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ARTICLE TYPE

## Adaptive Behavior of Redox-Active Gallium Carbenoid in Complexes with Molybdenum†‡

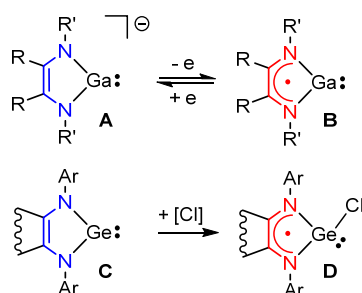
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Gallium(I) carbenoid derived from redox-active diimine 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene (dpp-bian) in complexes with molybdenum may serve either as neutral [(dpp-bian)Ga:] or anionic [(dpp-bian)Ga:]<sup>-</sup> two-electron donor depending on electronic state of the transition metal.

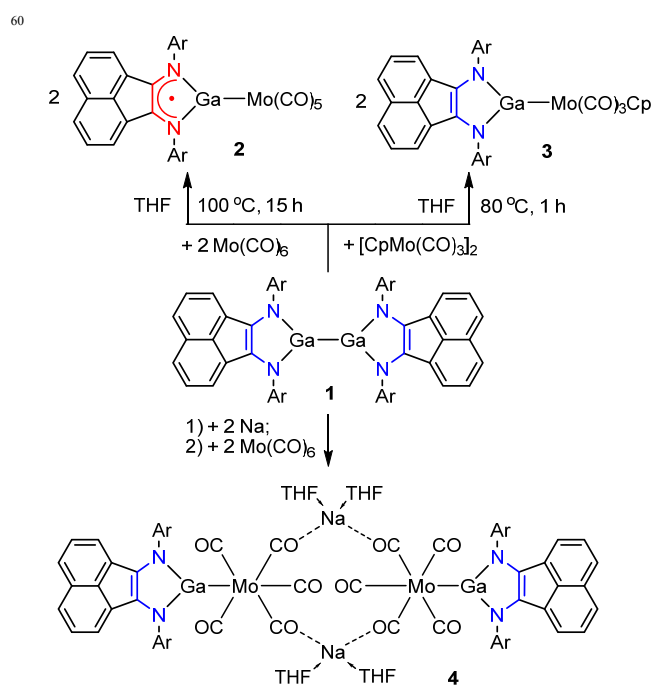
First anionic 1,3,2-imidazagalol (structure **A**, Scheme 1), namely [(*t*BuNCH)<sub>2</sub>Ga]<sup>-</sup>, has been reported by Schmidbaur and co-workers in 1999.<sup>1</sup> During the following decade, the chemistry of the related anion [(DAB)Ga:]<sup>-</sup> [DAB = (2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NCH)<sub>2</sub>] was intensively studied by Jones and co-workers.<sup>2</sup> They succeeded in preparing complexes of [(DAB)Ga:]<sup>-</sup> for most of the metals of the Periodic Table,<sup>3</sup> thus proving the versatility of [(DAB)Ga:]<sup>-</sup> as Ga-donor ligand. Anionic 1,3,2-imidazagalols are isoelectronic with neutral N-heterocyclic germynes (structure **C**, Scheme 1).<sup>4</sup> The latter compounds are the heavier analogues of Arduengo's carbenes, which now represent one of the most useful class of ligands. While the existence of radical species like **D** (Scheme 1) is proven,<sup>5</sup> neutral radicals of type **B** were neither observed as coordinated ligands nor as free species. Interestingly, radical R<sub>2</sub>Ga• (R = (2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NCH)<sub>2</sub>B) has been recently reported.<sup>6</sup>



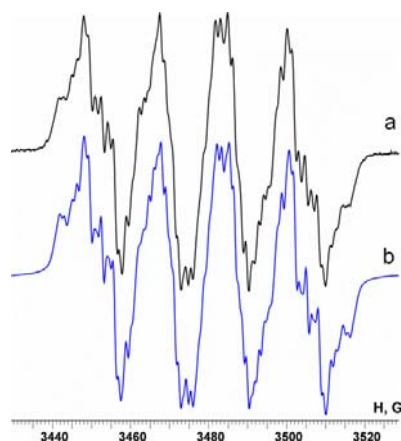
Scheme 1 N-Heterocyclic gallium and germanium carbenoids.

