doi:10.2533/chimia.2016.279 Chimia 70 (2016) 279–283 © Swiss Chemical Society

PH_3 as a Phosphorus Source for Phosphinidene–Carbene Adducts and Phosphinidene–Transition Metal Complexes.

Mark Bispinghoff[§]* and Hansjörg Grützmacher

[§]SCS-Metrohm Award for best oral presentation in Inorganic and Coordination Chemistry

Abstract: The parent phosphinidene–carbene adduct NHC=PH is a versatile synthon in main group chemistry and can act as an electronically flexible ligand for transition metals. Previously, it could only be synthesized with sterically demanding *N*-aryl substituents. This paper describes simple methods for the synthesis of NHC=PH adducts with varying steric demand from elemental phosphorus or easily accessible phosphorus sources. Furthermore, the reactivity of NHCs towards PH_3 was investigated. It was shown how a NHC inserts into the P–H bond of PH_3, which opens up a route to NHC=PH adducts from an imidazolium salt and PH_3. The adducts were used in the simple syntheses of bis(phosphinidene) mercury(II) and group 6 pentacarbonyl parent phosphinidene complexes. Their electronic and structural properties were investigated to elucidate the influence of the NHC on the phosphinidene and identify possible applications.

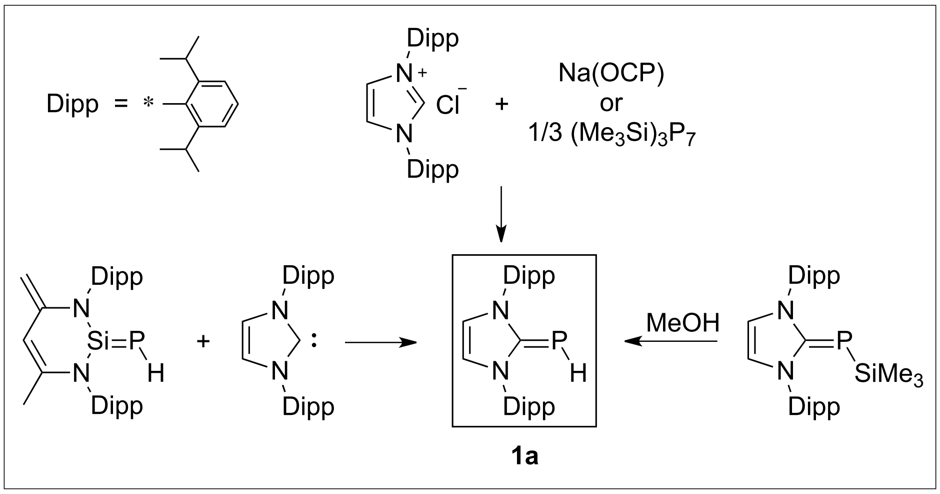
Keywords: Carbene insertion · N-Heterocyclic carbenes · Phosphine gas PH_3 · Phosphinidene complexes · Transition metal complexes

1. Introduction

Phosphinidenes are a highly reactive class of low-coordinate main group compounds, which easily oligomerize to cyclophosphanes.[1] Free phosphinidenes have eluded isolation so far. However, they can be stabilized in the presence of Lewis bases or in the coordination sphere of a metal.[2] Since their first preparation, *N*-heterocyclic carbenes (NHC) have been used for the stabilization of numerous main group species,[3] including substituted phosphinidenes PR.[4] Recently, the NHC-stabilized parent phosphinidene NHC=PH has been isolated using three different synthetic protocols (Scheme 1).[5–7]

The parent phosphinidene–carbene adduct ^{Dipp}NHC=PH **1a** (^{Dipp}NHC = bis(2,6-diisopropylphenyl)imidazol-2-ylidene) can be prepared from a phosphasilene and the corresponding carbene by H–P transfer.[5] It is also accessible from sodium phosphaethynolate, Na(OCP) or the substituted heptaphosphide $(Me_3Si)_3P_7$ and the corresponding imidazolium salt.[6] Furthermore, it can be obtained by methanolysis of ^{Dipp}NHC=$PSiMe_3$.[7]

The adduct **1a** has been used for the synthesis of carbene-supported P_3 and PAsP cations and radicals.[6] The reaction of **1a** with chlorophosphanes in presence of DABCO gives rise to NHC-substituted chlorodiphosphanes ^{Dipp}NHC=P-PClR and their cationic derivatives, [^{Dipp}NHC=P-PR]$^+$, which depending on the steric bulk of their substituents, can be isolated in monomeric or dimeric form.[8] Bertrand and co-workers have isolated the carbene-stabilized parent phosphenium cation [NHC-PH_2]$^+$ by treating a NHC=PH adduct featuring very bulky *N*-substituents with trifluorosulfonic acid.[9] These results indi-



Scheme 1. Several routes to parent phosphinidene-carbene adducts are described in literature.[5–7] However, they are limited to the use of the sterically demanding ^{Dipp}NHC.

