A Zwitterionic Heterobimetallic Gold–Iron Complex Supported by Bis(N-Heterocyclic Imine)Silyliumylidene

Franziska Hanusch, Dominik Munz, Jörg Sutter, Karsten Meyer, and Shigeyoshi Inoue*

Dedicated to Professor Matthias Driess on the occasion of his 60th birthday

Abstract: The facile synthesis of the first bis-N-heterocyclic imine-stabilized chlorosilyliumylidene is reported. Remarkably, consecutive reaction of 1 with PPh₃AuCl and K₂Fe(CO)₄ gives rise to the unique heterobimetallic complex 1,2-Mes-NH₂,C₆H₄-ClSiAuFe(CO)₄ (4). The overall neutral complex 4 bears an unusual linear Si–Au–Fe structure and a rare anagotic interaction between the d⁰-configured gold atom and a CH bond of the mesityl ligand. According to the computational analysis and Mössbauer spectroscopy, the formal Fe-oxidation state remains at −II. Thus, the electronic structure of 4 is best described as an overall neutral—yet zwitterionic—heterobimetallic “Si(II)–Au(I)–Fe(II)”-silyliumylidene complex, derived from double anion exchange. The computational analysis indicates strong hyperconjugative back donation from the gold(I) atom to the silyliumylidene ligand.

Introduction

Iron and gold engage in strong metallophilic interactions and show—both in homogeneous and heterogeneous phase—remarkable catalytic activity in industrial relevant processes, such as valorization of CO or hydrogenation of olefins. However, heterogeneous catalysts, including active clusters and nanoparticles, often suffer from agglomeration, non-uniform size distribution, and alloy segregation. Thus, the identification of novel preparative building blocks that ensure the ideal mixing of the alloy metals is of significant current importance. Heterobimetallic complexes arguably represent monomeric subunits of alloy clusters and feature a bifunctional metal core. Cooperativity between these two well-defined sites is believed to engender unusual chemical transformations, and may serve as models; hence, improving our understanding of heterogeneous reaction mechanisms. Still, defined small clusters or even heterobimetallic complexes with a monomeric Au–Fe unit are rare. So far, sterically demanding donor ligands, such as NHCs (N-heterocyclic carbenes) or phosphines, were applied for the isolation of these smallest units of the gold-iron alloy (Figure 1).

Figure 1. Selected examples for ligand stabilized monomeric (A, D, E) and dimeric (B, C) heterobimetallic Au-Fe complexes (Mes = 2,4,6-trimethylphenyl).

Silicon’s ability to partially mimic its lighter congener carbon, and to show metal-like behavior at the same time, has been a powerful concept for small molecule activation and preparation of novel materials. In recent years, silicon-based ligands beyond conventional silyl-ligands have been highlighted. Besides the nowadays well-known silylene ligands, silyliumylidenes are equally fascinating; yet, remain comparatively unexplored. Silyliumylidenes can serve as ligands in transition metal chemistry through their accessible lone pair of electrons, and their cationic nature offers coordination chemistry complementary to silylenes (Figure 2).

Hitherto known silyliumylidene metal complexes are mono- (J¹ₕ, J³ₕ, K⁷) or homobimetallic (I, K⁸) but, so far, no heterobimetallic silyliumylidene complex is reported. Even in silylene chemistry, examples are scarce and are mainly represented by bis(silylenes) or other multinuclear silylene systems. Due to the unique electronic properties of silyliumylidenes, we hypothesize them to be promising candidates to stabilize uncommon bonding motifs, such as
monomeric heterobimetallic Au–Fe complexes. Recently, we have shown that bis-NHIs (bis-N-heterocyclic imines/ bis-imidazoline-2-imines) are suitable for the stabilization of electron deficient main group complexes. Hence, we expect the strong donor abilities in combination with the chelating effect of bridged bis-NHIs to provide a significant advantage in the formation of reactive silyliumylides and their metal complexes. Herein, we present the synthesis of a bis-NH-stabilized silyliumylide ion and its reactivity towards the heavier chalcogenes. Indeed, elemental sulfur, selenium, and tellurium could be activated by stirring with the reaction took 48 hours in case of tellurium for complete conversion to 2c. Driess et al. proved G to be capable of sulfur activation to form the silathionium cation \( \text{G}^{+} \) and similar chalcogen activations were found for bis(NHC-stabilized silyliumylidenes). For bis(iminophosphorane) and amidinate- stabilized silyliumylide ions, the amidinate- type stabilized silyliumylide \( \text{K}^{+} \) (\( \delta^{29}(\text{Si}) = -3.3 \) ppm.)

