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Addition of *in situ* reduced amidinato-methylaluminium chloride to acetylenes†‡T. Chlupatý,<sup>a</sup> J. Turek,<sup>b</sup> F. De Proft,<sup>b</sup> Z. Růžicková<sup>a</sup> and A. Růžicka\*<sup>a</sup>

Two ethylene-bridged methylaluminium amidinates and one aluminium amidinate containing three terminal trimethylstannylethynyl groups interconnected by  $\pi$ -coordinated potassium ions were prepared *in situ*. The re-oxidation of the ethylene-bridged compound by iodine followed by further reduction using the same activation procedure demonstrated the versatility of the approach. The reactivity of an ethylene-bridged methylaluminium amidinate towards HCl was examined to demonstrate the building block concept. DFT calculations were performed to gain insight into the mechanism of the *in situ* activation of diphenylacetylene.

In the last few decades, the activation of various small molecules and unsaturated systems by low-valent main group metal complexes and their subsequent chemical transformations have attracted considerable attention.<sup>1</sup> The chemistry of low-valent aluminium<sup>2</sup> compounds, such as Al<sup>I</sup> and Al<sup>II</sup> compounds, developed considerably after the first stable species with an Al–Al arrangement, [(Me<sub>3</sub>Si)<sub>2</sub>CH]<sub>2</sub>Al–Al[CH(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>, was prepared and structurally characterized by Uhl<sup>3</sup> in 1988. However, the key milestone was the synthesis of a stable monomeric Al<sup>I</sup> species, an aluminium analogue of carbene decorated with a crowded bidentate diketiminato ligand reported in 2000 by Roesky and co-workers.<sup>4</sup> In addition to synthetic routes yielding new low-valent aluminium complexes, such as Al<sup>I</sup> species, dialumanes<sup>1i,2e,5</sup> and some metalloids/clusters,<sup>2g,h,6</sup> new reactivity patterns of the compounds towards smaller and larger molecules<sup>7</sup> were reported.

An important part of these synthetic and structural studies is the activation of the C–C multiple bond *via* either *in situ* generated Al<sup>I</sup>/Al<sup>II</sup> species or *via* the stepwise reaction with the isolable Al–Al/Al:Al' intermediate. The *in situ* reduction of diiodoaluminium *N,N*-diketiminato in the presence of an RC≡CR moiety (R = Ph or SiMe<sub>3</sub>)<sup>8</sup> and the stepwise activation of RC≡CR<sup>9</sup> (R = H, Ph, Me or SiMe<sub>3</sub>) by the isolable LAl<sup>I</sup> intermediate both afforded aluminacyclopropenes. However, dialuminacyclobutenes were obtained with organoaluminium compounds containing sterically demanding ligands from the *in situ* reduction by KC<sub>8</sub><sup>10</sup> and the stepwise reaction *via* the Al–Al fragment<sup>7b</sup> of Me<sub>3</sub>SiC≡CSiMe<sub>3</sub>. To the best of our knowledge, only examples of dinuclear aluminium ethylene bridged<sup>5a</sup> or double bridged compounds prepared from bis-amido-dialane and PhC≡CH<sup>5c</sup> followed by heating of the product in benzene (1,4-dialuminacyclohexadienes<sup>11</sup>) and PhC≡CPh, respectively, have been described. Pioneering studies of the reactivity of trialkyl aluminium compounds with acetylenes activated by UV light or sodium metal have also been published.<sup>5d,e</sup> Furthermore, the reaction of dichloroaluminium amide with an excess of alkali metal acetylides (Li,<sup>12</sup> Na and K<sup>12b</sup>) yielded ate complexes consisting of an ionic aluminium fragment carrying two or three terminal ethynyl groups involving alkali metal ions in bridging mode.

Herein, we report the synthesis, structural properties and reactivity of products resulting from the *in situ* reduction of chloromethylaluminium species supported by the NCN chelating amidinato ligand with various acetylenes. Our approach stemmed from previous work,<sup>13</sup> in which the preparation of the starting LAlMeCl (L = DippNC(Me)NDipp) and its reduction by a potassium mirror to yield LAlMe<sub>2</sub> and L<sub>2</sub>AlMe were investigated. The probable existence of transient LAlMe particles offers the possibility that they could be used in further studies as a trap for various unsaturated systems.