---

*Correspondence: M. Bispinghoff
Laboratory of Inorganic Chemistry
ETH Zürich
Vladimir-Prelog-Weg 1
CH-8093 Zürich
E-mail: bispinghoff@inorg.chem.ethz.ch

cate that NHC=PH adducts can be used as versatile synthons for the preparation of a variety of organophosphorus compounds.

Furthermore, NHC=PH adducts can act as versatile one- or two-electron ligands in transition metal complexes. Upon reaction with metal halogenide precursors, the carbene-stabilized phosphinidene unit NHC=P can bind covalently to metal centers and thus act as a one-electron ligand. By this method, the ruthenium and rhodium phosphinidene complexes [($^{\mathrm{Dipp}}$NHC=P)RuClL] (L = η^6-*p*-cymene) and [($^{\mathrm{Dipp}}$NHC=P)RhClL] (L = η^5-C_5Me_5) were prepared from $^{\mathrm{Dipp}}$NHC=PSiMe$_3$ and the corresponding dichloride precursors.[7]

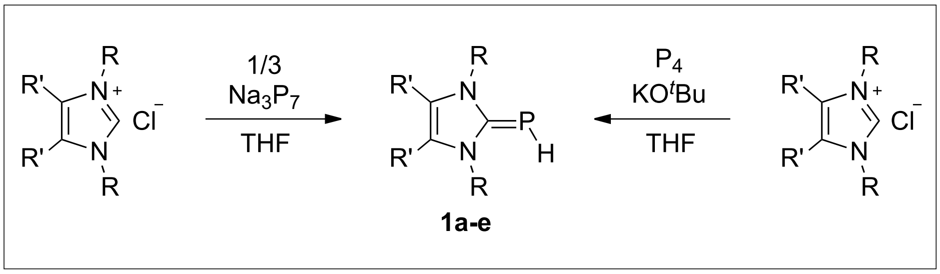
The phosphorus lone pair can also coordinate metal centers in a dative fashion, so that the NHC=PH unit acts as a two-electron ligand. Bertrand and co-workers have reacted a NHC=PH adduct with $Fe_2(CO)_9$, yielding the iron complex [(NHC=PH) Fe(CO)$_4$], in which the geometry around the phosphorus atom is trigonal pyramidal. Even though the natural bond analysis (NBO) analysis of the complex revealed a second lone pair on the P center, addition of excess $Fe_2(CO)_9$ did not lead to further coordination. This was assumed to be due to steric hindrance caused by the bulky Fe complex in conjugation with the very bulky NHC. Indeed, the second lone pair is accessible. If two equivalents of the linear gold complex [AuCl(tht)] (tht = tetrahydrothiophene) are added to the NHC=PH adduct, the bis-metal complex [(NHC=PH)(AuCl)$_2$] is formed.[9]

In this article, we review our work on versatile, direct routes to parent phosphinidene–NHC adducts and their use as transition metal ligands. Furthermore, we report on the synthesis and characterization of NHC=PH group 6 pentacarbonyl complexes.

2. Results and Discussion

The synthetic routes to NHC=PH adducts described above are limited to the use of NHCs with sterically demanding *N*-aryl substituents. Exposure of Na(OCP) or $(Me_3Si)_3P_7$ to *N*-alkylated imidazolium salts (*e.g.* 1,3-dimethylimidazolium chloride or 1,3-diisopropylimidazolium chloride) did not lead to NHC=PH adducts. As the large steric bulk of the *N*-aryl substituents can lead to steric hindrance of some reactions, we were interested in finding a more versatile access to NHC=PH adducts.

