

³¹P NMR Chemical Shifts of Carbene–Phosphinidene Adducts as an Indicator of the π -Accepting Properties of Carbenes**

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Since the discovery of the first stable carbene in 1988^[1] and the seminal report by Arduengo and co-workers in 1991 of the synthesis of a stable imidazol-2-ylidene,^[2] the number of stable carbenes has increased tremendously.^[3] Of particular interest is their use as ligands for transition metals, which has led to numerous breakthroughs in the field of homogenous catalysis.^[4]

It was first postulated that the excellent catalytic activity of transition-metal complexes bearing N-heterocyclic carbene (NHC) ligands was due to their strong σ -donating ability, coupled with almost no π -accepting character.^[5] However, recent computational studies as well as experimental evidence have shown that non-negligible π back donation occurs in the bonding between NHCs and transition metals.^[6] In a noteworthy example, Fürstner et al. showed that the π -acceptor properties of NHC ligands influence the outcome of gold-catalyzed reactions.^[6]

Several techniques have been developed to evaluate the donor properties of NHCs,^[7] such as calorimetric measurements of [Cp*RuCl] complexes,^[8] the ¹³C NMR chemical shifts of palladium(II) complexes,^[9] and the electrochemical E_0 value for various redox couples in a series of Ru^{III}/Ru^{II} complexes containing the NHC of interest.^[10] The most widely used method relies on the measure of the A_1 stretching frequency of CO ligands in nickel complexes [Ni(CO)₃(L)] (Tolman electronic parameter, TEP),^[11] or the average CO stretching frequencies of *cis*-[IrCl(CO)₂(L)] and *cis*-[RhCl(CO)₂(L)] complexes, which are easier to handle.^[12] These methods rely on the fact that the electron density from a ligand cannot only be passed on to the metal, but also onto the π^* orbital of CO ligands. Although all of these techniques provide a convenient way to evaluate the overall donor properties of carbenes, they are limited by the fact that they do not deconvolute the σ donation and the π back donation of carbene ligands.

Herein we report a convenient method that allows the evaluation of the π -acceptor properties of carbenes (and therefore the evaluation of their σ -donating properties). It is

mainly based on the ³¹P NMR chemical shift of the corresponding easily synthesized phenylphosphinidene–carbene adducts. These compounds can be represented by two extreme canonical structures: the resonance form **A** corresponds to a typical phosphalkene featuring a formal P=C double bond, whereas form **B** corresponds to a carbene–phosphinidene adduct featuring a P–C dative bond with two lone pairs of electrons at phosphorus (Figure 1).^[13,14]

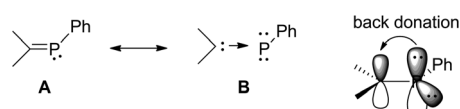
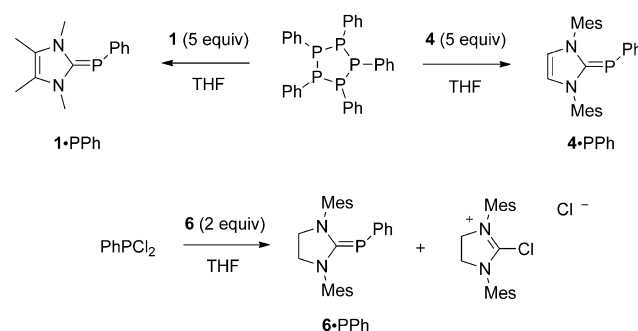


Figure 1. The two extreme canonical structures and bonding description of the carbene–phosphinidene adducts.

Some examples of carbene–phosphinidene adducts have been previously reported (Scheme 1).^[15,16] They were directly prepared in one step by reacting the free carbene with pentaphenylcyclopentaphosphane for **1** and **4** (Table 1) or with dichlorophenylphosphine for **6**.^[15] The main feature of these compounds is the very high-field ³¹P NMR chemical



Scheme 1. Previously reported syntheses of carbene–phosphinidene adducts **1**-PPh, **4**-PPh, and **6**-PPh.

