



One electron reduction transforms high-valent low-spin cobalt alkylidene into high-spin cobalt(II) carbene radical†

Amanda Grass,^a James A. Bellow,^a Gregory Morrison,^b Hans-Conrad zur Loye,^b Richard L. Lord^c* and Stanislav Groysman^b*^a

Cite this: *Chem. Commun.*, 2020, 56, 8416

Received 26th April 2020,
Accepted 17th June 2020

DOI: 10.1039/d0cc03028g

rsc.li/chemcomm

One electron reduction of formally $\text{Co}^{\text{IV}}(\text{OR})_2(\text{CPh}_2)$ forms the $[\text{Co}^{\text{II}}(\text{OR})_2(\text{CPh}_2)]^-$ anion. Whereas low-spin $\text{Co}(\text{OR})_2(=\text{CPh}_2)$ demonstrated significant alkylidene character, the high-spin $[\text{Co}(\text{OR})_2(\text{CPh}_2)]^-$ anion features a rare $\text{Co}(\text{II})$ -carbene radical. Treatment of $[\text{Co}(\text{OR})_2(\text{CPh}_2)][\text{CoCp}^*_2]$ with xylyl isocyanide triggers formation of two new C–C bonds, and is likely mediated by nucleophilic attack of deprotonated CoCp^*_2 on a transient ketenimine.

Transition metal carbene complexes are among the most important organometallic functionalities, catalyzing formation of new C–C, C–N, and C–O bonds.¹ The reactivity exhibited by transition metal carbenes is strongly correlated with their electronic structure.² While metal–carbenes can exhibit a broad spectrum of electronic structures, Fischer and Schrock carbenes (alkylidenes) clearly define the electrophilic and nucleophilic ends of the spectrum.^{1,2} Fischer carbenes are typically composed of middle or late low-valent transition metals surrounded by soft, strong-field ligands.³ Fischer carbenes demonstrate longer M=C bonds, nucleophilic metal centers, and electrophilic carbene carbons. In contrast, alkylidenes contain early, high-valent metal centers and often feature hard, weak-field ancillary ligation.^{4,5} Alkylidenes demonstrate shorter M=C bonds, electrophilic metals, and nucleophilic carbene carbons. More recently, metal carbene complexes featuring radical character on the carbene carbon received growing attention,^{6–8} in particular due to their pronounced ability to

promote C–H bond activation and C–C bond formation.^{9–12} Various types of metal carbenes require different types of metals/ligands that specifically stabilize a particular type of carbene complex. In this manuscript, we demonstrate that the carbene nature within a single metal/ligand system can be changed *via* a simple reduction.