The \( ^{29}\text{Si} \) NMR resonance for \( \text{I} \) was observed at \( \delta(\text{Si}) = 1.5 \) ppm, which is comparable to bis(iminophosphorane)-stabilized silyliumylide \( \text{G}^{+} \) (\( \delta^{29}(\text{Si}) = -3.3 \) ppm.) This indicates a similar coordination environment as well as a comparable electronic structure. In contrast, the \( ^{29}\text{Si} \) NMR resonance in NHC-stabilized silyliumylides \( \text{H}^{2+} \) (\( \delta^{29}(\text{Si}) = -58.4 \) ppm.) and \( \text{J}^{\text{Se}} \) (\( \delta^{29}(\text{Si}) = -68.8 \) ppm.) was observed at 26.7 ppm, which is comparable to bis(iminophosphorane). For bis(iminophosphorane) and amidinate-stabilized silyliumylides, \( \delta^{29}(\text{Si}) = -82.3 \) ppm. is shifted to higher fields. The structural similarity to \( \text{G} \) was confirmed by single-crystal X-ray diffraction (SC-XRD) analysis of colorless crystals grown from an ortho-difluorobenzene/diethylether solution. Compound \( \text{I} \) crystals in the triclinic space group \( P-1 \) with the Si-atoms in trigonal pyramidal geometry and the sum of bond angles around silicon being 273.9(2°) (Figure 3). The coordinated chlorine \( \text{ClI} \) protrudes from the puckered 5-membered \( \text{C}_{n}\text{Si}-\text{ring} \) at an angle of ca. 90°.

![Figure 3. Solid-state plot of the molecular structure of 1. Thermal ellipsoids are set at 50% probability. Hydrogen atoms, the counter anion and solvent molecules are omitted for clarity; mesityl-substituents are depicted as wireframe for simplicity. Selected bond length- and angles (°): Si–C1 2.37(4), Si–N5 1.829(18), Si–N6 1.8617(18), C1–N5 1.337(3), C4–N6 1.336(3); C1–Si1–N5 95.07(6), C1–Si1–N6 94.61(6).](image)

Results and Discussion

Upon reaction of the neutral ligand 1,2-(mes-NHIm)-C_{6}H_{4} (mes-NHIm = 1,3-bis(mesityl)-imidazolin-2-imine, mesityl = 2,4,6-trimethylphenyl) with an equimolar amount of Dopp-stabilized dichloro-silylene in toluene, chlorosilyliumylide \( \text{I} \) was isolated in 76% yield as a colorless, pearly solid (Scheme 1). Compound \( \text{I} \) is stable under inert conditions and soluble in acetonitrile, difluorobenzene, and pyridine, where-as it decomposes in chlorinated solvents, such as chloroform and dichloromethane.

![Scheme 1. Synthesis of bis-NHi-stabilized chlorosilyliumylide cation \( \text{I} \) (R = mesityl = 2,4,6-trimethylphenyl).](image)
with the coinage metal

Figure 4. Solid-state plot of the molecular structure of 2a. Thermal ellipsoids are set at 50% probability. Hydrogen atoms, the counter anion and solvent molecules are omitted for clarity; mesityl-substituents are depicted as wireframe for simplicity. Selected bond lengths [Å] and angles [°]: Si1–S1 1.9740(6), Si1–Cl1 2.0678(6), Si1–N5 1.7839(12), Si1–N6 1.7972(14), Cl1–N5 1.3446(19), N6–C4 1.3562(2); N5–Si1–N6 89.89(6), N5–Si1–S1 120.22(5), S1–Si1–Cl1 117.05(3), N5–Si1–Cl1 101.96(5).

