Main-Group Chemistry

DOI: 10.1002/anie.201301153

Phosphastannirane: A Phosphorus/Tin(II) Lewis Pair that Undergoes Alkyne and Alkene Addition**

*Sarah Freitag, Jens Henning, Hartmut Schubert, and Lars Wesemann**

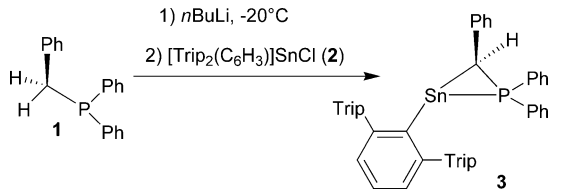
Dedicated to Professor Werner Uhl on the occasion of his 60th birthday

Research concerning frustrated Lewis pairs (FLPs) is currently of great interest. The groups of Stephan and Erker have recently published many articles about the activation of small molecules using inter- or intramolecular boron–phosphorus-based FLPs.[1] The perfluorinated arylborane $[B(C_6F_5)_3]$ and derivatives thereof act as the Lewis acid, whereas trialkyl- or triarylphosphines are very often the Lewis bases.[1c,e,2] Apart from B/P, combinations of C/B, N/B, and P/Al pairs were investigated as FLPs.[2,3] Reversible CO_2 coordination was found in reaction with a P,P-chelated stannylene $[(iPr_2P)_2N]_2Sn$.[4]

The focus of our current research is the chemistry of tin,[5] and especially the coordination chemistry of tin ligands.[6] We have characterized the first tripodal tin ligand[7] and reported recently on the coordination chemistry of a cyclic distannene.[8] This xanthene-based distannene shows as a twisted distannene side-on coordination of the Sn–Sn bond at Ni. To synthesize a bipodal tin ligand with two different donor sites, we started to investigate the chemistry of phosphino-substituted stannylenes. Herein we present the synthesis of a benzylphosphine-substituted stannylene. This molecule exhibits formation of the first three-membered Sn–C–P ring comprising a phosphorus–tin donor–acceptor interaction and a small angle at tin. Furthermore we found an interesting room-temperature reaction of the cyclic molecule **3** with terminal alkynes and 1-pentene, showing the Sn^{II}/P molecule acting like a FLP.

Benzyldiphenylphosphine (**1**) was lithiated and then reacted with isopropyl substituted *m*-terphenyltinchloride (**2**) to give the stannylene **3** in high yield (Scheme 1).[9] Orange crystals of the stannylene were obtained after several days of crystallization from a hexane solution of **3** at −20 °C. The stannylene **3** is very sensitive towards moisture and air and was characterized by elemental analysis, NMR spectroscopy in solution and the solid state, and single-crystal structure analysis.[10] In Figure 1 a,b the structure of the stannylene in the solid state is presented together with selected interatomic distances and angles.

The benzylphosphine-substituted stannylene forms a three membered Sn–C–P ring in the solid state that exhibits



Scheme 1. Formation of the cyclic Sn–C–P molecule **3**. Trip = 2,4,6-$iPr_3C_6H_2$.