Here we report for the first time the generation (in situ) of a heterocyclic radical [(dpp-bian)Ga:] (dpp-bian = 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene), which is rather stable when coordinated to a transition metal, e.g. molybdenum. On the other hand, we show here that, if required, electrons can be transferred from the transition metal centre to this radical, thus providing the formation of a gallen-anion. The interplay between [(dpp-bian)Ga:] and [(dpp-bian)Ga:]<sup>-</sup> is needed to ensure the stability of the 18 electron configuration at the transition metal.

The reaction between (dpp-bian)Ga–Ga(dpp-bian) (**1**) and an excess of Mo(CO)<sub>6</sub> proceeds in tetrahydrofuran (THF) at 100 °C (sealed glass ampoule). Within 15 hours, the reaction mixture turns from deep blue to green. The removal of the excess carbonyl reagent by sublimation and crystallisation of the product from benzene gives green crystals of (dpp-bian)Ga–Mo(CO)<sub>5</sub> (**2**) in 95 % yield (Scheme 2). A lack of signals in the <sup>1</sup>H NMR spectrum of compound **2** suggests its paramagnetic character. Indeed, EPR spectroscopy proves the presence of an unpaired electron in complex **2**. The interaction between compound **1** and [CpMo(CO)<sub>3</sub>]<sub>2</sub> also proceeds in THF, but under less drastic conditions (80 °C, 1 h) compared to compound **2**. The diamagnetic product (dpp-bian)Ga–Mo(CO)<sub>3</sub>Cp (**3**) was obtained in form of dark brown crystals (93 %) from 1,2-dimethoxyethane (Scheme 2). Reduction of compound **1** with two equivalents of sodium in THF resulted (in situ) in (dpp-bian)Ga–Na(THF)<sub>4</sub>,<sup>7</sup> which reacts with Mo(CO)<sub>6</sub> in THF at 25 °C within 1 h to give green carbonylate [(dpp-bian)Ga–Mo(CO)<sub>5</sub>]{Na(THF)<sub>2</sub>]<sub>2</sub> (**4**) (97 %) (Scheme 2).

Scheme 2 Syntheses of the compounds **2**, **3**, and **4**.

Compounds **2-4** are thermally quite robust: decomposition of crystalline samples takes place above 200 °C. The EPR signal of a solution of compound **2** (Figure 1) reveals a hyper-fine splitting (hfs) due to coupling of the unpaired electron with two pairs of protons, two equivalent  $^{14}\text{N}$  nuclei and the two magnetic gallium isotopes,  $^{69}\text{Ga}$  (60.11 %) and  $^{71}\text{Ga}$  (39.89 %).<sup>8</sup> The EPR spectrum unequivocally indicates the presence of the heterocyclic radical [(dpp-bian)Ga:] in complex **2**. This radical acts as a two-electron neutral  $\sigma$ -donor towards molybdenum, thus, providing the 18 electron configuration of the transition metal centre together with the five CO ligands. At that stage, we cannot conclude whether the back donation from molybdenum to unoccupied  $p_z$  orbital of gallium takes place. Alternatively, this orbital might be populated with lone pairs of the nitrogen atoms. Note, that in THF compound **2** exhibits thermochromism (green and red at ambient and low temperature, correspondingly). It seems to be reasonable to suggest that this phenomenon reflects the coordination of the solvent donor molecule to the empty gallium  $p$  orbital because not color alteration has been observed in non-coordinating solvent like toluene.