Motivated by our work on transition metal complexes of J, we also attempted the conversion of 1 with the coinage metal salts CuCl2, AgCl2, and Me3SbAuCl2, respectively (Scheme 2, middle reaction pathway). Adaptating the previously reported experimental procedure, 1 was treated with an equimolar amount of the precursor (or two equivalents in the case of Ag) to ensure complete conversion of poorly soluble precursor salt) at ambient temperature to furnish coinage metal complexes 3a–3c as colorless solids in good yields. Complexes 3 could be identified via 1H, 13C, and 29Si NMR techniques and mass spectrometry (ESI). Coordination of the corresponding transition metal causes a significant downfield shift in 29Si NMR for 3a δ(29Si) = +13.8 ppm, 3b +20.2 ppm (J90Ag = 592.8 Hz, J90Ag = 514.3 Hz), and 3c +18.2 ppm. Compound 3b features the up to now highest observed Si–Ag coupling constant with 592.8 Hz for the 109Ag nucleus. The shift for the gold complex 3c does not follow the expected downfield trend for the series of coinage metal complexes; we attribute this anomaly to relativistic effects.

SC-XRD analysis of compound 2a was carried out on colorless crystals grown from a MeCN/THF mixture. Upon addition of sulfur, the silicon atom adopts a tetrahedral coordination (Figure 4). The Si–S bond length (1.9740(6) Å) is in good agreement with other donor stabilized Si–S double bonds (1.96–2.08 Å) reported before and matches the Si–S bond in G3 (1.984(2) Å). The molecular structure of 2a serves as a representative for compounds 2 by replacing S for Se or Te. Compounds 2b and 2c were characterized by multinuclear NMR techniques, including 77Se (for 2b) and 125Te (for 2c) as well as mass spectrometry (ESI). All data are consistent and, therefore, suggest that 2b and 2c are isostructural with 2a.
54% yield. Neutral 4 is insoluble in benzene, fluorobenzene, and THF, sparingly soluble in acetonitrile and dissolves readily in pyridine. It is stable in pyridine solution up to 80°C according to 1H NMR monitoring.

SC-XRD analysis confirmed the heterobimetallic structure of 4. The silicon atom remains in a distorted tetrahedral coordination environment with the N–Si–N angle being strained to 87.80(13)°, as shown in Figure 5. As common for AuII complexes, the gold atom is nearly linearly coordinated with a Si–Au–Fe angle of 173.65(3)°. The Si–Au bond length (2.2676(9) Å) falls within the range of 2.246–2.363 Å for a Si(II)–Au complex.[23] The Au–Fe distance of 2.5305(6) Å matches related compound A (2.5168 Å) and is within the range of Au–Fe single bond lengths in small molecular gold-iron clusters (A–E: 2.516–2.567 Å). Moreover, comparatively short C–H···Au distances can be detected for the mesityl's ortho-methyl groups pointing towards the gold atom, indicating rare anagostic interactions. The shortest contact is detected for CH42···Au with 2.70(3) Å, while two more are slightly elongated (CH17···Au 2.87(6), CH33···Au 2.97(5) Å) but still shorter than Σvdw(H,Au) = 3.3 Å.[20] Also computationally, an anagostic interaction is found between the gold ion and a methyl group of the mesityl ligand (BP: 2.361 Å; PBE0: 2.445 Å; Figure 8). Although anagostic interactions of AuII complexes have been recently evidenced, C–H···Au interactions remain rare in general.[23] Also, anagostic C–H···Au interactions are a topic of current interest.[28] In contrast to agostic interactions that are understood as three-center-two-electron bonds between C–H and vacant d-orbitals of transition metals with rather short H–M distances and narrow C–H···M angles (≈1.8–2.3 Å; ≈90–140°), the weaker anagostic interactions are associated with filled d-orbitals, longer H–M distances and larger C–H···M angles (≈2.3–2.9 Å; ≈110–170°).[29] Consequently, MII (M = Cu, Ag, Au) complexes, that exclusively feature occupied d-orbitals, are good candidates to observe such contacts. The 29Si NMR spectrum of 4 displays a single resonance at δ(29Si) = +67.6 ppm. This is further downfield shifted compared to starting material 1 (+1.5 ppm) and precursor compound 3c (+18.2 ppm). Infrared (IR) vibrational spectroscopic measurements reveal the carbonyl stretching frequencies of 4 to occur at 1924, 1835, 1811, and 1796 cm⁻¹ (Table 1). The positions of these bands, which were reproduced by calculations at the ZORA-BP86-D3/def2-SVP level of theory,[20] is indicative for the donor properties, that is, combined o-donor/π-acceptor abilities of the “ligand” 3c, which coordinates anionic Fe(CO)₄ in 4. Compared to related compounds (cf. A, JFe, 1Fe–Fe(CO)₄, Na₂Fe(CO)₄, see Table 1) these bands are shifted to higher wavenumbers in case of zwitterionic 4.[31]