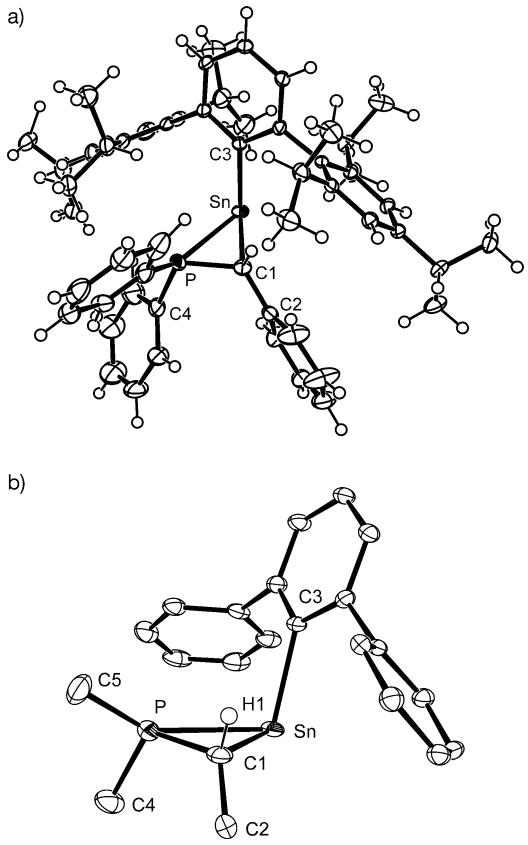


Figure 1. a) Molecular structure of stannylene **3** (ellipsoids set at 50% probability) in the solid state; the major contributor to the disordered structure is shown.[11] b) Detailed molecular structure of stannylene **3** (ellipsoids set at 50% probability) in the solid state without isopropyl groups, hydrogen atoms (except at the ring carbon), and phenyl groups at ring atoms. Selected bond lengths [Å] and angles [°]: Sn–C1 2.312(3), Sn–C3 2.217(2), Sn–P 2.663(1), P–C1 1.816(3); P-C1-Sn 79.3(1), Sn-P-C1 58.6(1), P-Sn-C1 42.1(1), P-Sn-C3 99.5(1), C1-Sn-C3 100.8(1), C2-C1-Sn 123.6(2), C5-P-C4 105.3(2).

[*] S. Freitag, J. Henning, Dr. H. Schubert, Prof. Dr. L. Wesemann
Institut für Anorganische Chemie, Universität Tübingen
Auf der Morgenstelle 18, 72076 Tübingen (Germany)
E-mail: lars.wesemann@uni-tuebingen.de

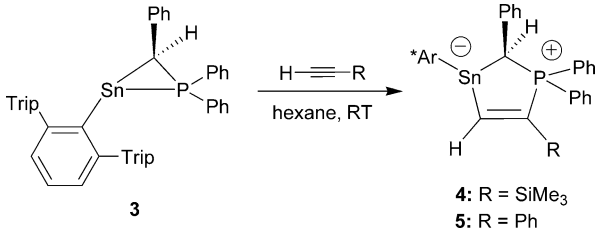
[**] This work was supported by the Fonds der Chemischen Industrie.
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201301153.

a Sn–P donor–acceptor bond. A three-membered ring with these elements is to the best of our knowledge unknown. Because of their interesting chemical properties, three-membered rings containing tin atoms have been an attractive synthetic goal.[12] The reason for the ring formation might be the steric shielding of the *m*-terphenyl substituent together with a combination of the Lewis acidity of the stannylene and the Lewis basicity of the phosphine substituent. Geminal donor–acceptor bonds between N and Si were studied extensively by Mitzel.[13] Obviously the phosphine reacts as a donor and forms an intramolecular bond with the tin atom, which is 2.663(1) Å long. The Sn–P distance in **3** lies in the range of published Sn–P bond lengths and belongs to the group of longer distances.[6a,14] The Sn–C1 bond (2.312(3) Å) is longer than Sn–C bond lengths in the Sn_2C ring (2.209(12), 2.196(12) Å) and comparable with bonds in benzyltin compounds.[12d,15] The P–C1 bond length inside the ring can be compared with P–C distances inside a phosphasilirane,[16] a phosphirane,[17] or known benzylphoshines.[18] The angles inside the ring (at C 79.3(1)°, P 58.6(1), Sn 42.1(1)°) are larger for carbon and phosphorus than comparable values in three-membered rings.[12d] The angle at tin however is the smallest angle at tin found in three-membered rings (Sn_2C 50.7, 51.1; Sn_3 60.0; Sn_2N 49.4, 49.2).[12a–d] The bond length of the substituent at tin (Sn–C3 2.2217(2) Å) can be compared with the published example, namely 2,6-$Trip_2(H_3C_6)$Sn-$SnMe_2C_6H_3$-2,6-$Trip_2$ (2.201(2 Å).[19]