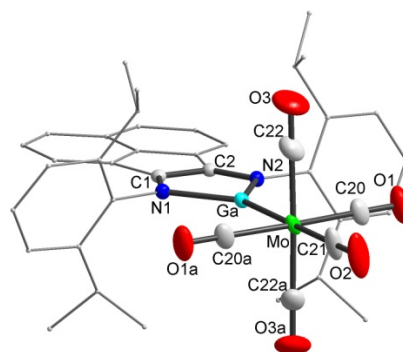


**Figure 1** EPR spectrum of compound **2**: (a) experimental spectrum (toluene, 293 K); (b) simulated spectrum ( $g_x = 2.0022$ ; hfs constants:  $a_x(2 \times ^{14}\text{N}) = 0.317$ ,  $a_x(2 \times ^1\text{H}) = 0.116$ ,  $a_x(2 \times ^{69}\text{Ga}) = 0.114$ ,  $a_x(^{69}\text{Ga}) = 1.542$ ,  $a_x(^{71}\text{Ga}) = 1.958$  mT).

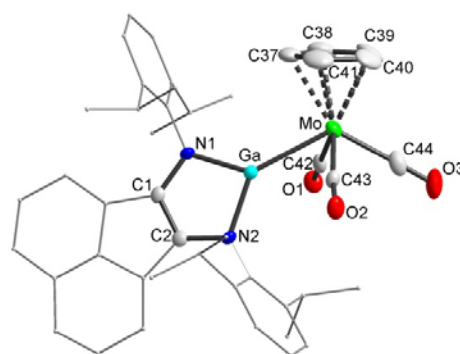
Compounds **3** and **4** are diamagnetic: their  $^1\text{H}$  NMR spectra reveal the expected signals for the dpp-bian ligands.<sup>†</sup> Thus, in complex **3** the isopropyl groups in dpp-bian give rise to two doublets ( $\delta$  1.34 and 1.15 ppm), and one septet ( $\delta$  3.83 ppm). The cyclopentadienyl protons in **3** result in a singlet at  $\delta$  4.40 ppm.

The molecular structures of compounds **2**, **3**, and **4** were determined by single crystal X-ray diffraction,<sup>§</sup> and are depicted in Figures 2, 3, and 4 respectively. Compound **2** and **4** represent octahedral  $\text{Mo}(0)$   $d_6$  complexes. Although the Mo–CO bonds in compound **2** lie within a narrow range (1.999(3)–2.042(2) Å), it is worth to mention, that the CO ligand trans-positioned to gallium exhibits the shortest bond to molybdenum. One might assume a weak back donation from the transition metal to the gallium in compound **2**. In complex **4** the Mo–CO bonds (2.004(1)–2.060(2) Å) are very similar to those in compound **2**. Compound **3** has a “four-leg piano stool geometry” and can be viewed as a molybdenum gallyl with a Ga–Mo covalent bond. The electron count for compound **3** indicates a 18 electron  $\text{Mo}(\text{II})$   $d_4$  complex. As in compounds **2** and **3**, the Mo–CO bonds lengths in complex **3** are close to each other (1.977(3)–2.004(4) Å).

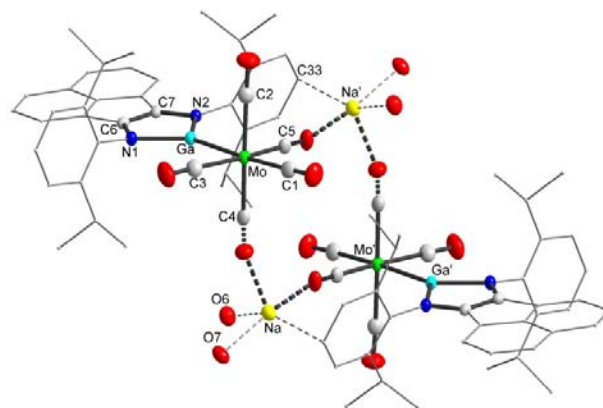
The Ga–Mo bonds in complexes **2**, **3**, and **4** are very much alike (**2**: 2.5352(3); **3**: 2.5608(4); **4**: 2.5678(3) Å) and can be compared with those bonds in  $(\text{Cp}^*\text{Ga})_6\text{Mo}$  (2.3844(6)–2.4930(7) Å),<sup>9</sup>  $(\text{Cp}^*\text{Ga})_3\text{Mo}(\text{CO})_3$  (2.5188(8)–2.5228(8) Å),<sup>9</sup>  $(\text{Cp}^*\text{Ga})_2\text{Mo}(\text{CO})_4$  (2.537(1) and 2.554(1) Å)<sup>11</sup> and  $\text{CpMo}(\text{CO})_2[(\text{GaL})_2(\text{OH})]$  ( $\text{L} = [\text{N}(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)]_2\text{CN}(\text{C}_6\text{H}_{11})_2$ ) (2.5728(9) and 2.5896(9) Å).<sup>12</sup>



