JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

COMMUNICATION

pubs.acs.org/JACS

Stabilization of the Heavy Methylene Analogues, GeH_2 and SnH_2, within the Coordination Sphere of a Transition Metal

S. M. Ibrahim Al-Rafia, Adam C. Malcolm, Sean K. Liew, Michael J. Ferguson, and Eric Rivard*

Department of Chemistry, University of Alberta, 11227 Saskatchewan Drive, Edmonton, Alberta, Canada T6G 2G2

Supporting Information

ABSTRACT: The heavy group 14 methylene analogues, EH_2, (E = Ge and Sn) have been stabilized via efficient methods, thus enabling the chemistry of these novel inorganic hydrides to be explored in depth.

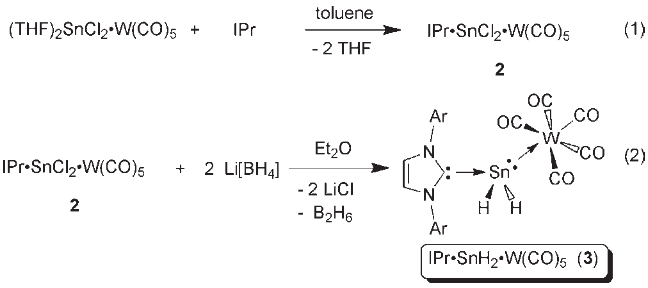
Chemical exploration of the heavy group 14 elements (E = Si−Pb) is largely motivated by a desire to compare their reactivity to that exhibited by the lightest congener, carbon.[1] In many instances, experimental verification of important bonding and reactivity patterns within this group are uncovered as a direct result of new advances in synthetic methodology. For example, the preparation of stable heavy element alkyne analogues, ArEEAr, relied upon the development of extremely bulky aryl ligands (Ar),[2] while the isolation of novel main group entities such as disilene :Si═Si:,[3a,3b] silanones ($R_2Si{=}O$)[3c] dihalosilylenes (:SiX_2),[3d,3e] and the dinitrogen analogues, P_2[3f] and PN,[3g] were recently achieved with the use of strongly donating N-heterocyclic carbenes (NHCs) as ligands.[4]

The highly reactive low oxidation state (+2) group 14 dihydrides, EH_2 (E = Si−Pb), have attracted considerable attention due to their potential role as intermediates in semiconductor syntheses[5] and metal-mediated bond-forming reactions;[6] moreover, these species represent direct chemical analogues to carbenes (CR_2).[7] The lightest member of this series, methylene, can be stabilized via $M{=}CH_2$ coordination (M = transition metal), and participates in many useful C−C bond-forming processes ranging from olefin metathesis[7b,7d] to carbonyl methylenations.[8] Due to a lack of suitable synthetic methods, illustrative coordination chemistry of the remaining heavy element parent dihydrides, EH_2, has been limited.[6b,9,10] In this communication we present efficient synthetic routes to stabilize the heavy group 14 hydrides, GeH_2 and SnH_2, in the presence of transition metals; this discovery should greatly facilitate the widespread study of these unusual main group hydrides.

We recently demonstrated that the highly reactive entity, germanium(II) dihydride, GeH_2, could be isolated at room temperature in the form of a carbene−borane bisadduct, $IPr\cdot GeH_2\cdot BH_3$ (**1**; IPr = $[(HCNAr')_2C:]$; Ar′ = 2,6-$^iPr_2C_6H_3$).[11,12] However attempts to isolate SnH_2 using our initial method were unsuccessful, presumably due to the instability of the tin hydride, $IPr\cdot SnH_2\cdot BH_3$.

On the basis of recent theoretical studies,[13] it was hoped that replacement of the Lewis acidic BH_3 group with the stronger electron acceptor $W(CO)_5$ would lead to the formation of more stable adducts, thus increasing the number of reactive species that could be intercepted and studied. To test the validity of this approach, we targeted the preparation of a stable complex of SnH_2. In general, tin(II) hydrides are highly unstable in the absence of very bulky anionic ligands,[14] and free stannylene, SnH_2, has only been identified in product mixtures Sn_xH_y via matrix isolation (<10 K).[10b] Starting from the readily available precursor, $(THF)_2SnCl_2\cdot W(CO)_5$,[15] the target hydride, $IPr\cdot SnH_2\cdot W(CO)_5$ (**3**), was synthesized in two high-yielding steps (Scheme 1).[16] Complex **3** represents the first stable transition-metal complex involving the heavy methylene congener, SnH_2, as a ligand.