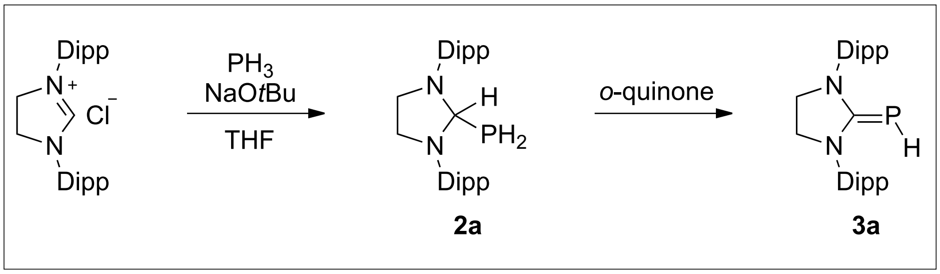
We have thus investigated different phosphorus sources and have shown that the NHC=PH adducts **1a**–**e** with *N*-substituents of varying steric bulk can be prepared from sodium heptaphosphide Na_3P_7 and even from elemental phosphorus, P_4 (Scheme 2).[10] Even though these phosphorus sources are easily accessible, they suffer from rather poor atom efficiency, as only one (in case of P_4) or three (in case of Na_3P_7) phosphorus atoms are incorporated into the NHC=PH adduct, whereas the others form bis(carbene) stabilized P(I) cations or insoluble polyphosphides.



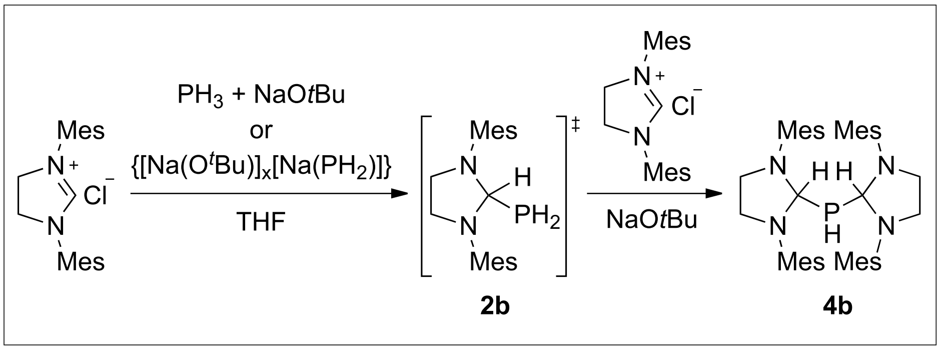
Scheme 2. NHC=PH adducts **1a**–**e** with NHCs of varying steric bulk are easily accessible from Na_3P_7 or P_4 and KO*t*Bu. a: R = Dipp, R' = H, b: R = Mes, R' = H, c: R = *i*Pr, R' = H, d: R = Me, R' = H, e: R = Me, R' = Me.[10]

To find a more atom efficient route, we envisioned the use of a mononuclear phosphorus source. Monophosphine (PH_3) has been employed as a versatile precursor to organophosphorus compounds.[11] Despite its limited usability in laboratories due to its high toxicity, it is considered a cheap and rather easy to handle phosphorus source industrially. Even though the reactivity of NHCs towards main group compounds has been studied extensively, their reactivity towards PH_3 remained unknown. We have shown that the saturated analogue of **1a**, DippNHC*=PH **3a** (DippNHC* = 1,3-bis(2,6- diisopropylphenyl)imidazolin-2-ylidene) can be synthesized from the corresponding imidazolium salt and PH_3 (Scheme 3). The *in situ* generated NHC inserts into the P–H bond of PH_3, giving rise to the phosphanyl-imidazolidine [DippNHC*-H]-[PH$_2$] **2**. This can subsequently be dehydrogenated with an *ortho*-quinone to the phosphinidene **3a**.[12]

This reaction is highly sensitive to the electronic properties of the NHC. Whereas the saturated $^{\mathrm{Dipp}}$NHC* reacts readily with PH_3, the unsaturated analogue $^{\mathrm{Dipp}}$NHC does not show any reaction. Furthermore, it is also sensitive to the steric properties of the NHC. If the related *N*-mesityl substituted $^{\mathrm{Mes}}$NHC* is exposed to PH_3, the bis(imidazolidine) phosphanyl species [$^{\mathrm{Mes}}$NHC*-H]$_2$-[PH] (**4b**) is formed selectively (Scheme 4). The ^{31}P-NMR spectrum exhibits a doublet of triplets at δ =



Scheme 3. The *in situ* generated carbene inserts into the P–H bond of PH_3, giving rise to a phosphanyl-imidazolidine **2a**, which can be subsequently dehydrogenated to the NHC=PH adduct **3a**.[12]



Scheme 4. If the mesityl-substituted imidazolium salt is used instead of the Dipp-substituted, the phosphanyl-imidazolidine **2b** reacts further to the bis(imidazolidine) phosphanyl **4b**, which cannot be dehydrogenated.

–40.9 ppm ($^1J_{PH}$ = 203 Hz, $^3J_{PH}$ = 18 Hz). As opposed to **2a**, which is easily dehydrogenated to **3a**, **4b** is stable against dehydrogenation.

