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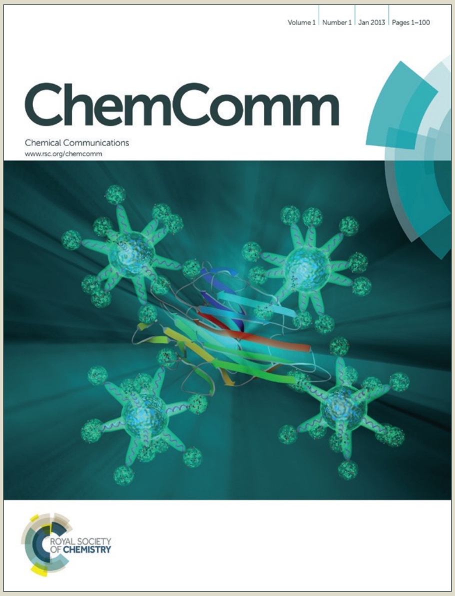

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Delivering carbide moieties to sulfide-rich clusters†

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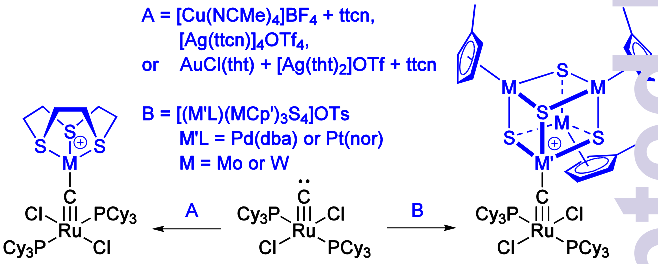
The propensity of the terminal ruthenium carbide Ru(C)Cl$_2$(PCy$_3$)$_2$ (RuC) to form carbide bridges to electron-rich transition metals enables synthetic routes to metal clusters with coexisting carbide and sulfide ligands. Electrochemical experiments show the Ru≡C moiety to exert a relatively large electron-withdrawing effect compared with PPh$_3$, effectively shifting redox potentials.

Carbide ligands in molecular metal sulfide clusters are rare in coordination chemistry. However, the active site FeMo-cofactor of nitrogenase contains a central carbide ligand[1] in a cluster structure composed of iron, molybdenum and sulfur. Naturally, the structural reports have influenced the views on the origin and plausible mechanistic roles of the central atom,[2] but as of yet, it is unclear if the carbide ligand serves in a structure directing or in a redox-modifying capacity. Molecular systems with carbide ligands in surroundings akin to those found in nitrogenase are pertinent synthetic goals allowing elucidation of this ligand in well-defined, isolated environments.

Terminal carbide complexes are known with molybdenum,[3, 4] tungsten,[5] ruthenium,[6, 7, 8] and osmium[9] as the central atoms. Elaboration at the carbide ligands through attachment of main group element fragments,[4, 5, 8, 9, 10] e.g. with H, C, Si, P, O, S, Se, Te, Cl, or I, offers a versatile route to otherwise inaccessible small molecules coordinated to the parent metal centres. Similarly, metallation of terminal carbide ligands[7, 11] paves the way for polynuclear carbide-bridged systems with incipient resemblance to the active site FeMo-cofactor in nitrogenase. In particular, incorporation of iron, molybdenum and sulfur is interesting as these elements make up the remainder of the constituent atoms in the FeMo-cofactor. Despite the growing number of carbide-bridged molecular systems,[12] synthetic systems that feature carbide in metal-sulfide clusters are scarce and only reported for rhenium.[13] This prompted us to decorate the unique corner of the cubane-like cluster complexes M$_3$S$_4$M′ (M = Mo, W, and M′ = Pd, Pt) with the terminal ruthenium carbide, Ru(C)Cl$_2$(PCy$_3$)$_2$ (**RuC**, Cy = cyclohexyl), as it binds readily to electron-rich transition metals (Mo, Rh, Ir, Pd, Pt, Ag and Au)[7, 11] which consequently allows elaboration to polynuclear carbide-bridged systems.



Scheme 1. Formation of carbide-bridged sulfur-rich complexes.