Prompted by its unexpected polar solubility properties and CO stretching IR bands, we aimed for further understanding of the bonding situation of 4. Whereas the structural data are consistent with gold in the formal oxidation state of +I, the iron center presents itself electron-rich, compared to Fe(CO)₄-containing complexes, such as 1Fe–Fe(CO)₄. Zero-field ⁵⁷Fe Mössbauer spectroscopy was performed to assess the complex’s electronic structure, (Figure 6 and Figure 7). Specifically, the Mössbauer isomer shift, δ, reflects the total x-orbital electron density at the nucleus, which is determined by the oxidation state, the coordination geometry, spin state, and, consequently, the metal-ligand distance as well as the degree of covalency.[32] The starting material K₂Fe(CO)₄, which is commonly assigned a formal oxidation state of −II, was re-investigated under the exact same conditions, for comparison.[33]

Intriguingly, K₂Fe(CO)₄ (δ = −0.19(1) mm s⁻¹) and 4 (δ = −0.14(1) mm s⁻¹) feature rather similar isomer shifts, which is indicative of similar electronic structures and, thus, physical oxidation states. The computational simulation of the ⁵⁷Fe Mössbauer isomer shift at the DKh2-TPSSh/def2-TZVPP

**Table 1**: Experimental (AT-IR) and computed (ZORA-BP86-D3B/def2-SVP) CO stretching frequencies (cm⁻¹) of 4 and relevant (gold-)iron carbonyl compounds.

| Compound             | Experimental | Calculated |
|----------------------|--------------|------------|
| 4[a]                 | 1924, 1835, 1811, 1796 | 1954, 1872, 1833, 1825 |
| A[b]                 | 1975, 1927, 1830, 1790 | 1926, 1866, 1843, 1818 |
| JFe                  | 2021, 1943, 1903, 1887 | 2027, 1958, 1915, 1895 |
| 1Fe–Fe(CO)₄[c]       | 2035, 1949, 1915 | 2022, 1959, 1934, 1920 |
| Na₂Fe(CO)₄[d]        | 1762         | 1787       |

[a] solid state, neat AT-IR. [b] solid state, neat, nujol-IR.
(Fe: CP(PPP)) level of theory matches the experimental finding almost perfectly, with a calculated isomer shift \( \Delta \theta \) of 0.16 mm s\(^{-1}\) for 4. The isomer shift can be rationalized by the removal of \( d \)-electron density from the iron center by the four CO ligands, resulting in a less-shielded positive charge and concentrated \( s \)-electron density at the iron nuclei. In this regard, experimental characteristics suggest 4 to be best described as zwitterionic L\(_2\)ClSi\(^+\)!Au\(^+\)!Fe\(^{II}\)\(_2\)(CO)\(_4\) (L\(_2\) = bis-NHI).

Electronic structure analysis was carried out using Intrinsis Bond Orbitals (IBOs) obtained by the BP86 (Figure S37) and PBE0 (Figure 8) functionals to further pinpoint the \( d \)-orbital population of the gold and iron atoms in 4. Both methods give consistent results corresponding to formally \( d^{10} \)-configured gold(+I) and iron(-II) ions. A dative interaction between the silicon lone pair (LP) and the gold metal is found with the weight of silicon amounting to 0.70 (Au: 0.30). This value, which is in the typical range of late transition metal NHC complexes, indicates a coordinative ligand-metal interaction of considerable covalency.