The ^{31}P NMR spectrum recorded in the solid state exhibits a signal for the cyclic molecule **3** at −50.3 ppm with a coupling constant with the tin atom $J_{Sn\text{-}P}$ of 364 Hz. In solution at room temperature, the molecule shows a resonance in the ^{31}P NMR spectrum at −38.6 ppm with a coupling constant of $J_{Sn\text{-}P}$ 82.7 Hz. This coupling constant is small in comparison to a variety of $^1J_{Sn\text{-}P}$ coupling constants (1682, 1628 Hz for Sn[P(Si*i*Pr$_3$)(SiF*t*BuTrip)]$_2$,[20] 1274 Hz for Sn[PPh-2,6-C_6H_3-$(CH_2NMe_2)_2$]$_2$,[14h] 1050 Hz for Sn[P(CH-$(SiMe_3)_2C_6H_4NMe_2$]$_2$,[14d] 767 Hz for $Ph_3Sn[\eta^2$-P,P-$MeP_3C_3tBu_3$]).[14e] We have studied the temperature dependence of the ^{31}P NMR resonance (80 °C, −36.8 ppm; −90 °C, −37.6 ppm) and the tin–phosphorus coupling in solution: cooling the sample from 80 °C to −90 °C results in an increase of the coupling constant from 14.5 Hz to 220 ± 20 Hz. The ^{119}Sn NMR resonance in solution at room temperature at 716 ppm lies between signals typical for triply coordinated Sn^{II} ($[SnPh_3]^-$ −98.4 ppm)[21] and signals for dialkylstannylenes with tin having a coordination number of two ([Sn-(*t*Bu)(C_6H_3-2,6-$Trip_2$)] 1904 ppm).[19] Owing to a half width of 290 Hz of the ^{119}Sn NMR signal, the coupling with the phosphorus atom was not detected. Attempts to obtain a ^{119}Sn NMR spectrum of compound **3** in the solid state were not successful. By evaluation of the spin–lattice relaxation time in ^{119}Sn solution NMR spectroscopy at variable temperature, we are able to estimate the chemical shift anisotropy to be ≥2000 ppm.[10,22] This probably accounts for the difficulties in observing the resonance in the solid state. The ring formation reaction (Scheme 1) is stereoselective, as we detect only one signal in solution in the ^{1}H NMR spectrum (3.67 ppm) for the CH unit of the ring and also only one signal in the ^{31}P NMR spectrum (−38.6 ppm). The tin and carbon atoms of the ring are centers of chirality, but we found formation of only one pair of enantiomers (*R*,*R* configuration shown in Figure 1). The reason for this diastereoselectivity might be due to the sterical requirements of the *m*-terphenyl ligand, which exhibits *trans* position to the phenyl group at the ring carbon atom.

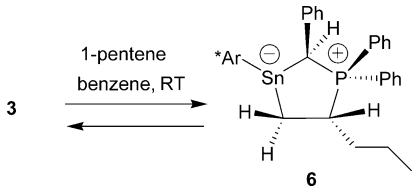
To better understand the bonding situation in the ring, we studied the molecule by DFT calculations on revPBE-D3(BJ)/TZP(all electrons) level of theory using the ADF program.[23] Full computational details are given in the Supporting Information. A geometry optimization starting from the crystal structure and subsequently a natural bond analysis (NBO) and an atoms-in-molecules analysis (AIM) were calculated. The NBO analysis indicates a donor–acceptor interaction of the phosphorus lone pair donating into a tin p orbital. Additionally, in the topological analysis of the electron density (AIM), a bond path and a bond critical point between the phosphorus and the tin is found, confirming a bonding interaction.

We started to investigate the chemistry of the cyclic stannylene in reactions of the small ring with unsaturated organic molecules. The addition of element–element bonds to alkynes has previously been carried out by using radical reaction conditions[24] or palladium catalysis.[25] Stannylene **3** reacts in a straightforward manner at room temperature with phenylacetylene or trimethylsilylacetylene under addition of the Sn–P bond to the triple bond to give phosphastannacyclopentenes **4** and **5**, respectively (Scheme 2).[26] In the case of



Scheme 2. Formation of the phosphastannacyclopentenes **4** and **5**. Ar* = 2,6-$Trip_2C_6H_3$.

