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Singlet (Phosphino)phosphinidenes are Electrophilic

Max M. Hansmann, Rodolphe Jazzar, and Guy Bertrand*

UCSD-CNRS Joint Research Laboratory (UMI 3555), Department of Chemistry and Biochemistry, University of California, San Diego, La Jolla, California 92093-0358, United States

Supporting Information

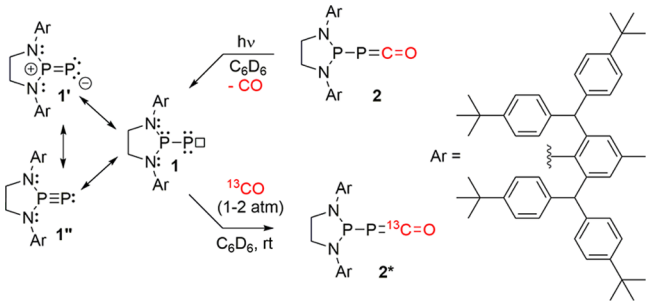
ABSTRACT: A room-temperature stable (phosphino)-phosphinidene reacts with carbon monoxide, stable singlet carbenes, including the poor π-accepting imidazol-2-ylidene, and phosphines giving rise to the corresponding phosphaketene, phosphinidene-carbene and phosphinidene-phosphine adducts, respectively. Whereas the electronic ground-state calculations indicate a PP multiple bond character in which the terminal phosphorus is negatively charged, the observed reactivity clearly indicates that (phosphino)phosphinidenes are electrophilic as expected for an electron-deficient species. This is further demonstrated by competition experiments as well as by the results of Fukui function calculations.

The isolation of singlet carbenes[1] and nitrenes,[2] featuring a formal valence sextet, was a paradigm shift in chemistry. Until recently, the heavier analogues of nitrenes, namely phosphinidenes [R−P], were postulated as short-lived intermediates,[3] only spectroscopically observable in the gas phase[4] and in matrices.[5] The difficulty in designing a stable phosphinidene can be attributed to the fact that most substituents have a triplet ground state, which makes them highly reactive. As is also the case with carbenes and nitrenes, computational studies predict that only strong π-donor substituents such as R_2N- or R_2P- could efficiently stabilize the singlet ground state.[6] Fritz et al.[7] and Frank et al.[8] generated a (phosphino)phosphinidene which was unstable and underwent dimerization and oligomerization. Thanks to the presence of a bulky substituent, however, our group recently succeeded in preparing a room-temperature stable (phosphino)-phosphinidene (**1**) (Scheme 1).[9]

As expected for a singlet phosphinidene, **1** features a high degree of multiple bond character between the two phosphorus centers as shown by resonance forms **1′** and **1″**. This is reflected in the very short P−P bond length (calcd 1.917 Å) and the large phosphorus−phosphorus coupling constant ($^1J_{PP}$ = 884 Hz).[9] Moreover, natural population analysis (NPA) indicates that the terminal P is negatively charged (−0.34 au), while the endocyclic P carries a large positive charge (+1.16 au). Based on these results, it could be expected that, similar to singlet carbenes and nitrenes, singlet phosphinidene **1** should be exclusively nucleophilic. However, herein we demonstrate that compound **1** is a powerful electrophile, as one could expect from a species featuring a valence sextet structure (**1**).

While the photolysis of the phosphaketene **2** in a quartz J-Young tube cleanly generates the phosphinidene **1**, we were curious to know if this species can also activate carbon monoxide