We have shown previously that **2a** can be obtained by either exposing the *in situ* generated ^{Dipp}NHC* to PH_3 or by the reaction between the imidazolium salt [^{Dipp}NHC*-H]-[Cl] and the sodium *tert*-butoxide/sodium dihydrogenphosphide aggregate {[Na(O^{t}Bu)]$_x$[Na(PH_2)]} (x ≈ 2.5).[12] In order to investigate the mechanism of the formation of **4b**, we monitored the reaction of [^{Mes}NHC*-H]-[Cl] with the Na(PH_2) aggregate by ^{31}P-NMR spectroscopy. After 15 min, the spectrum exhibited two sets of signals in an approximately 1:1 intensity ratio. One corresponded to **4b**, the other one, a triplet of doublets at δ = –144.1 ppm ($^3J_{PH}$ = 186 Hz, $^1J_{PH}$ = 18 Hz), can be attributed to the related phosphanyl-imidazolidine [^{Mes}NHC*-H]-[PH_2] **2b**. Over the course of 24 h, the mixture was converted quantitatively to the bis(imidazolidine) phosphanyl species **4b**. This suggests that the formation of **4b** from PH_3 or the Na(PH_2) aggregate proceeds *via* the formation of the phosphanyl-imidazolidine **2b**, which then reacts further with a second equivalent of [^{Mes}NHC*-H]-[Cl] under deprotonation with excess Na(O*t*Bu) to **4b** (Scheme 4). It is noted that the exposure of **2a** to Na(O*t*Bu) does not result in any reaction, which can be accounted for by the larger steric bulk of the *N*-substituents.

Single crystal X-ray diffraction was used to unambiguously identify the bis(imidazolidine) **4b** (Fig. 1). Its bond distances and angles are similar to those of the imidazolidine **2a** (Table 1). The C1–P1 as well as the N1–C1 and N2–C1 bond distances of **4b** do not differ significantly from those of **2a**. The C2–C3 distance in **4b** (1.487(5) Å) is shorter than in **2a** (1.526(2) Å) and the N1-C1-N2 bond angle (102.2(2) °) larger than in **2a** (101.5(1) °)

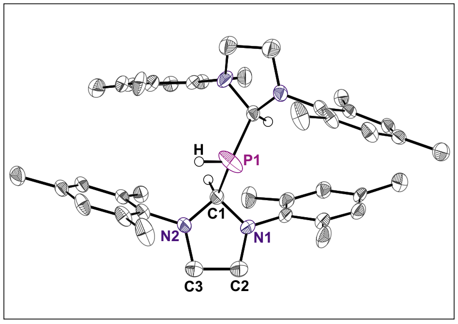
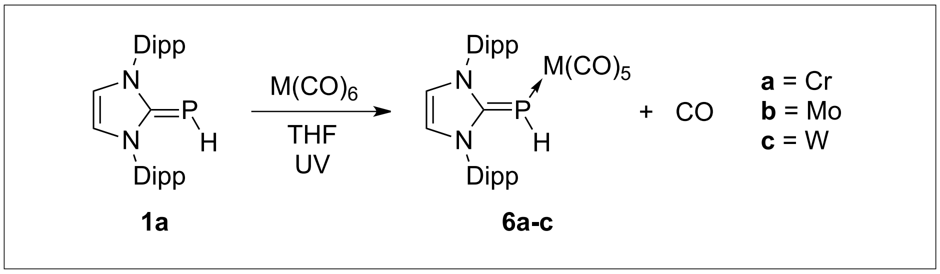


Fig. 1. ORTEP plot of the bis(imidazolidine) phosphanyl **4b**. Hydrogen atoms apart from the phosphorus and the carbene-C bound hydrogen atoms have been omitted for clarity. Thermal ellipsoids are shown at 50% probability.



Scheme 5. Group 6 pentacarbonyl complexes of the NHC=PH unit are easily accessible through CO replacement. Upon exposure of mixtures of **1a** and metal hexacarbonyls to UV radiation, the complexes **6a–c** are formed.