Thus, the reductive coupling (Scheme 1) of [DippNC(Me)NDipp]AlMeCl with either PhCCPh or 4-Me<sub>3</sub>Si-C<sub>6</sub>H<sub>4</sub>CCPh and potassium at room or lower temperatures yielded novel ethylene-bridged methylaluminium amidinates **1** (31%) and **2** (27%), respectively, along with aluminium amidinates LAlMe<sub>2</sub>

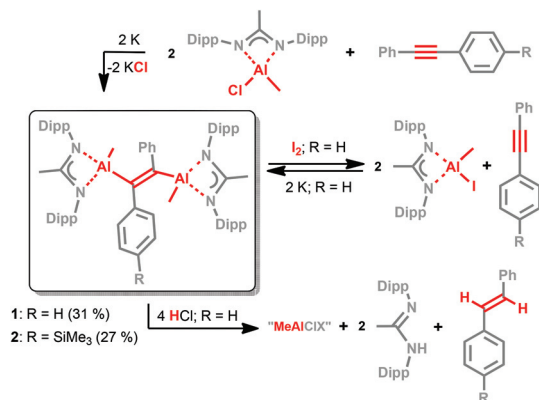
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†Dedicated to Dr Bohumil Štíbr on the occasion of his 75<sup>th</sup> birthday in recognition of his outstanding contributions to the area of boron chemistry.

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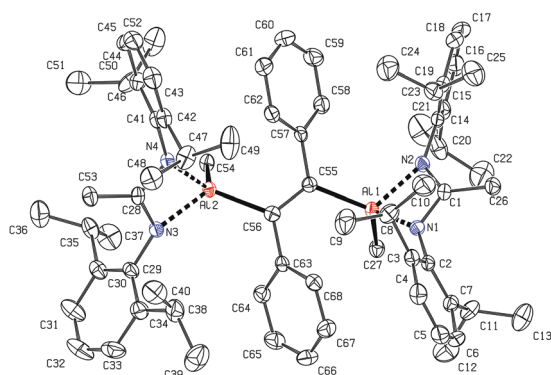




**Scheme 1** Synthesis of dinuclear ethylene-bridged methylaluminum amidinates (1, 2) with the three-component approach and the reactivity of 1 towards HCl and iodine.

and  $L_2AlMe$  ( $L = DippNC(Me)NDipp$ ) as side-products that could be removed by crystallization (ESI†). In addition, the blank test showed no reaction between both components without potassium. The *in situ* activation of acetylenes within the three-component framework affording aluminacycloprenes or dialuminacyclobutenes has been published by Roesky and others.<sup>8,10</sup>

1 (Fig. 1 and S5 in ESI†) and 2 (Fig. S6 and S7 in ESI†) were fully characterized by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy in C<sub>6</sub>D<sub>6</sub>, elemental analyses, and XRD. The structures of compounds 1 and 2 both contained four-coordinate aluminium atoms with a distorted tetrahedral arrangement of the substituents. The main feature of both dinuclear structures is the presence of an Al-C(Ph)=C(Ph)-Al chain fragment with twisted phenyl groups (torsion angles of 50.50 and 49.95°) in the *trans* configuration. This structural arrangement may predetermine the

