# Synthesis and Hydrogenation of Heavy Homologues of Rhodium Carbynes: [(Me₃P)₂(Ph₃P)Rh≡E-Ar*] (E = Sn, Pb)

*Max Widemann, Klaus Eichele, Hartmut Schubert, Christian P. Sindlinger, Steffen Klenner, Rainer Pöttgen, and Lars Wesemann**

*Abstract: Tetrylidynes [(Me₃P)₂(Ph₃P)Rh≡SnAr*] (10) and [(Me₃P)₂(Ph₃P)Rh≡PbAr*] (11) are accessed for the first time via dehydrogenation of dihydrides [(Ph₃P)₂RhH₂SnAr*] (3) and [(Ph₃P)₂RhH₂PbAr*] (7) (Ar* = 2,6-Trip₂C₆H₃, Trip = 2,4,6-triisopropylphenyl), respectively. Tin dihydride 3 was either synthesized in reaction of the dihydridostannate [Ar*SnH₂]⁻ with [(Ph₃P)₃RhCl] or via reaction between hydrides [(Ph₃P)₃RhH] and ½[(Ar*SnH)₂]. Homologous lead hydride [(Ph₃P)₂RhH₂PbAr*] (7) was synthesized analogously from [(Ph₃P)₃RhH] and ½[(Ar*PbH)₂]. Abstraction of hydrogen from 3 and 7 supported by styrene and trimethylphosphine addition yields tetrylidynes 10 and 11. Stannylidyne 10 was also characterized by ¹¹⁹Sn Mössbauer spectroscopy. Hydrogenation of the triple bonds at room temperature with excess H₂ gives the cis-dihydride [(Me₃P)₂-(Ph₃P)RhH₂PbAr*] (12) and the tetrahydride [(Me₃P)₂-(Ph₃P)RhH₂SnH₂Ar*] (14). Complex 14 eliminates spontaneously one equivalent of hydrogen at room temperature to give the dihydride [(Me₃P)₂(Ph₃P)RhH₂SnAr*] (13). Hydrogen addition and elimination at stannylene tin between complexes 13 and 14 is a reversible reaction at room temperature.*

## Introduction

The first example for a synthesis of a higher homologue of transition metal carbynes Cp(CO)₂Mo≡Ge-Ar′ was reported

[*] M. Widemann, Dr. K. Eichele, Dr. H. Schubert, Prof. Dr. L. Wesemann
Institut für Anorganische Chemie,
Eberhard Karls Universität Tübingen
Auf der Morgenstelle 18, 72076 Tübingen (Germany)
E-mail: lars.wesemann@uni-tuebingen.de

Dr. C. P. Sindlinger
Institut für Anorganische Chemie,
Georg-August Universität Göttingen
Tammannstrasse 4, 37077 Göttingen (Germany)

S. Klenner, Prof. Dr. R. Pöttgen
Institut für Anorganische und Analytische Chemie,
Universität Münster
Corrensstrasse 30, 48149 Münster (Germany)

Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under:
https://doi.org/10.1002/anie.202015725.

by Power and co-workers in 1996.[1] The nucleophilic anion [CpMo(CO)₃]⁻ was reacted with the electrophile Ar′GeCl at 50°C in THF (Ar′ = 2,6-Mes₂C₆H₃-, Mes = 2,4,6-trimethylphenyl). After elimination of a CO ligand the germylyne complex [Cp(CO)₂Mo≡GeAr′] was isolated as red crystals.[1] Following this procedure the analogous chromium and tungsten complexes featuring a triple bond with germanium were isolated. However, in these cases the stepwise formation of the germylyne was observed with the metalloorganogermylene [Cp(CO)₃M-GeAr*] (M = Cr, W) (Ar* = 2,6-Trip₂C₆H₃, Trip = 2,4,6-triisopropylphenyl) being an intermediate.[2] Filippou et al. reported a variety of compounds exhibiting a triple bond between a transition metal (M = Nb, Cr, Mo, W, Mn, Re, Fe, Ni, Pt) and a heavy element of the Group 14 (E = Si, Ge, Sn, Pb).[3] Three synthetic strategies for the synthesis of these carbyne homologues were reported: nucleophilic substitution at organotetrel halides by nucleophilic transition metal complexes;[1,2,3c,i] elimination of N₂/PMe₃ ligands and oxidative addition of organotetrel halides at transition metal complexes[3f,g,k–q] and formation of haloylidene complexes followed by halide abstraction.[3d,e] Hashimoto, Tobita and co-workers have synthesized tungsten germylyne and tungsten silylyne complexes by dehydrogenation using mesityl isocyanate, nitriles or stepwise proton and hydride abstraction with the hydrido hydrogermylene and hydrido hydrosilylene as starting materials.[4] Tilley and co-workers reported cationic silylyne complexes of molybdenum and osmium.[5] An amino germylyne complex of molybdenum was published by Jones et al.[6] Most recently Power et al. presented with the metathetical exchange between metal-metal triple bonds of transition metal molybdenum and main group metals Ge, Sn and Pb a very elegant synthetic method for the synthesis of carbyne homologues (Cp(CO)₂Mo≡E-Ar*, E = Ge, Sn, Pb).[7] Known homologues of transition metal carbyne complexes and new entries reported in this contribution are summarized in Figure 1.[8]

| V | Cr (Si, Ge) | Mn (Sn) | Fe (Ge, Sn) | Co | Ni (Si) |
|---|---|---|---|---|---|
| Nb (Si - Sn) | Mo (Si - Pb) | Tc | Ru | Rh (Sn, Pb) | Pd |
| Ta | W (Si - Pb) | Re (Ge) | Os (Si) | Ir | Pt (Si) |

known compounds          this work

**Figure 1.** Known homologues of transition metal carbyne complexes [L$_n$M≡E-R] and new entries reported in this contribution.[8]
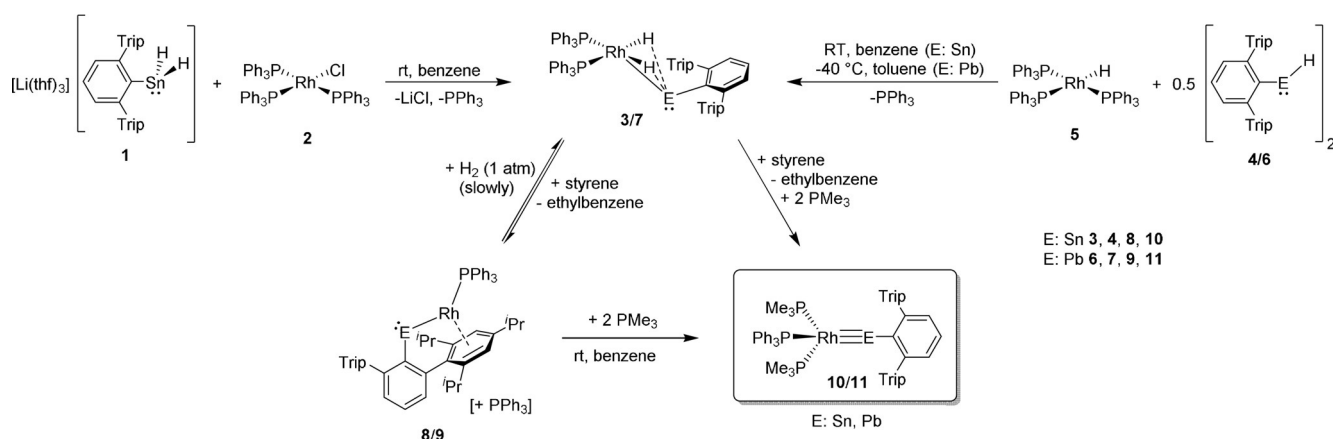
**Scheme 1.** Synthesis of hydride bridged rhodium tin and lead complexes **3**, **7**; Elimination of hydrogen and formation of the stannylidyne **10** and plumbylidyne **11**. [Trip = 2,4,6-tri(isopropyl)phenyl].

