

N-Heterocyclic Carbene–Phosphinidyne Transition Metal Complexes

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In memory of Reinhard Schmutzler

Abstract: The *N*-heterocyclic carbene–phosphinidene adduct $\text{IPr}=\text{PSiMe}_3$ is introduced as a synthon for the preparation of terminal carbene–phosphinidyne transition metal complexes of the type $[(\text{IPr}=\text{P})\text{ML}_n]$ ($\text{ML}_n = (\eta^6\text{-p-cymene})\text{RuCl}$ and $(\eta^5\text{-C}_5\text{Me}_5)\text{RhCl}$). Their spectroscopic and structural characteristics, namely low-field ^{31}P NMR chemical shifts and short metal–phosphorus bonds, show their similarity with arylphosphinidene complexes. The formally mononegative $\text{IPr}=\text{P}$ ligand is also capable of bridging two or three metal atoms as demonstrated by the preparation of bi- and trimetallic RuAu , RhAu , Rh_2 , and Rh_2Au complexes.

N-heterocyclic carbene (NHC) adducts of the p-block elements have received considerable interest ever since the isolation and structural characterization of the first stable carbenes of the imidazolin-2-ylidene type by Arduengo and co-workers in 1991.^[1,2] Following his observation that these carbenes react with S_8 to form imidazolin-2-thiones, Arduengo, together with Cowley, further demonstrated an analogous reaction with cyclic oligomers of alkyl- and arylphosphinidenes (e.g., pentaphenylcyclopentaphosphane, $(\text{PPh})_5$) to produce directly carbene–phosphinidene adducts of type **1** (Figure 1).^[3] Theoretical calculations^[4] and experimental studies^[5] revealed that these phosphorus(I) compounds can

be regarded as inversely polarized phosphaaalkenes, as illustrated by the resonance structures **1A–1C**.^[6] The Lewis base behavior of the imidazolin-2-ylidene adduct **1** ($\text{IMes}=\text{PPh}$ with $\text{R}=\text{Mes}$, $\text{R}'=\text{Ph}$) towards BH_3 was shown to be consistent with the availability of two lone pairs on the phosphorus atom.^[7] More recently, Bertrand showed that various carbene–phosphinidene adducts can be prepared by reaction of the respective carbene with dichlorophenylphosphine, followed by reduction with two equivalents of KC_8 , and that their ^{31}P NMR chemical shifts can serve as an indicator of the π -accepting properties of carbenes.^[8] Phosphinidene adducts of carbonyl-decorated NHCs or diaminocyclopropenylidenes were reported by Hudnall and co-workers and Alcarazo and co-workers,^[9,10] and related cationic dicarbene–phosphorus(I) species were described by the groups of Macdonald and Weigand.^[11,12]

Robinson's iconic phosphorus(0) compound **2** ("carbene-stabilized diphosphorus") represents another similar system, which was obtained by potassium graphite reduction of the carbene– PCl_3 adduct.^[13,14] Further reduction of **2** with lithium metal afforded **3**, which can be regarded as the lithiated form of the carbene-stabilized parent phosphinidene **4** ($\text{IPr}=\text{PH}$).^[15] The latter was first described by Driess and co-workers, who demonstrated that **4** can be generated by PH transfer from a phosphasilene to the NHC.^[16] Very recently, this compound was isolated in pure form by Grützmacher and co-workers from the corresponding imidazolium chloride, whereby either sodium phosphaaethynolate, $\text{Na}(\text{OCP})$, or $\text{P}_7(\text{TMS})_3$ ($\text{TMS}=\text{trimethylsilyl}$) served as the phosphorus source.^[17]

Independently of these approaches, we had been seeking access to compounds such as **4**, reflecting our long-standing interest in imidazolin-2-imine and imidazolin-2-iminato ligands.^[18] In particular, the latter monoanionic systems have found widespread use as ancillary ligands in homogeneous catalysts for alkyne metathesis and olefin polymerization.^[19,20] It was demonstrated that these ligands can act as $2\sigma,4\pi$ -electron donors towards early transition metals or metals in a higher oxidation state and might be regarded as isolobal analogues to dianionic imido systems (Figure 2).^[18,21] In a similar fashion, we envisaged that the corresponding anions bearing a phosphorus instead of a nitrogen atom in the 2-position of the imidazole ring might serve as phosphinidene analogues, which may be formally regarded as dinegative ligands in transition metal complexes of the type $[\text{L}_n\text{M}=\text{P}-\text{R}]$.^[22]

We initially followed Robinson's protocol (see above)^[15] by stirring a THF solution of the carbene– PCl_3 adduct with six equivalents of KC_8 for two days; after evaporation, **4** could be