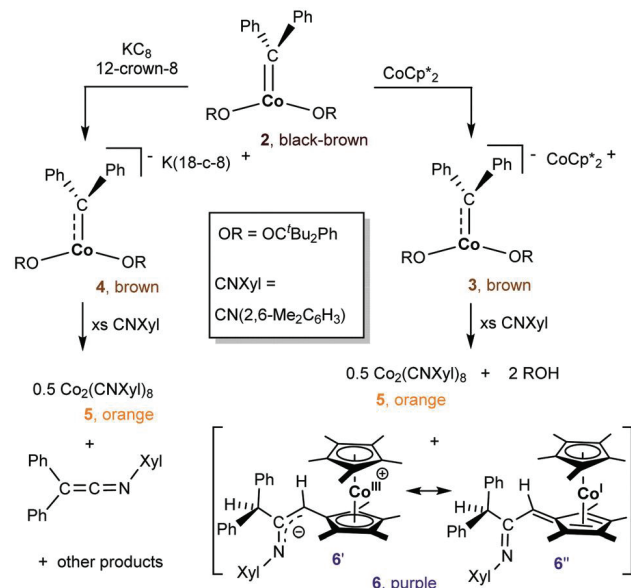
Isolable cobalt carbene complexes typically contain low-valent $\text{Co}(0)/\text{Co}(\text{I})$ metal centers ligated by Fischer-type carbenes.^{13–27} In contrast, $\text{Co}(\text{III})$ -carbene radicals have been proposed to mediate various C–C bond formation reactions. While the reactivity and electronic structures of these species have been thoroughly studied during the last decade, they are generally highly reactive and therefore elusive to isolation.^{28–31} As part of our studies targeting high-valent late transition metal complexes in weak-field ligand environments,^{32,33} we have reported the synthesis of $\text{Co}(\text{OR})_2(=\text{CPh}_2)$ (**2**, Scheme 1).³⁴ **2** was obtained by the reaction of diphenyldiazomethane with a cobalt(II) bis(alkoxide) precursor, $\text{Co}(\text{OR})_2(\text{THF})_2$ (**1**, OR = $\text{OC}^t\text{Bu}_2\text{Ph}$).^{35,36} **2** demonstrated a short Co–C bond of 1.773(3) Å (Fig. 1), and Co–O bonds significantly shorter than in **1**. Spectroscopic, magnetic, and computational studies suggested a low-spin ($S = 1/2$) high-valent cobalt structure intermediate between cobalt(III) antiferromagnetically coupled with a carbene radical and a genuine cobalt(IV) alkylidene.³⁴ The reaction of **2** with isocyanides, which proceeded *via* the initial isocyanide coordination to the metal, provided further evidence for its electrophilic alkylidene-like nature.^{37,38} **2** exhibited several electrochemical events by CV, with the first two (–1.2 V and –2.5 V) exhibiting quasi-reversible behavior. The accessibility of these reductions, particularly the first one, prompted us to investigate chemical reduction of **2**. Herein we demonstrate that one-electron reduction of $\text{Co}(\text{OR})_2(=\text{CPh}_2)$ retains the overall structure of the complex, while transforming the original low-spin high-valent “alkylidene” into a high-spin low-valent $\text{Co}(\text{II})$ -carbene with pronounced radical character at the carbene carbon. We also show that while the parent complex (**2**) exhibited efficient coupling of carbenes with isocyanides to

^a Department of Chemistry, Wayne State University, 5101 Cass Ave, Detroit, MI 48202, USA. E-mail: groysman@chem.wayne.edu

^b Department of Chemistry and Biochemistry, University of South Carolina, Columbia, SC 29208, USA

^c Department of Chemistry, Grand Valley State University, 1 Campus Dr, Allendale, MI 49401, USA. E-mail: lordri@gvsu.edu

† Electronic supplementary information (ESI) available: Experimental procedures, X-ray data collection/refinement details, NMR/IR/UV-vis spectra, and computational details. CCDC 1994783–1994786. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/d0cc03028g



Scheme 1 Synthesis and reactions of the reduced carbene complexes **3** and **4**.

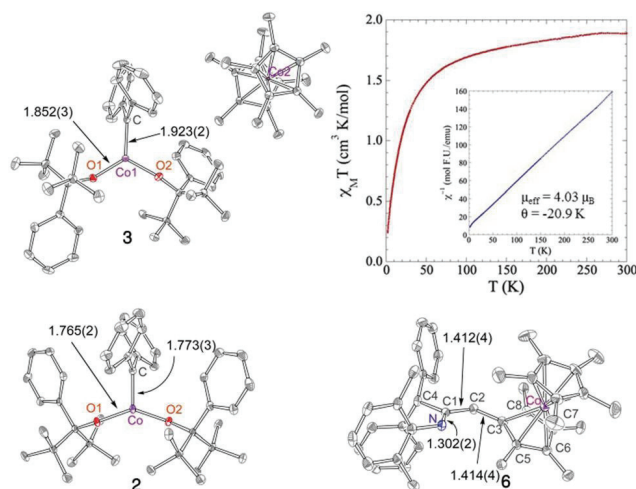


Fig. 1 Top: X-ray structure (50% probability ellipsoids) of **3** and its variable-temperature susceptibility data (measured at 1000 Oe). Bottom left: X-ray structure of **2**,³² 50% probability. Bottom right: X-ray structure of **6**, 50% probability ellipsoids. Selected bond lengths (Å) are presented above.

form ketenimines as final products, the formation of ketenimines by $[\text{Co}(\text{OR})_2(\text{CPh}_2)]^-$ can be followed by subsequent transformations, likely triggered by the anionic nature of the complex.