We are interested in hydrogen transfer of heavy group 14 elements and studied the reactivity of organoelement trihydrides of germanium and tin.[9] The base induced reductive elimination of hydrogen was investigated.[9a–c,10] Chemistry of cationic hydrides was explored after hydride abstraction from organoelement trihydrides.[9d,11] Deprotonation of trihydrides yields the highly reactive organoelement dihydrido anions of germanium and tin.[9e,f] Herein we report the use of anions [Ar*EH$_2$]$^-$ (E = Ge, Sn) and lead hydride [(Ar*Pb-H)$_2$] to synthesize rhodium element dihydrides [(Ph$_3$P)$_n$RhH$_2$EAr*] of Ge (n = 1) (Scheme 5), Sn and Pb (n = 2) (Scheme 1).[12] The tin and lead dihydride complexes were dehydrogenated in reaction with styrene to yield after PMe$_3$ addition the first examples for triple bonds between rhodium and tin or lead Rh≡E (E = Sn, Pb). Hydrogenation of the triple bonds Rh≡E is also presented.

## Results and Discussion

To further evaluate the nucleophilicity of the aryldihydridostannate (**1**) we explored the reactivity of this anion in reaction with tris(triphenylphosphine)rhodium chloride **2** (Scheme 1). In the product complex, a triphenylphosphine ligand and the chloride substituent at the rhodium atom were displaced by the dihydridostannate nucleophile. The hydride substituents were transferred from the tin atom to the rhodium and exhibit a contact to the tin atom. Following an alternative protocol, the Rh coordination compound **3** was synthesized in high yield (93%) reacting the low valent organotin hydride [(Ar*SnH)$_2$] **4** with rhodium hydride [(Ph$_3$P)$_3$RhH] **5** (Scheme 1). Since a lead homologue of stannate **1** is unknown the rhodium hydride route (Scheme 1) was used to synthesize a rhodium-lead complex. Due to thermal instability of the low valent lead hydride [(Ar*PbH)$_2$] **6** the reaction with the rhodium hydride was carried out at −40°C. The rhodium-lead dihydride **7** forms the same structural motif as the Rh-Sn compound **3**. However, this Rh-Pb complex decomposes at room temperature and must be stored below 0°C.

The hydride-bridged complexes **3** and **7** were characterized by NMR spectroscopy, elemental analyses and crystal structure determination. The molecular structure of **7** is shown in Figure 2. Details of the structure analyses and an ORTEP of the essentially isostructural molecular structure of **3** were placed in the Supporting Information.

In coordination compounds **3** and **7** two triphenylphosphine and two hydride ligands are square planar cis coordinated at rhodium with slightly shorter interatomic Rh-P and Rh-H distances in the tin case. The Rh-P distances [2.2741(7)–2.2897(9) Å] lie in the range of square planar coordinated (Ph$_3$P)$_2$Rh(I) fragments stabilized by *closo*-borates via BH-interaction or Cp$_2$WH$_2$ hydride coordination [2.2192(6)–2.2391(6) Å].[13] The hydride positions in **3** and **7** were localized using X-ray difference Fourier maps and refined with distance restraints. Budzelaar et al. studied the oxidative
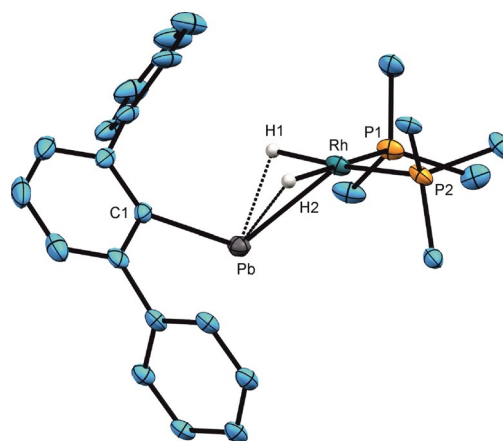


**Figure 2.** ORTEP of the molecular structure of **7**. Ellipsoids at 50% probability. $^i$Pr groups, phenyl rings of the PPh$_3$ ligand except the ipso-C atoms and CH hydrogen atoms are omitted for clarity. Interatomic distances in [Å] and angles [deg]: Pb–Rh 2.6361(3), Pb–H1 2.37(5), Pb–H2 2.15(4), Pb–C1 2.327(3), Rh–H1 1.71(5), Rh–H2 1.65(4), Rh–P1 2.2897(9), Rh–P2 2.2824(8), C1-Pb-Rh 114.0(1), C1-Pb-H2 97.6(12), C1-Pb-H1 83.0(12), H2-Pb-H1 63.0(17), P1-Rh-P2 104.17(3), P2-Rh-H2 82.1(15), P1-Rh-H2 171.1(15), P2-Rh-H1 171.0(17), P1-Rh-H1 84.3(17), H2-Rh-H1 90(2), Pb-Rh-H2 54.4(15), Pb-Rh-H1 62.0(17), Rh-Pb-H2 38.7(11), Rh-Pb-H1 39.4(12).[36]

addition of H-Sn$^n$Bu$_3$ at β-diiminate complexes of rhodium and found a Rh-Sn distance of 2.563(1) Å, Sn-H 2.27(4) Å and Rh-H 1.47(4) Å.[14] To compare, in complex **3** the observed Rh-Sn distance is 2.5262(3) Å, Sn-H 2.11(4) Å and Rh-H 1.59(4) Å long. In the lead case the Rh-Pb distance of 2.6361(3) Å can be compared with an example of PbCl$_2$ coordination [2.7561(7) Å] or plumbole coordination at rhodium [2.7601(5), 2.7712(5) Å].[15] The $^1$H NMR signals of the hydride substituents were found for **3** at −4.13 ppm ($J_{Rh-H}$ = 22 Hz, $J_{Sn-H}$ = 220 Hz) and for **7** at 3.62 ppm ($J_{Rh-H}$ = 21 Hz, $J_{Pb-H}$ = 124 Hz). The high frequency shift of the Rh-H signal of the lead derivative **7** can be explained with the influence of the heavy atom lead on the chemical shift of light atoms. The relativistic effects on NMR chemical shifts by spin-orbit coupling has been investigated by quantum chemical methods.[16] The $^{119}$Sn NMR signal of **3** found at 1728 ppm points toward an aryl rhodostannylene. Metallostannylenes of metals Cr, Mo and W exhibit signals at high frequencies in the range of 2116–3318 ppm.[17] The shift to lower frequency of compound **3** (1728 ppm) might be interpreted as an indicator for an increased coordination number caused by hydride Sn contacts. The same reasoning can be applied in the case of the $^{207}$Pb NMR signal of derivative **7**: the signal was found at 8195 ppm and should be compared with metalloplumbylenes investigated by Power's group [Cr, Mo, W: 9374–9563 ppm].[18]