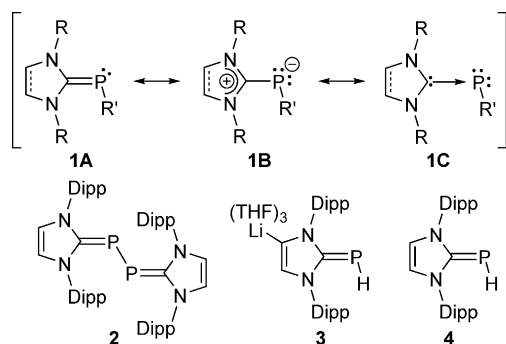


Figure 1. Selected *N*-heterocyclic carbene–phosphinidene adducts (2-phosphinideneimidazolines, Dipp = 2,6-diisopropylphenyl).

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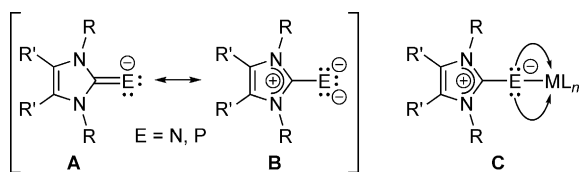
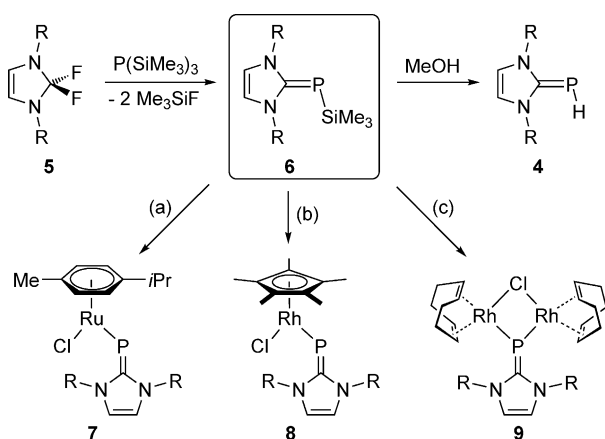


Figure 2. Resonance structures (A, B) of imidazolin-2-ynide ligands and their potential interaction with metals as 2σ,4π electron donors (C).

isolated as a pale yellow microcrystalline solid in 20% yield by column chromatography (neutral alumina, diethyl ether; see the Supporting Information (SI) for details). The ³¹P NMR signal at −133.9 ppm with a ¹J_{PH} coupling of 165.1 Hz is in excellent agreement with the values reported by Grützmacher and co-workers.^[17]

As an alternative entry, we chose *N,N'*-1,3-bis(2,6-diisopropylphenyl)-2,2-difluoroimidazoline (**5**, “PhenoFluor”) as a starting material, which was shown by Ritter et al. to be a highly versatile reagent for deoxyfluorination (for an X-ray crystal structure of **5**, see SI, Figure S37).^[23] The reaction of **5** with P(SiMe₃)₃ at 70 °C in toluene afforded the carbene–PSiMe₃ adduct **6** in high yield (83%) as a yellow crystalline solid (m.p. 149–151 °C) after evaporation of all volatiles (including Me₃SiF, Scheme 1).^[10b] The characteristic high-



Scheme 1. Synthesis of carbene–phosphinidyne transition metal complexes; R = 2,6-diisopropylphenyl (Dipp); a) 0.5 equiv [(η⁶-p-cymene)-RuCl₂]₂, b) 0.5 equiv [(η⁵-C₅Me₅)RhCl₂]₂, c) 1.0 equiv [Rh(cod)Cl]₂.

field ³¹P NMR signal is found at −129.5 ppm, and the ²⁹Si NMR spectrum exhibits a doublet at −4.48 ppm (¹J_{PSi} = 69.8 Hz). The molecular structure of **6** was also confirmed by X-ray diffraction analysis (Figure 3). The P–C bond length (1.7744(13) Å and 1.7800(13) Å for the two independent molecules) falls in the range observed for other carbene–phosphinidyne systems;^[3] it is longer, however, than found for **4** (1.752(1) Å;^[17] see SI for another polymorph of **4** with an almost identical P–C distance, Figure S34). The C1–P–Si angle is 110.71(4)°/106.40(4)°, which is less acute than usually observed.^[3] The TMS group is oriented with its silicon atom outside the plane of the imidazole ring, by 0.91/1.11 Å in two