We have recently reported the reaction between the adducts ^{Dipp}NHC=PH and ^{Dipp}NHC*=PH and mercury dichloride in presence of a strong base to obtain the bis(carbene-phosphinidenyl)mercury(II) complexes [(^{Dipp}NHC=P)$_2$Hg] (**5a**) and [(^{Dipp}NHC*=P)$_2$Hg] (**5b**), in which the mercury centers are coordinated linearly by two phosphinidene–carbene units. A comparison of the structural properties of the adducts **1a** and **3a** and the mercury complexes **5a** and **5b** revealed that the different electronic properties of the unsaturated versus saturated NHCs are not reflected in the structures.[12]

In addition to these findings, here we describe group 6 pentacarbonyl parent phosphinidene complexes of the structure [(^{Dipp}NHC=PH)M(CO)$_5$] (**6a–c**, M = Cr, Mo, W), in which the NHC=PH unit acts as a two-electron ligand. These complexes are easily accessible from the metal hexacarbonyls and the adduct **1a** (Scheme 5). Upon exposure of a THF solution of **1a** and the metal hexacarbonyl M(CO)$_6$ (M = Cr, Mo, W) to UV light at room temperature, one CO molecule is replaced by the ^{Dipp}NHC=PH unit. The conversion strongly depends on the CO-pressure in the reaction vessel. If the reaction is carried out in closed flask, the conversion of **1a** does not exceed 20%, whereas if it is connected to an argon Schlenk line with an overpressure valve, nearly-quantitative conversion is observed. Excess NHC=PH and M(CO)$_6$ were removed by washing with *n*-hexane, yielding the pentacarbonyl complexes as pale yellow powders in 65 to 82% yield.

The complexes exhibit doublets between –120.6 and –161.9 ppm ($^1J_{PH}$ = 214 to 217 Hz) in the ^{31}P-NMR spectra. Comparing the ^{31}P-NMR resonances of the free NHC=PH (δ = –136.7 ppm) to the resonances of the group 6 complexes, the coordination to chromium has a deshielding effect (δ = –120.6 ppm, Δδ = –16.1 ppm), whereas the coordination to molybdenum (δ = –147.3 ppm, Δδ = –10.6 ppm) and tungsten (δ = –161.9 ppm, Δδ = –25.2 ppm) has a shielding effect. The ^{31}P-NMR chemical shift is influenced by a local diamagnetic term, a paramagnetic term, the neighbor anisotropy effect and interatomic currents. The local diamagnetic term depends on the electron density around the phosphorus atom.[13] Coordination to a metal center leads to a lower electron density at the phosphorus atom and thus, a deshielded resonance is expected, as observed for chromium. However, heavy atoms can exhibit a strong neighbor anisotropy effect and thus a shielding influence on the ^{31}P-NMR resonance.[14,15] In case of molybdenum and tungsten, this effect appears to be stronger than the deshielding influence of the coordination of the lone pair. The same trend was observed in group 6 pentacarbonyl phosphine complexes, in which the

Table 1. Comparison of selected bond lengths and angles of [^{Dipp}NHCH][PH_2] (**2a**),[12] [^{Mes}NHC*-H]$_2$-[PH] (**4b**), ^{Dipp}NHC=PH (**1a**),[6] and the metal complexes [(DippNHC=PH)M(CO)$_5$] (**6a** = Cr, **6b** = Mo, **6c** = W) determined by single crystal X-ray difraction.

	2a	**4b**	**1a**	**6a**	**6b**	**6c**
C1–P1^a	1.885(2)	1.896(3)	1.752(1)	1.821(3)	1.804(3)	1.807(3)
P1–M^a	---	---	---	2.470(1)	2.619(1)	2.608(1)
N1–C1^a	1.454(2)	1.466(3)	1.373(1)	1.357(3)	1.360(3)	1.360(4)
N2–C1^a	1.456(2)	1.454(3)	1.373 (1)	1.357(3)	1.357(3)	1.359(4)
C2–C3^a	1.526(2)	1.486(4)	1.341 (2)	1.337(5)	1.337(4)	1.339(4)
N1–C1–N2^b	101.5(1)	102.1(2)	104.3(1)	105.7(3)	105.6(2)	105.5(2)
C1–P1–M^b	---	---	---	110.6(1)	114.5(1)	114.0(1)

^{a}Bond length given in Å. ^{b}Bond angle given in °.

^{31}P-NMR resonances become more shielded from chromium to tungsten.[14,15]

The ^{31}P-NMR spectrum of the tungsten complex **6c** exhibits ^{183}W-satellites (^{183}W: 14.3% abundant, I = ½) with a coupling constant of $^{1}J_{PW}$ = 48 Hz. The ^{183}W^{31}P coupling constant was shown to be a sensitive measure for the electronic properties of phosphine ligands and increases with the electronegativity of the phosphorus substituents.[16] For tungsten pentacarbonyl phosphine complexes [W(CO)$_5$PR$_3$] coupling constants between 142 Hz (R = Me$_3$Sn) and 485 Hz (R = F) have been reported.[16,17] The exceptionally small coupling constant observed here suggests that the NHC unit in **1a** serves as a strong electron donor. That is, the dipolar resonance structure NHC$^+$-P$^-$H strongly contributes to the electronic ground state.