Using the nucleophilic substitution procedure (Scheme 1) as the method to synthesize complex **3** two Sn−H bonds were activated, and the hydrides transferred to rhodium (for the transfer back to tin vide infra, Scheme 4). This reaction should be compared with the Ga-H activation studied by Aldridge and co-workers at rhodium (I).[19] The 1,2-hydrogen migration from tin, germanium and silicon to transition metals (Ru, Os, Mo, Hf) was studied intensively by Tilley and co-workers.[20] They discussed the equilibrium of hydride transfer between hydrido-metallostannylene (HM-Sn-R) and hydridostannylene (M–SnHR) with tin favouring energetically the hydridometallostannylene.[20a]

Examples for heavy Group 14 element metal dihydride complexes like [(Ph$_3$P)$_2$RhH$_2$EAr*] (E = Sn **3**; E = Pb **7**) are precedented in the literature for the following element combinations: Ge-Ru,[20e,h] Mo,[20i] W,[4d] Rh;[14] Sn-Os,[20g] Ru,[20a,b] Hf,[20f] Rh;[14] Pb-Ru.[20a]

The rhodium dihydride **3** reacts at room temperature with deuterium to give the dideuteride complex (see Supporting Information, Figures S11, S12). Both dihydrides **3** and **7** show reductive elimination of hydrogen and formation of the ylene complexes Ar*E-Rh(PPh$_3$) [E = Sn (**8**), E = Pb (**9**)] upon storage in solution at rt. However, in the tin case this hydrogen elimination is a very slow reaction and the lead compound also exhibits decomposition and formation of Ar*H. To selectively synthesize these ylene coordination compounds transfer of hydrogen from **3** and **7** to styrene was investigated (Scheme 1). Whereas the tin hydride **3** reacts overnight completely with styrene the lead hydride **7** shows the higher reactivity and the transfer is finished after 2 h. Both complexes **8** and **9** could be characterized as a mixture with PPh$_3$ which could not be separated from the rhodium complexes. Due to coordination of the rhodium atom at

a phenyl moiety of the terphenyl substituent in compounds **8** and **9** double sets of $^1$H and $^{13}$C NMR signals were found for the trip-substituents of the terphenyl group. This type of terphenyl-rhodium coordination is already known in the literature.[21] Both heteroelement NMR signals were found at high frequencies ($^{119}$Sn NMR **8**, 3112 ppm; $^{207}$Pb NMR **9**, 11269 ppm) in comparison to known organometallostannylenes or plumbylenes.[7,17,18,22] Cationic complex [Cp*W-(CO)$_3$Sn(NHC)][Al(OC(CF$_3$)$_3$)$_4$] exhibits a $^{119}$Sn NMR signal at very high frequency (3318 ppm).[17b]

In the tin case besides hydrogen transfer to styrene coordination of styrene was ascertained in solution with high concentrations of styrene (see Supporting Information for data of styrene complexes). Furthermore, in reaction with hydrogen and PPh$_3$ the stannylene complex **8** was transferred back to the hydride complex **3**. However, this oxidative addition of H$_2$ proceeds very slowly (Scheme 1).

To further investigate the hydrogen transfer products, reactions with trimethylphosphine were studied. Remarkably, as products of PMe$_3$ coordination in both cases the first examples for triple bond formation between rhodium and heavy Group 14 elements Sn and Pb were found (Scheme 1).

Both tetrylidyne complexes were crystallized from hexane at −40 °C as black-brown crystals in moderate yield (**10**, 61 %; **11**, 46 %). The molecular structure in the solid state was determined in both cases by single crystal X-ray diffraction (Figures 3 and 4).

Both Rh≡E (E = Sn 2.3856(2), E = Pb 2.4530(2) Å) bond lengths are by far the shortest bonds between these elements (CCDC search). The angles at tin or lead are close to linearity [Sn 174.6(1), Pb 174.2(1)°]. In both cases **10** and **11** the



**Figure 3.** ORTEP of the molecular structure of **10**. Ellipsoids at 50% probability. Hydrogen atoms are omitted for clarity. Interatomic distances in [Å] and angles [deg]: Rh–Sn 2.3856(2), Sn–C1 2.197(2), Rh–P1 2.2714(6), Rh–P2 2.2630(6), Rh–P3 2.2805(6), C1-Sn-Rh 174.6-(1), P2-Rh-P1 106.9(1), P2-Rh-P3 104.3(1), P1-Rh-P3 106.3(1), P2-Rh-Sn 108.7(2), P1-Rh-Sn 117.5(2), P3-Rh-Sn 112.3(2).[36]
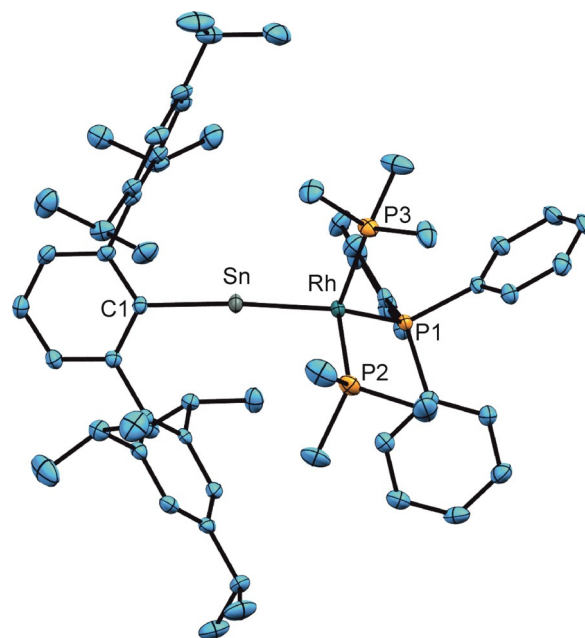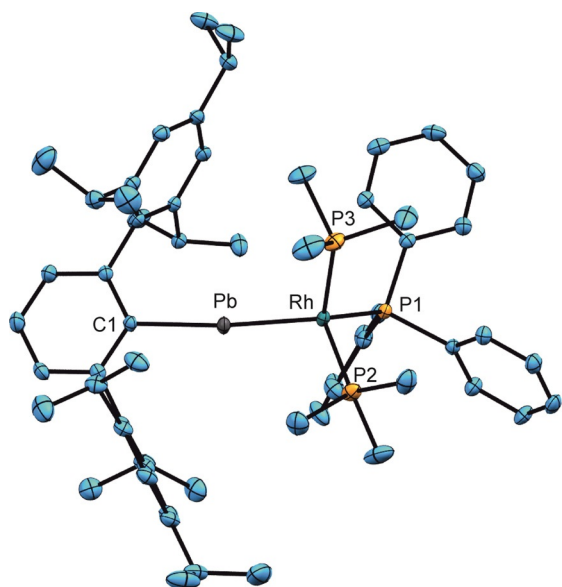
**Figure 4.** ORTEP of the molecular structure of **11**. Ellipsoids at 50% probability. Hydrogen atoms are omitted for clarity. Interatomic distances in [Å] and angles [deg]: Rh–Pb 2.4530(2), C1–Pb 2.2758(18), P3–Rh 2.2792(6), P1–Rh 2.2646(5), Rh–P2 2.2598(6), C1-Pb-Rh 174.2-(1), P2-Rh-P1 107.4(1), P2-Rh-P3 105.0(1), P1-Rh-P3 106.9(2), P2-Rh-Pb 108.2(2), P1-Rh-Pb 116.7(1), P3-Rh-Pb 111.9(2).[36]