Scheme 1. Generation of the (Phosphino)phosphinidene 1 with Its Resonance Structures 1′ and 1″ and Activation of ^{13}C-Labeled Carbon Monoxide to Form Phosphaketene 2*



to regenerate the phosphaketene **2**. Pressurizing 1−2 atm of ^{13}C-labeled carbon monoxide into a benzene solution of **1** at room temperature led quantitatively after 3 days to the ^{13}C labeled phosphaketene **2*** (see Figures S1−S4). This reaction could be monitored by ^{31}P NMR spectroscopy which showed two doublets of doublet at δ = −241.1 ppm [$^1J_{PP}$ = 262 Hz; $^1J_{PC}$ = 98 Hz] and δ = +172 ppm [$^1J_{PP}$ = 262 Hz; $^2J_{PC}$ = 22 Hz] and by IR spectroscopy [ν(CO) = 1875 cm^{-1} (**2***); 1922 cm^{-1} (**2**)]. Furthermore, the ketene carbon gave a strong ^{13}C NMR signal at δ = 194.3 ppm [J_{PC} = 98 and 22 Hz]. Note that although N-heterocyclic carbenes do not activate CO,[10,11] more electrophilic carbenes such as (cyclic) (alkyl)aminocarbenes (CAACs)[12] or diamidocarbenes (DACs)[13] are able to form the corresponding ketenes.[14]

In order to understand the thermodynamics and kinetics of the CO extrusion/incorporation process, we performed DFT calculations at various level of theory, using **I** and **II** (Dipp instead of Ar) as model compounds (Figure 1; see also SI for the comparison of Ph instead of Dipp). Depending on the functional, basis set, solvent model, etc., the reaction of **I** and carbon monoxide is predicted to be exergonic by 14.5 ± 1.8 kcal mol^{-1}, with an energy barrier of only 16.1 ± 1.9 kcal mol^{-1} (for a detailed theoretical analysis see Tables S18−S21). Therefore, this coupling reaction leading to **II** is thermally feasible, whereas the reverse process leading to the phosphinidene **I** can only easily proceed under irradiation, as observed experimentally.

While carbon monoxide can act either as a nucleophile and/or electrophile, we wondered if more genuine nucleophiles would be able to react with the (phosphino)phosphinidene **1**. We first chose a series of stable singlet carbenes. Upon mixing a toluene solution of phosphinidene **1** and CAAC **3a**,[12] we observed the

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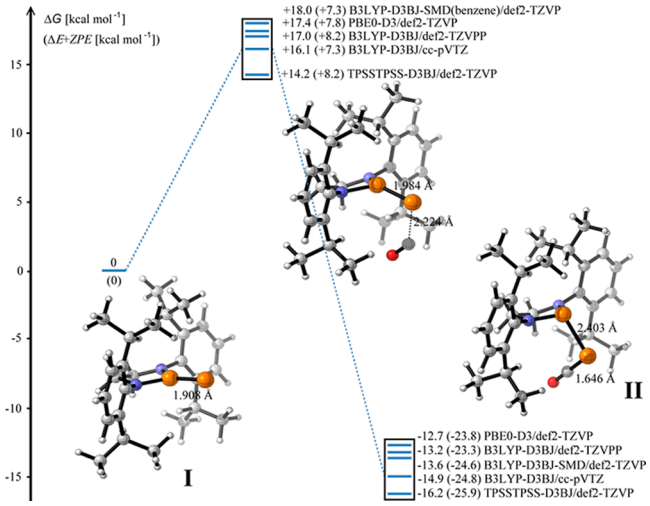
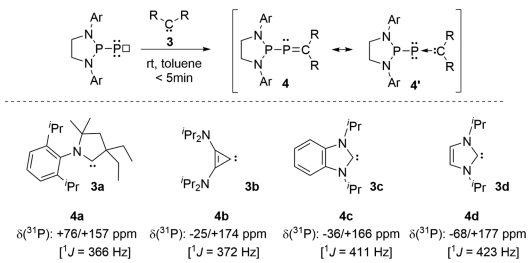


Figure 1. Reaction profile for the CO recombination at various (selected) levels of theory. Bond distances indicated at the B3LYP-D3BJ/TZVPP level of theory.

instantaneous coupling reaction leading to **4a** [^{31}P NMR: AX system at δ = +76 and +157 ppm ($^1J_{PP}$ = 366 Hz); $^{13}C_{carbene}$: 219 ppm ($^1J_{PC}/^2J_{PC}$ = 85/16 Hz)] (Scheme 2). CAAC **3a** is known to

