Carbene-Dichlorosilylene Stabilized Phosphinidenes Exhibiting Strong Intramolecular Charge Transfer Transition

Sudipta Roy,[†] Peter Stollberg,[†] Regine Herbst-Irmer,[†] Dietmar Stalke,*,[†] Diego M. Andrada,[‡] Gernot Frenking,*,[‡] and Herbert W. Roesky*,[†]

[†]Institut für Anorganische Chemie, Georg-August-Universität, Tammannstraße 4, 37077 Göttingen, Germany
[‡]Fachbereich Chemie, Philipps-Universität Marburg, Hans-Meerwein-Straße 35032 Marburg, Germany

Ⓢ Supporting Information

ABSTRACT: The unstable species dichlorosilylene was previously stabilized by carbene. The lone pair of electrons on the silicon atom of (carbene)$SiCl_2$ can form a coordinate bond with metal−carbonyls. Herein we report that (carbene)$SiCl_2$ can stabilize a phosphinidene (Ar−P, a carbene analogue) with the general formula carbene→$SiCl_2$→P−Ar (carbene = cyclic alkyl(amino) carbene (cAAC; **2**) and N-heterocyclic carbene (NHC; **3**)). Compounds **2** and **3** are stable, isolable, and storable at 0 °C (**2**) to room temperature (**3**) under an inert atmosphere. The crystals of **2** and **3** are dark blue and red, respectively. The intense blue color of **2** arises due to the strong intramolecular charge transfer (ICT) transition from $\pi_{Si=P}\rightarrow\pi^*_{cAAC}$. The electronic structure and bonding of **2**, **3** were studied by theoretical calculations. The HOMO of the molecule is located on the $\pi_{Si=P}$ bond, while the LUMO is located at the carbene moiety (cAAC or NHC). The dramatic change in color of these compounds from red (**3**, NHC) to blue (**2**, cAAC) is ascribed to the difference in energy of the LUMO within the carbenes (cAAC/NHC) due to a lower lying LUMO of cAAC.

Dichlorosilylene ($SiCl_2$) is an important intermediate chemical species[1] that is a heavier analogue of dichlorocarbene (CCl_2). It is well-known that in the presence of a base, $HSiCl_3$ can produce dichlorosilylene, which is stable only at low temperature (below −50 °C) and undergoes polymerization to produce polychlorosilane $(SiCl_2)_n$ when the temperature is raised.[1] Gaseous $SiCl_2$ is known for a long time but it condenses to polymeric $(SiCl_2)_n$ in solution.[1,2] N-Heterocyclic carbene (NHC) can stabilize the intermediate $SiCl_2$ as (NHC)$SiCl_2$ (**A**) via strong σ-donation[3] (Scheme S1). Theoretical calculations showed that NHC forms a strong donor NHC→Si σ-bond and the lone pair of electrons of (NHC)→(Si(:)Cl_2) resides on the silicon atom,[3] which can even be donated to metal carbonyls.[3a] Recently, it was observed that the cAAC (cyclic alkyl(amino) carbene) analogue of **A** has a singlet diradical character and hence the dimeric 1,4-diradical $(cAAC·)_2Si_2Cl_4$ (**B**) was isolated[4] instead of the monomeric (cAAC)Si(:)Cl_2. NHC and cAAC are inherently different from each other, since the HOMO−LUMO energy gap is smaller for the latter one (Figure S1).[5] The cAAC is now well-known as a stronger σ-donor and better π-acceptor when compared with those of NHCs.[5,6] Several radical species of

main group elements have been reported[7] using cAAC as a ligand. Moreover, cAAC induces diradicaloid character in ketene[8] and silylone,[9] since the LUMO of cAAC is lower in energy.

The strong σ-donor NHC is utilized as a ligand for the stabilization of monatomic carbon in the oxidation state zero. Such a class of compounds is coined as carbones (carbodicarbene), $(carbene)_2C$.[10,11] The central carbon atom of carbones L_2C possesses two lone pairs of electrons.[10−12] The heavier homologues, silylones L_2Si[9,13a] and germylones L_2Ge[13b,14] are also known. A related bonding situation is found in carbene stabilized phosphinidene complexes (carbene)PR where the strong π-backdonation of the R-P(:)$_2$ group leads to a substantial C=P double-bond character.[15] The π-backdonation decreases in heavier silicon analogues (silylene)PR.[16]