Treatment of the cold, dark brown solution of **2** in ether with decamethylcobaltacene (CoCp^*_2) resulted in a color change to lighter brown within minutes. Work-up and recrystallization from an ether/THF mixture led to the formation of brown X-ray quality crystals of $[\text{Co}(\text{OR})_2(\text{CPh}_2)][\text{CoCp}^*_2]$ (**3**). The composition of **3** was confirmed by X-ray structure determination and elemental analysis. The structure of **3** is given in Fig. 1. **3** consists of $[\text{Co}(\text{OR})_2(\text{CPh}_2)]^-$ anion and $[\text{CoCp}^*_2]^+$ cation in the

asymmetric unit. The structure of the $[\text{Co}(\text{OR})_2(\text{CPh}_2)]^-$ anion demonstrates a similar trigonal planar geometry to **2** comprised of two alkoxide and one carbene ligands. However, $[\text{Co}(\text{OR})_2(\text{CPh}_2)]^-$ also exhibits notable differences from **2**. The most significant difference between $[\text{Co}(\text{OR})_2(\text{CPh}_2)]^-$ in **3** and the structure of **2** is in the longer Co–C bond, 1.923(2) Å for **3** vs. 1.773(3) Å for **2**. Co–O bonds are also considerably longer (1.852(3) Å in **3**, 1.765(2) in **2**), and are close to Co–O bonds in **1** (1.849(1) Å), suggesting an oxidation state of Co(II).³⁶ Close examination of the brown crystals of $[\text{Co}(\text{OR})_2(\text{CPh}_2)][\text{CoCp}^*_2]$ revealed the presence of a second (polymorphic) structure (**3a**, see ESI†). While **3** crystallized in a triclinic cell, **3a** crystallizes in a monoclinic base-centered setting C_2/c ; both anion and cation feature crystallographic C_2 symmetry. Anions in **3** and **3a** are rotamers, differing by the alkoxide conformation (see Fig. S1, ESI† for the structure of **3a**). However, metric parameters obtained from the structure of **3a** are virtually identical to **3** (Co–C bond of 1.91(1) Å, Co–O bond of 1.861(5) Å), further supporting significant elongation of cobalt–ligand bonds as a result of one-electron reduction. Close inspection of the carbene aryl C–C bonds reveals slight bond distance alternation for both **3** and **2**, consistent with the radical nature of the carbene (see Fig. S22, ESI†).

In addition to X-ray crystallography, **3** was also investigated by ^1H NMR, UV-vis, and IR spectroscopy, and magnetic measurements. The ^1H NMR spectrum of **3** in $\text{THF}-d_8$ spans a wide range of 152 ppm (108 ppm to –44 ppm), consistent with its paramagnetic nature. The UV-vis spectrum of **3** exhibits peaks at 500, 648, and 712 nm. Magnetic measurements on **3** were conducted both in solution (Evans' method) and in solid state (magnetic susceptibility measurements, SQUID). Notably, the solution magnetic moment of 4.2(3) μ_B suggests a high-spin cobalt carbene, in contrast to the low-spin cobalt carbene **2** ($2.0 \pm 0.2 \mu_B$).³⁴ These observations were further supported by magnetic susceptibility measurements. Measurements were performed in the temperature range of 2 K to 300 K at 0.1 T. Both **2** and **3** follow Curie–Weiss behavior, as evidenced by the linear relationship between χ^{-1} vs. T . Fitting the susceptibility data gave effective magnetic moments of 2.19 μ_B for **2** and 4.03 μ_B for **3**, consistent with the solution magnetic data described above (Fig. 1 and Fig. S18, S19, ESI†).