The interest in the family of sulfide clusters, (MCp′)$_3$S$_4^+$ (M = Mo, W, Cp′ = methylcyclopentadienide), covers insertion of metal fragments into M$_3$S$_4$ forming cubane-like M$_3$S$_4$M′ clusters (M′ = Ru, Os, Co, Rh, Ir, Ni, Pd, Pt) and subsequent oxidation state manipulations and ligand exchange at M′.[14, 15, 16] With Ni, Pd or Pt as the unique corner, the M$_3$S$_4$M′ systems exhibit reversible electrochemistry,[15] and this offers an experimental handle on the ability of the carbide ligand to tune redox potentials when attached to M′. This is relevant in quantifying the electronic properties of bridging carbide ligands.

Here, we report the synthesis of complexes with **RuC** coordinated to M′ (Pd and Pt) in M$_3$S$_4$M′ complexes (M = Mo, W). To access structurally similar, but redox-wise simpler systems, we have also synthesized the systems (Cy$_3$P)$_2$Cl$_2$Ru≡C–M′(ttcn)$^+$ (M′ = Cu, Ag, Au) (ttcn = 1,4,7-trithiacyclononane).

When equimolar amounts of **RuC** and [(MCp′)$_3$S$_4$M′L]OTs (M = Mo or W, M′L = Pd(dba) or Pt(nor), OTs$^-$ p-toluenesulfonate, dba = dibenzylideneacetone, nor = norbornene) are dissolved in chloroform or dichloromethane, **RuC** displaces the olefin ligands and attaches to the M′ corner of the cubane moieties to form carbide bridges. This furnishes the family of carbide

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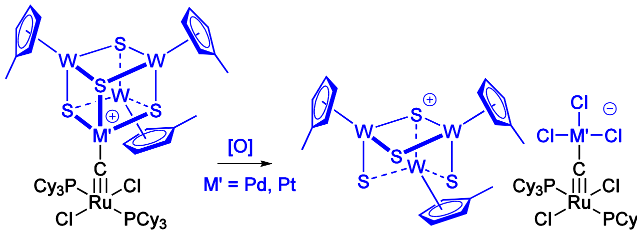
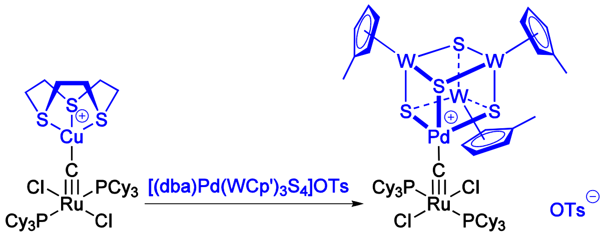


Scheme 2. Oxidation of carbide-bridged cluster complexes leads to the excision of M' that remains attached to the carbide ligand.



Scheme 3. Transmetallation reactions convert **6** to **3**.

decorated clusters $[(Cy_3P)_2Cl_2Ru{\equiv}C{-}M'S_4(MCp')_3]OTs$ (M = Mo, M′ = Pd (**1**), Pt (**2**); M = W, M′ = Pd (**3**), Pt (**4**), cf. Scheme 1). At the palladium centres, the reactions occur readily and are complete within few hours at room temperature; in stark contrast to this, the reactions that involve platinum are only complete within days (as determined by NMR), reflecting a marked kinetic robustness of platinum compared with palladium. In solution, the carbide-bridged complexes undergo slow oxidation that entails the excision of M′(0) from the cubane-based clusters and the persistence of the carbide-M′ bonds, ultimately affording $(Cp'M)_3S_4^+$ and $(Cy_3P)_2Cl_2Ru{\equiv}C{-}M'Cl_3^-$ (Scheme 2, see also ESI). The sulfur-ligated coinage metal complexes $Cu(ttcn)^+$, $[Ag_4(ttcn)_4]^{4+}$, and $Au(ttcn)^+$ react like the M_3S_4M' complexes and associate with the carbide ligand of **RuC** to afford $(Cy_3P)_2Cl_2Ru{\equiv}C{-}M'(ttcn)^+$ complexes (M′ = Cu (**5**), Ag (**6**), Au(**7**)). The $Cu(ttcn)^+$ fragment was generated *in situ* by reaction of ttcn with $[Cu(NCCH_3)_4]BF_4$ and similarly, $Au(ttcn)^+$ was generated from AuCl(tht) treated consecutively with $Ag(tht)_2OTf$ and ttcn (tht = tetrahydrothiophene, OTf^-= triflate). Together with the syntheses of **1** – **4**, this represents a route to metal centres with coordination spheres comprised solely of carbide and sulfur ligands.