The IBOs relating to the gold d\((xy)\) and d\((x^2-y^2)\) orbitals suggest orbital overlap with the methyl groups of the congesting mesityl substituents. The non-bonding Au d\((x')\) orbital shows large admixture of the 6s orbital, whereas the Au d\((xz)\) and d\((yz)\) orbitals indicate strong \( \pi \)-backbonding with the silyliumyldiene ligand. This hyperconjugative interaction, which is also reflected by a calculated L"owdin bond order of 1.56, is analogous to \( \pi \)-backbonding of isoelectronic phosphine ligands commonly applied in homogenous transition metal catalysis. Note that considerable research effort has been directed recently towards engineering cationic phosphine ligands for exceeding-ingly strong \( \pi \)-backbonding.

Also, all \( d \)-orbitals of the iron ion are fully populated, which gives rise to a formal oxidation state of −II. The Fe d\((xy)\), d\((xz)\), and d\((yz)\) orbitals engage in strong backbonding (contribution Fe: 0.75) with the CO ligands, which is in excellent agreement with the \( ^{57} \)Fe Mössbauer spectroscopic data (vide supra). Further, the Fe d\((x^2)\) orbital, associated with a dative bond to the gold atom, is quite covalent (contribution Fe: 0.58; contribution Au: 0.26). Both, the Hirshfeld as well as L"owdin (Figure S39) population analysis indicate accumulation of negative partial charge at the iron atom, whereas the positive partial charge is delocalized across the silyliumyldiene, gold ion, and the NHC moieties. We conclude that the computational analysis further supports a zwitterionic Si(II)\(^+\)!Au(I)\(^+\)!Fe(-II)\(^{2-}\) (4) electronic structure with considerably covalent Au–Si and, especially, Au–Fe (4') bonds, as represented by the mesomeric structures 4 and 4'.

**Conclusion**

In summary, the bis-NHI-stabilized silyliumyldiene 1 was isolated and studied for reactivity. The activation of elemental heavier chalcogens through the silyliumyldiene’s lone pair resulted in complexes 2a–2c, whereas coordination to group...
11 metals led to silyliumylidene-metal complexes 3a–3c. The first over-all neutral heterobimetallic silyliumylidene complex 4 was isolated via nonstandard anion exchange reaction using K₂Fe(CO)₉. The solid-state structure, spectroscopic analysis, and calculations of 4 reveal a rare anagotic interaction of the gold ion with the mesityl ligand, as well as strong donor and considerable π-backbonding capabilities of the silyliumylidene ligand 1. Computational analysis and 1⁹³Fe Mössbauer spectroscopy indicate 4 to feature a zwiterionic L¹ClSi⁺→Au⁻→Fe⁺(CO)₉ electronic structure. Investigations on bond activation reactions and catalytic applications of 1, 3 and 4 are currently ongoing in our group.

Acknowledgements

We are exceptionally grateful to the WACKER Chemie AG and European Research Council (SILION 63794) for financial support. Furthermore, we thank Dr. Alexander Pöthig for measurement and refinement of compound 1 and Kevin Frankiewicz (Prof. Dr. Fässler) for MS measurements. Computational resources by RRZ Erlangen are gratefully acknowledged, G. Knizia is thanked for providing a developer version of IBOView. Open access funding enabled and organized by Projekt DEAL.

Conflict of Interest

The authors declare no conflict of interest.