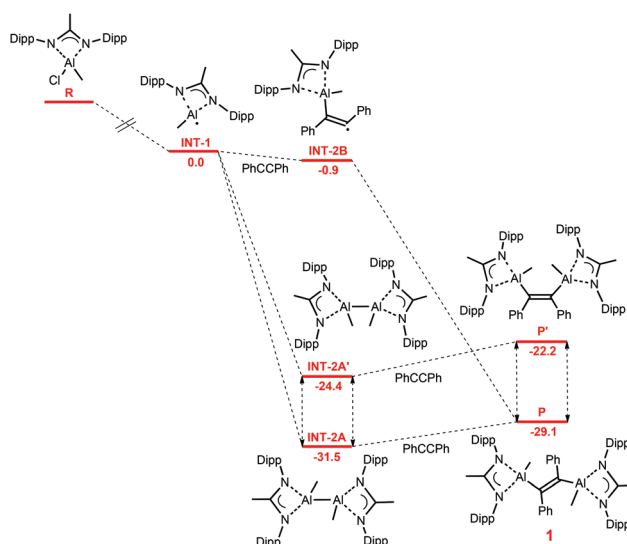


**Fig. 1** The molecular structure of 1 (ORTEP view, 30% probability level). Hydrogen atoms are omitted for clarity. Selected interatomic distances [Å] and angles [°]: N1–C1 1.337(3); N2–C1 1.337(3); N4–C28 1.333(3); N3–C28 1.333(3); C1–Al1 2.386(2); C28–Al2 2.368(2); Al1–C27 1.971(2); Al2–C54 1.980(2); N1–Al1 1.937(2); N2–Al1 1.976(2); N3–Al2 1.960(2); N4–Al2 1.938(2); Al1–C55 1.985(2); C55–C56 1.367(3); C56–Al2 1.987(3); N1–C1–N2 109.7(2); N3–C28–N4 110.4(2); C1–Al1–C55 129.10(9); C28–Al2–C56 132.30(9); Al1–C55–C56 120.06(18).

nature of the further reactivity of the complex and the structural design of the products. The diphenylethylene moiety (C=C found in 1 C55–C56 1.367(3) Å) serves as a linker (Al1–C55 1.985(2) and C56–Al2 1.987(3) Å in 1) between the two aluminium atoms decorated by bidentately bonded amidinates.

Two mechanisms were proposed by Roesky *et al.*<sup>8</sup> for the reduction of the similar aluminium complex  $LAlI_2$  in the presence of alkynes, *via* either the formation of the aluminium centred radical  $LAlI^{\cdot}$ , which couples with alkynes, or *via* the electron transfer from K to the alkyne and the formation of the radical anion  $K^+(RCCR)^{\cdot-}$ , which displaces the iodide in  $LAlI_2$ . In both pathways, the same intermediate,  $LAlI(RCCR)^{\cdot}$ , is formed, yielding the desired product *via* a further electron transfer reaction. For our system, the latter pathway could be ruled out because only one electron transfer reaction can take place; therefore, alkyne coupling would be observed instead of the formation of 1.

Based on these facts, DFT calculations were performed to elucidate a plausible reaction mechanism, suggesting one of the pathways described above and another possible pathway *via* an experimentally postulated dialumane intermediate<sup>5a</sup> (Fig. 2 and S16 in ESI†, Table S2 in ESI†). Both start with the reduction of the chloromethylaluminum complex **R** yielding radical **INT-1**. The first pathway comprises the formation of the dialumane intermediate with an *anti* (**INT-2A**) or *syn* conformation (**INT-2A'**), which subsequently reacts with diphenylacetylene to form the corresponding final product with the *trans* (**P**) or *cis* (**P'**) structural arrangement, respectively. The *trans* and *anti* isomers are 7.1 and 6.9 kcal mol<sup>-1</sup> lower in energy than the respective *cis* and *syn* isomers, which is in good agreement with the experimental results. Moreover, the prolonged reaction time and lower yields are consistent with the slightly positive  $\Delta G$  of the second step of the reaction



**Fig. 2** Energetic profiles (Gibbs free energies in kcal mol<sup>-1</sup>) for the *in situ* interaction of [DippNC(Me)NDipp]AlMeCl (**R**) with potassium and diphenylacetylene.



sequence. The second pathway is similar to the mechanism proposed by Roesky *et al.*,<sup>8</sup> suggesting the reaction of methylaluminium radical **INT-1** with diphenylacetylene, which generates intermediate **INT-2B**. The coupling of the aluminium-diphenylethylene radical **INT-2B** with methylaluminium radical **INT-1** forms the expected product **P** (**P'**). Similar to the first pathway, the rate-determining step of the reaction mechanism is the activation of a C≡C triple bond, which has a slightly negative  $\Delta G$ . Therefore, the second pathway seems to be more thermodynamically favourable; however, the negligible differences in  $\Delta G$  ( $-0.9$  vs.  $2.4$  kcal mol<sup>-1</sup>) mean that the first pathway cannot be excluded.