shift of the phosphorus center (**1**-PPh $\delta = -53.5$, **4**-PPh -23.0 , **6**-PPh -10.4 ppm) in comparison with the chemical shift usually displayed by typical, non-polarized phosphalkenes ($\delta = 230$ – 420 ppm).^[16] These high-field chemical shifts indicate that the phosphorus atom in these adducts is electron-rich, in agreement with resonance form **B**. This is confirmed by single-crystal diffraction studies, as these adducts display C_{carb}–P bonds (**1**-PPh 1.794, **4**-PPh 1.763, **6**-PPh 1.746 Å) that are significantly longer than those in nonconjugated phosphalkenes (1.65–1.67 Å).^[16,17] Moreover, the P–C_{Ph} bonds are not coplanar with the imidazole rings, and according to

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Table 1: ^{31}P NMR and ^{13}C NMR chemical shifts ($\text{P}=\text{C}$) for the adducts **1**·PPh–**16**·PPh (recorded in C_6D_6 unless otherwise indicated), Tolman electronic parameter (TEP), and ^{13}C NMR chemical shifts for the corresponding carbenes **1**–**16**.

Carbene	Carbene-PPh adduct $\delta^{31}\text{P}$	$\delta^{13}\text{C}$	Carbene TEP	$\delta^{13}\text{C}$	Carbene	Carbene-PPh adduct $\delta^{31}\text{P}$	$\delta^{13}\text{C}$	Carbene TEP	$\delta^{13}\text{C}$
1 ^[18a] 	−53.5 ^[a]	169.1 ^[a]	2051.7 ^[c]	213.7	9 ^[18f] 	34.9	199.9	2047 ^[e]	282.0
2 ^[18b] 	−61.2	167.8	2051.7 ^[c]	210.5	10 ^[18g] 	39.7	180.3	2050 ^[e]	260.56
3 ^[18c] 	−34.6	177.4	2054.0 ^[c]	221.6	11 ^[18h] 	69.5	199.7	2037 ^[f]	255.5
4 ^[18a] 	−23.0	170.0 ^[a]	2050.7 ^[d]	219.7	12 ^[18i] 	57.0	192.0	2054 ^[e]	254.4
5 ^[18d] 	−18.9	172.9	2051.5 ^[d]	220.6	13 ^[18j] 	56.2	191.3	2042.2 ^[e]	319.0
6 ^[18d] 	−10.4	184.3 ^[a]	2051.5 ^[d]	243.8	14 ^[18j] 	68.9	208.1	2048.5 ^[f]	309.4
7 ^[18d] 	−10.2 ^[b]	186.9 ^[b]	2052.2 ^[d]	244.0	15 ^[18k] 	126.3 ^[b]	217.2 ^[b]	2043.8 ^[f]	330.5
8 ^[18e] 	14.8	186.5	2044	245.1	16 ^[18l] 	−34.9	138.5	2045 ^[f]	185.5

[a] The NMR spectrum was recorded in $[\text{D}_8]\text{thf}$. [b] The NMR spectrum was recorded in CDCl_3 . [c] Computational value.^[23] [d] Determined experimentally from $\text{LNi}(\text{CO})_3$ complex.^[24] [e] Value calculated by linear regression from the experimentally measured $\nu_{\text{CO}}^{\text{av}}$ of the $[\text{IrCl}(\text{CO})_2\text{L}]$ complex.^[12b] [f] Value calculated by linear regression taking the experimentally measured $\nu_{\text{CO}}^{\text{av}}$ of the $[\text{RhCl}(\text{CO})_2\text{L}]$ complex.^[7]

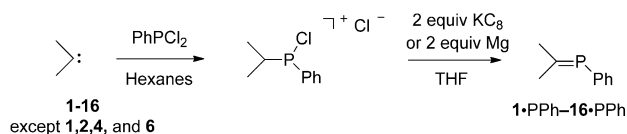
the ^1H and ^{13}C NMR spectra recorded in solution at room temperature, there is free rotation around the $\text{C}_{\text{carb}}-\text{P}$ bonds.

It is obvious that an increase of the π -accepting property of the carbene favors the back donation of the lone pair of the phosphorus atom to the vacant p orbital of the carbene center, therefore increasing the contribution of resonance form **A**. Consequently, the ^{31}P NMR chemical shift of carbene–phosphinidene adducts should provide a straightforward method to evaluate the π -acceptor property of the carbene: the more π -accepting the carbene is, the further downfield the chemical shift of the phosphorus nucleus will be.