Scheme 2. PC Coupling Reaction between Stable Carbenes and the Stable Phosphinidene 1



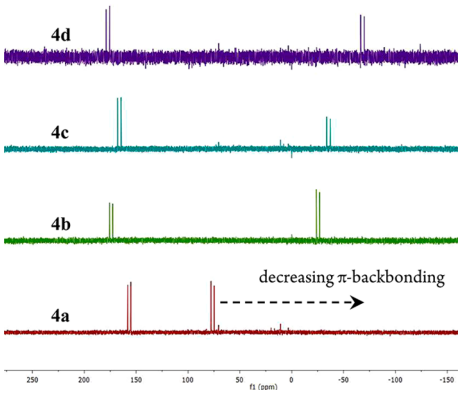


Figure 2. ^{31}P NMR π-accepting scale based on phosphinidene **1**.

possess a small singlet−triplet gap with a low-lying LUMO,[15] but we found that less electrophilic carbenes such as cyclopropenylidene **3b**,[16] benzimidazol-2-ylidene **3c**,[17] and even imidazol-2-ylidene **3d**[18] also reacted instantaneously with phosphinidene **1** (Figure 2). The variation of the ^{31}P NMR shift of the phosphorus bound to carbon is in very good agreement with our recently reported π-accepting scale of carbene-phosphinidene adducts ($R_2C \rightarrow PPh$),[19] with no significant effect of the second phosphorus atom (see Table S1 and Figure S6). The PC bond ranges from a phosphorus−carbon π-bond (**4**) to a phosphinidene−carbene dative bond (**4′**) as reflected in the very low- and high-field ^{31}P chemical shifts, respectively (**4a**: +76 ppm; **4d**: −68 ppm).

In the case of the cyclopropenylidene-phosphinidene adduct **4b**, we were able to obtain single crystals suitable for an X-ray diffraction study (Figure 3). The cyclopropenylidene moiety

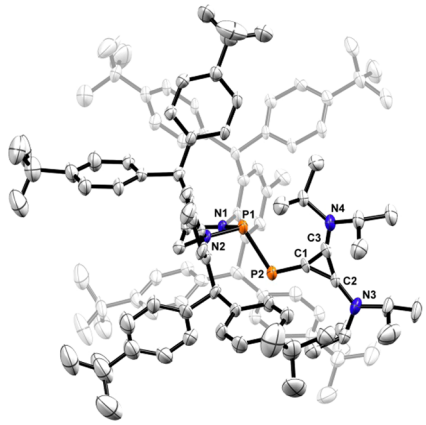


Figure 3. X-ray crystal structure of the phosphinidene-carbene adduct **4b**. Toluene solvent molecules and hydrogen atoms omitted for clarity; 50% probability thermal ellipsoids; selected bond lengths [Å] and angles [°]: P1−P2 2.193(2); P1−N1 1.744(5); P1−N2 1.706(4); P2−C1 1.746(6); C1−C3 1.396(8); C1−C2 1.405(8); C2−C3 1.345(9); C3−N4 1.354(8); C2−N3 1.345(7); N1−P1−N2 89.3(2); P1−P2 C1 101.4(2); C2−C1 C3 57.4(4); P1−P2−C1−C2 178.9(7).

nicely fits into the phosphinidene pocket. The P−C bond length [1.746(6) Å] is clearly longer than in typical phosphaalkenes (1.65 Å), but shorter than a genuine C−P single bond (∼1.80−1.85 Å).[20] This bond length correlates well with previously reported carbene-phosphinidene adducts, which indicate that the $C(p_\pi)-P(p_\pi)$ bond is not well developed and thus **4b** should be seen as a highly polarized phosphaalkene.[21]