The solid-state structures of the complexes **6a–c** were determined by single crystal X-ray diffraction. Fig. 2 depicts the structure of the tungsten complex **6c** as an example. Selected bond lengths and angles are listed in comparison to those of **1a** in Table 1. The significant contraction of the C1–P1 bond and the widening of the N1-C1-N2 bond angle upon coordination of **1a** to the metal pentacarbonyls can be attributed to the large steric demand of the pentacarbonyls. The P1–M distances of the molybdenum and tungsten complexes **6b** (2.619 Å) and **6c** (2.608 Å) are about 0.15 Å longer than the distance of the chromium complex **6a** (2.470 Å). Furthermore, the C1-P1–M bond angles of **6b** and **6c** are about 4° wider than the angle of **6a**. Both effects can be attributed to the larger atomic radii and larger steric demand of molybdenum and tungsten versus chromium. The P–M distances observed here are longer than typical distances of group 6 metal phosphines M-PR$_3$ (Cr: 2.31–2.33 Å, Mo: 2.52 Å, W: 2.54 Å for M-PPh$_3$) and phosphides M-PR$_2$ (Cr: 2.32 Å, Mo: 2.39 Å).[18]

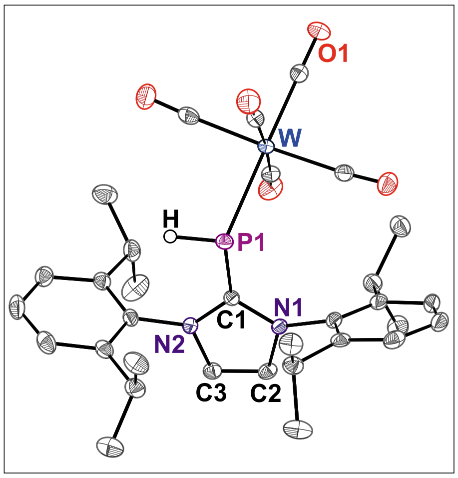


Fig. 2. ORTEP plot of the ^{Dipp}NHC=PH tungsten pentacarbonyl complex **6c**. Hydrogen atoms apart from the phosphorus bound hydrogen atoms have been omitted for clarity. Thermal ellipsoids are shown at 50% probability.

In order to quantify the steric demand of NHC ligands, Cavallo and Nolan proposed the use of the 'percent buried volume' %V_{Bur}, which is defined as the percent of potential coordination sphere around a metal occupied by the ligand and calculated from crystallographic data.[19] For the ^{Dipp}NHC=PH ligand **1a** a percent buried volume of %V_{Bur} = 30.4% was obtained. This value is smaller than that of PPh$_3$ (%V_{Bur} = 34.5%) and corresponds to the value of P*n*Bu$_3$ (%V_{Bur} = 30.4%). It is considerably smaller than that of the corresponding ^{Dipp}NHC in the complex [^{Dipp}NHCAuCl] (%V_{Bur} = 39.0%).[20] This lower steric hindrance of the metal center despite the bulky substituents on the NHC can be attributed to the larger distance between the metal and the NHC. Correspondingly, metal complexes with NHC=PH ligands could be interesting candidates for homogenous catalysis as their metal centers suffer from less steric hindrance than their NHC counterparts.

3. Conclusion

Parent phosphinidene–carbene adducts NHC=PH with varying steric bulk have been synthesized from elemental phosphorus P$_4$ or the easily accessible phosphorus sources Na$_3$P$_7$, (Me$_3$Si)$_3$P$_7$ and Na(OCP). Furthermore, *N*-heterocyclic carbenes were shown to insert into a P–H bond of PH$_3$, giving rise to a phosphanyl–imidazolidine, which can be dehydrogenated to the NHC=PH adduct. The interaction between PH$_3$ and N-heterocyclic carbenes strongly depends on the steric and electronic properties of the NHC. The NHC=PH adducts can act as electronically flexible ligands and can be used to generate bis(phosphinidene) mercury(II) complexes of the structure [(NHC=P)$_2$Hg]. Moreover, group 6 pentacarbonyl complexes of the structure [(^{Dipp}NHC=PH)M(CO)$_5$] are easily obtained by photolysis of solutions containing NHC=PH and metal hexacarbonyls. Calculations of the percent buried volume revealed only low coverage of the metal center by the NHC=PH ligand despite its sterically demanding substituents. This might prove useful for the application in homogenous catalysis, as the ligand keeps the metal sufficiently free for catalytic interaction and still provides kinetic stabilization to the complexes. Accordingly, further investigations of metal complexes with NHC=PH ligands, which can be used in homogeneously catalyzed reactions, are planned.