**Figure 5.** $^{119}Sn$ Mössbauer spectrum of complex **10**. The green ($\delta = 0.54(2)$ mm s$^{-1}$, 6(1) %) and ocher ($\delta = 3.73(4)$ mm s$^{-1}$, 5(1) %) sub-signals correspond to minor Sn$^{IV}$ and Sn$^{II}$ impurity phases.

rhodium atom is nearly tetrahedrally coordinated by the three phosphines and the Group 14 ligand. The Group 14 elements show signals in the $^{119}Sn$ and $^{207}Pb$ NMR spectra at 1149 ppm (**10**: ddt, $^1J_{119Sn-103Rh} = 762$ Hz, $^2J_{119Sn-31P} = 294$ Hz, $^2J_{119Sn-31P} = 185$ Hz) and 5729 ppm (**11**: d, $^1J_{207Pb-103Rh} = 1050$ Hz). The chemical shifts of the tetrylidynes lie in the range of complexes featuring triple bonds with molybdenum Mo≡E (Sn: 1021 ppm, Pb 9660 ppm) or niobium Nb≡Sn 829.7 ppm.[3c,7] In the $^{13}C\{^1H\}$ NMR spectra the signals for the ipso carbon atom connected at tin or lead exhibit the signal at highest frequency (Sn: 188.0 ppm, Pb 274.7 ppm). The shift to high frequencies of the plumbylidyne can be compared with the plumbylidynes published by Filippou et al. exhibiting signals at 280.6, 279.1, 278.7 ppm.[3l,m] The shift of the $^{13}C$ NMR signals to high frequencies can be rationalized by the influence of the heavy atom lead on the chemical shift of the neighbouring atom.[16]

Probing the electronic structure including NBO analyses suggests the E-Rh bonding to be primarily composed of two π-type bonds that constitute from filled Rh d-orbitals donating into a set of empty p-orbitals at the tetrel element. NBO analyses further suggest that the σ-interactions stem from a strongly E-located near pure s-orbital pair of electrons that, according to second order perturbation analysis strongly donates into an empty Rh 5s-orbital. The extent of this donation is significantly stronger for Sn (162 kcal mol$^{-1}$) than for Pb (108 kcal mol$^{-1}$). An only partial contribution of a triple-bond Lewis structure description is in line with Löwdin bond indices for E-Rh pairs of ca. 2($\pm$0.1). (See Supporting Information for further information)

In the case of the stannylidyne complexes of molybdenum and tungsten Mössbauer spectroscopic studies were carried
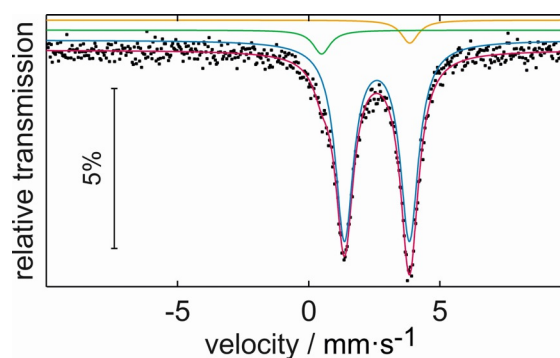
out.[23] A sample of the rhodium stannylidyne **10** was also investigated by $^{119}Sn$ Mössbauer spectroscopy to get further insight into the oxidation state of the tin atom. In Figure 5 the $^{119}Sn$ Mössbauer spectrum of compound **10** is presented together with a simulation ($\delta = 2.63(1)$ mm s$^{-1}$, $\Delta E_Q = 2.47$-(1) mm s$^{-1}$, $\Gamma = 0.82(1)$ mm s$^{-1}$). The isomer shift found for **10** and the quadrupole splitting are close to the values found for stannylidyne complexes of molybdenum and tungsten ($\delta$: 2.38–2.50 mm s$^{-1}$; $\Delta E_Q$: 1.81–2.82 mm s$^{-1}$). Furthermore, the isomer shift of distannyne (Ar*Sn≡SnAr*, $\delta$: 2.69, $\Delta E_Q$: 3.73) lies also in this range, which was interpreted as tin in oxidation state (II).[23,24] The differences in the quadrupole splitting can be attributed to the varying geometry at the transition metal since in all examples the tin atoms are further substituted by a terphenyl substituent. The largest $\Delta E_Q$ points toward a less symmetrical substituent on the transition metal.[23,24] The anisotropy of the tin atom was further investigated by $^{119}Sn$ CP/MAS NMR spectroscopy (see in the Supporting Information Figure S51).

Since the presented [Rh]≡Sn-Ar* and [Rh]≡Pb-Ar* complexes were synthesized in a reductive elimination sequence of hydrogen (Scheme 1) the reactivity of these compounds **10** and **11** towards hydrogen was of interest and the results are shown in Scheme 2.

Both compounds show an addition reaction of hydrogen at rt. The stannylidyne **10** adds two equivalents of hydrogen whereas the plumbylidyne **11** reacts with one equivalent. Hydrogenation of higher homologues of transition metal carbynes is, to the best of our knowledge, so far an unknown reaction.[8,25] Power and co-workers studied the reactivity of unique heavy element alkyne homologues of germanium and tin.[26] Digermyne [Ar†Ge≡GeAr†] exhibits a hydrogenation at rt to give a mixture of dihydride [Ar†GeH=GeHAr†] and tetrahydride [Ar†GeH₂-GeH₂Ar†] (Ar† = C₆H₃-2,6(C₆H₃-2,6-iPr₂)₂),[27] whereas the distannyne [Ar†Sn≡SnAr†] shows a reversible addition and elimination of one equivalent of hydrogen at 80°C.[28] The addition of hydrogen at amido-distannyne and amido-digermyne was presented by Jones et al.[29]

Based on NMR spectroscopy in the process of the formation of tetrahydride **14**, the addition product of one equivalent hydrogen complex **13** is an intermediate (Scheme 2), which could also be synthesized by reacting the
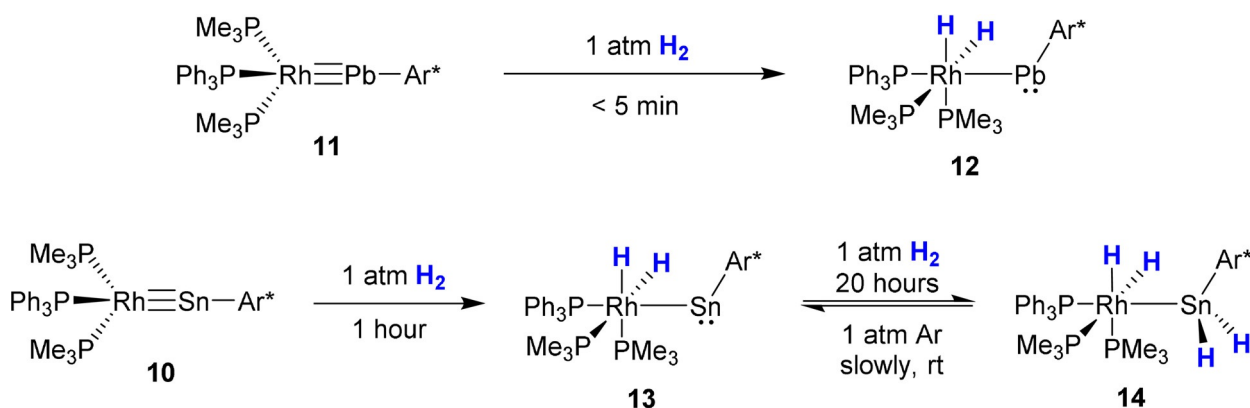
**Scheme 2.** Hydrogenation of the rhodium tetrylidyne complexes **10** and **11** at rt.
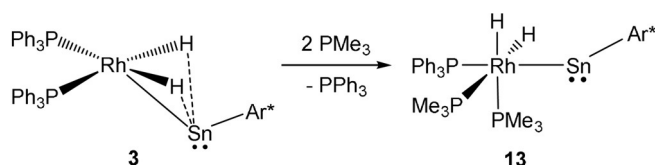