Over the last three decades several research groups (F. Bickelhaupt,[17] E. Niecke,[18] M. Driess,[16,19] R. Corriu,[20] A. Sekiguchi,[21] A. Baceiredo,[22] C. Cui,[23] D. Scheschkewitz,[24] S. Inoue[25]) developed various synthetic routes for the preparation of phosphasilenes; however, the majority of these reported synthetic methods follow either the hydrogen halide or lithium fluoride elimination route. Meanwhile, a bisphosphasilene was prepared by the activation of P_4 with silylenes.[26] Recently, M. Driess et al. have illustrated the nature of bonding between a cyclic silylene (LSi:) and a P−H group in LSi=PH (L = HC(CMe[2,6-$iPr_2C_6H_3N$])$_2$).[16] However, to the best of our knowledge there are no reports so far on the phosphasilenes with functional chlorides on the silicon atom. In this communication we report first on an easy access to the precursor of composition Ar−P($SiCl_3$)$_2$, and then the novel synthesis, characterization, and theoretical calculations of carbene-dichlorosilylene stabilized phosphinidenes with the general formula carbene→$SiCl_2$→P-Tip (Scheme 1; carbene = cAAC; **2**), NHC; **3** (Scheme S3) and Tip = 2,4,6-triisopropylphenyl). Theoretical calculations showed that there is a strong intramolecular charge transfer transition (ICT) from $\pi_{Si=P}\rightarrow\pi^*_{cAAC}$ that is responsible for the unusual dark blue color of **2**.

The intermediate species $SiCl_2$ is *in situ* generated[1,27] (reacting $HSiCl_3$ with Et_3N in toluene in 1:1 molar ratio) below −80 °C and reacted with Tip-PCl_2 in 2:1 molar ratio (Scheme 1) to obtain Tip-P($SiCl_3$)$_2$ (**1**) as light yellow crystals in 70% yield. Previously, R-P($SiCl_3$)$_2$ compounds (R = Ph, Dip, iPr) were only

Scheme 1. Synthetic Route of cAAC→SiCl$_2$→P-Tip (2a–c)
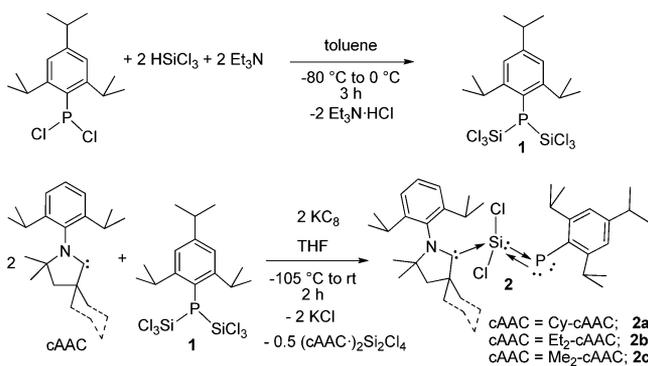
studied by NMR and mass spectrometry and reported to be unstable at room temperature. None of them was characterized by X-ray single crystal diffraction.[27] Previous theoretical studies suggested that a highly substituted aromatic group could increase the stability of R-P(SiCl$_3$)$_2$.[28] **1** is very sensitive to air and moisture. It is stable at room temperature under an inert atmosphere for months and decomposes above 88 °C. After the successful synthesis of **1** in good yield, it was further utilized as a precursor for the preparation of compounds **2-3** (Schemes 1, S3). Treatment of **1** with cAAC in the presence of KC$_8$ in 1:2:2 molar ratio in THF resulted in the formation of a dark blue solution. The dark blue blocks of compounds cAAC→SiCl$_2$→P-Tip (**2**) (cAAC = Cy-cAAC (**2a**), Et$_2$-cAAC (**2b**), and Me$_2$-cAAC (**2c**)) were obtained from *n*-hexane in 45–50% yield. To investigate the generality of this synthetic route, NHC [:C{N(2,6-*i*Pr$_2$C$_6$H$_3$)(CH)}$_2$] was employed instead of cAAC. The analogous compound NHC→SiCl$_2$→P-Tip (**3**) was obtained as bright red crystalline solid (see SI) in 90% yield.