The electronic structure of the anionic fragment of **3** (denoted **3'** for simplicity) was investigated by DFT calculations at the B3LYP/6-31G(d) level of theory,^{39–42} based on our earlier study on **2**.³⁴ Singlet and triplet states corresponding to anti- and ferromagnetically coupled low-spin Co(II) and carbene radical were found to be higher (+15–16 kcal mol^{–1}) in free energy than the triplet and quintet states corresponding to anti- and ferromagnetically coupled high-spin Co(II) and carbene radical. These latter two states are only separated by 1 kcal mol^{–1} in free energy. DFT predicts the triplet state to be lowest in electronic and free energy, so our analysis focuses on that state. Mulliken spin analysis of the $[\text{Co}(\text{OR})_2]$ and $[\text{CPh}_2]$ fragments shows spins of 2.87 and –0.87, in contrast to 1.89 and –0.89 for **2**.³⁴ This suggests reduction occurs primarily at the Co center of **2**. Corresponding orbitals are shown in Fig. 2. Based on these data, and similar analyses for the quintet

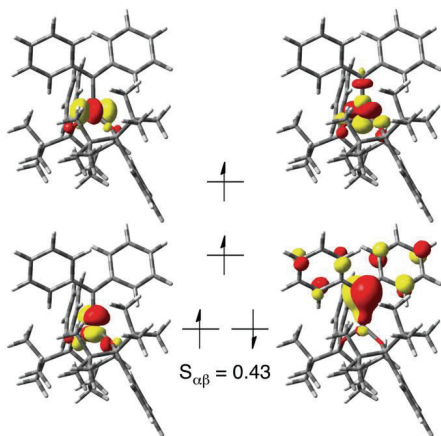
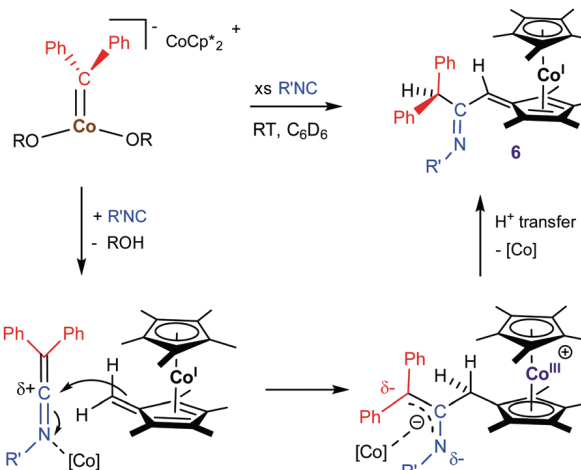


Fig. 2 Corresponding orbital diagram (iso = 0.05 a.u.) of **3'**.

(see ESI[†]), we interpret **3'** to be a high-spin cobalt(II) ion antiferromagnetically coupled to a carbene radical anion with thermal population of the corresponding ferromagnetic state. This interpretation is consistent with the magnetic data, where a fit of χT results in a small, negative coupling constant between the high-spin Co(II) and carbene radical, $J/k_B < -10$ K (see ESI[†]).