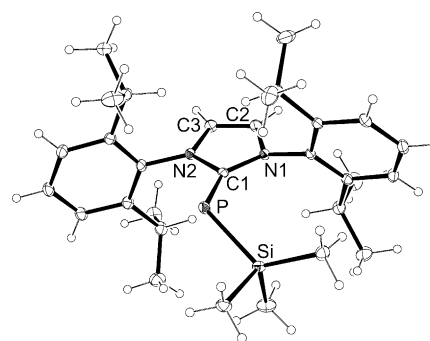


Figure 3. ORTEP diagram of one of the two independent molecules of **6** with thermal displacement parameters drawn at 50% probability level. Selected bond length [Å] and angles [°] (molecule 1/molecule 2): P–Si 2.2135(5)/2.2161(5), P–C1 1.7744(13)/1.7800(13), N1–C1 1.3786(16)/1.3779(17), N2–C1 1.3781(15)/1.3742(17); Si–P–C1 110.71(4)/106.40(4), P–C1–N1 135.79(9)/135.29(10), P–C1–N2 119.94(9)/120.47(10), N1–C1–N2 103.83(10)/104.04(11).

independent molecules. Desilylation of **6** is easily achieved by stirring in methanol to furnish **4** in good yield.

N-Silylated imidazolin-2-imines have been widely used for the preparation of imidazolin-2-iminato complexes of type **C** (Figure 2).^[18,24] We thus expected that **6** would be equally useful for the formation of metal–phosphorus bonds by reaction with metal halides and release of the corresponding trimethylsilyl halide. In view of the chemistry of related phosphinidene complexes,^[22g,25–27] the dimeric complexes [(η⁶-p-cymene)RuCl₂]₂ and [(η⁵-C₅Me₅)RhCl₂]₂ were chosen as starting complexes, and their reaction with two equivalents of **6** furnished the Ru^{II} and Rh^{III} complexes **7** and **8** as dark green solids in satisfactory yield (74%). Both complexes are highly sensitive to air and moisture, but can be stored without noticeable decomposition for several months in an inert glove-box atmosphere. Their ³¹P NMR spectra show characteristic low-field signals at 531.5 ppm (**7**) and 551.8 ppm (d, ¹J_{RhP} = 95.5 Hz, **8**), which reveals their phosphinidene–metal character.^[22g] Nevertheless, the resonances for related authentic phosphinidene complexes are usually found at significantly lower field, and for instance, the phosphine-supported [(η⁶-p-cymene)(PCy₃)Ru(PMes*)]^[25c] and [(η⁵-C₅Me₅)(PPh₃)Rh(PMes*)]^[26b] (Mes* = 2,4,6-tri-*tert*-butylphenyl) show resonances at 813 and 868 ppm; the reported ¹J_{RhP} coupling of 69 Hz is smaller than found for **8**. The ¹H NMR spectra of **7** and **8** at room temperature show broad signals, indicating dynamic behavior in solution, presumably by rotation around the phosphorus–carbon bonds. At low temperature, two septets (quartet of quartets) and four doublets are observed for the isopropyl CH and CH₃ hydrogen atoms, respectively, in agreement with the expected C_s-symmetry (see SI for variable-temperature NMR studies, Figures S13 and S22).

The molecular structure of **7** was established by X-ray diffraction analysis (Figure 4), confirming the formation of a complex with a terminal carbene–phosphinidyne ligand. The Ru metal is in a pseudo-trigonal planar (two-legged piano stool) environment with a P–Ru–Cl angle of 94.24(2)°. Together with a Ru–P–C1 angle of 112.80(7)° and a Ru–P bond length of 2.2099(6) Å, these structural features are very

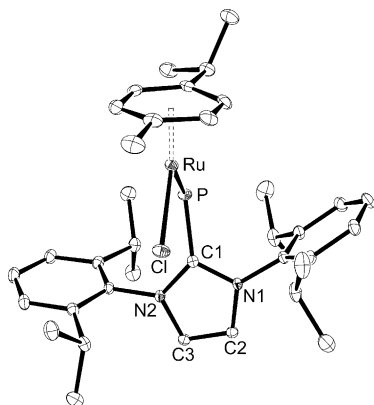


Figure 4. ORTEP diagram of **7** with thermal displacement parameters drawn at 50% probability level. Selected bond length [Å] and angles [°]: Ru–P 2.2099(6), Ru–Cl 2.3956(6), P–Cl 1.824(2), N1–C1 1.363(3), N2–C1 1.360(3); Ru–P–Cl 112.80(7), P–Ru–Cl 94.24(2), P–Cl–N1 123.67(16), P–Cl–N2 129.41(17), N1–C1–N2 105.47(18).