**Scheme 3.** Selective synthesis of the intermediate dihydride **13**.

dihydride complex **3** with two equivalents of trimethylphosphine (Scheme 3).

The tetrahydride **14** shows a spontaneous reductive elimination of hydrogen at rt. However, this elimination is a slow reaction and by NMR spectroscopy the reversibility of the hydrogen elimination and addition (**13** ⇌ **14**) was probed and confirmed experimentally (Scheme 2, Supporting Information Figures S7–10). Hydrogenation of the metallostannylene **13** can be compared with the addition of hydrogen at a metallosilylene or germylene.[3d, 30] The described reversible hydrogenation is a rare case for a stannylene exhibiting a reversible room temperature hydrogenation reaction. Reversible addition and elimination of hydrogen is known for the well-studied distannyne. The equilibrium between hydrogen, distannyne and low valent dihydride was studied at 80 °C.[28] Pápai, Ashley and co-workers investigated the base induced reversible hydrogenation of diorganostannylene [Sn-{CH(SiMe$_3$)$_2$}$_2$]. Hydrogenation was observed at 4 bar H$_2$ in the presence of Et$_3$N acting as a catalyst and the elimination of H$_2$ was demonstrated at room temperature in reaction of the dihydride with DBU.[31] Bis(boryl) substituted stannylene was shown to add hydrogen at rt by Aldridge and co-workers.[32]

Hydrogenation products **12**, **13** and **14** were characterized by single crystal X-ray diffraction and NMR spectroscopy. In Figures 6 and 7 an ORTEP of the molecular structures of **12** and **14** is presented (see Supporting Information for an ORTEP of the molecular structure of **13**).

The Rh−Sn bond length of 2.5797(1) Å found in **14** is much longer than the triple bond (Table 1) and can be compared with single bonds between these elements.[15,33] The signal for the RhH$_2$ moiety was found in the $^1$H NMR spectrum at −11.24 ppm and the SnH$_2$ group shows a signal at 4.31 ppm. Both ranging in the chemical shift range typical of Rh-H and Sn-H signals.[9b,c,34] The RhH$_2$ unit of **13** shows
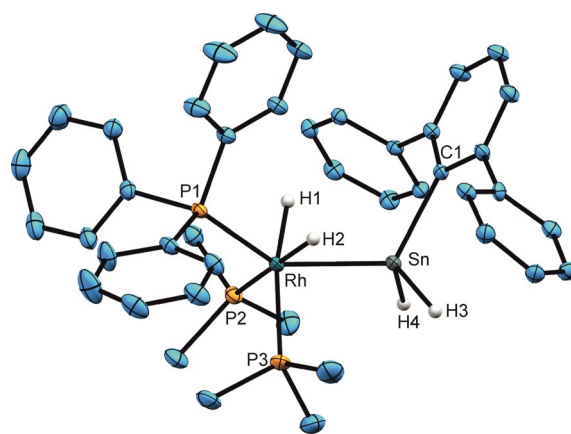


**Figure 6.** ORTEP of the molecular structure of **14**. Ellipsoids at 50% probability. Hydrogen atoms and $^i$Pr groups are omitted for clarity. Only Rh-H and Sn-H hydride atoms are shown. Interatomic distances in [Å] and angles [deg]: Rh–Sn 2.5797(1), Sn–C1 2.212(1), P1–Rh 2.3084(3), Rh–P2 2.3295(4), Rh–P3 2.3323(4), Sn–H3 1.891(15), Sn–H4 1.891(15), Rh–H1 1.57(2), Rh–H2 1.54(3), C1-Sn-Rh 118.2(1), P1-Rh-P2 106.18(1), P1-Rh-P3 106.18(1), P2-Rh-P3 96.61(1), P1-Rh-Sn1 143.53(1), P2-Rh-Sn 101.27(1), P3-Rh-Sn 93.82(1).[36]
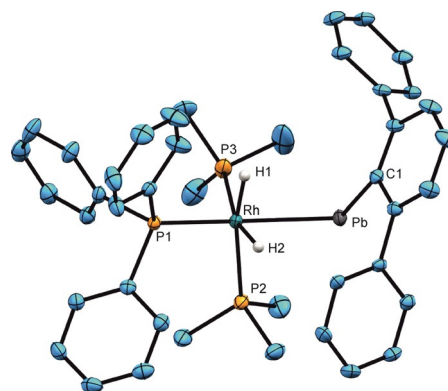


**Figure 7.** ORTEP of the molecular structure of **12**. Ellipsoids at 50% probability. Hydrogen atoms and $^i$Pr groups are omitted for clarity. Only Rh-H hydride atoms are shown. Interatomic distances in [Å] and angles [deg]: Rh–Pb 2.6697(2), Pb–C1 2.316(2), P3–Rh 2.3080(7), Rh–P2 2.3286(7), Rh–P1 2.3329(6), Rh–H1 1.33(4), Rh–H2 1.58(4), C1-Pb-Rh 115.14(6), P3-Rh-P2 100.19(3), P3-Rh-P1 103.57(2), P2-Rh-P1 103.37(2), P3-Rh-Pb 97.16(2), P2-Rh-Pb 88.28(2), P1-Rh-Pb 153.82-(2).[36]

**Table 1:** Selected data of compounds **3**, **7–14**.

| | Rh–Sn [Å] | Rh–Pb [Å] | δ ($^{119}$Sn)[a] | δ ($^{207}$Pb)[a] | δ ($^{103}$Rh)[a] |
|---|---|---|---|---|---|
| **3** | 2.5262(3) | | 1727 | | −8503 |
| **7** | | 2.6361(3) | | 8195 | −8057 |
| **8** | | | 3112 | | |
| **9** | | | | 11 269 | |
| **10** | 2.3856(2) | | 1149 | | |
| **11** | | 2.4530(2) | | 5729 | |
| **12** | | 2.6697(2) | | 11 733 | −8321 |
| **13** | 2.59289(17) | | 3296 | | −8529 |
| **14** | 2.5797(1) | | −244 | | −9440 |

[a] in ppm.