2 demonstrated facile carbene-transfer reactivity with isocyanides (including xylyl and adamantyl isocyanide).³⁷ To understand reactivity differences between **2** and **3**, the reactivity of **3** with xylyl isocyanide was also investigated. Addition of excess xylyl isocyanide (CNXyl) to **3** manifested a color change to dark purple. Recrystallization of the crude reaction mixture from ether produced two different types of crystals: larger orange and smaller purple. As the orange and the purple products exhibited similar solubility and crystallized together, the only route to separate these products was *via* mechanical separation. X-ray diffraction studies carried out on the orange crystals revealed previously reported structure of Co₂(CNXyl)₈ (**5**, Scheme 1).⁴³ ¹H NMR spectrum of the isolated orange product was also consistent with Co₂(CNXyl)₈. Structural determination of the purple crystals revealed the intriguing product **6**. **6** can be approximated by two resonance structures: zwitterionic form **6'** Ph₂C(H)C(NXyl)C(H)[Cp(Me)₄Co^{III}Cp*] that contains decamethylcobaltocenium covalently linked to enamide with delocalized negative charge, and form **6''**, that contains Cp*-Co(I)-tetramethylfulvene further conjugated to the (C1=N) imine. The X-ray structure of **6** (Fig. 1) is in agreement with **6''**. The bond distances within the NC1C2C3 fragment and relatively narrow dihedral angle between the [NC1C2] plane and tetramethylfulvene (~18°) are consistent with the delocalized conjugated system. The formulation of the metal fragment as tetramethylfulvene-Co(I) is further supported by a significantly longer Co–C3 bond 2.216(3) compared with bonds to other carbons (Co–C5/C6/C7/C8, 2.011–2.064 Å). ¹H NMR spectrum of isolated **6** (C₆D₆) is consistent with the solid-state structure, containing a singlet for the allylic Ph₂C(H)C proton at 3.82 ppm and a singlet for the vinylic proton at 5.34 ppm (see ESI[†]). **6** likely originates from the activation of decamethylcobaltocene by transient ketenimine Ph₂C=C=N(Xyl). Observation of the



Scheme 2 Possible mechanism for the formation of **6**. R' = xylyl.

previously reported Ph₂C=C=N(Ad)³⁷ in the reaction of **3** with adamantyl isocyanide lends further support for the postulated Ph₂C=C=N(Xyl) intermediate.

What is the mechanism behind the formation of **6**? Decamethylcobaltocenium (and related species) has been previously demonstrated to undergo deprotonation to form the tetramethylfulvene complex (resonance form of deprotonated CoCp*₂⁺).^{44–47} It is feasible that the initial deprotonation of decamethylcobaltocenium by RO[–] is followed by a nucleophilic attack on Ph₂C=C=N(Xyl).⁴⁸ In support of this mechanism, ROH was observed in the reaction mixture. No ligand decomposition products consistent with alkoxide radicals were observed by NMR.³⁶ The reaction is completed by proton transfer from the (Cp*) methylene position to the benzylic position and formal reduction of the metal, to form the fully conjugated product (Scheme 2). However, we cannot rule out that the formation of **6** is initiated *via* radical H-atom abstraction from the Cp*-methyl group, as H-atom abstraction has been also previously demonstrated for the decamethylcobaltocenium ion,⁴⁹ and ketenimines have been shown to exhibit radical reactivity in the presence of radical initiators.⁵⁰

To obtain further insight into the reaction, we have also prepared the potassium salt of the reduced carbene, [Co(OR)₂(CPh₂)] [K(18-crown-6)] (**4**). **4** was obtained by the reduction of **2** with potassium graphite (KC₈), followed by the addition of 18-crown-6 (Scheme 1). The complex was characterized by UV-vis, IR, and elemental analysis. The UV-vis spectrum of **4** (peaks at 503, 651, and 712 nm) closely resembles the spectrum of **3** (500, 648, and 712 nm). We also note that treatment of **2** with two equivalents of CoCp*₂ or KC₈ did not result in a doubly reduced species, forming again complexes **3** and **4**, respectively. The reaction of cobaltocenium-free **4** with xylyl isocyanide leads to the observation of stable ketenimine³⁷ (in addition to **5**), consistent with the absence of relatively acidic CoCp*₂⁺, and providing further support for the mechanism depicted in Scheme 2.

In summary, we demonstrated that one-electron reduction of the high-valent alkylidene-like formally Co^{IV}(OR)₂(=CPh₂) (**2**) produced low-valent carbene-like [Co^{II}(OR)₂(–CPh₂*)][–] product, which was isolated as [Co(OR)₂(CPh₂)] [CoCp*₂] (**3**) or

[Co(OR)₂(CPh₂)] [K(18-crown-6)] (4). Treatment of [Co(OR)₂(CPh₂)] [CoCp*₂] with xylyl isocyanide led to the formation of compound 6 and Co₂(CNXyl)₈ (5). The formation of the intriguing conjugated product 6 likely proceeded *via* nucleophilic attack of deprotonated decamethylcobaltocenium on pre-formed ketenimine. Consistently, substitution of the decamethylcobaltocenium counterion by potassium counterion led to the observation of the corresponding ketenimine and Co₂(CNXyl)₈. Our future studies will focus on the design of new cobalt-carbene species featuring related, yet more stable alkoxide ligand environments and the investigation of their reactivity.