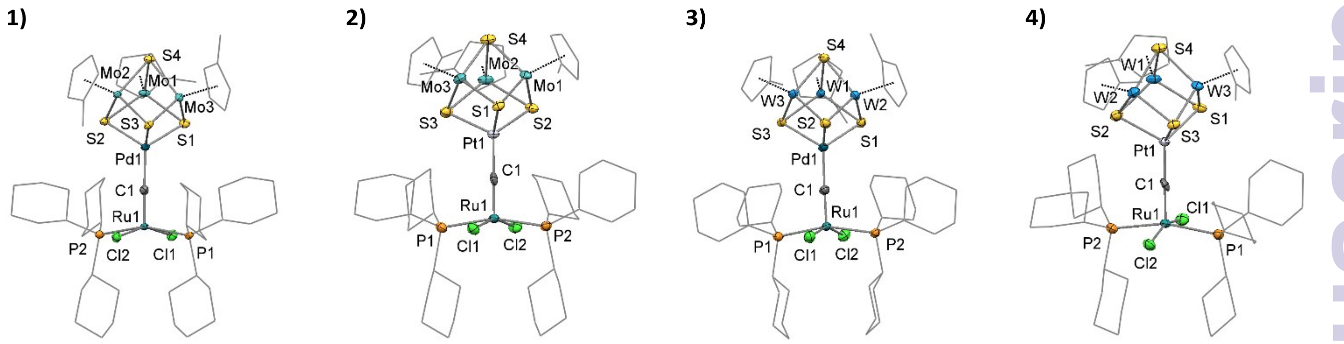
The formation of **1** – **7** is in concord with the multiplets observed by ^1H-NMR and the singlets (PCy_3) observed by ^{31}P-NMR spectroscopies (cf. ESI). Moreover, mass spectrometry (MS) reveals fragments with the m/z ratios expected for the cations in **1** – **7** (cf. ESI). Yet, the most characteristic signature of the complexes are the ^{13}C-NMR resonances from the bridging carbide ligands. These signals (378 – 432 ppm) fall far outside the normal range for organic and most organometallic carbons; moreover, **2**, **4**, and **6** display large coupling constants involving platinum and silver, which attests to non-fluxional bonding in solution. The NMR data from **2** and **4** further lend credence to the assignment of Pt as zero-valent, since the magnitude of the coupling constants ($J_{Pt\text{-}C}$ = 2417 – 2600 Hz) is nearly doubled compared with systems containing **RuC** coordinated to *bona fide* Pt(II) centres (1283 – 1396 Hz).[11] This parallels the magnitude difference typically observed for phosphines coordinated to Pt(0) and Pt(II).[16, 17] NMR also allows evaluation of the relative stabilities of the carbide complexes; for instance, when solutions of **5** are treated with $[(WCp')_3S_4Pd(dba)]OTs$, ^{31}P and ^1H resonances from **3** appear.

7 is too unstable to be isolated from its reaction mixtures and converts into the starting material $(Cy_3P)_2Cl_2Ru{\equiv}C{-}AuCl$, suggesting chloride uptake. However, MS spectra show an isotope cluster matching the cation of **7** (m/z = 1121), and the ^{13}C-NMR spectrum shows the characteristic resonance from a bridging carbide ligand (δ_C = 414 ppm), far from the carbide resonances of $(Cy_3P)_2Cl_2Ru{\equiv}C{-}AuCl$ and $\{(Cy_3P)_2Cl_2Ru{\equiv}C\}_2Au^+$ (both 395 ppm). This suggests that **7**, despite its instability, is analogous to **5** and **6**.

Single crystal X-ray structure determinations of **1** – **6** confir the structures inferred using NMR and MS (molecul structures: Figure 1, selected metrics: Table 1). Qualitatively, – **6** contain square-based pyramidal ruthenium centres with carbide ligand on the apical position acting as a linear bridge to palladium, platinum, copper and silver; additionally, the th sulfur ligators impose a tetrahedral coordination environment on the heterometals. **1** – **5** feature ruthenium-carbide bo that are elongated slightly (2.2 – 4.1%) compared with the trip bond in parent **RuC** (1.632(6) Å).[7] Curiously, the ruthenium carbide bond in **6** is comparable, and perhaps even shorter tha the triple bond in **RuC**. In fact, the bond is near record-short as it ranks among the 0.01% shortest Ru–C bonds in the Cambridge Structural Database. Moreover, the bonds between th bridging carbide and the heterometals are relatively shor compared with representative heterometal-carbon bonds (P shortest 7.7 – 16.6%, Pt: 4.1 – 5.3%, Cu: 9.2%, Ag: 20.5%, se ESI). This agrees with suggestions[11, 18] that **RuC** acts as a accepting ligand towards electron-rich transition metals, enforcing short carbide-heterometal bonds. In the case of **1** – , the bulk of the **RuC** and the S_3-donor units necessitate separation, which imparts a tendency for the carbide bridges to become linear. This steric requirement is less urgent coordination partners with compact ligand spheres, for instance with linear or square planar ligand arrangements, and these often exhibit larger deviations from linearity (172.9 – 180°).[7,