Based on the reactions with carbenes exhibiting a low degree of backbonding, we decided to test phosphines as the coupling partner. One equiv of triphenylphosphine reacted instantaneously with phosphinidene **1** to afford the phosphine adduct **5a**, which was identified by its typical ^{31}P NMR AMX system [+164 ($^1J/^2J$ = 390 Hz/93 Hz); +38 ($^1J/^2J$ = 561 Hz/93 Hz); −114 ppm ($^1J/^1J$ = 561 Hz/390 Hz) (Scheme 3). Strikingly, more basic phosphines such as trimethyl-, tri-*n*-butyl-, tricyclohexyl, and even the sterically bulky tri-*t*-butylphosphine also reacted with **1** to give the corresponding adducts **5b−e** (see Table S2). In the case of adduct **5c**, a single crystal X-ray diffraction study was performed (Figure 4). The P1−P2 bond length [2.1967(10) Å] is very similar to that of the carbene adduct **4b** and in the typical range for a P−P single bond. The P2−P3 bond length [2.1064(11) Å] is in the range of those previously observed for structurally related adducts [2.077−2.136].[22]

Phosphine adducts of phosphinidenes ($R_3P \rightarrow PR$) have previously been reported[23] and used as phospha-Wittig reagents.[24] Some of them were generated from $(PhP)_5$ and $(PCF_3)_4$,[23] which are potential triplet-phosphinidene precursors. However, mechanisms not involving a phosphinidene intermediate could also explain the formation of these phospha-Wittig reagents.[25] Our results unambiguously show these adducts can indeed be obtained from free singlet phosphinidenes. Calculations at the B3LYP-D3/def2-TZVP level of theory predict that

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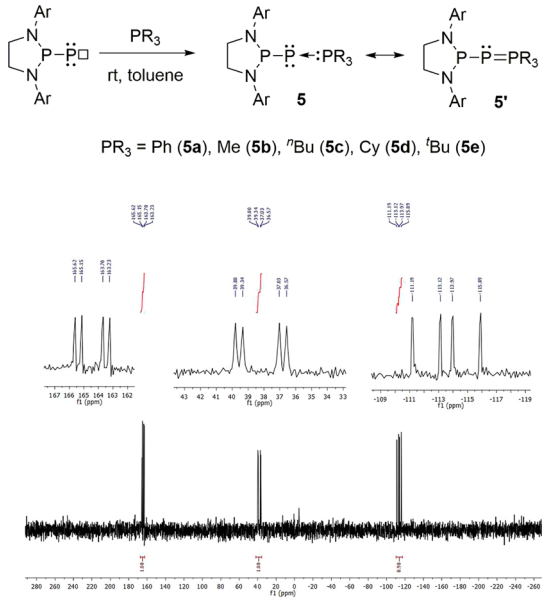
Scheme 3. Phosphinidene-Phosphine Coupling Reactions and ^{31}P NMR of adduct 5a (PPh_3)



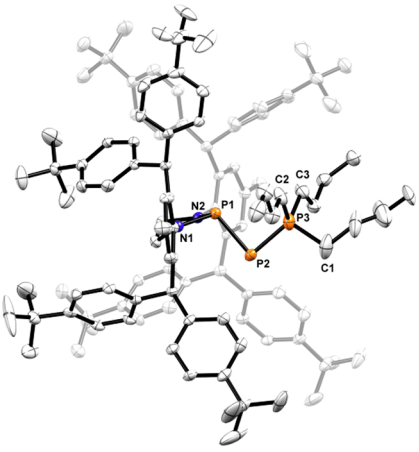


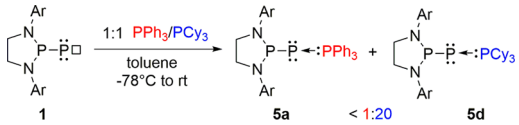
Figure 4. X-ray crystal structure of the phosphinidene-phosphine adduct **5c**. Toluene solvent molecules and hydrogen atoms omitted for clarity; 50% probability thermal ellipsoids; selected bond lengths [Å] and angles [°]: P1−P2 2.1967(10); P1−N1 1.726(2); P1−N2 1.724(2); P2−P3 2.1064(11); P3−C1 1.850(4); P3−C2 1.826(4); P3−C3 1.830(4); P1−P2−P3 91.19(4).

the reaction of **I** with PMe_3 is fairly exergonic ($\Delta G = -25.4$ kcal mol^{-1}) with a low reaction barrier ($\Delta G^{\ddagger} = +7.2$ kcal mol^{-1}) (see Figure S12).