a signal at −8.60 ppm in the typical range for transition metal hydrides and the signal of the tin atom was found at 3296 ppm (d, $^{1}J_{119Sn-103Rh}$ = ca. 350 Hz) in the $^{119}$Sn NMR spectrum (Table 1).[17,34a]

The Rh−Pb bond length of 2.6697(2) Å found in **12** is longer than the triple bond and slightly shorter than Rh−Pb single bonds found in the literature.[15a,35] The signal for the protons of the RhH$_2$ group was found in the $^1$H NMR spectrum at −6.71 ppm. For the lead atom a signal at very high frequency 11733 ppm was found in the $^{207}$Pb NMR spectrum (Table 1). Compound **9** exhibits also a signal at very high frequency (**9**, 11269 ppm). Both resonances lie at exceptionally high frequencies and only few examples in this chemical shift range were found: metalloplumbylenes Cp-(CO)$_3$MPbAr* (M = Cr, 9563 ppm; Mo, 9659 ppm; W, 9374 ppm).[18] Furthermore the $^{31}$P NMR signal of the PPh$_3$ ligand in *trans*-position to the plumbylene ligand was found at very high frequency 321.6 ppm (dt, $^{1}J_{103Rh-31P}$ = 103 Hz, $^{2}J_{31P-31P}$ = 6.5 Hz, PPh$_3$). In comparison compound **13** exhibits for the PPh$_3$ ligand a signal at 93.1 and compound **14** at 47.1 ppm. This substantial high frequency NMR chemical shift found in **12** is likely to be attributed to the influence of the plumbylene ligand. This is another example for the HALA effect discussed for heavy atoms due to spin-orbit coupling.[16] In contrast the effect of the plumbylene exerted on the directly bonded rhodium, expressed by the $^{103}$Rh chemical shift is relatively small (compare $^{103}$Rh NMR data for compounds **3**, **7** and **12**, **13** in Table 1). In the series of compounds analyzed by $^{103}$Rh NMR spectroscopy a deshielding effect of ca. 1000 ppm of the Group 14 ligand at rhodium was observed: low valent ligand (plumbylene, stannylene −8057 to −8529 ppm) versus germyl and stannyl (−9131 to −9440 ppm) (Supporting Information Table S4).

With the formation of rhodium dihydride **13** (Scheme 3) the sequence of hydride transfer from the tin atom of the dihydridostannate **1** into the bridging position in compound **3** to the rhodium atom was completed. Transfer of both hydride substituents from the transition metal back to the tin atom was realized in reaction with chelating phosphine dmpe [dmpe: bis(dimetyhlphosphino)ethane]. This intramolecular hydrogen transfer is a remarkable example for a reductive elimination at a transition metal in combination with an oxidative addition of a ligand in the first coordination sphere. In comparison to **3** [1727 ppm (dt, $^{1}J_{119Sn-103Rh}$ = ca. 150 Hz, $^{2}J_{119Sn-1H}$ = ca. 240–250 Hz)] and **13** [3296 ppm (d, $^{1}J_{119Sn-103Rh}$ =

ca. 350 Hz)] the $^{119}$Sn NMR signal of **15** was found at lower frequencies in the typical area for higher coordination numbers at tin [−325 ppm (dt (br), $^{1}J_{119Sn-103Rh}$ = 392 Hz, $^{1}J_{119Sn-1H}$ = 740 Hz)]. The increased Sn-H coupling constant in **15** is another proof for the hydrogen transfer to form a sp$^3$-tin atom (Scheme 4). An ORTEP of the molecular structure of **15** was placed in the Supporting Information.
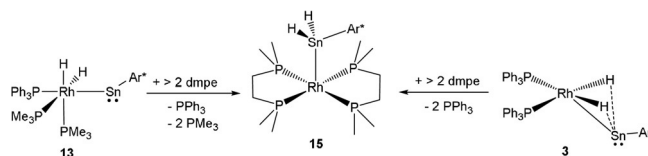


**Scheme 4.** Hydrogen transfer to tin.

Finally, the homologous germate anion [Ar*GeH$_2$]$^-$ was also reacted with the rhodium electrophile **2** to give (Ph$_3$P)RhGeH$_2$Ar* (**16**) (Scheme 5 and Supporting Information for ORTEP of the reaction product). In this complex a Ge−Rh bond was formed; the hydride substituents stay at the germanium atom and a phenyl moiety of the terphenyl substituent shows $\eta^6$-coordination at rhodium. Obviously, due to the higher stability of the Ge−H bond the hydride substituents were not transferred to rhodium and a complex comparable with the dihydrides **3** and **7** was not formed. Furthermore, in comparison to the stannate anion **1**, the germate anion is the stronger element-centered nucleophile.[9e]
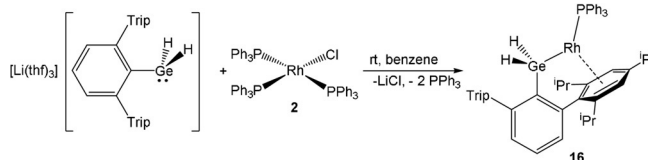


**Scheme 5.** Reaction of [Ar*GeH$_2$]$^-$ with [(Ph$_3$P)$_3$RhCl].

## Conclusion

Following a sequence of hydride transfer from tin or lead to rhodium and reductive elimination of hydrogen from the rhodium dihydride complexes tin and lead tetrylidynes featuring a Rh≡Sn or Rh≡Pb triple bond were synthesized. The polar triple bonds of the rhodium tetrylidynes add one (Pb case) or two (Sn case) equivalents of hydrogen at room temperature. The addition of two equivalents of hydrogen in the tin case is a stepwise procedure, with the hydrogenation of the rhodium and formation of a metallostannylene as the first hydrogenation. The second hydrogenation is a room temperature reversible reaction between stannylene tin and hydrogen.

## Conflict of interest

The authors declare no conflict of interest.

**Keywords:** hydrogenation · leadhydride · rhodiumhydride · tetrylidyne · tinhydride

[1] R. S. Simons, P. P. Power, *J. Am. Chem. Soc.* **1996**, *118*, 11966–11967.

[2] L. Pu, B. Twamley, S. T. Haubrich, M. M. Olmstead, B. V. Mork, R. S. Simons, P. P. Power, *J. Am. Chem. Soc.* **2000**, *122*, 650–656.