Scheme 1. Synthesis of the Tin(II) Dihydride, $IPr\cdot SnH_2\cdot W(CO)_5$ 3



As shown in Figure 1, $IPr\cdot SnH_2\cdot W(CO)_5$ (**3**) features a central SnH_2 moiety flanked by electron-donating IPr and electron-accepting $W(CO)_5$ groups. The respective $Sn{-}C_{IPr}$ and Sn−W bond lengths are 2.230(6) and 2.7703(9) Å, and the latter distance is shorter than the $Sn{-}C_{IPr}$ distance in $IPr\cdot SnCl_2$ [2.341(8) Å],[11] suggesting the presence of a stronger $C_{IPr}{-}Sn$ donor/acceptor interaction in **3**. In addition, the $Sn{-}W{-}CO_{trans}$ unit is nearly linear with an observed Sn−W−C(1) angle of 176.1(2)°. The Sn−W distance in **3** is slightly elongated (∼0.05 Å) in relation to the dative Sn−W bond lengths found within the dianionic cluster $\{Sn_6[W(CO)_5]_6\}^{2-}$ and the tin(II) alkoxide adduct $\{[(^tBuO)_2Sn]_2\}\cdot W(CO)_5$.[17]

The presence of a stable tin(II) dihydride group in **3** was further supported by NMR spectroscopy. Namely, the SnH_2 moiety was detected at 5.56 ppm in the ^1H NMR spectrum, while a triplet at −309 ppm was observed in the proton-coupled ^{119}Sn NMR spectrum ($^1J_{Sn-H}$ = 1158 Hz) along with additional satellite resonances due to coupling with tungsten ($^1J_{Sn-W}$ = 828 Hz; see Figure S3a, Supporting Information).[18] The

Received: November 25, 2010
Published: December 28, 2010

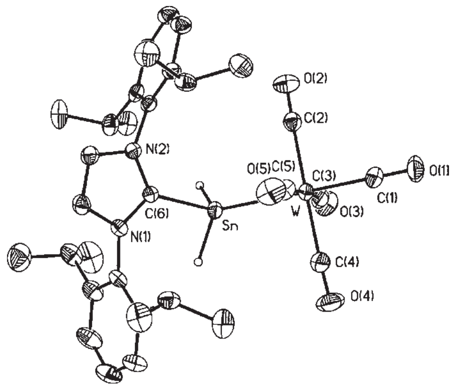
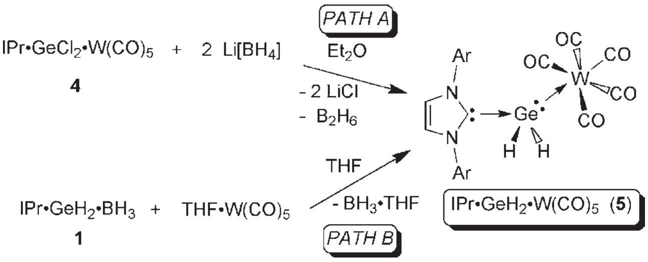


Figure 1. Thermal ellipsoid (30%) plot of IPr·SnH$_2$·W(CO)$_5$ (**3**). Carbon-bound hydrogen atoms and hexane solvate have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Sn—W 2.7703(9), Sn—C(6) 2.230(6), Sn—H 1.81(11) and 1.67(10), W—C(1) 1.961(7), W—C(2—5) 2.006(9) to 2.042(8); C(6)—Sn—W 120.06(14), Sn—W—C(1) 176.1(2), Sn—W—C(2—5) 84.6(2) to 91.7(2).

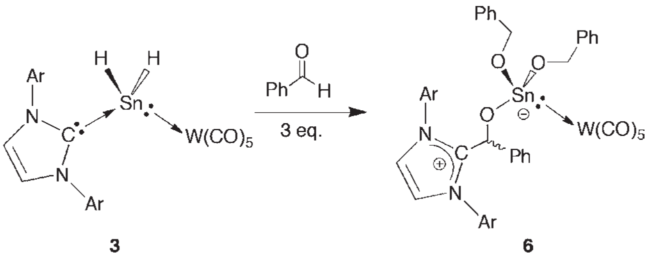
Scheme 2. Parallel Synthetic Routes to IPr·GeH$_2$·W(CO)$_5$ 5