similar to those established for arene–ruthenium phosphinidene complexes, for example, P–Ru–P 85.98(14)°, Ru–P–C 110.5(4)°, and Ru–P 2.205(3) Å in $[(\eta^6\text{-}p\text{-cymene})(\text{PCy}_3)\text{Ru}(\text{PMe}_2^*)]$.^[25c] It should be noted that the carbene moiety adopts a *Z* orientation facing the chlorine atom, and a preliminary X-ray crystal structure of **8** established the same configuration.^[28] In contrast, the majority of related phosphinidene–metal complexes display an *E* configuration of the M=P bond in the solid state, which can be ascribed to the presence of sterically more demanding co-ligands such as phosphines and NHCs.^[25–27] In contrast, the *Z* form is found for the less congested carbonyl complex $[(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})\text{Ir}(\text{PMe}_2^*)]$,^[26a] and density functional theory (DFT) calculations on model compounds of the type (*E*)- and (*Z*)- $[(\eta^5\text{-C}_5\text{H}_5)(\text{L})\text{M}(\text{PH})]$ (M = Co, Rh, Ir; L = CO, PH₃) reveal similar energies with the *Z* isomer tending to be slightly more stable.^[26b] Overall, the spectroscopic and structural properties of **7** and **8**, and also theoretical calculations,^[29] suggest a close similarity to the bonding situation in ruthenium- and rhodium–phosphinidene complexes and are therefore in agreement with the assignment of a metal–phosphorus double bond.^[22,25–27] For comparison, the recently published Grubbs-type ruthenium complex $[\text{RuCl}_2(\text{IMes}=\text{PPh})(\text{PPh}_3)(\text{CHPh})]$ exhibits a markedly longer Ru–P bond (2.3643(7) Å) than **7**.^[30]

The carbene–P(SiMe₃) adduct **6** was also reacted with one equivalent of $[\text{Rh}(\text{cod})\text{Cl}]_2$ (cod = 1,5-cyclooctadiene) in toluene, affording the bimetallic rhodium(I) complex **9** as a dark red solid in 66% isolated yield. Attempts to substitute the second bridging chlorine atom failed, and the introduction of a second phosphorus ligand is probably prevented by steric congestion. The ³¹P NMR spectrum exhibits a triplet at 15.3 ppm with a ¹J_{RhP} coupling of 52.5 Hz, which is, as expected, at significantly higher field than observed for the monometallic complexes **7** and **8**. X-ray diffraction analysis confirmed the formation of a binuclear complex with approximate mirror symmetry (r.m.s.d. 0.28 Å) and with the phosphorus atom residing in an acute trigonal-pyramidal environment with an angle sum of 293.6° (Figure 5, top). The

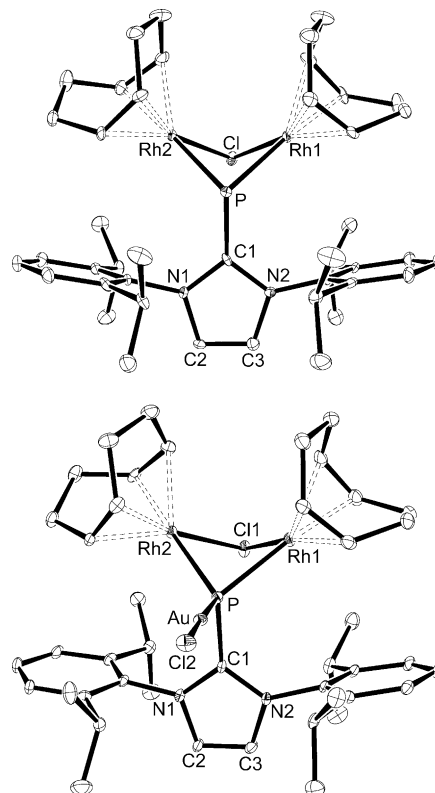


Figure 5. ORTEP diagram of **9** (top) and **9-AuCl** (bottom) with thermal displacement parameters drawn at 50% probability level. Selected bond length [Å] and angles [°]: In **9**: Rh1–P 2.3613(4), Rh1–Cl 2.4349(4), Rh2–P 2.3689(4), Rh2–Cl 2.4302(4), P–Cl 1.8056(17); P–Rh1–Cl 84.426(14), P–Rh2–Cl 84.368(14), Rh1–P–Rh2 75.391(12), Rh1–Cl–Rh2 72.957(11), C1–P–Rh1 110.43(5), C1–P–Rh2 107.79(5), N1–C1–N2 104.02(14). In **9-AuCl**: Rh1–P1 2.3457(13), Rh1–Cl1 2.4056(13), Rh2–P 2.3382(13), Rh2–Cl1 2.4268(13), P–Cl 1.855(5), Au–P 2.2712(12), Au–Cl2 2.3340(12); P–Rh1–Cl1 83.12(4), P–Rh2–Cl1 82.82(4), Rh1–P–Rh2 78.31(4), Rh1–Cl1–Rh2 75.47(4), C1–P–Rh1 112.46(15), C1–P–Rh2 115.48(15), N1–C1–N2 105.7(4), P–Au–Cl2 176.95(5).