**Figure 2** Molecular structure of compound **2**. Thermal ellipsoids are drawn at 50 % probability. Selected bond lengths (Å) and angles (°): Ga–N(1) 1.979(1), Ga–N(2) 1.979(1), Ga–Mo 2.5352(3), Mo–C(20) 2.042(2), Mo–C(20a) 2.042(2), Mo–C(21) 1.999(3), Mo–C(22) 2.032(2), Mo–C(22a) 2.032(2), N(1)–C(1) 1.333(2), N(2)–C(2) 1.333(2), C(1)–C(2) 1.426(3), N(2)–Ga–N(1) 83.50(7).



**Figure 3** Molecular structure of compound **3**. Thermal ellipsoids are drawn at 50 % probability. Selected bond lengths (Å) and angles (°): Ga–N(1) 1.877(2), Ga–N(2) 1.884(3), Ga–Mo 2.5608(4), Mo–C(42) 1.977(3), Mo–C(43) 1.986(3), Mo–C(44) 2.004(4), Mo–C(37) 2.355(4), Mo–C(38) 2.358(4), Mo–C(39) 2.338(4), Mo–C(40) 2.323(4), Mo–C(41) 2.348(4), N(1)–C(1) 1.385(4), N(2)–C(2) 1.387(4), C(1)–C(2) 1.385(4), N(2)–Ga–N(1) 89.97(11).



**Figure 4** Molecular structure of compound **4**. Thermal ellipsoids are drawn at 50 % probability. Carbon atoms of THF molecules are omitted for clarity. Selected bond lengths (Å) and angles (°): Ga–N(1) 1.903(1), Ga–N(2) 1.917(1), Ga–Mo 2.5678(3).

Mo–C(1) 2.021(2), Mo–C(2) 2.055(1), Mo–C(3) 2.060(2), Mo–C(4) 2.013(1), Mo–C(5) 2.004(1), N(1)–C(6) 1.390(2), N(2)–C(7) 1.383(2), C(6)–C(7) 1.364(2), Na–C(33) 2.843(2), N(2)–Ga–N(1) 87.13(5).

Noteworthy, an attempted synthesis of the analogue of compound **5** by reacting CpMo(CO)<sub>3</sub>Cl with [K(tmeda)]<sup>+</sup>[(DAB)Ga]<sup>–</sup> (DAB = (2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NCH<sub>2</sub>)<sub>2</sub>) failed.<sup>13</sup>

The most significant difference between molecule **2** and molecules **3** and **4** is related to the geometries of the gallium heterocycles. Every reduction state of dpp-bian has its own structural “fingerprint”. While evolving from the neutral, to the radical-anionic, and further to the dianionic state of dpp-bian, the C(1)–N(1) and C(2)–N(2) bonds become longer, and the middle C(1)–C(2) bond becomes shorter.<sup>14</sup> In complex **2** these key bonds (N(1)–C(1) 1.333(2), N(2)–C(2) 1.333(2), C(1)–C(2) 1.426(3) Å) point out to the radical-anionic character of the dpp-bian ligand. Note, few other gallium species that consist of radical-anionic ligands have been reported.<sup>15</sup> However, all of them represent Ga(III) derivatives. In comparison to complex **2**, the C–N bonds within the metalacycles in compound **3** and **4** are about 0.05 Å longer, indicating the presence of a dpp-bian dianion in these complexes. Further, as anticipated, the Ga–N bonds in compounds **3** and **4** are notably shorter than those in compound **2**.