Compounds **2a–c** were synthesized by controlling the reaction temperature and the molar ratio of the precursor and the reducing agent. A 1:2:2 molar ratio of **1**, cAAC, and KC$_8$ was cooled to −105 °C using a frozen THF bath and separately the solvent was cooled to the same temperature. Precooled THF was added via a canula, the resultant solution was stirred for 5 min at this temperature and then at −78 °C for another 30 min. Then the temperature was slowly raised to room temperature over 25 min. The resultant dark blue-purple (for **2a–c**) solution was stirred for 1 h at room temperature and the graphite was separated by filtration. The solvent was removed under vacuum and the product was extracted with *n*-hexane. Dark blue blocks of **2a–c** were formed when concentrated solutions were stored at 0 °C in a refrigerator. The crystals of **2a–c** were separated by filtration. The NHC analogue (**3**) was prepared by the similar synthetic method (see SI). A 2:1 mixture of THF and toluene was utilized for the synthesis of **3** due to the partial solubility of NHC in THF.

The solutions of **2a–c** in *n*-hexane are stable at −32 to 0 °C for months. The crystals of **2a–c** are stable at 0 °C for more than 3 months in an inert atmosphere. **2a–c**, and **3** decompose above 170 (**2a**), 165 (**2b–c**), and 201 °C (**3**), respectively. ^{29}Si NMR spectra of **2a**, **2b**, **2c**, and **3** show doublet at −6.56 ($J_{Si–P}$ = 198.4 Hz), −7.48 ($J_{Si–P}$ = 203.6 Hz), −7.89 ($J_{Si–P}$ = 195.5 Hz), and −19.12 ($J_{Si–P}$ = 197.7 Hz) ppm, respectively, which are upfield shifted when compared with that of (+19.06 ppm) (NHC)SiCl$_2$ (**A**).[3b] The ^{31}P resonances of **2a/2b/2c** and **3** appeared at −123.09/−122.30/−123.27, and −141.24 ppm, respectively which are in line with the expected poorer π-accepting property of NHC.[6] The ^{13}C resonances of **2a–c** (C$_{carbene}$) were observed

in the range of 208.05−211.44 ppm, which are upfield shifted when compared with those of free carbenes (309.4 and 304.2 ppm for Cy-cAAC and Me$_2$-cAAC) but close to those of Cy-cAAC→SiCl$_4$ (207.0 ppm) and Me$_2$-cAAC→SiCl$_4$ (206.1 ppm).[29] The UV–vis spectra of **2a–b** were recorded in THF which show broad (500−900 nm) absorption bands at 665 and 680 nm, respectively, while the corresponding (400−600 nm) value was 475 nm for **3** (see SI for details).

Single crystal X-ray structure determinations of **2a**, **2c**, and **3** revealed that all of them have similar molecular structures and hence the structural aspects of **2a** are only described here (for **2c**, **3** see SI). Compound **2a** crystallizes in space group *Pbca*. The molecular structure of **2a** shows that the central SiCl$_2$ unit is bound to one carbene (Cy-cAAC) and one phosphorus atom of the P-Tip group. The silicon atom adopts a distorted tetrahedral geometry while the phosphorus atom attends a bent geometry. The phosphorus atom is bound to one silicon (Si1−P1 2.1225(9) Å) and one carbon atom (P1−C24 1.874(2) Å) of the Tip group. The Cy-cAAC and Tip-P units of **2a** are oriented in a *trans*-position (*E*) (C1−Si1−P1−C24 torsion angle 169.24°) with respect to the central Si−P bond. The C$_{cAAC}$-Si and C$_{cAAC}$-N bond distances of **2a** are 1.945(2) and 1.308(3) Å, respectively, which are close to those values (1.944(2) and 1.303(2) Å) found in Me$_2$-cAAC→SiCl$_4$.[29] The carbene carbon atom adopts a trigonal planar geometry with a sum of angles of 359.8° which is close to that of Me$_2$-cAAC→SiCl$_4$ (360°).[29] The above-mentioned bond data of **2a** suggest that the bond between the carbene carbon atom and the silicon atom is a coordinate bond (C → Si) rather than an electron sharing single bond (∼1.84 Å).[30]