4. Experimental

4.1 *Materials and Methods*

All reactions were carried out under argon using either standard Schlenk techniques or an argon-filled glove box. Solvents were purified using an Innovative Technology PureSolv MD 7 solvent purification system. All reagents were used as received from commercial suppliers unless otherwise stated. The compounds ^{Dipp}NHC=PH (**1a**),[10] [^{Mes}NHC*-H]-[Cl][21] and{[Na(O*t*Bu)]$_x$[Na(PH$_2$)]} (x ≈ 2.5)[22] were synthesized following literature procedures. Reactions involving PH$_3$ gas were carried out in a setup and following a procedure described by Pringle and co-workers[23] and PH$_3$ electronic grade, > 99.9995% was used.

UV irradiation was carried out with a mercury vapor pressure lamp (Heraeus TQ 150, 150 W) inside a quartz dip tube in a temperature-controlled water bath. X-ray single crystal diffraction studies were performed on a Bruker Smart APEX or an Oxford XCalibur S diffractometer, both equipped with a molybdenum X-ray tube (λ = 0.7107 Å).

Percent buried volume %V_{Bur} was calculated using the user friendly online tool Samb*V*ca available at *www.molnac.unisa.it/OMtools/sambvca.php* with the default parameters as suggested by Cavallo and co-workers (sphere radius R = 3.5 Å, M–P distance d = 2.10 Å, Bondi radii[24] scaled by 1.17, mesh spacing s = 0.05 Å, including H-atoms).[25]

4.2 Synthetic Procedures

4.2.1 *Synthesis of [MesNHC*-H]$_2$-[PH] (4b)*

A suspension of the imidazolium salt [^{Mes}NHC*-H]-[Cl] (257 mg, 0.75 mmol) and sodium *tert*-butoxide (96 mg, 1.0 mmol) in THF (15 mL) was treated with PH$_3$ as described previously for the synthesis of [^{Dipp}NHC*-H]-[PH$_2$].[12] Volatiles were removed under reduced pressure from the yellow suspension and the product extracted with *n*-hexane (3x 3 mL). Removal of the solvent under reduced pressure and recrystallization from *n*-hexane yielded **4b** as a pale yellow, crystalline solid (280 mg, 0.433 mmol, 57%). Single crystals suitable for X-ray diffraction were obtained from a saturated *n*-hexane solution at –30 °C.

4.2.2 *Synthesis of the Complexes [(DippNHC=PH)M(CO)$_5$] (**6a-c**, M = Cr, Mo, W)*

In a 200 mL Schlenk tube, **1a** (210 mg, 0.500 mmol) and the equimolar amount of the corresponding metal hexacarbonyl were dissolved in THF (20 mL). The flask was connected to an argon Schlenk line fitted with an overpressure valve set to 0.1 bar overpressure and exposed to UV radiation.

The reaction was monitored by ^{31}P-NMR spectroscopy. After radiation times of 5 to 10 h, maximum conversions of 90–95% were observed. The solvent was removed under reduced pressure and the residue washed with *n*-hexane (5x 5 mL) to remove excess starting materials. Recrystallization from boiling toluene gave the complexes as yellow crystalline solids in 65–82 % yield. Single crystals suitable for X-ray diffraction were obtained from saturated toluene solutions at –30 °C (M = Cr) or from saturated toluene solutions layered with *n*-hexane (M = Mo, W).

Supplementary Information

The structures discussed here have been deposited with the Cambridge Structural Database under the numbers CCDC 1446562, 1446676, 1446858, 1446859.

Acknowledgements

We thank the European Union (Marie Curie ITN SusPhos, Grant Agreement No. 317404) for financial support. Furthermore, M.B. thanks the Swiss Chemical Society and Metrohm for the SCS-Metrohm Award for the best oral presentation in Inorganic and Coordination Chemistry.

Received: January 18, 2016

[1] a) K. Lammertsma in 'New Aspects in Phosphorus Chemistry III', Ed.: J.-P. Majoral, Springer, Berlin Heidelberg, **2003**; b) Z. Benko, R. Streubel, L. Nyulaszi, *Dalton Trans.* **2006**, 4321.

[2] H. Aktaş, J. C. Slootweg, K. Lammertsma, *Angew. Chem. Int. Ed.* **2010**, *49*, 2102.