The tetrahedrally coordinated M′ centres and the three sulfu ligators form relatively short bonds for M′ = Cu, bonds o intermediate length for Pd and Pt, and relatively long bonds f Ag. The distances between M′ and the centroids defined by th three coordinating S atoms increases in the order $Mo_3S_4 < W_3S$ < ttcn. The decreased flexibility of M_3S_4 as compared to ttc makes the incomplete cubane clusters undergo conformation changes with greater reluctance, thus limiting the departure of M′ from the S_3 ligand plane.

Electrochemical studies offer insigths into the thermodyna associated with redox processes, and for the carbide-bridge cluster systems this enables assessment of the electro withdrawing capability of **RuC** as a ligand. The electrochemist of $[(MCp')_3S_4M'L]^+$ (M = Mo, W; M′ = Pd, Pt) has been established with PPh_3 as the unique ligand L,[15] and thus these systems offer a highly suitable frame of reference for comparisons with **1** – **3**.



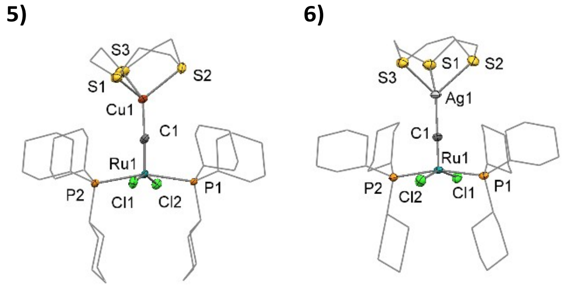


Table 1. Metrics (Å, °) for cluster complexes and cluster models

Complex	Ru–C	M′–C	Ru–C–M′	M′–S$^{\$}$	M′–S$_c$*
1	1.672(3)	1.971(3)	178.3(2)	2.393	1.093
2	1.689(7)	1.896(7)	178.2(5)	2.378	1.084
3	1.668(5)	1.959(5)	178.1(3)	2.413	1.136
4	1.699(9)	1.874(9)	178.8(6)	2.404	1.138
5	1.653(4)	1.876(4)	177.3(2)	2.339	1.274
6	1.622(7)	2.098(7)	176.9(5)	2.562	1.571

$^{\$}$Average. *M′–S$_c$ is the distance from M′ to the centroid of its three ligating S.

Figure 1 molecular structures of the complex cations **1** – **6**. Thermal ellipsoids correspond to the 50% probability level. Hydrogen atoms, solvent molecules [Et_2O, $CHCl_3$], and counterions [$(Cy_3P)_2Cl_2RuC–PdCl_3^-$ (**1**, **3**), OTs^- (**2**, **4**), BF_4^- (**5**), OTf^- (**6**)] are omitted. Carbons from Cy, Cp′, and ttcn are shown as wirefram

In dichloromethane solution, the electrochemical behaviour of **1**, **2**, and **3** is qualitatively identical: cyclic voltammograms (cf. SI) display one reversible reduction process and one reversible oxidation process. In addition, there are signs of an extra partially reversible oxidation process ocurring about 0.4 V above the reversible oxidation process. This parallels the redox processes observed for the analogous phosphine substituted cubane clusters as these display a single reversible one-electron reduction wave and oxidation by two electrons in a two-electron process. Hereby, the formal substitution of **RuC** for PPh_3 leads to similar redox chemistries. This suggests that **RuC** introduces a perturbation on the redox potentials in the $[(MCp')_3S_4M']^+$ core that does not engage the ruthenium centre directly. In addition, the lack of reversible electrochemistry for the ttcn complexes **5** and **6** is pursuant to the electrochemical processes occuring within the M_3S_4M' clusters but not within the **RuC** ligand.