1-pentene, the reaction with an excess of the olefin takes one day at room temperature to reach completion (Scheme 3). After dissolving crystals of **6** in benzene, the formation of an equilibrium mixture between the trinuclear cycle **3**, olefin, and cyclopentane **6** was detected. The new five-membered ring molecules **4**–**6** were characterized by elemental analyses, NMR spectroscopy, and in the case of **4** and **6** by X-ray crystal structure analysis. The reaction of the P–Sn bond with the



Scheme 3. Formation of the phosphastannacyclopentane **6**. Ar* = 2,6-$Trip_2C_6H_3$.

acetylenes and 1-pentene can be monitored by a shift to low field for the ^{31}P NMR signal and shift to high field for the ^{119}Sn NMR signal for **4**–**6** in comparison to the starting material. In the case of the olefinic proton of molecule **4** coupling with all three heteroatoms, $^{3}J_{P\text{-}H}$ 73.8 Hz, $^{3}J_{Si\text{-}H}$ 10.3 Hz, and $^{2}J_{Sn\text{-}H}$ 54.8 Hz was observed. Coupling between the tin and phosphorus atoms was only detected in the case of molecule **6** in the ^{31}P NMR spectrum. The signal in the ^{119}Sn NMR is too broad ($\Delta\nu_{1/2} = (135 \pm 10)$ Hz) to allow detection of the coupling ($^{2}J_{Sn\text{-}P} = 30.5$ Hz). As only the isomer in which the terminal carbon atom of the alkynes or olefin has formed a bond to the tin atom, the formations of the five-membered rings are regioselective reactions. Furthermore, the reaction with the olefin is also diastereoselective, as we form a new center of chirality and detect only one signal in the ^{31}P NMR spectrum, and therefore only one pair of enantiomers out of four possible pairs was formed.

The structure of the cyclic molecules **4** (Figure 2) and **6** (Figure 3) can be compared with a bicyclic distannide published by Veith et al.[26b] In the addition products **4** and

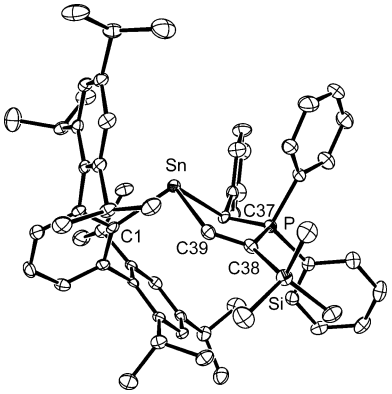


Figure 2. Molecular structure of stannylene **4** (ellipsoids set at 50% probability) in the solid state.[11] All hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Sn–C39 2.216(3), Sn–C1 2.261(3), Sn–C37 2.331(3), P–C37 1.779(3), P–C38 1.796(3), Si–C38 1.895(3), C38–C39 1.348(4); C39-Sn-C37 79.6(1), C37-P-C38 106.7(1), P-C37-Sn 102.5(1), C39-C38-P 111.5(2), C38-C39-Sn 123.0(2), C1-Sn-C39 92.8(1), C1-Sn-C37 108.4(1).

6, a three-coordinate stannide anion and a four-coordinate phosphonium cation are formed. The sum of the C-Sn-C angles of molecules **4** (280.8°) and **6** (282.9°) are smaller than the sum of angles in $[Ph_3Sn]^-$ (290.3°). This might be an effect of the small C-Sn-C angle inside the ring of **4** (79.6°(1)) and **6** (84.5(1)°). In the unsaturated molecule **4**, a large C1-Sn-C37 angle of 108.4(1)° was found, which is due to steric requirements of the phenyl and terphenyl substituent. The angles at the tetrahedrally coordinated phosphorus atom can be compared with angles found in a bicyclic distannide or other cyclic FLP addition products.[1b,26b] As expected, the C–C distances inside the rings **4** and **6** are elongated towards a double and single bond.[1b,3f] The angle at the carbon inside the three-membered ring **3** (79.3(1)°) shows an enlargement of more than 20° upon addition of the unsaturated organic molecules (**4** 102.5(1)°, **6** 105.1(1)°). The terphenyl substituent

