% p-, and 0.22% d-) character, which indicated 100% P localization.

The WBI of the phosphorus centre in **I** (2.629) is misleading as the "three bonds" that the phosphorus forms are derived from the $C_{carbene}$–P σ bond, the P–C_{Ph} σ bond and a donor–acceptor interaction involving the p-type lone-pair on the phosphorus atom with a $C_{carbene}$–N π* orbital.

We have shown that CDCs may be used to prepare novel phosphaalkenes in a one-pot redox reaction which affords the desired phosphaalkenes in moderate yields. The nature of the P–C bond was fully interrogated using a combination of ^{31}P NMR, X-ray crystallographic, and DFT methods. These results demonstrated that DAC → PPh adducts lie toward the canonical phosphaalkene end of the continuum between forms **A** and **B**, whereas the monoaminoamido carbene (MAAC) and CAAC-derived adducts, that exhibited weaker π bonds, lie in the middle, and compound **I** lies toward the established phosphinidene structure.[15] Our current efforts are focused on exploring the reactivity of compounds **1·PPh–3·PPh** to compare to other known phosphaalkenes.

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Notes and references

‡ Treatment with $(PhP)_5$ according to ref. 15 was also unsuccessful.
§ During the course of our work, Bertrand and co-workers independently prepared **3·PPh** using a different methodology (ref. 16). In our report, **3·PPh** was prepared in higher yield using our TMSOTf one-pot redox route.
¶ All triflate salts were characterized by ^{1}H and ^{19}F NMR, and the trilfate salt **[1·Cl][OTf]** was further characterized by X-ray diffraction. During the synthesis of **2·PPh**, approximately 29% of the crude product mixture was the dimer of carbene **2**, resulting in a lower yield of the desired phosphaalkene.
‖ Due to the lack of crystallographic data for compounds **3·PPh** and **III**, the optimized geometries from the DFT analyses were used as input geometries for NBO analyses.

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