[3] a) L. J. Murphy, K. N. Robertson, J. D. Masuda, J. A. Clyburne in 'N-Heterocyclic Carbenes', Ed.: S. P. Nolan, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, **2014**; b) C. D. Martin, M. Soleilhavoup, G. Bertrand, *Chem. Sci.* **2013**, *4*, 3020; c) D. J. D. Wilson, S. A. Couchman, J. L. Dutton, *Inorg. Chem.* **2012**, *51*, 7657; d) Y. Wang, G. H. Robinson, *Inorg. Chem.* **2011**, *50*, 12326; e) O. Back, B. Donnadieu, P. Parameswaran, G. Frenking, G. Bertrand, *Nat. Chem.* **2010**, *2*, 369.

[4] a) A. J. Arduengo, J. C. Calabrese, A. H. Cowley, H. V. R. Dias, J. R. Goerlich, W. J. Marshall, B. Riegel, *Inorg. Chem.* **1997**, *36*, 2151; b) A. J. Arduengo, Dias,H. V. Rasika, J. C. Calabrese, *Chem. Lett.* **1997**, *26*, 143; c) A. J. Arduengo III, J. Carmalt, Claire, A. C. Clyburne, Jason, H. Cowley, Alan, R. Pyati, *Chem. Commun.* **1997**, 981.

[5] K. Hansen, T. Szilvási, B. Blom, E. Irran, M. Driess, *Chem. Eur. J.* **2014**, *20*, 1947.

[6] A. M. Tondreau, Z. Benkő, J. R. Harmer, H. Grützmacher, *Chem. Sci.* **2014**, *5*, 1545.

[7] A. Doddi, D. Bockfeld, T. Bannenberg, P. G. Jones, M. Tamm, *Angew. Chem. Int. Ed.* **2014**, *53*, 13568.

[8] A. Beil, R. J. Gilliard, H. Grützmacher, *Dalton Trans.* **2016**, DOI: 10.1039/C5DT03014E.

[9] L. Liu, D. A. Ruiz, F. Dahcheh, G. Bertrand, *Chem. Commun.* **2015**, *51*, 12732.

[10] M. Cicač-Hudi, J. Bender, S. H. Schlindwein, M. Bispinghoff, M. Nieger, H. Grützmacher, D. Gudat, *Eur. J. Inorg. Chem.* **2015**, DOI: 10.1002/ejic.201501017.

[11] B. A. Trofimov, S. N. Arbuzova, N. K. Gusarova, *Russ. Chem. Rev.* **1999**, *68*, 215.

[12] M. Bispinghoff, A. M. Tondreau, H. Grützmacher, C. A. Faradji, P. G. Pringle, *Dalton Trans.* **2015**, DOI: 10.1039/C5DT01741F.

[13] K. J. Packer, *J. Chem. Soc.* **1963**, 960.

[14] S. O. Grim, D. A. Wheatland, W. McFarlane, *J. Am. Chem. Soc.* **1967**, *89*, 5573.

[15] M. F. Guns, E. G. Claeys, G. P. van der Kelen, *J. Mol. Struct.* **1979**, *54*, 101.

[16] E. O. Fischer, L. Knauss, R. L. Keiter, J. G. Verkade, *J. Organomet. Chem.* **1972**, *37*, C7.

[17] H. Schumann, H.-J. Kroth, *Z. Naturforsch., B: Chem. Sci.* **1977**, *32*, 768.

[18] F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, Orpen, A. Guy, R. Taylor, *J. Chem. Soc., Perkin Trans. 2* **1987**, S1.

[19] A. C. Hillier, W. J. Sommer, B. S. Yong, J. L. Petersen, L. Cavallo, S. P. Nolan, *Organometallics* **2003**, *22*, 4322.

[20] H. Clavier, S. P. Nolan, *Chem. Commun.* **2010**, *46*, 841.

[21] K. M. Kuhn, R. H. Grubbs, *Org. Lett.* **2008**, *10*, 2075.

[22] M. Podewitz, J. D. van Beek, M. Wörle, T. Ott, D. Stein, H. Rüegger, B. H. Meier, M. Reiher, H. Grützmacher, *Angew. Chem. Int. Ed.* **2010**, *49*, 7465.

[23] J. H. Downing, J. Floure, K. Heslop, M. F. Haddow, J. Hopewell, M. Lusi, H. Phetmung, Orpen, A. Guy, P. G. Pringle, R. I. Pugh, D. Zambrano-Williams, *Organometallics* **2008**, *27*, 3216.

[24] A. Bondi, *J. Phys. Chem.* **1964**, *68*, 441.

[25] A. Poater, B. Cosenza, A. Correa, S. Giudice, F. Ragone, V. Scarano, L. Cavallo, *Eur. J. Inorg. Chem.* **2009**, 1759.