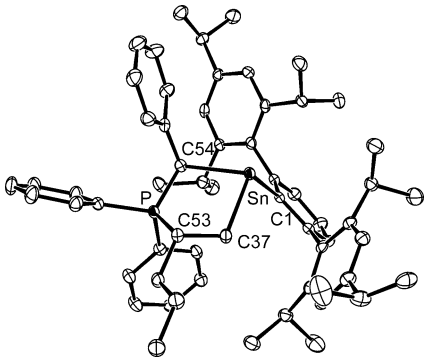


Figure 3. Molecular structure of the cyclic molecule **6** (ellipsoids set at 50% probability) in the solid state. All hydrogen atoms are omitted for clarity.[11] Selected bond lengths [Å] and angles [°]: Sn–C1 2.278(2), Sn–C37 2.246(3), Sn–C54 2.381(2), C53–C37 1.541(3), C53–P 1.837(2), P–C54 1.777(3); C1-Sn-C37 98.7(1), C1-Sn-C54 99.7(1), C37-Sn-C54 84.5(1), C54-P-C53 109.1(1), P-C54-Sn 105.1(1), Sn-C37-C54 113.0(2), C37-C53-P 104.7(2).

exhibits a longer bond with the tin atoms (**3** 2.217(2), **4** 2.261(3), **6** 2.278(2) Å), which is probably due to steric requirements of the larger rings **4** and **6**. These observed Sn–C bond lengths can be compared with interatomic Sn–C distances of this substituent from Power et al.[19]

In conclusion, the observed Sn–P addition at a triple or double bond can be compared with the reaction of B/P and Al/P frustrated Lewis pairs with terminal acetylenes and olefins.[1b,d,3e–g] This formation shows the same regioselectivity, but in the case of the Al/P pair, higher temperatures (70 °C) are necessary for completion of the reaction. Furthermore, Toshimitsu and Tamao described a phosphine-coordinated silylene as an intermediate, which reacts at 110 °C with diphenylacetylene to result in the addition of a Si–P bond. However at the end they found transfer of an aryl group from the phosphorus to silicon.[27] In comparison to those examples, the three-membered ring **3** shows high reactivity with respect to addition of unsaturated organic molecules.

Received: February 8, 2013
Published online: April 15, 2013

Keywords: alkynes · Lewis pairs · olefins · phosphorus · tin

[1] a) D. W. Stephan, G. Erker, *Angew. Chem.* **2010**, *122*, 50–81; *Angew. Chem. Int. Ed.* **2010**, *49*, 46–76; b) C. M. Mömming, S. Frömel, G. Kehr, R. Fröhlich, S. Grimme, G. Erker, *J. Am. Chem. Soc.* **2009**, *131*, 12280–12289; c) P. Spies, G. Erker, G. Kehr, K. Bergander, R. Fröhlich, S. Grimme, D. W. Stephan, *Chem. Commun.* **2007**, 5072–5074; d) J. S. J. McCahill, G. C. Welch, D. W. Stephan, *Angew. Chem.* **2007**, *119*, 5056–5059; *Angew. Chem. Int. Ed.* **2007**, *46*, 4968–4971; e) A. Stute, G. Kehr, R. Fröhlich, G. Erker, *Chem. Commun.* **2011**, *47*, 4288–4290.

[2] G. Ménard, D. W. Stephan, *Angew. Chem.* **2012**, *124*, 8397–8400; *Angew. Chem. Int. Ed.* **2012**, *51*, 8272–8275.