In conclusion, in the present work we invented a new redox-active ligand – heterocyclic gallium carbenoid. Since it is sensitive to the electronic configuration of the coordination centre and may behave adaptively, we believe that this ligand can be used to tune the reactivity of transition metal complexes. One of the phenomena that could be observed in the metal complexes of this ligand is redox-isomerism. In the case of compound **2**, its redox-isomers may have the following electronic distribution: [(dpp-bian)<sup>1–</sup>Ga–Mo<sup>0</sup>(CO)<sub>5</sub>] and [(dpp-bian)<sup>2–</sup>Ga–Mo<sup>+1</sup>(CO)<sub>5</sub>]. Indeed, the former isomer is reported in this paper. In order to detect the second one, temperature dependent spectroscopic and magnetic measurements are required. To get more insight in the electronic structure of the complexes reported, and especially to find out whether back donation takes place, theoretical and experimental studies are required. We also plan to synthesize and characterize complexes of heterocyclic gallium carbenoids derived from dpp-bian with metals of the s, p and f blocks of the Periodic Table.

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## Notes and references

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- † Electronic Supplementary Information (ESI) available: Ref. 3, details of syntheses and the <sup>1</sup>H NMR spectra. CCDC references 1004674 (**2**), 1004675 (**3**) and 1004676 (**4**). For ESI and crystallographic data in CIF or other electronic format see DOI: XX.XXX/XXXXXXX.
- ‡ This article is part of the *ChemComm* ‘Non-innocent ligands’ web themed issue.
- § The X-ray data for **2**, **3** and **4** were collected at 100(2) K on a Bruker AXS D8 Quest Photon, an Oxford Xcalibur Eos and a Bruker AXS Smart