four-membered Rh1–P–Cl–Rh2 ring adopts a butterfly-like conformation with acute (< 90°) angles and an angle of 109.9° between the Rh1–P–Cl and Rh2–P–Cl planes. Again, a *Z* configuration can be assigned with regard to the orientation of the carbene moiety. The Rh–P bond lengths are 2.3613(4) and 2.3689(4) Å, which are similar to the values reported for the phosphido-bridged complex $[\text{Rh}_2(\text{cod})_2(\mu\text{-}t\text{Bu}_2\text{P})(\mu\text{-Cl})]$.^[31]

Since phosphinidenes are known to bridge metal atoms and to support metal clusters, in particular in a μ_3 -binding mode,^[32] we explored the reactivity of **9** toward $[(\text{Me}_2\text{S})\text{AuCl}]$. Mixing the two compounds in THF afforded **9-AuCl** in almost quantitative yield. Gold coordination to phosphorus is indicated by a pronounced high-field shift of the ³¹P NMR signal, which is found as a triplet at –16.6 ppm with ¹J_{RhP} = 94.0 Hz, significantly larger than for **9**. The X-ray crystal structures of **9** and **9-AuCl** are very similar (Figure 5), with the Rh1–P–Cl–Rh2 ring of the latter preserving its butterfly geometry with a slightly increased angle of 112.2° between the Rh1–P–Cl and Rh2–P–Cl planes. Gold coordination affords a slight shortening of the Rh–P bond, that is,

Rh1–P 2.3457(13) Å, Rh2–P 2.3382(13) Å, and an elongation of the P–Cl bond (1.8056(17) Å in **9** versus 1.855(5) Å in **9**·AuCl). The P–Au–Cl2 angle of 176.95(5)° is close to linearity, and the Au–P and Au–Cl bond lengths of 2.2712(12) Å and 2.3340(12) Å, respectively, fall in the range expected for gold–phosphine complexes of the type [Au(PR₃)Cl].^[33]

Preliminary auration studies were also carried out with the mononuclear Ru and Rh complexes **7** and **8**, and their reaction with one equivalent of [(Me₂S)AuCl] afforded the bimetallic complexes **7**·AuCl and **8**·AuCl as dark green solids in analytically pure form. Again, the ³¹P NMR signals are shifted to higher field relative to the starting materials and are found at 261.2 ppm (**7**·AuCl) and at 229.7 ppm (**8**·AuCl), with the latter exhibiting a smaller ¹J_{RhP} coupling of 55.1 Hz than observed for **8** (95.5 Hz). Suitable single crystals for X-ray diffraction analysis of these bimetallic compounds have not been obtained to date, but for steric reasons, we tentatively propose C_s-symmetric structures, in which the Z configuration of **7** and **8** are preserved, with the Cl–M–P–Au chains arranged in a zig–zag-fashion.

The carbene–phosphinidene adduct IPr=PSiMe₃ (**6**) proved to be a useful synthon for the preparation of both terminal and bridging N-heterocyclic carbene–phosphinidyne transition metal complexes, and we envisage its potential use for the synthesis of a wide range of d- and f-block metal complexes. The spectroscopic and structural similarities to terminal arylphosphinidene complexes suggest that these ligands are in an isolobal relationship and that double bond character can also be tentatively assigned to the metal–phosphorus bond in the terminal ruthenium and rhodium complexes **7** and **8**.^[22g,34] It might also be interesting to note that metal complexes containing carbene–phosphinidene adducts of type **1** and related species can be regarded as carbene-stabilized phosphinidene–metal complexes,^[10a,30] and indeed, trapping of the phosphinidene complex [(PhP)W(CO)₅] by addition of a stable diaminocyclopropenylidene has been reported.^[35] Likewise, complexes such as **7** and **8** might be formally regarded as NHC-stabilized terminal phosphinidyne (or phosphido) metal complexes^[36] of the type NHC→P≡ML_n, and the possibility of interconversion between these species will be further explored.