We carried out DFT calculations on **2a** and **3** in order to elucidate the bonding situation in the molecules. The optimized bond lengths and angles of **2a** are in good agreement with the experimental values (Figure 1). A comparison between the
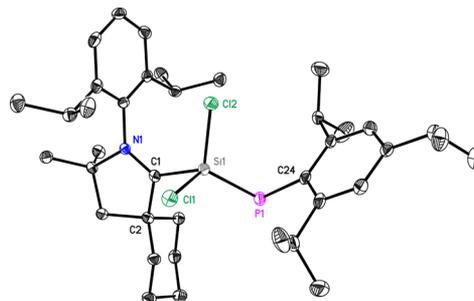

Figure 1. Crystal structure of **2a**. Anisotropic displacement parameters are depicted at the 50% probability level. Hydrogen atoms are omitted for clarity.

calculated structures of **2a** and **3** indicates (Figure S13) very similar geometries where the Si1−C1 and P1−Si1 bonds in the NHC complex **3** are slightly shorter than in **2a**. We then analyzed the bonding situation at the M06-2X/def2-TZVPP level of theory in model compounds **2M** and **3M** where the Dip substituents at the cAAC and NHC donors moieties and the isopropyl substituents at P-Tip are replaced by methyl groups. The optimized geometries of the model compounds are very similar to those of **2a** and **3** (Figure S14).

Natural bond orbital (NBO) calculations of **2M** and **3M** support the bonding picture in the molecules in terms of donor–acceptor interactions D→SiCl$_2$→P-Tip (D = cAAC, NHC). Figure 2 shows the NBOs of **2M** that are relevant for the
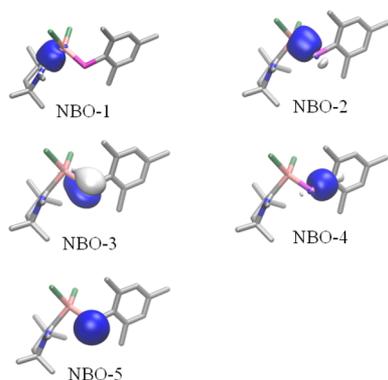
Figure 2. Shape of some relevant natural bond orbitals of **2M** at M06-2X/def2-TZVPP.

discussion. The NBOs of **3M** are very similar (Figure S15), and therefore they are not shown here. Table 1 gives the polarization

Table 1. NBO Results at M06-2X/def2-TZVPP of the Molecules 2M and 3M[a]

	2M		
NBO	occ.	classification	P(A−B)
1	1.92	C (77.8%) − Si (22.2%)	0.63
2	1.90	Si (42.7%) − P (57.3%)	1.30
3	1.70	Si (15.1%) − P (84.9%)	
4	1.96	P (38.3%) − C (61.7%)	0.98
5	1.92	LP P(62.8% s; 37.0% p)	
charge			
q(cAAC)	+0.25		
q(SiCl₂)	+0.34		
q(P−Ar)	−0.59		

	3M		
NBO	occ.	classification	P(A−B)
1	1.92	C (77.9%) − Si (22.1%)	0.66
2	1.89	Si (42.7%) − P (57.3%)	1.30
3	1.80	Si (15.1%) − P (84.9%)	
4	1.95	P (38.3%) − C (61.7%)	0.98
5	1.91	LP P(62.8% s; 37.0% p)	
charge			
q(NHC)	+0.37		
q(SiCl₂)	+0.26		
q(P−Ar)	−0.63		

[a]Occupation and polarization of the NBOs, Wiberg bond orders (P) and partial charges (q).

of the two-center orbitals and the hybridization of the lone-pair NBO-5. The NBOs 1, 2, and 4 are identified as σ-bonding orbitals of C−Si, Si−P, and P−C bonds.

The NBO-5 is the σ lone-pair orbital at phosphorus. The NBO-3 is classified by the standard parameters as Si−P π-bonding orbital. The calculated polarization reveals that NBO-3 is largely localized at the phosphorus end (84.9%). Thus, it can be considered as phosphorus π-lone pair orbital which is engaged in some Si ← P π-backdonation. This is further corroborated by an energy decomposition analysis that suggests that the (carbene)-SiCl₂−PAr orbital interactions in **2M** are built up of 73.3% σ-donation and 15.5% π-backdonation with 11.2% polarization (Table S7). The values for **3M** are very similar, namely, 77.3% σ-donation, 14.0% π-backdonation, and 8.7% polarization. The Wiberg bond order of the Si−P bonds suggests partial double

bond character (Table 1). This picture fits into the Dewar−Chatt−Duncanson model of simultaneous σ donation and π-backdonation. The compounds may also be sketched with formal charges at C1 (+) and P1 (−). We prefer the writing as D→SiCl₂→P-Tip because it directly specifies the formation of the covalent bonds between the three moieties. The calculated partial charges suggest that the fragments D and SiCl₂ are overall donors and P−Ar is an acceptor.