[3] a) P. A. Chase, D. W. Stephan, *Angew. Chem.* **2008**, *120*, 7543–7547; *Angew. Chem. Int. Ed.* **2008**, *47*, 7433–7437; b) D. Holschumacher, T. Bannenberg, C. G. Hrib, P. G. Jones, M. Tamm, *Angew. Chem.* **2008**, *120*, 7538–7542; *Angew. Chem. Int.*

Ed. **2008**, *47*, 7428 – 7432; c) P. A. Chase, T. Jurca, D. W. Stephan, *Chem. Commun.* **2008**, 1701 – 1703; d) V. Sumerin, F. Schulz, M. Nieger, M. Leskelä, T. Repo, B. Rieger, *Angew. Chem.* **2008**, *120*, 6090 – 6092; *Angew. Chem. Int. Ed.* **2008**, *47*, 6001 – 6003; e) M. A. Dureen, D. W. Stephan, *J. Am. Chem. Soc.* **2009**, *131*, 8396 – 8397; f) C. Appelt, H. Westenberg, F. Bertini, A. W. Ehlers, J. C. Slootweg, K. Lammertsma, W. Uhl, *Angew. Chem.* **2011**, *123*, 4011 – 4014; *Angew. Chem. Int. Ed.* **2011**, *50*, 3925 – 3928; g) S. Roters, C. Appelt, H. Westenberg, A. Hepp, J. C. Slootweg, K. Lammertsma, W. Uhl, *Dalton Trans.* **2012**, *41*, 9033 – 9045.

[4] D. A. Dickie, E. N. Coker, R. A. Kemp, *Inorg. Chem.* **2011**, *50*, 11288 – 11290.

[5] a) T. Marx, B. Mosel, I. Pantenburg, S. Hagen, H. Schulze, L. Wesemann, *Chem. Eur. J.* **2003**, *9*, 4472 – 4478; b) T. Gädt, L. Wesemann, *Organometallics* **2007**, *26*, 2474 – 2481; c) M. Kirchmann, K. Eichele, F. M. Schappacher, R. Pöttgen, L. Wesemann, *Angew. Chem.* **2008**, *120*, 977 – 980; *Angew. Chem. Int. Ed.* **2008**, *47*, 963 – 966; d) J.-A. Dimmer, M. Hornung, T. Wütz, L. Wesemann, *Organometallics* **2012**, *31*, 7044 – 7051.

[6] a) M. Wagner, K. Dorogov, M. Schürmann, K. Jurkschat, *Dalton Trans.* **2011**, *40*, 8839 – 8848; b) D. Heitmann, T. Pape, A. Hepp, C. Mück-Lichtenfeld, S. Grimme, F. E. Hahn, *J. Am. Chem. Soc.* **2011**, *133*, 11118 – 11120; c) M. Kilian, H. Wadepohl, L. H. Gade, *Organometallics* **2008**, *27*, 524; d) M. F. Lappert, P. P. Power, *J. Chem. Soc. Dalton Trans.* **1985**, 51; e) M. Veith, A. Müller, L. Stahl, M. Nötzel, M. Jarczyk, V. Huch, *Inorg. Chem.* **1996**, *35*, 3848 – 3855; f) R. D. Adams, E. Trufan, *Organometallics* **2008**, *27*, 4108 – 4115; g) J. Martincová, R. Jambor, M. Schürmann, K. Jurkschat, J. Honzíček, F. A. Almeida Paz, *Organometallics* **2009**, *28*, 4778 – 4782; h) J.-Q. Wang, B. Wahl, T. F. Fässler, *Angew. Chem.* **2010**, *122*, 6742 – 6745; *Angew. Chem. Int. Ed.* **2010**, *49*, 6592 – 6595.

[7] C. Nickl, K. Eichele, D. Joosten, T. Langer, F. M. Schappacher, R. Pöttgen, U. Englert, L. Wesemann, *Angew. Chem.* **2011**, *123*, 5886 – 5889; *Angew. Chem. Int. Ed.* **2011**, *50*, 5766 – 5769.

[8] J. Henning, L. Wesemann, *Angew. Chem.* **2012**, *124*, 13041 – 13045; *Angew. Chem. Int. Ed.* **2012**, *51*, 12869 – 12873.

[9] a) M. M. Olmstead, R. S. Simons, P. P. Power, *J. Am. Chem. Soc.* **1997**, *119*, 11705 – 11706; b) R. S. Simons, L. Pu, M. M. Olmstead, P. P. Power, *Organometallics* **1997**, *16*, 1920 – 1925; c) H. Lei, J.-D. Guo, J. C. Fettinger, S. Nagase, P. P. Power, *Organometallics* **2011**, *30*, 6316 – 6322.