deutero analogue IPr·SnD$_2$·W(CO)$_5$, **3D**, was also prepared and gave a diagnostic quintet resonance in the ^{119}Sn{^{1}H} NMR spectrum ($^1J_{\text{Sn-D}}$ = 179 Hz; Figure S3b, Supporting Information).[18] A weak Sn—H band was detected at 1786 cm^{-1} in the IR spectrum of **3**, and assignment of this band in the presence of proximal carbonyl vibrations was achieved using a combination of deuterium labeling and theoretical work.[18] For comparison, the Fe(II) stannane complex, [Fe{PPh(OEt)$_2$}$_4$(SnH$_3$)$_2$], exhibits a Sn—H vibration at 1755 cm^{-1},[19] while the terminal Sn—H bonds in the asymmetric tin hydride, Ar″SnSn(H)$_2$Ar″ (Ar″ = C$_6$H-2,6(C$_6$H$_2$-2,4,6-^{i}Pr$_3$)$_2$-3,5-^{i}Pr$_2$) were located at 1783 and 1810 cm^{-1}.[20] Congruent with the stabilizing influence of the IPr and W(CO)$_5$ groups in **3**, this complex is stable to 141 °C under a nitrogen atmosphere; however, complete decomposition of **3** occurred in hot toluene (100 °C, 1.5 days) to give an insoluble black precipitate, along with IPr, IPr·W(CO)$_5$, and the dihydroimidazole [(HCNAr)$_2$CH$_2$] as soluble products.[18]

The related germanium complex, IPr·GeH$_2$·W(CO)$_5$ (**5**), was prepared by two distinct routes as summarized in Scheme 2; the latter route, BH$_3$/W(CO)$_5$ metathesis, proceeded in a higher yield starting from the readily available carbene—borane bisadduct **1**.[11] The GeH$_2$ transfer chemistry outlined in Path B is noteworthy as it could represent a general method to install reactive GeH$_2$ groups onto a variety of metal centers.[6] Compound **5** has an overall structure that is analogous to the tin hydride analogue **3** (Figure S1, Supporting Information)[16,18] with Ge—C$_{\text{IPr}}$ and Ge—H distances [2.0151(18) and 1.42(3) Å] that are similar to the values found in IPr·GeH$_2$·BH$_3$, **1**.[11] The corresponding Ge—W distance in **5** [2.6318(2) Å] is significantly longer than the Ge—W distance [2.4289(8) Å] within the hydrogermylene, Cp*(CO)$_2$(H)W = Ge(H)[C(SiMe$_3$)$_3$],[21a] and is in the range typically observed for W—Ge single bonds (2.50−2.75 Å).[21b] The long W—Ge distance, in conjunction with our theoretical calculations,[18] support the lack of appreciable W—Ge π-bonding in **5**.

Scheme 3. Hydrostannylation/Insertion Reaction Involving Benzaldehyde and 3



The GeH$_2$ group in IPr·GeH$_2$·W(CO)$_5$ (**5**) was detected as a singlet in the ^{1}H NMR spectrum at 4.23 ppm, while the associated Ge—H vibration was located at 1981 cm^{-1} in the IR spectrum, and both values are in the range expected for low oxidation state Ge(II) hydrides;[22] for spectral comparison the deutero complex, IPr·GeD$_2$·W(CO)$_5$ **5D**, was also prepared.[18] Complex **5** is a colorless solid that is highly moisture sensitive; however, this species displays enhanced thermal stability relative to that of the tin analogue **3** and was found to be entirely stable for extended periods of time in hot toluene (100 °C, 16 h).

The bonding in **3** and **5** was further examined by theoretical methods (B3LYP/cc-pVDZ-pp)[18] using the model complexes, [(HCNMe)$_2$C]·EH$_2$·W(CO)$_5$ (E = Ge and Sn). In both cases, polar dative C$^{\delta-}$—E$^{\delta+}$ bonding was observed, while the W—E interactions were dominated by donation of a :EH$_2$ lone pair into empty W—C σ* orbitals to give linear E—W—C$_{\text{trans}}$ arrays (W—E Wiberg bond index = 0.42 and 0.43; for E = Ge and Sn, respectively). As anticipated on the basis of electronegativities,[23] the hydrogen atoms within the EH$_2$ units were calculated to be hydridic. This prediction was borne out in the observed reactivity of the Sn—H linkages in **3** with the electrophile, benzaldehyde. As shown in Scheme 3, the racemic insertion product **6** was isolated as the sole tin-containing species in 46% yield (Figure S2, Supporting Information).[16,18] Although the exact mechanism for this process is under investigation, the related hydrostannylation of ketones by Sn(II) hydrides has been reported;[24] despite the presence of stabilizing IPr and W(CO)$_5$ groups in **3**, functional chemistry involving the encapsulated SnH$_2$ unit is still possible.