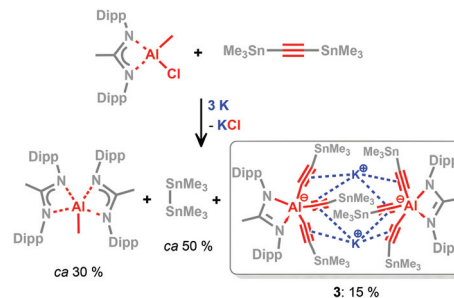
Finally, the two radicals occurring in the proposed reaction pathways were investigated. **INT-1** is an aluminium-centered radical (Mulliken spin density at Al 82%), whereas for **INT-2B** the spin density is more delocalized (Mulliken spin density at C<sub>ethylene</sub> 58%) in the  $\pi$ -system of the phenyl ring (Fig. S15 in ESI†).

The oxidation of **1** by molecular iodine produced a clear mixture of diphenylacetylene and [DippNC(Me)NDipp]AlMeI (Fig. S1 and S2 in ESI†). <sup>1</sup>H and <sup>13</sup>C NMR of the reaction mixture are shown in Fig. S9 and S10 in the ESI.† The reaction mixture was used without further workup for a re-reduction using the same method. The reaction proceeded to the same product (**1**) in 34% yield. In addition, oxidizing **1** with oxygen gas afforded a complex mixture of products, mainly consisting of benzil and DippNC(Me)NHDipp, along with a small amount of diphenylacetylene and other by-products.

The importance of the structural arrangement of the diphenylethylene moiety is demonstrated by the reactivity of complex **1** towards small molecules (Scheme 1). Based on the <sup>1</sup>H (Fig. S11†) and <sup>13</sup>C NMR spectra (Fig. S12†) and the EI-MS results (Fig. S14 in ESI†), the chemical transformation of the diphenylethylene fragment by two equivalents of HCl to *trans*-stilbene was quantitative. This hydrogen substitution process was completed by the formation of amidine DippNC(Me)NHDipp (<sup>1</sup>H, <sup>13</sup>C NMR and EI-MS), and an unidentified methylaluminium chloride-containing species (Fig. S13 in ESI†) as by-products formed due to the decomposition of the initially formed [DippNC(Me)NDipp]AlMeCl.

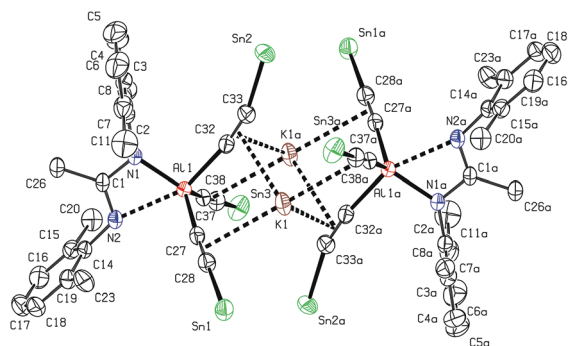
The analogous *in situ* reduction of [DippNC(Me)NDipp]AlMeCl in the presence of bis(trimethylstannyl)acetylene (Scheme 2) resulted in the formation of *ca.* 15% ate complex **3** identified by NMR and XRD. In the reaction mixture, aluminium amidinate **3** was accompanied by major by-products Me<sub>3</sub>SnSnMe<sub>3</sub> ( $-109$  ppm in the <sup>119</sup>Sn NMR spectrum)<sup>14</sup> and L<sub>2</sub>AlMe (L = DippNC(Me)NDipp).<sup>13</sup> This structural arrangement on the aluminum atom is not entirely surprising. Some examples of these rare types of aluminium ate complexes have been obtained from the reaction of amido-aluminium dichloride with a large excess of alkali metal acetylide.<sup>12</sup> Most probably, the potassium atom attacks the Sn–C bond in the first step to form KCCSnMe<sub>3</sub>,<sup>15</sup> which further reacts with the MeAlCl fragment of the starting component.