The carbenes **1**–**16**^[18] selected for this study are listed in Table 1. All of the corresponding adducts (except **1**·PPh, **2**·PPh, **4**·PPh, and **6**·PPh) have been prepared using a synthetic pathway that can be applied to a wider range of carbenes than the methods described in Scheme 1. In the first step, the carbene is reacted with one equivalent of dichlorophenylphosphine in hexanes or benzene, and the resulting salt is then filtered out from the solution. Then, without further purification, this salt is treated with two equivalents of KC_8 or magnesium in THF, and subsequent workup affords the

corresponding carbene–phenylphosphinidene adduct (Scheme 2).

Table 1 and Figure 2 show that the ^{31}P NMR chemical shifts of the carbene–phosphinidene adducts vary over a wide range (−61.2 to +126.3 ppm). This is already apparent when



Scheme 2. Preparation of carbene–phosphinidene adducts using dichlorophenylphosphine. **2**·PPh has been prepared from the free carbene **2** and pentaphenylcyclopentaphosphane; the preparation of **1**·PPh, **4**·PPh, and **6**·PPh was already reported, as shown in Scheme 1.

considering the diaminocarbene series **1**–**11**. The ^{31}P NMR signal of the unsaturated NHC adducts **4**·PPh and **5**·PPh (−23.0 and −18.9 ppm) are at significantly higher field than those of the saturated NHC adducts **6**·PPh and **7**·PPh (−10.4 and −10.2 ppm), which have the same substituents on the

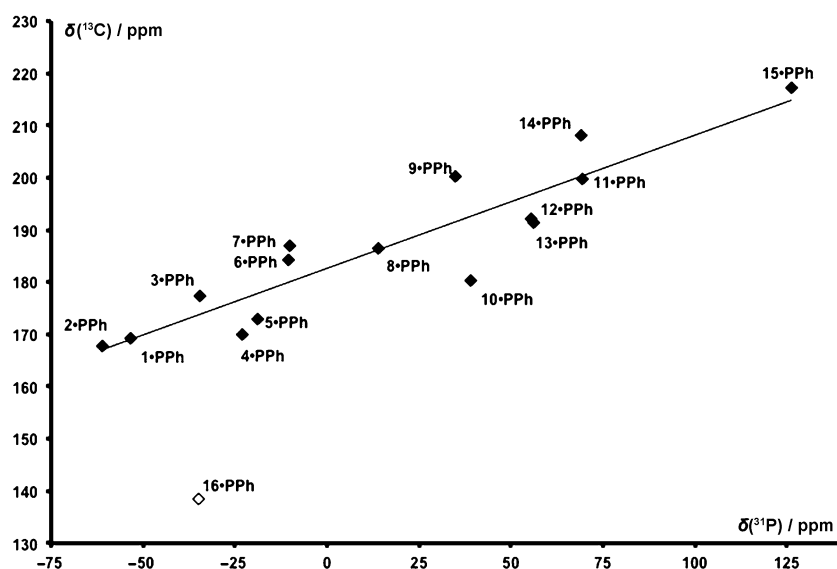


Figure 2. Plots of observed ^{13}C NMR chemical shifts of the adducts **1-PPh**–**16-PPh** against the ^{31}P NMR chemical shift. The plots represented by \blacklozenge have been considered in the straight-line correlation, whereas **16-PPh** (\diamond) has been omitted.