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- [1] a) A. J. Arduengo III, R. L. Harlow, M. Kline, *J. Am. Chem. Soc.* **1991**, *113*, 361–363; b) A. J. Arduengo III, H. V. R. Dias, R. L. Harlow, M. Kline, *J. Am. Chem. Soc.* **1992**, *114*, 5530–5534.
- [2] a) D. Bourissou, O. Guerret, F. P. Gabbaï, G. Bertrand, *Chem. Rev.* **2000**, *100*, 39–91; b) N. Kuhn, A. Al-Sheikh, *Coord. Chem. Rev.* **2005**, *249*, 829–857; c) R. C. Fischer, P. P. Power, *Chem. Rev.* **2010**, *110*, 3877–3923; d) M. Scheer, G. Balázs, A. Seitz, *Chem. Rev.* **2010**, *110*, 4236–4256; e) Y. Wang, G. H. Robinson, *Inorg. Chem.* **2011**, *50*, 12326–12337; f) M. N. Hopkinson, C. Richter, M. Schedler, F. Glorius, *Nature* **2014**, *510*, 485–496.
- [3] a) A. J. Arduengo III, H. V. R. Dias, J. C. Calabrese, *Chem. Lett.* **1997**, 143; b) A. J. Arduengo III, J. C. Calabrese, A. H. Cowley, H. V. R. Dias, J. R. Goerlich, W. J. Marshall, B. Riegel, *Inorg. Chem.* **1997**, *36*, 2151–2158; alternatively, such adducts could be prepared by reaction of PhPCl₂ with two equivalents of a free carbene.
- [4] a) G. Frison, A. Sevin, *J. Organomet. Chem.* **2002**, *643*–644, 105–111; b) G. Frison, A. Sevin, *J. Chem. Soc. Perkin Trans. 2* **2002**, 1692–1697; c) P. Rosa, C. Gouverd, G. Bernardinelli, T. Berclaz, M. Geoffroy, *J. Phys. Chem. A* **2003**, *107*, 4883–4892.
- [5] L. Weber, *Eur. J. Inorg. Chem.* **2000**, 2425–2441.
- [6] For a revealing discussion of the pros and cons of using arrows for the description of carbene–element adducts, see: a) D. Himmel, I. Krossing, A. Schnepf, *Angew. Chem. Int. Ed.* **2014**, *53*, 370–374; *Angew. Chem.* **2014**, *126*, 378–382; b) G. Frenking, *Angew. Chem. Int. Ed.* **2014**, *53*, 6040–6046; *Angew. Chem.* **2014**, *126*, 6152–6158; c) D. Himmel, I. Krossing, A. Schnepf, *Angew. Chem. Int. Ed.* **2014**, *53*, 6047–6048; *Angew. Chem.* **2014**, *126*, 6159–6160.
- [7] A. J. Arduengo III, C. J. Carmalt, J. A. C. Clyburne, A. H. Cowley, R. Pyati, *Chem. Commun.* **1997**, 981–982.
- [8] O. Back, M. Henry-Ellinger, C. D. Martin, D. Martin, G. Bertrand, *Angew. Chem. Int. Ed.* **2013**, *52*, 2939–2943; *Angew. Chem.* **2013**, *125*, 3011–3015.
- [9] a) R. R. Rodrigues, C. L. Dorsey, C. A. Arceneaux, T. W. Hudnall, *Chem. Commun.* **2014**, *50*, 162–164; b) C. L. Dorsey, B. M. Squires, T. W. Hudnall, *Angew. Chem. Int. Ed.* **2013**, *52*, 4462–4465; *Angew. Chem.* **2013**, *125*, 4558–4561.
- [10] a) M. Alcarazo, K. Radkowski, G. Mehler, R. Goddard, A. Fürstner, *Chem. Commun.* **2013**, *49*, 3140–3142; b) Alcarazo also reported the reaction of 1-chloro-2,3-diaminocyclopropenium salts with P(SiMe₃)₃ to produce phosphorus(III) tricationic species, see J. Petušková, M. Patil, S. Holle, C. W. Lehmann, W. Thiel, M. Alcarazo, *J. Am. Chem. Soc.* **2011**, *133*, 20758–20760.
- [11] B. D. Ellis, C. A. Dyker, A. Decken, C. L. B. Macdonald, *Chem. Commun.* **2005**, 1965–1967.
- [12] K. Schwedtmann, M. H. Holthausen, K.-O. Feldmann, J. J. Weigand, *Angew. Chem. Int. Ed.* **2013**, *52*, 14204–14208; *Angew. Chem.* **2013**, *125*, 14454–14458.
- [13] Y. Wang, Y. Xie, P. Wei, R. B. King, H. F. Schaefer III, P. v. R. Schleyer, G. H. Robinson, *J. Am. Chem. Soc.* **2008**, *130*, 14970–14971.
- [14] a) Y. Wang, Y. Xie, M. Y. Abraham, P. Wei, H. F. Schaefer III, P. v. R. Schleyer, G. H. Robinson, *Chem. Commun.* **2011**, *47*, 9224–9226; b) Y. Wang, Y. Xie, P. Wei, H. F. Schaefer III, P. R. Schleyer, G. v. H. Robinson, *J. Am. Chem. Soc.* **2013**, *135*, 19139–19142; c) D. Gudat, *Angew. Chem. Int. Ed.* **2014**, *53*, 4753–4754; *Angew. Chem.* **2014**, *126*, 4849–4851.
- [15] Y. Wang, Y. Xie, M. Y. Abraham, R. J. Gilliard, Jr., P. Wei, H. F. Schaefer III, P. v. R. Schleyer, G. H. Robinson, *Organometallics* **2010**, *29*, 4778–4780.
- [16] a) K. Hansen, T. Szilvási, B. Blom, S. Inoue, J. Epping, M. Driess, *J. Am. Chem. Soc.* **2013**, *135*, 11795–11798; b) K. Hansen, T. Szilvási, B. Blom, E. Irran, M. Driess, *Chem. Eur. J.* **2014**, *20*, 1947–1956.
- [17] A. M. Tondreau, Z. Benkö, J. R. Harmer, H. Grützmacher, *Chem. Sci.* **2014**, *5*, 1545–1554.
- [18] X. Wu, M. Tamm, *Coord. Chem. Rev.* **2014**, *260*, 116–138.
- [19] a) S. Beer, C. G. Hrib, P. G. Jones, K. Brandhorst, J. Grunenberg, M. Tamm, *Angew. Chem. Int. Ed.* **2007**, *46*, 8890–8894; *Angew. Chem.* **2007**, *119*, 9047–9051; b) S. Beer, K. Brandhorst, C. G. Hrib, X. Wu, B. Haberlag, J. Grunenberg, P. G. Jones, M. Tamm, *Organometallics* **2009**, *28*, 1534–1545; c) B. Haberlag, X. Wu, K. Brandhorst, J. Grunenberg, C. G. Daniliuc, P. G. Jones, M. Tamm, *Chem. Eur. J.* **2010**, *16*, 8868–8877; d) S. Lysenko, C. G. Daniliuc, P. G. Jones, M. Tamm, *J. Organomet. Chem.* **2013**, *744*,