Square wave voltammetry further quantifies the potentials of the redox processes (Table 2). Compared with the PPh_3 complexes, the first reduction and first oxidation processes occur at slightly higher potentials in the **RuC** complexes. Additionally, the second oxidation process in the **RuC** complexes occurs at significantly higher potentials than in the PPh_3 complexes thus suggesting that **RuC** exerts a stronger electron withdrawing effect on the cubane moiety than does PPh_3. This agrees with spectroscopic studies where **RuC** formally replaces PPh_3 as a ligand towards an {IrCl(CO)} fragment: here, the CO stretching frequency is larger for the carbide complex owing to **RuC** being a more potent π-accepting ligand than PPh_3.[11] In conclusion, the electrochemical results demonstrate that the introduction of the Ru≡C moiety in th M_3S_4M' clusters serves to tune their redox potentials.

We have demonstrated a versatile route to molecular system with carbide ligands installed in metal-sulfide clusters, using th terminal carbide complex $Ru(C)Cl_2(PCy_3)_2$ (**RuC**) as the carbid source. Metrics pertaining to the carbide bridges suggest **RuC** t be a relatively strong π-accepting ligand, and electrochemic processes in the cluster complexes occur at higher potentials than in the corresponding complexes where PPh_3 replaces C as ligand. Thus, **RuC** interacts with the metal centres with a considerable degree of electron withdrawal. This demonstrates the ability of the carbide ligand to tune redox potentials metal sulfide clusters. Reductive conditions are known induce aggregation in metal-sulfide clusters,[19] and in th context, cleaving of the Ru≡C triple bonds to incorporate th carbide ligands in metal clusters with all-sulfur ligand sphere represents the natural extension towards clusters modelling th FeMo-cofactor of nitrogenase.

Table 2. Redox potentials for complexes **1 – 3** and their PPh_3 analogues (square wa voltammetry, taking $E^{\ominus\prime}_{2+/3+}$ of ferrocene-ferrocenium as 0).

Complex	$E^{\ominus\prime}_{+/0}$ / V	$E^{\ominus\prime}_{+/2+}$ / V	$E^{\ominus\prime}_{2+/3+}$ / V
1	–1.40	0.48	0.88
$[(Cp'Mo)_3S_4Pd(PPh_3)]^+$	–1.47	0.32	0.32
2	–1.41	0.42	0.84
$[(Cp'Mo)_3S_4Pt(PPh_3)]^+$	–1.56	0.39	0.39
3	–1.68	0.32	0.72
$[(Cp'W)_3S_4Pd(PPh_3)]^+$	–1.79	0.16	0.16