In conclusion, the first transition-metal complexes of the heavy methylenes, GeH$_2$ and SnH$_2$, have been prepared. The facile and general nature of the reported donor/acceptor synthetic strategy should lead to a wider chemical exploration of reactive main group hydrides, especially within the context of controlled cluster and nanoparticle synthesis,[25] and the development of viable reduction pathways such as C—F bond hydrodefluorination.[26]

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Full experimental and theoretical details along with crystallographic data for **3**, **5** and **6** .

This material is available free of charge via the Internet at http://pubs.acs.org).

■ AUTHOR INFORMATION

Corresponding Author
erivard@ualberta.ca

■ ACKNOWLEDGMENT

We thank NSERC of Canada (E.R. and A.C.M), the Canada Foundation for Innovation and Alberta Innovates (E.R. and S.M.I.A) for financial support. We also thank Profs. Josef Takats and Mariusz Klobukowski, and Dr. Guibin Ma for providing valuable advice.

■ REFERENCES

(1) *The Chemistry of Organic Germanium, Tin and Lead*; Rappoport, Z., Ed.; Wiley VCH: New York, 2003; Vol. 2.

(2) (a) Pu, L.; Twamley, B.; Power, P. P. *J. Am. Chem. Soc.* **2000**, *122*, 3524. (b) Phillips, A. D.; Wright, R. J.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **2002**, *124*, 5930. (c) Stender, M.; Phillips, A. D.; Wright, R. J.; Power, P. P. *Angew. Chem., Int. Ed.* **2002**, *41*, 1785. (d) Wiberg, N.; Vasisht, S. K.; Fischer, G.; Mayer, P. *Z. Anorg. Allg. Chem.* **2004**, *630*, 1823. (e) Sekiguchi, A.; Kinjo, R.; Ichinohe, M. *Science* **2004**, *305*, 1755. (f) Sugiyama, Y.; Sasamori, T.; Hosoi, Y.; Furukawa, Y.; Takagi, N.; Nagase, S.; Tokitoh, N. *J. Am. Chem. Soc.* **2006**, *128*, 1023.

(3) (a) Wang, Y.; Robinson, G. H. *Chem. Commun.* **2009**, 5201. (b) Wang, Y.; Xie, Y.; Wei, P.; King, R. B.; Schaefer, H. F., III; Schleyer, P. v. R.; Robinson, R. H. *Science* **2008**, *321*, 1069, (c) Xiong, Y.; Yao, S.; Driess, M. *J. Am. Chem. Soc.* **2009**, *131*, 7562. (d) Ghadwal, R. S.; Roesky, H. W.; Merkel, S.; Henn, J.; Stalke, D. *Angew. Chem., Int. Ed.* **2009**, *48*, 5683. (e) Filippou, A. C.; Chernov, O.; Schnakenburg, G. *Angew. Chem., Int. Ed.* **2009**, *48*, 5687. (f) Kinjo, R.; Donnadieu, B.; Bertrand, G. *Angew. Chem., Int. Ed.* **2010**, *34*, 5930. (g) Back, O.; Donnadieu, B.; Parameswaran, P.; Frenking, G.; Bertrand, G. *Nature Chem.* **2010**, *2*, 369.

(4) (a) Arduengo, A. J., III; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1991**, *113*, 361. For examples of carbene-stabilization throughout the main group, see: (b) Wang, Y.; Quillian, B.; Wei, P.; Wannere, C. S.; Xie, P.; King, R. B.; Schaefer, H. F., III; Schleyer, P. v. R.; Robinson, G. H. *J. Am. Chem. Soc.* **2007**, *129*, 12412. (c) Masuda, J. D.; Schoeller, W. W.; Donnadieu, B.; Bertrand, G. *J. Am. Chem. Soc.* **2007**, *129*, 14180. (d) Quillian, B.; Wei, P.; Wannere, C. S.; Schleyer, P. v. R.; Robinson, G. H. *J. Am. Chem. Soc.* **2009**, *131*, 3168. (e) Dutton, J. L.; Ragogna, P. J. *Inorg. Chem.* **2009**, *48*, 1722. (f) Sidiropoulos, A.; Jones, C.; Stasch, A.; Klein, S.; Frenking, G. *Angew. Chem., Int. Ed.* **2009**, *48*, 9701. (g) Bonyhady, S. J.; Collis, D.; Frenking, G.; Holzmann, N.; Jones, C.; Stasch, A. *Nature Chem.* **2010**, *2*, 865.