- 7–14; e) B. Haberlag, M. Freytag, P. G. Jones, M. Tamm, *Adv. Synth. Catal.* **2014**, 356, 1255–1265.
- [20] a) M. Tamm, S. Randoll, E. Herdtweck, N. Kleigrew, G. Kehr, G. Erker, B. Rieger, *Dalton Trans.* **2006**, 459–467; b) S. H. Stelzig, M. Tamm, R. M. Waymouth, *J. Polym. Sci. Part A* **2008**, 46, 6064–6070; c) M. Sharma, H. Yameen, B. Tumanskii, S. A. Filimon, M. Tamm, M. Eisen, *J. Am. Chem. Soc.* **2012**, 134, 17234–17244; d) K. Nomura, H. Fukuda, W. Apisuk, A. Trambitas, B. Kitiyanan, M. Tamm, *J. Mol. Catal. A* **2012**, 363–364, 501–511; e) W. Apisuk, A. G. Trambitas, B. Kitiyanan, M. Tamm, K. Nomura, *J. Polym. Sci. Part A* **2013**, 51, 2575–2580; f) D. Shoken, M. Sharma, M. Botoshansky, M. Tamm, M. S. Eisen, *J. Am. Chem. Soc.* **2013**, 135, 12592–12595; g) K. Nomura, B. Bahuleyan, S. Zhang, P. Veerasha Sharma, S. Katao, A. Igarashi, A. Inagaki, M. Tamm, *Inorg. Chem.* **2014**, 53, 607–623.
- [21] K. Panda, A. G. Trambitas, T. Bannenberg, C. G. Hrib, S. Randoll, P. G. Jones, M. Tamm, *Inorg. Chem.* **2009**, 48, 5462–5472.
- [22] a) A. H. Cowley, *Acc. Chem. Res.* **1988**, 21, 81–87; b) A. H. Cowley, *Acc. Chem. Res.* **1997**, 30, 445–451; c) D. W. Stephan, *Angew. Chem. Int. Ed.* **2000**, 39, 314–329; *Angew. Chem.* **2000**, 112, 322–338; d) F. Mathey, *Angew. Chem. Int. Ed.* **2003**, 42, 1578–1604; *Angew. Chem.* **2003**, 115, 1616–1643; e) S. Greenberg, D. W. Stephan, *Chem. Soc. Rev.* **2008**, 37, 1482–1489; f) R. Waterman, *Dalton Trans.* **2009**, 18–26; g) H. Aktas, J. C. Slootweg, K. Lammertsma, *Angew. Chem. Int. Ed.* **2010**, 49, 2102–2113; *Angew. Chem.* **2010**, 122, 2148–2159.
- [23] a) P. Tang, W. Wang, T. Ritter, *J. Am. Chem. Soc.* **2011**, 133, 11482–11484; b) F. Sladojevich, S. I. Arlow, P. Tang, T. Ritter, *J. Am. Chem. Soc.* **2013**, 135, 2470–2473.
- [24] a) M. Tamm, S. Randoll, T. Bannenberg, E. Herdtweck, *Chem. Commun.* **2004**, 876–877; b) M. Tamm, D. Petrovic, S. Randoll, S. Beer, T. Bannenberg, P. G. Jones, J. Grunenberg, *Org. Biomol. Chem.* **2007**, 5, 523–530.
- [25] a) A. T. Termaten, T. Nijbacker, M. Schakel, M. Lutz, A. L. Spek, K. Lammertsma, *Chem. Eur. J.* **2003**, 9, 2200–2208; b) R. Menye-Biyogo, F. Delpech, A. Castel, H. Gornitzka, P. Rivère, *Angew. Chem. Int. Ed.* **2003**, 42, 5610–5612; *Angew. Chem.* **2003**, 115, 5768–5770; c) R. Menye-Biyogo, F. Delpech, A. Castel, V. Pimienta, H. Gornitzka, P. Rivière, *Organometallics* **2007**, 26, 5091–5101.
- [26] a) A. T. Termaten, T. Nijbacker, M. Schakel, M. Lutz, A. L. Spek, K. Lammertsma, *Organometallics* **2002**, 21, 3196–3202; b) A. T. Termaten, H. Aktas, M. Schakel, A. W. Ehlers, M. Lutz, A. L. Spek, K. Lammertsma, *Organometallics* **2003**, 22, 1827–1834.