- Apex diffractometers respectively (MoK $\alpha$ -radiation,  $\omega$ -scan technique,  $\lambda$  = 0.71073 Å). The structures were solved by direct methods and were refined on  $F^2$  using SHELXTL.<sup>16</sup> All hydrogen atoms were placed in calculated positions and were refined in the riding model. Area-detector scaling and absorption corrections for **2** and **4** were performed using SADABS,<sup>17</sup> for **3** using SCALE3 ABSPACK.<sup>18</sup> Complex **3** contains disordered *i*Pr and Ar groups of dpp-bian ligand. In **4** a solvate molecule of benzene is disordered over two positions about an inversion center.
- Crystal data for **2**: C<sub>41</sub>H<sub>40</sub>GaMoN<sub>2</sub>O<sub>5</sub>,  $M_r$  = 806.41, orthorhombic (*P*bcn),  $a$  = 17.1431(12),  $b$  = 15.7892(11),  $c$  = 14.4285(11) Å,  $\alpha$  =  $\beta$  =  $\gamma$  = 90°,  $V$  = 3905.4(5) Å<sup>3</sup>,  $Z$  = 4,  $d_{\text{calc}}$  = 1.371 Mg/m<sup>3</sup>,  $\mu$  = 1.055 mm<sup>–1</sup>,  $\theta$  = 2.94–28.00°,  $-22 \leq h \leq 22$ ,  $-20 \leq k \leq 20$ ,  $-19 \leq l \leq 19$ , refls. collected/unique 44584/4708 [ $R_{\text{int}}$  = 0.0224], max./min. trans. 0.7109/0.4063, data/restraints/parameters 4708/24/233, GOF on  $F^2$  1.044,  $R$  [ $I > 2\sigma(I)$ ]  $R_1$  = 0.0242,  $wR_2$  = 0.0646, largest diff. peak and hole 0.757/–0.435 e<sup>–</sup>Å<sup>–3</sup>.
- Crystal data for **3**: C<sub>44</sub>H<sub>45</sub>GaMoN<sub>2</sub>O<sub>5</sub>,  $M_r$  = 815.48, monoclinic (*P*2<sub>1</sub>),  $a$  = 8.82154(13),  $b$  = 38.0697(5),  $c$  = 11.69917(16) Å,  $\beta$  = 97.2432(13)°,  $V$  = 3897.62(9) Å<sup>3</sup>,  $Z$  = 4,  $d_{\text{calc}}$  = 1.390 Mg/m<sup>3</sup>,  $\mu$  = 1.054 mm<sup>–1</sup>,  $\theta$  = 3.13–32.41°,  $-12 \leq h \leq 13$ ,  $-57 \leq k \leq 56$ ,  $-16 \leq l \leq 17$ , refls. collected/unique 88721/25974 [ $R_{\text{int}}$  = 0.0567], max./min. trans. 1.00000/0.92352, data/restraints/parameters 25974/317/1120, GOF on  $F^2$  1.016,  $R$  [ $I > 2\sigma(I)$ ]  $R_1$  = 0.0499,  $wR_2$  = 0.0872, largest diff. peak and hole 0.744/–0.820 e<sup>–</sup>Å<sup>–3</sup>.
- Crystal data for **4**: C<sub>104</sub>H<sub>118</sub>Ga<sub>2</sub>Mo<sub>2</sub>N<sub>4</sub>Na<sub>2</sub>O<sub>14</sub>,  $M_r$  = 2025.32, triclinic (*P*–1),  $a$  = 12.1620(17),  $b$  = 12.7895(18),  $c$  = 16.926(2) Å,  $\alpha$  = 72.066(2)°,  $\beta$  = 83.271(2)°,  $\gamma$  = 85.462(2)°,  $V$  = 2485.0(6) Å<sup>3</sup>,  $Z$  = 1,  $d_{\text{calc}}$  = 1.353 Mg/m<sup>3</sup>,  $\mu$  = 0.855 mm<sup>–1</sup>,  $\theta$  = 2.01–26.00°,  $-14 \leq h \leq 14$ ,  $-15 \leq k \leq 15$ ,  $-20 \leq l \leq 20$ , refls. collected/unique 21538/9683 [ $R_{\text{int}}$  = 0.0184], max./min. trans. 0.825/0.7262, data/restraints/parameters 9683/6/595, GOF on  $F^2$  1.036,  $R$  [ $I > 2\sigma(I)$ ]  $R_1$  = 0.0282,  $wR_2$  = 0.0729, largest diff. peak and hole 0.731/–0.397 e<sup>–</sup>Å<sup>–3</sup>.
- E. S. Schmidt, A. Jockisch and H. Schmidbaur, *J. Am. Chem. Soc.*, 1999, **121**, 9758.
  - R. J. Baker, R. D. Farley, C. Jones, M. Kloth and D. M. Murphy, *Dalton Trans.*, 2002, 3844.
  - (a) R. J. Baker and C. Jones, *Coord. Chem. Rev.* 2005, **149**, 1857; (b) C. Jones, A. Stasch and W. D. Woodul, *Chem. Commun.* 2009, 113; (c) S. T. Liddle, J. McMaster, D. P. Mills, A. J. Blake, C. Jones and W. D. Woodul, *Angew. Chem., Int. Ed.* 2009, **48**, 1077; (d) C. Jones, D. P. Mills, R. P. Rose and A. Stasch, *Dalton Trans.* 2008, 4395; (e) P. L. Arnold, S. T. Liddle, J. McMaster, C. Jones and D. P. Mills, *J. Am. Chem. Soc.* 2007, **129**, 5360; (f) C. Jones, D. P. Mills, J. A. Platts and R. P. Rose, *Inorg. Chem.* 2006, **45**, 3146; (h) S. Aldridge, R. J. Baker, N. D. Coombs, C. Jones, R. P. Rose, A. Rossin and D. J. Willock, *Dalton Trans.* 2006, 3313; (i) R. J. Baker, C. Jones and D.M. Murphy, *Chem. Commun.* 2005, 1339; (j) R. J. Baker, C. Jones, D. P. Mills, M. Kloth and D. M. Murphy, *Chem. Eur. J.* 2005, **11**, 2972; (k) R. J. Baker, C. Jones, M. Kloth and J. A. Platts, *Angew. Chem., Int. Ed.* 2003, **43**, 2660.
  - (a) M. Asay, C. Jones and M. Driess, *Chem. Rev.*, 2011, **111**, 354; (b) S. S. Sen, S. Khan, S. Nagendran and H. W. Roesky, *Acc. Chem. Res.*, 2012, **45**, 578; (c) S. Inoue and M. Driess, *Angew. Chem., Int. Ed.*, 2011, **50**, 5614; (d) I. L. Fedushkin, A. A. Skatova, V. A. Chudakova, N. M. Khvoynova and A. Yu. Baurin, *Organometallics*, 2004, **23**, 3714.
  - (a) I. L. Fedushkin, N. M. Khvoynova, A. Yu. Baurin, G. K. Fukin, V. K. Cherkasov and M. P. Bubnov, *Inorg. Chem.*, 2004, **43**, 7807; (b) B. Tumanskii, P. Pine, Y. Apeloig, N. J. Hill and R. West, *J. Am. Chem. Soc.*, 2005, **127**, 8248; (c) G. A. Abakumov, V. K. Cherkasov, A. V. Piskunov, I. A. Aivaz'yan and N. O. Druzhkov, *Dokl. Chem.*, 2005, **404**, 189.
  - A. V. Protchenko, D. Dange, J. R. Harmer, C. Y. Tang, A. D. Schwarz, M. J. Kelly, N. Phillips, R. Tirfoin, K. H. Birjumar, C. Jones, N. Kaltsoyannis, P. Mountford and S. Aldridge, *Nature Chem.*, 2014, **6**, 315.
  - I. L. Fedushkin, A. N. Lukoyanov, A. N. Tishkina, G. K. Fukin, K. A. Lyssenko and M. Hummert, *Chem.–Eur. J.*, 2010, **16**, 7563.
  - J. Emsley, *The Elements*, Clarendon Press, Oxford, 1991, 251.
  - T. Cadenbach, T. Bollermann, C. Gemel, I. Fernandez, M. von Hopffgarten, G. Frenking and R. A. Fischer, *Angew. Chem. Int. Ed.*, 2008, **47**, 9150.