nitrogen atoms. This is consistent with the increased π -accepting properties of the latter, as already observed by Nolan using a series of $[(\text{NHC})\text{Pt}(\text{dmsO})(\text{Cl})_2]$ complexes.^[6b] This was confirmed by variable-temperature NMR experiments performed on **5-PPh** and **7-PPh**. Indeed, compound **7-PPh** displays broad signals in the room temperature ^1H and ^{13}C NMR spectra that are due to slow rotation around the $\text{P}=\text{C}$ bond; in contrast, the room-temperature NMR spectra of **5-PPh** contain only sharp signals. By lowering the temperature, we were able in both cases to observe the splitting of the signals attributed to the *i*Pr groups of the Dipp substituents (the absence of rotation around the $\text{P}=\text{C}$ bond makes the Dipp group unsymmetrical). The coalescence temperatures allowed us to determine the enthalpy of activation for the rotation process, and indeed the value is much higher in the case of **7-PPh** (**5-PPh**, $T_c = 180\text{ K}$, $\Delta G^\ddagger = 34\text{ kJ mol}^{-1}$; **7-PPh**, $T_c = 293\text{ K}$, $\Delta G^\ddagger = 58\text{ kJ mol}^{-1}$). Even subtle changes in the electronic structure of the carbenes give noticeable differences in the ^{31}P NMR chemical shift of the corresponding phenylphosphinidene adducts. This is apparent when **2-PPh** is compared to **3-PPh**. As observed by Heinicke et al. using rhodium complexes,^[6f] extension of the π system of the NHCs by annelation increases the π -accepting property of the carbene, resulting here in a significant downfield shift of the ^{31}P NMR signal ($\Delta\delta(\text{3-PPh}-\text{2-PPh}) = 26.6\text{ ppm}$). N-alkyl-substituted NHCs **1** and **2** give ^{31}P NMR signals at higher field than those of corresponding N-aryl substituted NHCs **4** and **5**, as expected from replacement of inductive donor groups by π -accepting groups.

The trend observed for the ^{31}P NMR chemical shifts of phosphinidene adducts of six-membered ring carbenes **8–10** is in excellent agreement with their expected π -accepting properties. Indeed, the superior electrophilicity of **9** compared to **8** has been demonstrated computationally and experimentally; it is attributed to the pyramidalization of one

of the nitrogen atoms of NHC **9**.^[18f] The carbonyl group of **10** is of course a π -acceptor and withdraws electron density from the carbene p orbital. Because of the difference in ring size, it is risky to draw a firm conclusion when comparing five-membered NHC **7-PPh** and six-membered NHC **8-PPh**. However, the apparent increased electrophilicity of **8**, indicated by the ^{31}P NMR chemical shift, might result from the increased flexibility of the six-membered compared to the five-membered ring skeleton, which allows for the pyramidalization of the nitrogen centers. Along this line, the ^{31}P NMR signal of carbene adduct **11-PPh** appears to be the most deshielded of the diaminocarbene series **1–11**, which argues for a substantial electrophilic character of **11**. Indeed, calculations showed that for an acyclic diaminocarbene, one of the nitrogen centers of its adducts is pyramidalized, preventing the lone pair to interact with the carbene vacant orbital.^[19] Based on the different

reactivity of NHC–gold and acyclic diaminocarbene–gold complexes, Hong et al.^[20] drew the same conclusion.

As expected from the presence of only one p donor substituent, and in agreement with previous studies on their reactivity,^[19,21] (alkyl)(amino)carbenes **13–15** are much more π -accepting than diaminocarbenes, and indeed their phenylphosphinidene adducts give ^{31}P NMR signals at much lower fields. Note that there is a noticeable difference between the ^{31}P NMR chemical shifts observed for the adducts **13-PPh** and **14-PPh**, which are obtained from electronically very similar carbenes. This is mainly due to the difference of stereochemistry around the $\text{P}=\text{C}$ double bond. It has been reported that in phosphamidines, *E* isomers give rise to a higher chemical shift in the ^{31}P NMR spectra than *Z* isomers.^[17,22] Owing to the steric hindrance of the menthyl moiety, the phosphalkene **13-PPh** possesses a *Z* configuration, whereas **14-PPh**, prepared from the less sterically demanding carbene **14** possesses an *E* configuration, as confirmed by x-ray diffraction studies.^[25] Note also that the adduct of the acyclic (alkyl)(amino)carbene **15** appears at even lower field (+126.3 ppm), as observed in the diaminocarbene series, and for the same reasons.

Finally, **16-PPh** gives a ^{31}P NMR signal at high field (−34.9 ppm), which might indicate that cyclopropenylidene **16** has π -acceptor properties similar to unsaturated NHCs **1–5**. Although this assumption is reasonable owing to the aromaticity of this carbene, the ring strain could have a tremendous influence on the observed chemical shift.