(5) (a) Isobe, C.; Cho, H. −C.; Sewell, J. E. *Surf. Sci.* **1993**, *295*, 117. (b) Weerts, W. L. M.; de Croon, M. H. J. M.; Marin, G. B. *J. Electrochem. Soc.* **1998**, *145*, 1318.

(6) (a) Waterman, R.; Hayes, P. G.; Tilley, T. D. *Acc. Chem. Res.* **2007**, *40*, 712 and references therein. (b) Gusev, D. G.; Fontaine, F.-G.; Lough, A. J.; Zargarian, D. *Angew. Chem. Int. Ed.* **2003**, *42*, 216.

(7) (a) Fischer, E. O. *Adv. Organomet. Chem.* **1976**, *14*, 1. (b) Schrock, R. R. *Acc. Chem. Res.* **1979**, *12*, 98. (c) Bourissou, D.; Guerret, O.; Gabbaï, F. P.; Bertrand, G. *Chem. Rev.* **2000**, *100*, 39. (d) Grubbs, R. H, Ed. *Handbook of Metathesis*; Wiley-WCH: Weinheim, 2008. (e) Hahn, F. E.; Jahnke, M. C. *Angew. Chem., Int. Ed.* **2008**, *47*, 3122. (f) Diez-González, S.; Marion, N.; Nolan, S. P. *Chem. Rev.* **2009**, *109*, 3612. For the reviews on the chemistry of heavy divalent tetrelenes ($:ER_2$, E = Si−Pb), see: (g) Petz, W. *Chem. Rev.* **1986**, *86*, 1019. (h) Mizuhata, Y.; Sasamori, T.; Tokitoh, N. *Chem. Rev.* **2009**, *109*, 3479.

(8) (a) Tebbe, F. N.; Parshall, G. W.; Ovenall, D. W. *J. Am. Chem. Soc.* **1979**, *101*, 5074. (b) Schwab, P.; France, M. B.; Ziller, J. W.; Grubbs, R. H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2039. (c) Scott, J.; Mindiola, D. J. *Dalton Trans.* **2009**, 8463.

(9) (a) Smith, G. R.; Guillory, W. A. *J. Chem. Phys.* **1972**, *56*, 1423. (b) Wang, X.; Andrews, L.; Chertihin, G. V.; Souter, P. F. *J. Phys. Chem. A* **2002**, *106*, 6302. (c) Lemierre, V.; Chrostowska, A.; Dargelos, A.; Baylère, P.; Leigh, W. J.; Harrington, C. R. *Appl. Organometal. Chem.* **2004**, *18*, 676. (d) Smith, T. C.; Clouthier, D. J.; Sha, W.; Adam, A. G. *J. Chem. Phys.* **2000**, *113*, 9567.

(10) Theoretical studies predict singlet ground states for the heavy group 14 hydrides, EH_2, and a reduced propensity for $M = EH_2$ π-bonding, see: (a) Jacobsen, H.; Ziegler, T. *Inorg. Chem.* **1996**, *35*, 775. (b) Frison, G.; Sevin, A. *J. Chem. Soc., Perkin Trans. 2* **2002**, 1692. (c) Lein, M.; Szabó, A.; Kovács, A.; Frenking, G. *Faraday Discuss.* **2003**, *124*, 365.

(11) Thimer, K. C.; Al-Rafia, S. M. I.; Ferguson, M. J.; McDonald, R.; Rivard, E. *Chem. Commun.* **2009**, 7119.

(12) For examples of donor/acceptor stabilization, see: (a) Burford, N.; Cameron, T. S.; LeBlanc, D. J.; Losier, P.; Sereda, S.; Wu, G. *Organometallics* **1997**, *16*, 4712. (b) Vogel, U.; Timoshkin, A. Y.; Scheer, M. *Angew. Chem., Int. Ed.* **2001**, *40*, 4409. (c) Rupar, P. A.; Jennings, M. C.; Ragogna, P. J.; Baines, K. M. *Organometallics* **2007**, *26*, 4109. (d) Li, J.; Merkel, S.; Henn, J.; Meindl, K.; Doring, A.; Roesky, H. W.; Ghadwal, R. S.; Stalke, D. *Inorg. Chem.* **2010**, *49*, 775.