We also calculated the excitation energies of **2M** and **3M** using TD-DFT at the M06-2X/def2-TZVPP level in order to understand the different colors of the compounds **2a-c** (dark blue) and **3** (red). The HOMO−LUMO excitation of **2M** was calculated at 489.6 nm while the corresponding excitation of **3M** was calculated at 395.6 nm (Figure 3). The theoretical data are
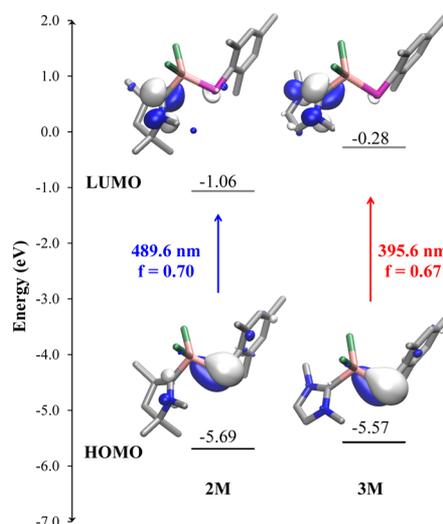

Figure 3. Calculated excitation energies, oscillator strength f and differences of the HOMO and LUMO of 2 and 3 M at M06-2X/def2-TZVPP.

smaller than the experimental values (of **2−3**), which may partly be due to the larger substituents at the donor moieties which may lead to a more delocalized LUMO. The shift of the absorption band for **2M** toward higher wave numbers by 94 nm is also smaller than the experimentally observed differences of 190 nm (**2a**) and 185 nm (**2c**) but the trend nicely agrees with the color change of **2a−c** vs **3**. The HOMO of **2−3** is located on the $\pi_{Si=P}$ bond while the LUMO is located at the carbene moiety (cAAC or NHC). The red (**3**, NHC) and blue (**2**, cAAC; band range 500−900 nm) colors are due to the intramolecular charge transfer (ICT) transition from $\pi_{Si=P} \rightarrow \pi^*_{carbene}$. The LUMO is lower in energy for cAAC than that of NHC compounds by 0.78 eV. All previously reported phosphinidenes are found to be colorless to yellow[16−25] except bisphosphasilene (L(N-TMS₂)Si═P—P═P—Si(N-TMS₂)L; L = C(N-tBu)₂Ph), which is not suitable for studying ICT due to electronic π-conjugation.[26] So far only blue colored anthracenyl-substituted trialkyldisilene[31a] and 3-silylene-2-silaaziridine[31b] show ICT due to electronic transitions from $\pi_{Si=Si} \rightarrow \pi^*_{anthracene}$ and $\pi_{Si=C} \rightarrow \pi^*_{anthracene}$, respectively. The napthalene and phenanthrene analogues are yellow in color. The low lying π^* orbital is required for ICT transition for which anthracene is suitable.[31]

In conclusion, we have developed a novel synthetic route for the preparation of carbene-dichlorosilylene stabilized phosphinidenes (**2−3**). The reaction of **1** with cAAC in the presence of KC₈ in 1:2:2 in THF led to the formation of dark blue

compounds cAAC→SiCl$_2$→P-Tip (**2a−c**), which are stable even in air for a few hours. The crystals of **2a−c** are stable for months at 0 °C in an inert atmosphere. When the cAAC is replaced by NHC, the color changes to dark red (**3**). The stability of compound **3** is lower in air, whereas its thermal stability is higher when compared with that of **2**. Theoretical calculation showed that the (carbene)SiCl$_2$ forms a coordinate bond (Cl$_2$Si → P) with the phosphorus atom of the P-Tip group. Thus, there are two pairs of electrons on the phosphorus atom with σ and π symmetry with the latter engaging in some π-backdonation. The HOMO of the molecule is located on the $\pi_{Si=P}$ bond while the LUMO is located at the carbene moiety (cAAC or NHC). The change in color of these compounds from red (**3**, NHC) to blue (**2**, cAAC) is due to the lower lying LUMO of cAAC. Compounds **2a−c** are the first examples of carbene-dichlorosilylene stabilized phosphinidenes that show ICT transition from $\pi_{Si=P}$→π^*_{cAAC}.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Syntheses of **1**, **2**, **3**; UV−vis, crystal structure determination of **1**, **2a**, **2c**, and **3**, and theoretical details. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Authors
dstalke@chemie.uni-goettingen.de
frenking@chemie.uni-marburg.de
hroesky@gwdg.de

Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

■ REFERENCES

(1) (a) Schmeisser, M.; Voss, P. *Z. Anorg. Allg. Chem.* **1964**, *334*, 50. (b) Schenk, P. W.; Bloching, H. *Z. Anorg. Allg. Chem.* **1964**, *334*, 57. (c) See SI for more refs.

(2) Koe, J. R.; Powell, D. R.; Buffy, J. J.; Hayase, S.; West, R. *Angew. Chem., Int. Ed.* **1998**, *37*, 1441; *Angew. Chem.* **1998**, *110*, 1514.

(3) (a) Ghadwal, R. S.; Azhakar, R.; Roesky, H. W. *Acc. Chem. Res.* **2013**, *46*, 444. (b) Ghadwal, R. S.; Roesky, H. W.; Merkel, S.; Henn, J.; Stalke, D. *Angew. Chem., Int. Ed.* **2009**, *48*, 5683; *Angew. Chem.* **2009**, *121*, 5793 and references herein.

(4) Mondal, K. C.; Dittrich, B.; Maity, B.; Koley, D.; Roesky, H. W. *J. Am. Chem. Soc.* **2014**, *136*, 9568.

(5) Martin, D.; Soleilhavoup, M.; Bertrand, G. *Chem. Sci.* **2011**, *2*, 389.

(6) (a) Back, M.; Henry-Ellinger, M.; Martin, C. D.; Martin, D.; Bertrand, G. *Angew. Chem., Int. Ed.* **2013**, *52*, 2939; *Angew. Chem.* **2013**, *125*, 3011. (b) Martin, D.; Canac, Y.; Lavallo, V.; Bertrand, G. *J. Am. Chem. Soc.* **2014**, *136*, 5023.

(7) Martin, C. D.; Soleilhavoup, M.; Bertrand, G. *Chem. Sci.* **2013**, *4*, 3020.

(8) Lavallo, V.; Canac, Y.; Donnadieu, B.; Schoeller, W. W.; Bertrand, G. *Angew. Chem., Int. Ed.* **2006**, *45*, 3488; *Angew. Chem.* **2006**, *118*, 3568.

(9) Mondal, K. C.; Roesky, H. W.; Schwarzer, M. C.; Frenking, G.; Niepötter, B.; Wolf, H.; Herbst-Irmer, R.; Stalke, D. *Angew. Chem., Int. Ed.* **2013**, *52*, 2963; *Angew. Chem.* **2013**, *125*, 3036.

(10) Tonner, R.; Öxler, F.; Neumüller, B.; Petz, W.; Frenking, G. *Angew. Chem., Int. Ed.* **2006**, *45*, 8038; *Angew. Chem.* **2006**, *118*, 8206.

(11) (a) Dyker, C. A.; Lavallo, V.; Donnadieu, B.; Bertrand, G. *Angew. Chem.* **2008**, *120*, 3250; *Angew. Chem., Int. Ed.* **2008**, *47*, 3206. (b) Fürstner, A.; Alcarazo, M.; Goddard, R.; Lehmann, C. W. *Angew. Chem., Int. Ed.* **2008**, *47*, 3210; *Angew. Chem.* **2008**, *120*, 3254.

(12) (a) Schmidbaur, H. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 907; *Angew. Chem.* **1983**, *95*, 980. (b) Morosaki, T.; Suzuki, T.; Wang, W.-W.; Nagase, S.; Fujii, T. *Angew. Chem., Int. Ed.* **2014**, *53*, 9569; *Angew. Chem.* **2014**, *126*, 9723.

(13) (a) Xiong, Y.; Yao, S.; Inoue, S.; Epping, J. D.; Driess, M. *Angew. Chem.* **2013**, *125*, 7287; *Angew. Chem., Int. Ed.* **2013**, *52*, 7147. (b) Xiong, Y.; Yao, S.; Tan, G.; Inoue, S.; Driess, M. *J. Am. Chem. Soc.* **2013**, *135*, 5004.

(14) See SI.