- [27] a) H. Aktas, J. C. Slootweg, M. Schakel, A. W. Ehlers, M. Lutz, A. L. Spek, K. Lammertsma, *J. Am. Chem. Soc.* **2009**, 131, 6666–6667; b) H. Aktas, J. C. Slootweg, A. W. Ehlers, M. Lutz, A. L. Spek, K. Lammertsma, *Organometallics* **2009**, 28, 5166–5172.
- [28] X-ray crystallographic analysis performed several times on crystals of **8** resulted in crystallographic data of only modest quality. Therefore, the structure is not included in the main text (see Figure S40 and Table S6 in the SI). Nevertheless, the data are sufficient to demonstrate the connectivity, thereby confirming the presence of a bent Rh–P–C moiety (110.2(2)°). The Rh–P bond length of 2.1968(16) Å falls in the range found for rhodium–phosphinidene complexes, for example, Rh–P 2.1903(4) Å in $[(\eta^5\text{-C}_5\text{Me}_5)(\text{PPh}_3)\text{Rh}(\text{PMes}^*)]$.^[26b]
- [29] The bonding situation in **6**, **7**, and **8** was further analyzed by DFT calculations at the B3PW91/6-311G(d,p) level of theory and by NBO analyses (see SI, Section S4). For instance, Wiberg bond indices (WBI) of 1.48 (Ru–P) and 1.30 (Rh–P) were calculated for the metal–phosphorus bonds in **7** and **8**; these values are smaller but close to those reported for Schrock-type carbene complexes, see V. H. Gessner, F. Meier, D. Uhrich, M. Kaupp, *Chem. Eur. J.* **2013**, 19, 16729–16739.
- [30] T. G. Larocque, G. G. Lavoie, *New J. Chem.* **2014**, 38, 499–502.
- [31] A. M. Arif, R. A. Jones, M. H. Seeberger, B. R. Whittlesey, T. C. Wright, *Inorg. Chem.* **1986**, 25, 3943–3949.
- [32] a) G. Huttner, K. Knoll, *Angew. Chem. Int. Ed. Engl.* **1987**, 26, 743–760; *Angew. Chem.* **1987**, 99, 765–783; for two recent publications, see: b) Y. Lv, C. E. Kefalidis, J. Zhou, L. Maron, X. Leng, Y. Chen, *J. Am. Chem. Soc.* **2013**, 135, 14784–14796; c) K. Wang, G. Luo, J. Hong, X. Zhou, L. Weng, Y. Luo, L. Zhang, *Angew. Chem. Int. Ed.* **2014**, 53, 1053–1056; *Angew. Chem.* **2014**, 126, 1071–1074.
- [33] P. G. Jones, *Gold Bull.* **1981**, 14, 102–118.
- [34] A. W. Ehlers, E. J. Baerends, K. Lammertsma, *J. Am. Chem. Soc.* **2002**, 124, 2831–2838.
- [35] N. H. T. Huy, B. Donnadiou, G. Bertrand, F. Mathey, *Chem. Asian J.* **2009**, 4, 1225–1228.
- [36] a) B. P. Johnson, G. Balázs, M. Scheer, *Top. Curr. Chem.* **2004**, 232, 1–23; b) B. P. Johnson, G. Balázs, M. Scheer, *Coord. Chem. Rev.* **2006**, 250, 1178–1195; c) G. Balázs, L. Gregoriades, M. Scheer, *Organometallics* **2007**, 26, 3058–3075.