Table 1 and more clearly Figure 2 show that in the carbene-PPh adducts, the variation of the ^{13}C NMR chemical shift of the former carbene carbon follows the same trend as the ^{31}P NMR chemical shift. Indeed, when the point corresponding to **16-PPh** is omitted, a linear correlation can be obtained with a fair correlation coefficient R^2 of 0.91. However, the range of the ^{13}C NMR chemical shifts is of

course narrower than the ^{31}P NMR chemical shifts, and the time of acquisition on the spectrometer is much longer.

Table 1 shows that the ^{31}P NMR chemical shift of the carbene–phenylphosphinidene adducts does not correlate with the TEP of the corresponding carbenes. This confirms that these two parameters are representative of two different properties, and an examination of the data strongly suggests that indeed the TEP and the ^{31}P NMR chemical shift gives a good indication of the overall donating and π -accepting properties, respectively. Importantly, a comparison of the two scales allows for an evaluation of the relative pure σ -donor abilities of carbenes. As a first illustration, the ^{31}P NMR signal of the benzoimidazol-2-ylidene adduct **3**-PPh (-34.6 ppm) is at higher field than that of the thiazol-2-ylidene adduct **12**-PPh ($+57.0$ ppm), in line with the expected poorer π -accepting properties of **3** (which is due to the better p donation of nitrogen compared to sulfur). Concomitantly, benzoimidazol-2-ylidene **3** and thiazol-2-ylidene **12** have the same TEP value (2054 cm^{-1}), arguing that they have similar overall donating properties. As a consequence, it can be concluded that **12** is significantly more σ -donating than **3** as expected, because sulfur is more electropositive than nitrogen. In another good example, according to the TEP values, the acyclic diaminocarbene **11** (2037 cm^{-1}) is a better overall donor than the acyclic (alkyl)(amino)carbene **15** (2043.8 cm^{-1}). However, because **11** is a much weaker π acceptor than **15**, it is quite reasonable to believe that **11** is a weaker σ donor than **15**, in line with the relative electronegativity of nitrogen and carbon. This is confirmed when comparing the data for classical NHCs **1–7** and cyclic (alkyl)(amino)carbenes **13** and **14**. From the TEP values of NHCs **1–7** and CAACs **13** and **14** (2050.7 – 2054.0 versus 2042.2 – 2048.5 cm^{-1}), it is clear that **13** and **14** are stronger overall donors; however, ^{31}P NMR chemical shifts indicate that **13** and **14** ($+56.2$ and $+68.9$ ppm) are also stronger π acceptors than **1–7** (-61.2 to -10.2 ppm). Therefore these data allow concluding that CAACs **13** and **14** are much stronger σ donors than classical NHCs **1–7**, in perfect agreement with calculations.^[19]

In summary, this work demonstrates that the ^{31}P NMR chemical shift of carbene–phenylphosphinidene adducts gives a good indication of the relative π -accepting properties of carbenes. These adducts can be easily prepared in two steps, by reaction of the carbene with dichlorophenylphosphine followed by reduction with Mg or KC_8 , and they do not have to be purified. In marked contrast with the narrow range of TEP values, the ^{31}P NMR chemical shifts of these main-group-element adducts are considerably spread out, and are very sensitive to subtle changes in the electronic structures of carbenes. For example, noticeable differences are observed when imidazol-2-ylidenes are compared with their saturated homologues, but also with the corresponding annulated version. Knowing both the TEP value and the ^{31}P NMR chemical shift of the corresponding carbene–phosphinidene adduct allows for an evaluation of the relative pure σ -donating properties of carbenes.

Experimental Section

Representative synthesis of **11**-PPh: Dichlorophenylphosphine (0.186 g, 1.04 mmol) was added at room temperature to a solution of carbene **11** (0.220 g, 1.04 mmol) in hexane (10 mL). Immediately, a bright yellow precipitate was generated. The mixture was then stirred overnight and the mixture filtered using a cannula. The solids were washed with diethyl ether ($2 \times 10\text{ mL}$) and dried under reduced pressure. Magnesium (0.050 g, 2.08 mmol) was added, followed by the addition of THF (8 mL). The mixture was then stirred at room temperature overnight and the volatiles removed under reduced pressure. The product was extracted with benzene (15 mL). After removing the volatiles under reduced pressure, compound **11**-PPh was obtained as a bright yellow oil; yield 74% (0.246 g, 0.77 mmol). Further experimental details are available in the Supporting Information.

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