[10] See the Supporting Information.

[11] Crystal structure of compound **3** shows disorder in the solid state. For further details, see the Supporting information. CCDC 923361, 923362, and 923363 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[12] a) F. J. Brady, C. J. Cardin, D. J. Cardin, M. A. Convery, M. M. Devereux, G. A. Lawless, *J. Organomet. Chem.* **1991**, *421*, 199 – 203; b) H. Grützmacher, H. Pritzkow, *Angew. Chem.* **1991**, *103*, 976 – 978; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1017 – 1018; c) P. Alvarez-Bercedo, A. D. Bond, R. Haigh, A. D. Hopkins, G. T. Lawson, M. McPartlin, D. Moncrieff, M. E. Gonzalez Mosquera, J. M. Rawson, A. D. Woods, D. S. Wright, *Chem. Commun.* **2003**, 1288 – 1289; d) L. Baiget, H. Ranaivonjatovo, J. Escudié, H. Gornitzka, *J. Am. Chem. Soc.* **2004**, *126*, 11792 – 11793; e) S. Masamune, L. R. Sita, *J. Am. Chem. Soc.* **1985**, *107*, 6390 – 6391.

[13] N. W. Mitzel, K. Vojinović, R. Fröhlich, T. Foerster, H. E. Robertson, K. B. Borisenko, D. W. H. Rankin, *J. Am. Chem. Soc.* **2005**, *127*, 13705 – 13713.

[14] a) M. Driess, K. Merz, C. Monse, *Chem. Commun.* **2003**, 2608 – 2609; b) O. Fuhr, D. Fenske, *Z. Anorg. Allg. Chem.* **2004**, *630*, 244 – 246; c) B. P. Johnson, S. Almstätter, F. Dielmann, M. Bodensteiner, M. Scheer, *Z. Anorg. Allg. Chem.* **2010**, *636*, 1275 – 1285; d) K. Izod, J. Stewart, W. Clegg, R. W. Harrington, *Organometallics* **2010**, *29*, 108 – 116; e) M. Brym, M. D. Francis, G. Jin, C. Jones, D. P. Mills, A. Stasch, *Organometallics* **2006**, *25*, 4799 – 4807; f) M. Westerhausen, M. W. Oßberger, A. Keilbach, C. Gückel, H. Piotrowski, M. Suter, H. Nöth, *Z. Anorg. Allg. Chem.* **2003**, *629*, 2398 – 2407; g) M. Westerhausen, M. H. Digeser, H. Nöth, W. Ponikwar, T. Seifert, K. Polborn, *Inorg. Chem.* **1999**, *38*, 3207 – 3214; h) T. Řezníček, L. Dostál, A. Růžička, R. Jambor, *Eur. J. Inorg. Chem.* **2012**, 2983 – 2987.

[15] M. F. Lappert, W.-P. Leung, C. L. Raston, B. W. Skelton, A. H. White, *J. Chem. Soc. Dalton Trans.* **1992**, 775 – 785.

[16] M. J. M. Vlaar, A. W. Ehlers, F. J. J. de Kanter, M. Schakel, A. L. Spek, M. Lutz, N. Sigal, Y. Apeloig, K. Lammertsma, *Angew. Chem.* **2000**, *112*, 4296 – 4299; *Angew. Chem. Int. Ed.* **2000**, *39*, 4127 – 4130.

[17] J. C. Slootweg, F. J. J. de Kanter, M. Schakel, M. Lutz, A. L. Spek, S. I. Kozhushkov, A. de Meijere, K. Lammertsma, *Chem. Eur. J.* **2005**, *11*, 6982 – 6993.

[18] a) D. Duncan, E. G. Hope, K. Singh, A. M. Stuart, *Dalton Trans.* **2011**, *40*, 1998 – 2005; b) W. E. McEwen, C. E. Sullivan, R. O. Day, *Organometallics* **1983**, *2*, 420 – 425.