- 10 M. Cokoja, T. Steinke, C. Gemel, T. Welzel, M. Winter, K. Merz and R. A. Fischer, *J. Organomet. Chem.*, 2003, **684**, 277.
- 11 P. Jutzi, B. Neumann, L. O. Schebaum, A. Stammer and H.-G. Stammer, *Organometallics*, 1999, **18**, 4462.
- 5 12 C. Jones, A. Stasch, G. J. Moxey, P. C. Junk and G. B. Deacon, *Eur. J. Inorg. Chem.*, 2009, 3593.
- 13 R. J. Baker, R. D. Farley, C. Jones, D. P. Mills, M. Kloth and D. M. Murphy, *Chem.–Eur. J.*, 2005, **11**, 2972.
- 14 I. L. Fedushkin, A. A. Skatova, V. A. Dodonov, V. A. Chudakova, N. L. Bazyakina, A. V. Piskunov, S. V. Demeshko and G. K. Fukin, *Inorg. Chem.*, 2014, **53**, 5159.
- 10 15 (a) S. Hasenzahl, W. Kaim, T. Stahl, *Inorg. Chim. Acta*, 1994, **225**, 23; (b) T. Pott, P. Jutzi, W. Kaim, W. W. Schoeller, B. Neumann, A. Stammer, H.-G. Stammer and M. Wanner, *Organometallics*, 2002, **21**, 3169; (c) R. J. Baker, C. Jones, D. P. Mills, G. A. Pierce, M. Waugh, *Inorg. Chim. Acta*, 2008, **361**, 427; (e) T. W. Myers and L. A. Berben, *Inorg. Chem.*, 2012, **51**, 1480.
- 15 16 Sheldrick, G. M. SHELXTL v.6.14, Structure Determination Software Suite, Bruker AXS, Madison, Wisconsin, USA, 2003.
- 20 17 Sheldrick, G. M. SADABS v.2012/1, Bruker/Siemens Area Detector Absorption Correction Program, Bruker AXS, Madison, Wisconsin, USA, 2012.
- 18 SCALE3 ABSPACK. Empirical Absorption Correction. CrysAlisPro–Software Package Agilent Technologies, 2012.

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