(13) Krapp, A.; Frenking, G. *J. Am. Chem. Soc.* **2008**, *49*, 16646.

(14) (a) Eichler, B. E.; Power, P. P. *J. Am. Chem. Soc.* **2000**, *122*, 8785. (b) Pineda, L. W.; Jancik, V.; Starke, K.; Oswald, R. B.; Roesky, H. W. *Angew. Chem., Int. Ed.* **2006**, *45*, 2602.

(15) Balch, A. L.; Oram, D. E. *Organometallics* **1988**, *7*, 155.

(16) Crystallographic data for **3**, **5**, and **6**: recorded at 173 K with Mo Kα radiation ($\lambda = 0.71073$): **3·(0.25 hexane)** $a = 14.330(6)$ Å, $b = 19.457(8)$ Å, $c = 26.718(10)$ Å, $\alpha = \beta = \gamma = 90°$, orthorhombic, space group *Pbca*, $Z = 8$, $R1 = 0.0446$ for 8542 ($I > 2\sigma(I)$) data, $wR2$ (all data) = 0.1600; **5·THF** $a = 14.6626(5)$ Å, $b = 19.5017(6)$ Å, $c = 26.3383(8)$ Å, $\alpha = \beta = \gamma = 90°$, orthorhombic, space group *Pbca*, $Z = 8$, $R1 = 0.0175$ for 8727 ($I > 2\sigma(I)$) data, $wR2$ (all data) = 0.0474; **6·Et_2O** $a = 17.910(4)$ Å , $b = 13.236(3)$Å, $c = 23.515(5)$ Å, $\alpha = \beta = \gamma = 90°$, orthorhombic, space group $Pna2_1$, $Z = 4$, $R1 = 0.0227$ for 12822 ($I > 2\sigma(I)$) data, $wR2$ (all data) = 0.0515. CCDC-788842 (**3**), CCDC-788843 (**5**), CCDC-804481 (**6**) 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.

(17) (a) Renner, G.; Kircher, P.; Huttner, G.; Rutsch, P.; Heinze, K. *Eur. J. Inorg. Chem.* **2001**, 973. (b) Veith, M.; Ehses, M.; Huch, V. *New. J. Chem.* **2005**, *29*, 154.

(18) See the Supporting Information for more details.

(19) Albertin, G.; Antoniutti, S.; Castro, J. *Organometallics* **2010**, *29*, 3808.

(20) Peng, Y.; Brynda, M.; Ellis, B. D.; Fettinger, J. C.; Rivard, E.; Power, P. P. *Chem. Commun.* **2008**, 6042.

(21) (a) Hashimoto, H.; Tsubota, T.; Fukuda, T.; Tobita, H. *Chem. Lett.* **2009**, *38*, 1196. (b) Hashimoto, H.; Fukuda, T.; Tobita, H. *New. J. Chem.* **2010**, *34*, 1723.

(22) (a) Ding, Y.; Hao, H.; Roesky, H. W.; Noltemeyer, M.; Schmidt, H.-G. *Organometallics* **2001**, *20*, 4806. (b) Spikes, G. H.; Fettinger, J. C.; Power, P. P. *J. Am. Chem. Soc.* **2005**, *127*, 12232.

(23) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed., Cornell University Press: Ithaca, NY, 1960.

(24) Jana, A.; Roesky, H. W.; Schulzke, C. *Inorg. Chem.* **2009**, *48*, 9543.

(25) (a) Brynda, M.; Herber, R.; Hitchcock, P. B.; Lappert, M. F.; Nowik, I.; Power, P. P.; Protchenko, A. V.; Ruzicka, A.; Steiner, J. *Angew. Chem., Int. Ed.* **2006**, *45*, 4333. (b) Pacher, A.; Schrenk, C.; Schnepf, A. *J. Organomet. Chem.* **2010**, *695*, 941.

(26) (a) Douvris, C.; Ozerov, O. V. *Science* **2008**, *321*, 1188. (b) Jana, A.; Samuel, P. P.; Tavcar, G.; Roesky, H. W.; Schulke, C. *J. Am. Chem. Soc.* **2010**, *132*, 10164.