The signals corresponding to terminally bonded trimethylstannylethynyl groups in **3** were found at 110.1 (broad signal



**Scheme 2** Reduction of [DippNC(Me)NDipp]AlMeCl in the presence of bis(trimethylstannyl)acetylene.

for C–Al) and 97.2 ppm (for C–Sn) in the <sup>13</sup>C NMR spectrum, and at  $-88$  ppm in the <sup>119</sup>Sn NMR spectrum (116.2 and  $-81$  ppm, respectively, for Me<sub>3</sub>SnCCSnMe<sub>3</sub>). This agrees well with the data for the previously described ate complexes [LAl(C≡C–Ph)<sub>3</sub>]M (M = Li, Na or K; broad signal at  $\sim 110$  ppm)<sup>12b</sup> and [LAl(C≡C–SiMe<sub>3</sub>)<sub>3</sub>]Li (95.3 ppm for C–Si).<sup>12a</sup> The chemical shift of the central carbon atom of the NCN moiety (165.9 ppm) in the <sup>13</sup>C NMR spectrum indicates the presence of an anisobidentately bonded ligand, which was also supported by the XRD analyses of **3** (N1–Al1 1.881(4); N2–Al1 2.413(4)). The structure of centrosymmetric dimer **3** (Fig. 3 and S8†) displays distorted trigonal bipyramidal geometry (C–Al–C angles 100.46°, 100.65° and 116.04°) around both five-coordinated aluminium atoms with Al–C distances of 1.970(3), 1.974(3) and 2.041(4) Å. The [(DippNC(Me)NDipp)Al–(C≡C–SnMe<sub>3</sub>)<sub>3</sub>]<sup>−</sup> cores are stabilized by  $\pi$ -coordination (2.986–3.223 Å, comparable with {[LAl(C≡C–Ph)<sub>3</sub>]M}<sub>2</sub> (M = Na or K)<sup>12b</sup>) with two potassium atoms, each atom being connected to four ethynyl groups.



**Fig. 3** The molecular structure of **3** (ORTEP view, 50% probability level). Hydrogen atoms and methyl groups from the trimethylstannyl and 2,6-diisopropylphenyl moiety are omitted for clarity. Selected interatomic distances [Å] and angles [°]: N1–C1 1.350(5); N2–C1 1.293(4); N1–Al1 1.881(4); N2–Al1 2.413(4); Al1–C37 1.974(3); Al1–C27 1.970(3); Al1–C32 2.041(4); C37–C38 1.214(4); K1–C27 3.014(4); K1–C28 3.030(4); K1–C32 2.986(3); K1–C32a 2.989(3); K1–C33 3.233(4); K1–C33a 3.220(4); K1–C37a 3.036(3); K1–C38a 3.050(4); N1–C1–N2 113.3(4); C1–Al1–C27 106.42(15); C27–Al1–C32 100.46(15).



The internal ethynyl groups, which are bridged by two potassium atoms, have K–C distances (K1–C32a vs. K1–C33a, see caption of Fig. 3) that are different by 0.23 Å, whereas the other K–C distances were similar to K1–C32a. The Al–C≡C fragment was not linear (angles from 170.53° to 176.15°) in 3 or in structures of  $\{[LAl(C\equiv C-Ph)_3]M\}_2$  (M = Li, Na or K)<sup>12b</sup> and this could be explained by the small energy difference between the linear and non-linear Al–C≡C arrangements.

In conclusion, we described the *in situ* activation of an unsaturated CC multiple bond *via* the reduction of amidinato-methylaluminium chloride in the presence of various acetylenes. The reaction was partially reversible by the oxidation of iodine with re-reduction. The structure of the products is strongly affected by the nature of the C≡C group substituents (C substituent vs. Sn substituent). Moreover, we proposed two possible reaction mechanisms for model compound 1 by using DFT calculations. In addition, the use of the building block concept was demonstrated by the reactivity of 1 towards HCl resulting in the formation of *trans*-stilbene.