Keywords: anagotic interactions - gold - iron - silicon - zwiterionic complexes

[1] a) H. Schmidtbaur, A. Schier, Chem. Soc. Rev. 2008, 37, 1931 –1951; b) P. Pykkö, Chem. Rev. 1997, 97, 597–636.
[2] a) Y. Zhang, J. Zhang, B. Zhang, R. Si, B. Han, F. Hong, Y. Niu, L. Sun, L. Li, B. Qiao, K. Sun, J. Huang, M. Haruta, Nat. Commun. 2020, 11, 558; b) S. Yamazoe, K. Koyasu, T. Tsukuda, Acc. Chem. Res. 2014, 47, 816–824; c) G. J. Hutchings, ACS Cent. Sci. 2018, 4, 1095–1101; d) A. S. K. Hashmi, Chem. Rev. 2007, 107, 3180–3211; e) S. A. Shahzad, M. A. Sajid, Z. A. Khan, D. Canseco-Gonzalez, Synth. Commun. 2017, 47, 735–755; f) I. Bauer, H.-J. Knölker, Chem. Rev. 2015, 115, 3170–3387; g) D. Wei, C. Darcel, Chem. Soc. Rev. 2019, 119, 2550–2610; h) A. Fürstenr, ACS Cent. Sci. 2016, 2, 778–789.
[3] a) B. Chatterjee, W.-C. Chang, S. Jena, C. Werlé, ACS Catal. 2020, 10, 14024–14055; b) B. G. Cooper, J. W. Napoline, C. M. Thomas, Catal. Rev. 2012, 54, 1 –40; c) P. Buchwalter, J. J. Rosé, P. Braunstein, Chem. Rev. 2015, 115, 28 –126; d) R. C. Cammarota, L. J. Clouston, C. C. Lu, Coord. Chem. Rev. 2017, 334, 100 –111; e) M. R. Elsby, R. T. Baker, Chem. Soc. Rev. 2020, 49, 8933–8987.
[4] a) K. M. Koczkur, S. Mordikdous, L. Polavarapu, S. E. Krabalak, Dalton Trans. 2015, 44, 17883–17905; b) Y. Mikami, A. Dhalakshamamorthy, M. Alvaro, H. Garcia, Catal. Sci. Technol. 2013, 3, 58–69.
[5] a) B. Berti, M. Bortoluzzi, C. Cersa, C. Femoni, M. C. Iapalucci, R. Mazzoni, S. Zacchini, Eur. J. Inorg. Chem. 2020, 2191–2202; b) B. Berti, M. Bortoluzzi, C. Cersa, C. Femoni, M. C. Iapalucci, R. Mazzoni, F. Vaccà, S. Zacchini, Eur. J. Inorg. Chem. 2019, 3084–3093; c) G. Wang, T. T. Ponduru, Q. Wang, L. Zhao, G. Frenking, H. V. R. Dias, Chem. Eur. J. 2017, 23, 17222–17226; d) M. Bortoluzzi, C. Cesari, I. Ciabatti, C. Femoni, M. Hayatifar, M. C. Iapalucci, R. Mazzoni, S. Zacchini, J. Cluster Sci. 2017, 28, 705–723; e) P. Braunstein, M. Knorr, A. Tiripicchio, M. Tiripicchio Camellini, Inorg. Chem. 1992, 31, 3685–3687; f) U. Schubert, E. Kunz, M. Knorr, J. Müller, Chem. Rev. 1987, 120, 1079–1085; g) C. E. Briant, K. P. Hall, D. M. P. Mingos, J. Chem. Soc. Chem. Commun. 1983, 843–845.
Schaper, C. Ganter, Organometallics 2013, 32, 5269–5272;
c) G. P. Junor, J. Lorkowski, C. M. Weinstein, R. Jazkar, C. Pietraszuk, G. Bertrand, Angew. Chem. Int. Ed. 2020, 59, 22028–22033; Angew. Chem. 2020, 132, 22212–22217.
[21] a) S. Yao, X. Xiong, M. Driess, Chem. Eur. J. 2010, 16, 1281–1288; b) R. Tacke, C. Kobelt, J. A. Baus, R. Bertermann, C. Burschka, Dalton Trans. 2015, 44, 14959–14974.
[22] a) S. R. Alvarado, I. A. Shortt, H.-J. Fan, J. Vela, Organometallics 2015, 34, 4023–4031; b) T. P. A. Ruberu, H. R. Albright, B. Callis, B. Ward, J. Cisneros, H.-J. Fan, J. Vela, ACS Nano 2012, 6, 5348–5359.