[3] a) P. Ghana, M. I. Arz, U. Chakraborty, G. Schnakenburg, A. C. Filippou, *J. Am. Chem. Soc.* **2018**, *140*, 7187–7198; b) P. Ghana, M. I. Arz, G. Schnakenburg, M. Straßmann, A. C. Filippou, *Organometallics* **2018**, *37*, 772–780; c) A. C. Filippou, D. Hoffmann, G. Schnakenburg, *Chem. Sci.* **2017**, *8*, 6290–6299; d) A. C. Filippou, B. Baars, O. Chernov, Y. N. Lebedev, G. Schnakenburg, *Angew. Chem. Int. Ed.* **2014**, *53*, 565–570; *Angew. Chem.* **2014**, *126*, 576–581; e) A. C. Filippou, P. Ghana, U. Chakraborty, G. Schnakenburg, *J. Am. Chem. Soc.* **2013**, *135*, 11525–11528; f) A. C. Filippou, U. Chakraborty, G. Schnakenburg, *Chem. Eur. J.* **2013**, *19*, 5676–5686; g) A. C. Filippou, A. Barandov, G. Schnakenburg, B. Lewall, M. van Gastel, A. Marchanka, *Angew. Chem. Int. Ed.* **2012**, *51*, 789–793; *Angew. Chem.* **2012**, *124*, 813–817; h) A. C. Filippou, O. Chernov, G. Schnakenburg, *Chem. Eur. J.* **2011**, *17*, 13574–13583; i) A. C. Filippou, O. Chernov, K. W. Stumpf, G. Schnakenburg, *Angew. Chem. Int. Ed.* **2010**, *49*, 3296–3300; *Angew. Chem.* **2010**, *122*, 3368–3372; j) A. C. Filippou, N. Weidemann, G. Schnakenburg, *Angew. Chem. Int. Ed.* **2008**, *47*, 5799–5802; *Angew. Chem.* **2008**, *120*, 5883–5886; k) A. C. Filippou, N. Weidemann, A. I. Philippopoulos, G. Schnakenburg, *Angew. Chem.* **2006**, *118*, 6133–6137; l) A. C. Filippou, N. Weidemann, G. Schnakenburg, H. Rohde, A. I. Philippopoulos, *Angew. Chem. Int. Ed.* **2004**, *43*, 6512–6516; *Angew. Chem.* **2004**, *116*, 6674–6678; m) A. C. Filippou, H. Rohde, G. Schnakenburg, *Angew. Chem.* **2004**, *116*, 2293–2297; n) A. C. Filippou, P. Portius, A. I. Philippopoulos, H. Rohde, *Angew. Chem. Int. Ed.* **2003**, *42*, 445–447; *Angew. Chem.* **2003**, *115*, 461–464; o) A. C. Filippou, A. I. Philippopoulos, G. Schnakenburg, *Organometallics* **2003**, *22*, 3339–3341; p) A. C. Filippou, P. Portius, A. I. Philippopoulos, *Organometallics* **2002**, *21*, 653–661; q) A. C. Filippou, A. I. Philippopoulos, P. Portius, D. U. Neumann, *Angew. Chem. Int. Ed.* **2000**, *39*, 2778–2781; *Angew. Chem.* **2000**, *112*, 2881–2884.

[4] a) T. P. Dhungana, H. Hashimoto, M. Ray, H. Tobita, *Organometallics* **2020**, *39*, 4350–4361; b) T. Fukuda, T. Yoshimoto, H. Hashimoto, H. Tobita, *Organometallics* **2016**, *35*, 921–924; c) H. Hashimoto, T. Fukuda, H. Tobita, M. Ray, S. Sakaki, *Angew. Chem. Int. Ed.* **2012**, *51*, 2930–2933; *Angew. Chem.* **2012**, *124*, 2984–2987; d) H. Hashimoto, T. Tsubota, T. Fukuda, H. Tobita, *Chem. Lett.* **2009**, *38*, 1196–1197; e) T. Watanabe, H. Hashimoto, H. Tobita, *Angew. Chem. Int. Ed.* **2004**, *43*, 218–221; *Angew. Chem.* **2004**, *116*, 220–223.

[5] a) B. V. Mork, T. D. Tilley, *Angew. Chem. Int. Ed.* **2003**, *42*, 357–360; *Angew. Chem.* **2003**, *115*, 371–374; b) P. G. Hayes, Z. Xu, C. Beddie, J. M. Keith, M. B. Hall, T. D. Tilley, *J. Am. Chem. Soc.* **2013**, *135*, 11780–11783.

[6] J. Hicks, T. J. Hadlington, C. Schenk, J. Li, C. Jones, *Organometallics* **2013**, *32*, 323–329.

[7] J. D. Queen, A. C. Phung, C. A. Caputo, J. C. Fettinger, P. P. Power, *J. Am. Chem. Soc.* **2020**, *142*, 2233–2237.

[8] S. Saini, A. Agarwal, S. K. Bose, *Dalton Trans.* **2020**, *49*, 17055–17075.

[9] a) C. P. Sindlinger, L. Wesemann, *Chem. Sci.* **2014**, *5*, 2739–2746; b) C. P. Sindlinger, A. Stasch, H. F. Bettinger, L. Wesemann, *Chem. Sci.* **2015**, *6*, 4737–4751; c) C. P. Sindlinger, W. Grahneis, F. S. W. Aicher, L. Wesemann, *Chem. Eur. J.* **2016**, *22*, 7554–7566; d) F. Diab, F. S. W. Aicher, C. P. Sindlinger, K. Eichele, H. Schubert, L. Wesemann, *Chem. Eur. J.* **2019**, *25*, 4426–4434; e) J.-J. Maudrich, F. Diab, S. Weiß, M. Widemann, T. Dema, H. Schubert, K. M. Krebs, K. Eichele, L. Wesemann, *Inorg. Chem.* **2019**, *58*, 15758–15768; f) J.-J. Maudrich, M. Widemann, F. Diab, R. H. Kern, P. Sirsch, C. P. Sindlinger, H. Schubert, L. Wesemann, *Chem. Eur. J.* **2019**, *25*, 16081–16087.

[10] a) J.-J. Maudrich, C. P. Sindlinger, F. S. W. Aicher, K. Eichele, H. Schubert, L. Wesemann, *Chem. Eur. J.* **2017**, *23*, 2192–2200; b) F. S. W. Aicher, K. Eichele, H. Schubert, L. Wesemann, *Organometallics* **2018**, *37*, 1773–1780.

[11] C. P. Sindlinger, F. S. W. Aicher, L. Wesemann, *Inorg. Chem.* **2017**, *56*, 548–560.

[12] a) S. Weiß, H. Schubert, L. Wesemann, *Chem. Commun.* **2019**, *55*, 10238–10240; b) J. Schneider, C. P. Sindlinger, K. Eichele, H. Schubert, L. Wesemann, *J. Am. Chem. Soc.* **2017**, *139*, 6542–6545.

[13] a) E. Molinos, S. K. Brayshaw, G. Kociok-Köhn, A. S. Weller, *Organometallics* **2007**, *26*, 2370–2382; b) A. Rifat, N. J. Patmore, M. F. Mahon, A. S. Weller, *Organometallics* **2002**, *21*, 2856–2865; c) N. W. Alcock, O. W. Howarth, P. Moore, G. E. Morris, *Chem. Commun.* **1979**, 1160–1162.

[14] N. Zhang, R. S. Sherbo, G. S. Bindra, D. Zhu, P. H. M. Budzelaar, *Organometallics* **2017**, *36*, 4123–4135.

[15] a) A. K. Swarnakar, M. J. Ferguson, R. McDonald, E. Rivard, *Dalton Trans.* **2016**, *45*, 6071–6078; b) M. Saito, M. Nakada, T. Kuwabara, R. Owada, S. Furukawa, R. Narayanan, M. Abe, M. Hada, K. Tanaka, Y. Yamamoto, *Organometallics* **2019**, *38*, 3099–3103.

[16] J. Vícha, J. Novotný, S. Komorovsky, M. Straka, M. Kaupp, R. Marek, *Chem. Rev.* **2020**, *120*, 7065–7103.

[17] a) B. E. Eichler, A. D. Phillips, S. T. Haubrich, B. V. Mork, P. P. Power, *Organometallics* **2002**, *21*, 5622–5627; b) Y. N. Lebedev, U. Das, G. Schnakenburg, A. C. Filippou, *Organometallics* **2017**, *36*, 1530–1540.