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## Notes and references

- For example see: (a) P. P. Power, *Chem. Rev.*, 1999, **99**, 3463; (b) P. P. Power, *Nature*, 2010, **463**, 171; (c) I. Resa, E. Carmona, E. Gutierrez-Puebla and A. Monge, *Science*, 2004, **305**, 1136; (d) Y. Peng, B. D. Ellis, X. Wang, J. C. Fettinger and P. P. Power, *Science*, 2009, **325**, 1668; (e) S. P. Green, C. Jones and A. Stasch, *Science*, 2007, **318**, 1754; (f) M. Asay, C. Jones and M. Driess, *Chem. Rev.*, 2011, **111**, 354; (g) S. Harder, *Chem. Rev.*, 2010, **110**, 3852; (h) P. P. Power, *Chem. Rev.*, 2003, **103**, 789; (i) S. J. Bonyhady, D. Collis, G. Frenking, N. Holzmann, C. Jones and A. Stasch, *Nat. Chem.*, 2010, **2**, 865; (j) C. Jones, *Coord. Chem. Rev.*, 2010, **254**, 1273; (k) Y. Li, K. C. Mondal, J. Lubben, H. Zhu, B. Dittrich, I. Purushothaman, P. Parameswaran and H. W. Roesky, *Chem. Commun.*, 2014, **50**, 2986.
- For example see: (a) R. J. Wehmschulte, in *Low Valent Organoaluminum (+I, +II) Species*, in *Topics in Organometallic Chemistry*, ed. S. Woodward and S. Dagorne, Springer Verlag, Berlin Heidelberg, 2013, vol. 41, pp. 91–124; (b) H. W. Roesky and S. S. Kumar, *Chem. Commun.*, 2005, 4027; (c) S. P. Sarish, B. Nekoueshahraki, A. Jana, H. W. Roesky, T. Schulz and D. Stalke, *Chem. – Eur. J.*, 2011, **17**, 890; (d) K. Nagata, T. Agou and N. Tokitoh, *Angew. Chem., Int. Ed.*, 2014, **53**, 3881; (e) R. J. Wright, A. D. Phillips and P. P. Power, *J. Am. Chem. Soc.*, 2003, **125**, 10784; (f) H. W. Roesky and S. S. Kumar, *Chem. Commun.*, 2005, 4027; (g) A. Schnepf and H. Schnöckel, *Angew. Chem., Int. Ed.*, 2002, **41**, 3532; (h) C. Schnitter, H. W. Roesky, C. Röpken, R. Herbst-Irmer, H.-G. Schmidt and M. Noltemeyer, *Angew. Chem., Int. Ed.*, 1998, **37**, 1952; (i) S. Nagendran and H. W. Roesky, *Organometallics*, 2008, **27**, 457; (j) H. W. Roesky, *Inorg. Chem.*, 2004, **43**, 7284.
- W. Uhl, *Z. Naturforsch., B: Chem. Sci.*, 1988, **43**, 1113.
- (a) C. Cui, H. W. Roesky, H.-G. Schmidt, M. Noltemeyer, H. Hao and F. Cimpoesu, *Angew. Chem., Int. Ed.*, 2000, **39**, 4274; (b) X. Li, X. Cheng, H. Song and Ch. Cui, *Organometallics*, 2007, **26**, 1039.
- (a) Y. Zhao, Y. Liu, Y. Lei, B. Wu and X.-J. Yang, *Chem. Commun.*, 2013, **49**, 4546; (b) T. Agou, K. Nagata, H. Sakai, Y. Furukawa and N. Tokitoh, *Organometallics*, 2012, **31**, 3806; (c) I. L. Fedushkin, M. V. Moskalev, A. N. Lukoyanov, A. N. Tishkina, E. V. Baranov and G. A. Abakumov, *Chem. – Eur. J.*, 2012, **18**, 11264; (d) H. Lehmkuhl, J. Čuljković and H. Nehl, *Liebigs Ann. Chem.*, 1973, **4**, 666–691; (e) H. Hoberg and F. Aznar, *Angew. Chem., Int. Ed.*, 1980, **19**, 146–148; (f) Y. Zhao, Y. Liu, L. Yang, J.-G. Yu, S. Li, B. Wu and X.-J. Yang, *Chem. – Eur. J.*, 2012, **18**, 6022; (g) K. S. Klimek, C. Cui, H. W. Roesky, M. Noltemeyer and H.-G. Schmidt, *Organometallics*, 2000, **19**, 3085; (h) S. G. Minasian and J. Arnold, *Chem. Commun.*, 2008, 4043; (i) R. J. Wehmschulte, K. Ruhlandt-Senge, M. M. Olmstead, H. Hope, B. E. Sturgeon and P. P. Power, *Inorg. Chem.*, 1993, **32**, 2983.
- For examples see: (a) A. Purath and H. Schnöckel, *J. Organomet. Chem.*, 1999, **579**, 373; (b) C. Dohmeier, C. Robl, M. Tacke and H. Schnöckel, *Angew. Chem., Int. Ed.*, 1991, **30**, 564; (c) P. Yang, R. Koppe, T. Duan, J. Hartig, G. Hadiprono, B. Pilawa, I. Keilhauer and H. Schnöckel, *Angew. Chem., Int. Ed.*, 2007, **46**, 3579; (d) N. Wiberg, T. Blank, W. Kaim, B. Schwederski and G. Linti, *Eur. J. Inorg. Chem.*, 2000, 1475; (e) A. Purath and H. Schnöckel, *J. Organomet. Chem.*, 1999, **579**, 373; (f) C. Dohmeier, C. Robl, M. Tacke and H. Schnöckel, *Angew. Chem., Int. Ed.*, 1991, **30**, 564; (g) P. Yang, R. Koppe, T. Duan, J. Hartig, G. Hadiprono, B. Pilawa, I. Keilhauer and H. Schnöckel, *Angew. Chem., Int. Ed.*, 2007, **46**, 3579.
- (a) H. Zhu, J. Chai, V. Chandrasekhar, H. W. Roesky, J. Magull, D. Vidovic, H.-G. Schmidt, M. Noltemeyer, P. P. Power and W. A. Merrill, *J. Am. Chem. Soc.*, 2004, **126**, 9472; (b) T. Agou, K. Nagata and N. Tokitoh, *Angew. Chem., Int. Ed.*, 2013, **52**, 10818; (c) Y. Peng, H. Fan, V. Jancik, H. W. Roesky and R. Herbst-Irmer, *Angew. Chem., Int. Ed.*, 2004, **43**, 6190; (d) X. Li, X. Cheng, H. Song and C. Cui, *Organometallics*, 2007, **26**, 1039; (e) Z. Yang, X. Ma, R. B. Oswald, H. W. Roesky and M. Noltemeyer, *J. Am. Chem. Soc.*, 2006, **128**, 12406; (f) R. J. Wright, M. Brynda and P. P. Power, *Angew. Chem., Int. Ed.*, 2006, **45**, 5953.
- C. Cui, S. Köpke, R. Herbst-Irmer, H. W. Roesky, M. Noltemeyer, H.-G. Schmidt and B. Wrackmeyer, *J. Am. Chem. Soc.*, 2001, **123**, 9091.
- H. Zhu, R. B. Oswald, H. Fan, H. W. Roesky, Q. Ma, Z. Yang, H.-G. Schmidt, M. Noltemeyer, K. Starke and N. S. Hosmane, *J. Am. Chem. Soc.*, 2006, **128**, 5100.