Notes and references

1. K. M. Lancaster, M. Roemelt, P. Ettenhuber, Y. Hu, M. W. Ribbe, F. Neese, U. Bergmann and S. DeBeer, *Science*, 2011, **334**, 974-977; T. Spatzal, M. Aksoyoglu, L. Zhang, S. L. A. Andrade, E. Schleicher, S. Weber, D. C. Rees and O. Einsle, *Science*, 2011, **334**, 940-940; J. A. Wiig, Y. Hu, C. C. Lee and M. W. Ribbe, *Science*, 2012, **337**, 1672-1675; J. A. Wiig, C. C. Lee, Y. Hu and M. W. Ribbe, *J. Am. Chem. Soc.*, 2013, **135**, 4982-4983; K. M. Lancaster, Y. Hu, U. Bergmann, M. W. Ribbe and S. DeBeer, *J. Am. Chem. Soc.*, 2013, **135**, 610-612.
2. W. Orme-Johnson, *Science*, 1992, **257**, 1639-1640; B. E. Smith, *Science*, 2002, **297**, 1654-1655; S. Ramaswamy, *Science*, 2011, **334**, 914-915.
3. J. C. Peters, A. L. Odom and C. C. Cummins, *Chem. Commun.*, 1997, DOI: 10.1039/A704251E, 1995-1996.
4. T. Agapie, P. L. Diaconescu and C. C. Cummins, *J. Am. Chem. Soc.*, 2002, **124**, 2412-2413.
5. A. E. Enriquez, P. S. White and J. L. Templeton, *J. Am. Chem. Soc.*, 2001, **123**, 4992-5002.
6. R. G. Carlson, M. A. Gile, J. A. Heppert, M. H. Mason, D. R. Powell, D. V. Velde and J. M. Vilain, *J. Am. Chem. Soc.*, 2002, **124**, 1580-1581; T. J. Morsing, A. Reinholdt, S. P. A. Sauer and J. Bendix, *Organometallics*, 2015, DOI: 10.1021/acs.organomet.5b00803; E. F. van der Eide, P. E. Romero and W. E. Piers, *J. Am. Chem. Soc.*, 2008, **130**, 4485-4491.
7. A. Hejl, T. M. Trnka, M. W. Day and R. H. Grubbs, *Chem. Commun.*, 2002, DOI: 10.1039/B207903H, 2524-2525.
8. P. E. Romero, W. E. Piers and R. McDonald, *Angew. Chem., Int. Ed.*, 2004, **43**, 6161-6165; S. R. Caskey, M. H. Stewart, J. E. Kivela, J. R. Sootsman, M. J. A. Johnson and J. W. Kampf, *J. Am. Chem. Soc.*, 2005, **127**, 16750-16751; M. L. Macnaughtan, M. J. A. Johnson and J. W. Kampf, *J. Am. Chem. Soc.*, 2007, **129**, 7708-7709.
9. M. H. Stewart, M. J. A. Johnson and J. W. Kampf, *Organometallics*, 2007, **26**, 5102-5110.
10. C. C. Cummins, *Angew. Chem., Int. Ed.*, 2006, **45**, 862-870; S. R. Caskey, M. H. Stewart, M. J. A. Johnson and J. W. Kampf, *Angew. Chem., Int. Ed.*, 2006, **45**, 7422-7424; Y. Mutoh, N. Kozono, M. Araki, N. Tsuchida, K. Takano and Y. Ishii, *Organometallics*, 2010, **29**, 519-522; J. B. Greco, J. C. Peters, T. A. Baker, W. M. Davis, C. C. Cummins and G. Wu, *J. Am. Chem. Soc.*, 2001, **123**, 5003-5013.
11. A. Reinholdt, J. E. Vibenholt, T. J. Morsing, M. Schau-Magnussen, N. E. A. Reeler and J. Bendix, *Chem. Sci.*, 2015, **6**, 5815-5823.
12. S. Kato, I. Noda, M. Mizuta and Y. Itoh, *Angew. Chem., Int. Ed. Engl.*, 1979, **18**, 82-83; I. Noda, S. Kato, M. Mizuta, N. Yasuoka and N. Kasai, *Angew. Chem., Int. Ed. Engl.*, 1979, **18**, 83-83; M. R. Churchill and H. J. Wasserman, *Inorg. Chem.*, 1981, **20**, 4119-4123; D. Mansuy, J. P. Lecomte, J. C. Chottard and J. F. Bartoli, *Inorg. Chem.*, 1981, **20**, 3119-3121; V. L. Goedken, M. R. Deakin and L. A. Bottomley, *J. Chem. Soc., Chem. Commun.*, 1982, DOI: 10.1039/C39820000607, 607-608; S. L. Latesky and J. P. Selegue, *J. Am. Chem. Soc.*, 1987, **109**, 4731-4733; G. Rossi, V. L. Goedken and C. Ercolani, *J. Chem. Soc., Chem. Commun.*, 1988, DOI: 10.1039/C39880000046, 46-47; F. Scherbaum, A. Grohmann, B. Huber, C. Krüger and H. Schmidbaur, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 1544-1546; F. Scherbaum, A. Grohmann, G. Müller and H. Schmidbaur, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 463-465; O. Steigelmann, P. Bissinger and H. Schmidbaur, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 1399-1400; W. Beck, W. Knauer and C. Robl, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 318-320; M. Etienne, P. S. White and J. L. Templeton, *J. Am. Chem. Soc.