[19] B. E. Eichler, P. P. Power, *Inorg. Chem.* **2000**, *39*, 5444 – 5449.

[20] M. Driess, R. Janoschek, H. Pritzkow, S. Rell, U. Winkler, *Angew. Chem.* **1995**, *107*, 1746 – 1749; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1614 – 1616.

[21] U. Englich, K. Ruhlandt-Senge, F. Uhlig, *J. Organomet. Chem.* **2000**, *613*, 139 – 147.

[22] T. B. Grindley, R. D. Curtis, R. Thangarasa, R. E. Wasylishen, *Can. J. Chem.* **1990**, *68*, 2102 – 2110.

[23] a) E. Van Lenthe, E. J. Baerends, *J. Comput. Chem.* **2003**, *24*, 1142 – 1156; b) E. van Lenthe, A. Ehlers, E.-J. Baerends, *J. Chem. Phys.* **1999**, *110*, 8943 – 8953; c) G. te Velde, F. M. Bickelhaupt, E. J. Baerends, C. Fonseca Guerra, S. J. A. van Gisbergen, J. G. Snijders, T. Ziegler, *J. Comput. Chem.* **2001**, *22*, 931 – 967; d) J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1996**, *77*, 3865 – 3868; e) Y. Zhang, W. Yang, *Phys. Rev. Lett.* **1998**, *80*, 890 – 890; f) G. C. Fonseca, J. G. Snijders, G. te Velde, E. J. Baerends, *Theor. Chim. Acta* **1998**, *99*, 391 – 403; g) ADF2012, SCM, Theoretical Chemistry, Vrije Universiteit Amsterdam, www.scm.com, **2012**; h) NBO 5.0, Theoretical Chemistry Institute, University of Wisconsin, Madison, **2001**; i) J. I. Rodríguez, R. F. W. Bader, P. W. Ayers, C. Michel, A. W. Götz, C. Bo, *Chem. Phys. Lett.* **2009**, *472*, 149 – 152; j) S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.* **2010**, *132*, 154104 – 154119; k) S. Grimme, S. Ehrlich, L. Goerigk, *J. Comput. Chem.* **2011**, *32*, 1456 – 1465.

[24] a) H. Schumann, P. Jutzi, M. Schmidt, *Angew. Chem.* **1965**, *77*, 912 – 912; *Angew. Chem. Int. Ed. Engl.* **1965**, *4*, 869 – 869; b) T. N. Mitchell, H.-J. Belt, *J. Organomet. Chem.* **1990**, *386*, 167 – 176.

[25] a) T. N. Mitchell, H. Killing, R. Dicke, R. Wickenkamp, *J. Chem. Soc. Chem. Commun.* **1985**, 354 – 355; b) S.-K. Kang, Y.-H. Ha, B.-S. Ko, Y. Lim, J. Jung, *Angew. Chem.* **2002**, *114*, 353 – 355; *Angew. Chem. Int. Ed.* **2002**, *41*, 343 – 345; c) T. E. Nielsen, S. L. Quement, D. Tanner, *Synthesis* **2004**, 1381 – 1390; d) R. R. Singidi, A. M. Kutney, J. C. Gallucci, T. V. RajanBabu, *J. Am. Chem. Soc.* **2010**, *132*, 13078 – 13087.

[26] a) G. Märkl, D. Matthes, *Tetrahedron Lett.* **1976**, *17*, 2599 – 2602; b) M. Veith, V. Huch, *J. Organomet. Chem.* **1986**, *308*, 263 – 279.

[27] a) K. Tamao, M. Asahara, T. Saeki, A. Toshimitsu, *J. Organomet. Chem.* **2000**, *600*, 118 – 123; b) K. Tamao, M. Asahara, T. Saeki, S. Feng, A. Kawachi, A. Toshimitsu, *Chem. Lett.* **2000**, 660 – 661; c) A. Toshimitsu, T. Saeki, K. Tamao, *J. Am. Chem. Soc.* **2001**, *123*, 9210 – 9211.