In order to ascertain the electrophilic character of the phosphinidene **1**, we performed a competition experiment (Scheme 4). When treating **1** at −78 °C with a 1:1 mixture of PPh_3/PCy_3 and warming the solution to room temperature, we observed a clear preference for the formation of the tricyclohexylphosphine adduct **5d** over the corresponding triphenylphosphine adduct **5a** (>20:1) (see SI). No thermal equilibration of this mixture was obtained at room temperature. This result strongly suggests that the phosphinidene **1** acts as an electrophile since it binds faster to the more nucleophilic, although bulkier, tricyclohexylphosphine.

The reaction of the singlet phosphinidene **1** with phosphines is surprising since the related singlet carbenes do not usually react

Scheme 4. Competition Experiment with Phosphines



with strong Lewis bases,[26] with the exception of transient electrophilic carbenes, such as dihalogenocarbenes.[27] To understand the counterintuitive electrophilic reactivity of **1**, we first calculated the Mulliken, Hirshfeld, and natural charges of the model compound **I**. In all cases, the phosphinidene phosphorus has a partial negative charge (−0.30, −0.23, −0.33e), while the adjacent inner phosphorus atom has a considerable positive charge (+0.28, +0.21, +1.10e). However, electrophilic reactivity is typically related to the LUMO of a molecule.[28] Therefore, we modeled the electrophilicity of the phosphinidene with the condensed Fukui functions, a classical computational tool to investigate the electron affinity or ionization potential (see SI). These properties are related to the nucleophilic (f_k^-) and electrophilic (f_k^+) properties of molecules/atoms.[29] The terminal phosphorus center has a large positive condensed (Hirshfeld) Fukui index f_k^+ of 0.26, which is in agreement with the electrophilic reactivity of this atom (for the visualization of the $f_k^+(r)/f_k^-(r)$ functions and the calculations of global and local electrophilicity indices, which are also in agreement with an electrophilic center, see SI). Likewise, f_k^- shows a large, positive value (0.35), which, together with the positive f_k^+ index, indicates an amphiphilic species (we have already reported that **1** reacts with electron-poor alkenes).[9] The calculated isosurface of the dual descriptor[30] at the B3LYP-D3BJ/6-31G(d) level nicely supports this amphiphilic description showing areas prone for both nucleophilic and electrophilic attack at the terminal phosphinidene P atom (Figure 5; for a quantitative analysis see SI).

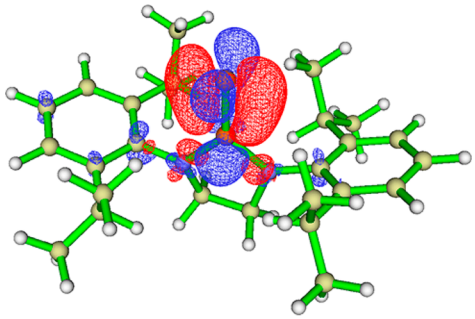


Figure 5. Calculated isosurface of the dual descriptor $\Delta f(r)$ at the B3LYP-D3BJ/6-31G(d) level of theory showing the phosphinidene center prone for both nucleophilic (blue; $\Delta f(r) > 0$) and electrophilic attack (red; $\Delta f(r) < 0$) (at an isovalue of 0.004).

In conclusion we have shown experimental evidence that despite its PP multiple bond character and the presence of a negative charge on the phosphinidene center, **1** acts as an electrophile. This is probably due to the reluctance of the tricoordinated phosphorus to be planar. As can be seen on the transition state of the reaction of **1** with CO (Figure 1), the approach of a nucleophile induces the bending of the internal P and a lengthening of the PP bond, which gives a formal valence sextet structure to the terminal P.

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■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b04232.

Experimental details and data. CCDC 1474876 (**4b**) and CCDC 1474877 (**5c**) contain the crystallographic data (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*guybertrand@ucsd.edu

Notes

The authors declare no competing financial interest.

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