[18] L. Pu, P. P. Power, I. Boltes, R. Herbst-Irmer, *Organometallics* **2000**, *19*, 352–356.

[19] J. A. B. Abdalla, A. Caise, C. P. Sindlinger, R. Tirfoin, A. L. Thompson, A. J. Edwards, S. Aldridge, *Nat. Chem.* **2017**, *9*, 1256–1262.

[20] a) P. W. Smith, R. C. Handford, T. D. Tilley, *Organometallics* **2019**, *38*, 4060–4065; b) H.-J. Liu, M. S. Ziegler, T. D. Tilley, *Angew. Chem.* **2015**, *127*, 6722–6726; c) H.-J. Liu, J. Guihaumé, T. Davin, C. Raynaud, O. Eisenstein, T. D. Tilley, *J. Am. Chem. Soc.* **2014**, *136*, 13991–13994; d) M. E. Fasulo, E. Calimano, J. M. Buchanan, T. D. Tilley, *Organometallics* **2013**, *32*, 1016–1028; e) M. E. Fasulo, T. D. Tilley, *Chem. Commun.* **2012**, *48*, 7690–7692; f) J. Guihaumé, C. Raynaud, O. Eisenstein, L. Perrin, L. Maron, T. D. Tilley, *Angew. Chem. Int. Ed.* **2010**, *49*, 1816–1819; *Angew. Chem.* **2010**, *122*, 1860–1863; g) P. G. Hayes, C. W. Gribble, R. Waterman, T. D. Tilley, *J. Am. Chem. Soc.* **2009**, *131*, 4606–4607; h) P. G. Hayes, R. Waterman, P. B. Glaser, T. D.

Tilley, *Organometallics* **2009**, *28*, 5082–5089; i) A. Shinohara, J. McBee, T. D. Tilley, *Inorg. Chem.* **2009**, *48*, 8081–8083.

[21] K. M. Krebs, S. Freitag, J. J. Maudrich, H. Schubert, P. Sirsch, L. Wesemann, *Dalton Trans.* **2018**, *47*, 83–95.

[22] a) B. Wrackmeyer, in *Annual Reports on NMR Spectroscopy*, Vol. 38 (Ed.: G. A. Webb), Academic Press, San Diego, **1999**, pp. 203–264; b) B. Wrackmeyer, K. Horchler, in *Ann. Rep. NMR Spec.*, Vol. 22 (Ed.: G. A. Webb), Academic Press, San Diego, **1990**, pp. 249–306.

[23] H. Rohde, M. Menzel, F. Renz, A. C. Filippou, *Hyperfine Interact.* **2008**, *185*, 129–132.

[24] G. H. Spikes, J. R. Giuliani, M. P. Augustine, I. Nowik, R. H. Herber, P. P. Power, *Inorg. Chem.* **2006**, *45*, 9132–9136.

[25] T. Chu, G. I. Nikonov, *Chem. Rev.* **2018**, *118*, 3608–3680.

[26] a) L. Pu, B. Twamley, P. P. Power, *J. Am. Chem. Soc.* **2000**, *122*, 3524–3525; b) P. P. Power, *Acc. Chem. Res.* **2011**, *44*, 627–637; c) Y. Peng, X. Wang, J. C. Fettinger, P. P. Power, *Chem. Commun.* **2010**, *46*, 943–945; d) Y. Peng, B. D. Ellis, X. Wang, J. C. Fettinger, P. P. Power, *Science* **2009**, *325*, 1668–1670; e) Y. Peng, M. Brynda, B. D. Ellis, J. C. Fettinger, E. Rivard, P. P. Power, *Chem. Commun.* **2008**, 6042–6044; f) P. P. Power, *Organometallics* **2007**, *26*, 4362–4372; g) C. Cui, M. M. Olmstead, J. C. Fettinger, G. H. Spikes, P. P. Power, *J. Am. Chem. Soc.* **2005**, *127*, 17530–17541; h) C. Cui, M. M. Olmstead, P. P. Power, *J. Am. Chem. Soc.* **2004**, *126*, 5062–5063; i) L. Pu, A. D. Phillips, A. F. Richards, M. Stender, R. S. Simons, M. M. Olmstead, P. P. Power, *J. Am. Chem. Soc.* **2003**, *125*, 11626–11636; j) A. D. Phillips, R. J. Wright, M. M. Olmstead, P. P. Power, *J. Am. Chem. Soc.* **2002**, *124*, 5930–5931; k) M. Stender, A. D. Phillips, R. J. Wright, P. P. Power, *Angew. Chem. Int. Ed.* **2002**, *41*, 1785–1787; *Angew. Chem.* **2002**, *114*, 1863–1865.

[27] G. H. Spikes, J. C. Fettinger, P. P. Power, *J. Am. Chem. Soc.* **2005**, *127*, 12232–12233.

[28] S. Wang, T. J. Sherbow, L. A. Berben, P. P. Power, *J. Am. Chem. Soc.* **2018**, *140*, 590–593.

[29] a) C. Jones, T. J. Hadlington, *Chem. Commun.* **2014**, *50*, 2321–2323; b) J. Li, C. Schenk, C. Goedecke, G. Frenking, C. Jones, *J. Am. Chem. Soc.* **2011**, *133*, 18622–18625.

[30] K. Inomata, T. Watanabe, Y. Miyazaki, H. Tobita, *J. Am. Chem. Soc.* **2015**, *137*, 11935–11937.

[31] R. C. Turnell-Ritson, J. S. Sapsford, R. T. Cooper, S. S. Lee, T. Földes, P. A. Hunt, I. Pápai, A. E. Ashley, *Chem. Sci.* **2018**, *9*, 8716–8722.

[32] A. V. Protchenko, J. I. Bates, L. M. A. Saleh, M. P. Blake, A. D. Schwarz, E. L. Kolychev, A. L. Thompson, C. Jones, P. Mountford, S. Aldridge, *J. Am. Chem. Soc.* **2016**, *138*, 4555–4564.

[33] a) M. Kilian, H. Wadepohl, L. H. Gade, *Organometallics* **2008**, *27*, 524; b) M. Kilian, H. Wadepohl, L. H. Gade, *Eur. J. Inorg. Chem.* **2008**, 1892–1900; c) J. Martincová, R. Dostálová, L. Dostál, A. Růžička, R. Jambor, *Organometallics* **2009**, *28*, 4823–4828.

[34] a) C. Cheng, J. F. Hartwig, *J. Am. Chem. Soc.* **2014**, *136*, 12064–12072; b) L. Turculet, J. D. Feldman, T. D. Tilley, *Organometallics* **2004**, *23*, 2488–2502.

[35] G. Thiele, Y. Franzke, F. Weigend, S. Dehnen, *Angew. Chem. Int. Ed.* **2015**, *54*, 11283–11288; *Angew. Chem.* **2015**, *127*, 11437–11442.

[36] Deposition Number(s) 2042784 (for **3**), 2042791 (for **7**), 2042794 (for **8b**), 2042785 (for **8**), 2042787 (for **10**), 2042786 (for **11**), 2042790 (for **12**), 2042792 (for **13**), 2042789 (for **14**), 2042788 (for **15**), and 2042793 (for **16**) contain(s) the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.