*, 1991, **113**, 2324-2325; H. Schmidbaur, B. Brachthäuser, O. Steigelmann and H. Beruda, *Chem. Ber.*, 1992, **125**, 2705-2710; H. L. Miller, P. T. Wolczanski and A. L. Rheingold, *J. Am. Chem. Soc.*, 1993, **115**, 10422-10423; F. P. Gabbaï, A. Schier, J. Riede and H. Schmidbaur, *Chem. Ber.*, 1997, **130**, 111-114; A. Kienast, L. Galich, K. S. Murray, B. Moubaraki, G. Lazarev, J. D. Cashion and H. Homborg, *J. Porphyrins Phthalocyanines*, 1997, **1**, 141-157; L. Galich, A. Kienast, H. Hückstädt and H. Homborg, *Z. Anorg. Allg. Chem.*, 1998, **624**, 1235-1242; A. Caselli, E. Solari, R. Scopelliti and C. Floriani, *J. Am. Chem. Soc.*, 2000, **122**, 538-539; S. H. Hong, M. W. Day and R. H. Grubbs, *J. Am. Chem. Soc.*, 2004, **126**, 7414-7415; E. Solari, S. Antonijevic, S. Gauthier, R. Scopelliti and K. Severin, *Eur. J. Inorg. Chem.*, 2007, **2007**, 367-371; W. Knauer and W. Beck, *Z. Anorg. Allg. Chem.*, 2008, **634**, 2241-2245; I. A. Cade, A. F. Hill and C. M. A. McQueen, *Organometallics*, 2009, **28**, 6639-6641; A. L. Colebatch, R. L. Cordiner, A. F. Hill, K. T. H. D. Nguyen, R. Shang and A. C. Willis, *Organometallics*, 2009, **28**, 4394-4399; S. Takemoto, H. Morita, K. Karitani, H. Fujiwara and H. Matsuzaka, *J. Am. Chem. Soc.*, 2009, **131**, 18026-18027; J.-H. Jia and Q.-M. Wang, *J. Am. Chem. Soc.*, 2009, **131**, 16634-16635; R. L. Cordiner, A. F. Hill, R. Shang and A. C. Willis, *Organometallics*, 2010, **30**, 139-144; J.-H. Jia, J.-X. Liang, Z. Lei, Z. X. Cao and Q.-M. Wang, *Chem. Commun.*, 2011, **47**, 4739-4741; A. F. Hill, M. Sharma and A. C. Willis, *Organometallics*, 2012, **31**, 2538-2542; R. D. Young, A. F. Hill, G. E. Cavigliasso and R. Stranger, *Angew. Chem., Int. Ed.*, 2013, **52**, 3699-3702; E. S. Borren, A. F. Hill, R. Shang, M. Sharma and A. C. Willis, *J. Am. Chem. Soc.*, 2013, **135**, 4942-4945; S. Takemoto, J. Ohata, K. Umetani, M. Yamaguchi and H. Matsuzaka, *J. Am. Chem. Soc.*, 2014, **136**, 15889-15892; S. I. Kallane, T. Braun, M. Teltewskoi, B. Braun, R. Herrmann and R. Laubenstein, *Chem. Commun.*, 2015, **51**, 14613-14616.
13. Y. V. Mironov, N. G. Naumov, S. G. Kozlova, S.-J. Kim and V. E. Fedorov, *Angew. Chem., Int. Ed.*, 2005, **44**, 6867-6871; Y. V. Mironov, Y. M. Gayfulin, S. G. Kozlova, A. I. Smolentsev, M. S. Tarasenko, A. S. Nizovtsev and V. E. Fedorov, *Inorg. Chem.*, 2012, **51**, 4359-4367.
14. K. Herbst, L. Dahlenburg and M. Brorson, *Inorg. Chem.*, 2004, **43**, 3327-3328; K. Herbst, M. Monari and M. Brorson, *Inorg. Chem.*, 2001, **40**, 2979-2985; K. Herbst, M. Monari and M. Brorson, *Inorg. Chem.*, 2002, **41**, 1336-1338; K. Herbst, E. Söderhjelm, E. Nordlander, L. Dahlenburg and M. Brorson, *Inorg. Chim. Acta*, 2007, **360**, 2697-2703.
15. K. Herbst, P. Zanello, M. Corsini, N. D'Amelio, L. Dahlenburg and M. Brorson, *Inorg. Chem.*, 2003, **42**, 974-981.
16. K. Herbst, B. Rink, L. Dahlenburg and M. Brorson, *Organometallics*, 2001, **20**, 3655-3660.
17. J. Autschbach and T. Ziegler, *J. Chem. Phys.*, 2000, **113**, 936-947.
18. A. Krapp and G. Frenking, *J. Am. Chem. Soc.*, 2008, **130**, 16646-16658; G. Frenking, R. Tonner, S. Klein, N. Takagi, T. Shimizu, A. Krapp, K. K. Pandey and P. Parameswaran, *Chem. Soc. Rev.*, 2014, **43**, 5106-5139.
19. R. P. Pesavento, C. P. Berlinguette and R. H. Holm, *Inorg. Chem.*, 2007, **46**, 510-516.