[23] a) C. W. So, H. W. Roesky, R. B. Oswald, A. Pal, P. G. Jones, Dalton Trans. 2007, 5241–5244; b) A. Meltzer, S. Inoue, C. Prasang, M. Driess, J. Am. Chem. Soc. 2010, 132, 3038–3046; c) S. Yao, X. Xiong, M. Brym, M. Driess, Chem. Asian J. 2008, 3, 113–118; d) S. H. Zhang, H. X. Yeong, C. W. So, Chem. Eur. J. 2011, 17, 3490–3499.
[24] P. Schwerdtfeger, Heteroat. Chem. 2002, 13, 578–584.
[25] a) M. Theil, P. Jutzi, B. Neumann, A. Stammer, H.-G. Stammer, J. Organomet. Chem. 2002, 662, 34–42; b) T. Troade, A. Prades, R. Rodriguez, R. Mirgalet, A. Baceiredo, N. Saffon-Merceron, V. Branchadell, T. Kato, Inorg. Chem. 2016, 55, 8234–8240.
[26] a) S. R. Alvarado, Inorg. Mater. 2001, 37, 871–885.
[27] a) F. Rekhroukh, L. Estévez, C. Bijani, K. Miqueu, A. Amgoune, D. Bourissou, Angew. Chem. Int. Ed. 2016, 55, 3414–3418; Angew. Chem. 2016, 128, 3475–3479; b) M. Rigoulet, S. Massou, E. D. Sosa Carrio, S. Mallet-Ladeira, A. Amgoune, K. Miqueu, D. Bourissou, Proc. Natl. Acad. Sci. USA 2019, 116, 46–51; c) M. Kumar, J. S. Francisco, J. Am. Chem. Soc. 2020, 142, 6001–6006; d) H. Darmandeh, J. Löffler, N. V. Tzouras, B. Dereli, T. Scherpf, K.-S. Feichtner, S. Vanden Broeck, K. Van Hecke, M. Saab, C. S. I. Cazin, L. Cavallo, S. P. Nolan, V. H. Däschlein-Gessner, Angew. Chem. Int. Ed. 2021, 60, 21014–21024; Angew. Chem. 2021, 133, 21182–21192.
[28] a) W. Scherer, A. C. Dunbar, J. E. Barquera-Lozada, D. Schmitz, G. Eickerling, D. Kratzert, D. Stalke, A. Lanza, P. Macchi, N. P. M. Casati, J. Ebad-Allah, C. Kunzsch, Angew. Chem. Int. Ed. 2015, 54, 2505–2509; Angew. Chem. 2015, 127, 2535–2539; b) H. Schmidbaur, H. G. Raubheimer, L. Dobrzańska, Chem. Rev. 2014, 43, 345–380.
[29] G. dos Passos Gomes, G. Xu, X. Zhu, L.-M. Chamoreau, Y. Zhang, O. Bistri-Aslanoff, S. Roland, I. V. Alabugin, M. Sollogoub, Chem. Eur. J. 2021, 27, 8127–8142.
[30] a) F. Neese, Wiley Interdiscip. Rev.: Comput. Mol. Sci. 2012, 2, 73–78; b) F. Neese, Wiley Interdiscip. Rev.: Comput. Mol. Sci. 2018, 8, e1327.
[31] S. Warrant, L. Postigo, B. Royo, Organometallics 2013, 32, 893–897.
[32] F. Neese, Inorg. Chim. Acta 2002, 337, 181–192.
[33] R. J. Ward, D. Pivordi, A. Carpenter, M. L. Tarlton, S. P. Kelley, L. Maron, K. Meyer, J. R. Walensky, Organometallics 2021, 40, 1411–1415.
[34] P. T. Wołczanski, Organometallics 2017, 36, 622–631.
[35] D. Munz, K. Meyer, Nat. Rev. Chem. 2021, 5, 422–439.
[36] G. Knizia, J. Chem. Theory Comput. 2013, 9, 4834–4843.
[37] a) D. Munz, Organometallics 2018, 37, 275–289; b) C. Lepetit, V. Maraval, Y. Canac, R. Chauvin, Coord. Chem. Rev. 2016, 308, 59–75.
[38] a) L. D. M. Nicholls, M. Alcarazo, Chem. Lett. 2019, 48, 1–13; b) M. Alcarazo, Acc. Chem. Res. 2016, 49, 1797–1805.
[39] CCDC 2085156 (1), 2085157 (2a), and 2085158 (4) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Manuscript received: June 18, 2021
Accepted manuscript online: August 19, 2021
Version of record online: September 22, 2021