- 10 C. Cui, X. Li, Ch. Wang, J. Zhang, J. Cheng and X. Zhu, *Angew. Chem., Int. Ed.*, 2006, **45**, 2245.
- 11 (a) C. Üffing, A. Ecker, R. Köppe, K. Merzweiler and H. Schnöckel, *Chem. – Eur. J.*, 1998, **4**, 2142; (b) H. Hoberg, V. Gotor, A. Milchereit, C. Krüger and J. C. Sekutowski, *Angew. Chem., Int. Ed.*, 1977, **16**, 539.
- 12 (a) M. Schiefer, N. D. Reddy, H.-J. Ahn, A. Stasch, H. W. Roesky, A. C. Schlicker, H.-G. Schmidt, M. Noltemeyer and D. Vidovic, *Inorg. Chem.*, 2003, **42**, 4970; (b) M. Schiefer, H. Hatop, H. W. Roesky, H.-G. Schmidt and M. Noltemeyer, *Organometallics*, 2002, **21**, 1300.
- 13 T. Chlupatý, M. Bílek, J. Moncol, Z. Růžicková and A. Růžička, *J. Organomet. Chem.*, 2015, **786**, 48.
- 14 D. L. Freeman, J. D. Odom, W. R. Nutt and L. Lebioda, *Inorg. Chem.*, 1997, **36**, 2718.
- 15 N. V. Komarov, A. A. Andreev and O. G. Shein, *Russ. Chem. Bull.*, 1994, **43**, 1048.