(15) See SI for all the references.

(16) (a) Driess, M.; Block, S.; Brym, M.; Gamer, M. T. *Angew. Chem., Int. Ed.* **2006**, *45*, 2293; *Angew. Chem.* **2006**, *118*, 2351. (b) Hansen, K.; Szilvasi, T.; Blom, B.; Inoue, S.; Epping, J.; Driess, M. *J. Am. Chem. Soc.* **2013**, *135*, 11795. (c) Hansen, K.; Szilvasi, T.; Blom, B.; Irran, E.; Driess, M. *Chem.—Eur. J.* **2014**, *20*, 1947.

(17) Smit, C. N.; Lock, F. M.; Bickelhaupt, F. *Tetrahedron Lett.* **1984**, *25*, 3011.

(18) (a) Niecke, E.; Klein, E.; Nieger, M. *Angew. Chem., Int. Ed.* **1989**, *28*, 751; *Angew. Chem.* **1989**, *101*, 792. (b) Bender, H. R. G.; Niecke, E.; Nieger, M. *J. Am. Chem. Soc.* **1993**, *115*, 3314. (c) Lange, D.; Klein, E.; Bender, H.; Niecke, E.; Nieger, M.; Pietschnig, R.; Schoeller, W. W.; Ranaivonjatovo, H. *Organometallics* **1998**, *17*, 2425.

(19) (a) Driess, M. *Angew. Chem., Int. Ed.* **1991**, *30*, 1022; *Angew. Chem.* **1991**, *103*, 979. (b) Driess, M.; Rell, S.; Pritzkow, H. *J. Chem. Soc., Chem. Commun.* **1995**, 253. (c) Driess, M.; Pritzkow, H.; Rell, S.; Winkler, U. *Organometallics* **1996**, *15*, 1845. (d) Driess, M.; Block, S.; Brym, M.; Gamer, M. T. *Angew. Chem.* **2006**, *118*, 2351; *Angew. Chem., Int. Ed.* **2006**, *45*, 2293. (e) Hansen, K.; Szilvasi, T.; Blom, B.; Inoue, S.; Epping, J.; Driess, M. *J. Am. Chem. Soc.* **2013**, *135*, 11795. (f) Hansen, K.; Szilvasi, T.; Blom, B.; Irran, E.; Driess, M. *Chem.—Eur. J.* **2014**, *20*, 1947.

(20) Corriu, R.; Lanneau, G.; Priou, C. *Angew. Chem., Int. Ed.* **1991**, *30*, 1130; *Angew. Chem.* **1991**, *103*, 1153.

(21) Lee, V. Y.; Kawei, M.; Sekiguchi, A.; Ranaivonjatovo, H.; Escudie, J. *Organometallics* **2009**, *28*, 4262.

(22) Gau, D.; Kato, T.; Saffon-Merceron, N.; Cossio, F. P.; Baceiredo, A. *J. Am. Chem. Soc.* **2009**, *131*, 8762.

(23) Cui, H.; Zhang, J.; Cui, C. *Organometallics* **2013**, *32*, 1.

(24) Willmes, P.; Cowley, M. J.; Hartmann, M.; Zimmer, M.; Huch, V.; Scheschkewitz, D. *Angew. Chem., Int. Ed.* **2014**, *53*, 2216; *Angew. Chem.* **2014**, *126*, 2248.

(25) Breit, N. C.; Szilvasi, T.; Inoue, S. *Chem.—Eur. J.* **2014**, *20*, 9312.

(26) Khan, S.; Michel, R.; Sen, S. S.; Roesky, H. W.; Stalke, D. *Angew. Chem.* **2011**, *123*, 11990; *Angew. Chem., Int. Ed.* **2011**, *50*, 11786.

(27) See SI for the contributions of du Mont et al.

(28) Pietschnig, R.; Orthaber, A. *Eur. J. Inorg. Chem.* **2006**, 4570.

(29) See SI.

(30) See SI.

(31) (a) Iwamoto, T.; Kobayashi, M.; Uchiyama, K.; Sasaki, S.; Nagendran, S.; Isobe, H.; Kira, M. *J. Am. Chem. Soc.* **2009**, *131*, 3156. (b) Iwamoto, T.; Ohnishi, N.; Akasaka, N.; Ohno, K.; Ishida, S. *J. Am. Chem. Soc.* **2013**, *135*, 10606.