S. G. and R. L. L. are grateful to the National Science Foundation (NSF) for current support under grant number CHE-1855681. We thank Mr R. F. J. (Roel) Epping (Universiteit van Amsterdam) and Prof. Joel S. Miller (The University of Utah) for helpful discussions. Magnetic measurements (GM and HCzL) acknowledge DOE award DE-SC0016574. Experimental characterization was carried out at Lumigen Instrument Center of Wayne State University. Amanda Grass is a Knoller Fellow.

Conflicts of interest

There are no conflicts to declare.

Notes and references

- R. A. Moss and M. P. Doyle, *Contemporary Carbene Chemistry*, Wiley, Hoboken, New Jersey, 2013, ISBN: 1118730267.
- T. Strassner, *Top. Organomet. Chem.*, 2004, **13**, 1–20.
- K. H. Doetz and J. Stendel, *Chem. Rev.*, 2009, **109**, 3227–3274.
- R. R. Schrock and C. Coperet, *Organometallics*, 2017, **36**, 1884–1892.
- R. R. Schrock, *Chem. Commun.*, 2005, 2773–2777.
- P. Cui and V. M. Iluc, *Chem. Sci.*, 2015, **6**, 7343–7354.
- A. P. Deziel, M. R. Hoffbauer and V. M. Iluc, *Organometallics*, 2019, **38**, 879–887.
- P. Cui, M. R. Hoffbauer, M. Vyushkova and V. M. Iluc, *Dalton Trans.*, 2019, **48**, 9663–9668.
- W. I. Dzik, X. P. Zhang and B. de Bruin, *Inorg. Chem.*, 2011, **50**(20), 9896–9903.
- C. te Grotenhuis and B. de Bruin, *Synlett*, 2018, 2238–2250.
- S. P. Heins, W. D. Morris, T. R. Cundari, S. N. MacMillan, E. B. Lobkovsky, N. M. Livezey and P. T. Wolczanski, *Organometallics*, 2018, **37**, 3488–3501.
- X. Cui and X. P. Zhang, Asymmetric C–H Functionalization by Transition Metal-Catalyzed Carbene Transfer Reactions, in *Comprehensive Organic Synthesis II*, ed. P. Knochel and G. Molander, Amsterdam, Elsevier, 2nd edn, 2014, vol. 7, pp. 86–120.
- J. Du, W. Chen, Q. Chen, X. Leng, Y.-S. Meng, S. Gao and L. Deng, *Organometallics*, 2020, **39**, 729–739.
- D. Wang, Q. Chen, X. Leng and L. Deng, *Inorg. Chem.*, 2018, **57**, 15600–15609.
- S. L. Marquard, M. W. Bezpalko, B. M. Foxman and C. M. Thomas, *J. Am. Chem. Soc.*, 2013, **135**, 6018–6021.
- D. J. Harrison, S. I. Gorelsky, G. M. Lee, I. Korobkov and R. T. Baker, *Organometallics*, 2013, **32**, 12–15.
- J. T. Fuller, D. J. Harrison, M. C. Leclerc, R. T. Baker, D. H. Ess and R. P. Hughes, *Organometallics*, 2015, **34**, 5210–5213.
- G. M. Lee, D. J. Harrison, I. Korobkov and R. T. Baker, *Chem. Commun.*, 2014, **50**, 1128–1130.
- T. Ikeno, I. Iwakura and T. Yamada, *J. Am. Chem. Soc.*, 2002, **124**, 15152–15153.
- L. Jordi, J. M. Moreto, S. Ricart, J. M. Vinas, M. Mejias and E. Molins, *Organometallics*, 1992, **11**, 3507–3510.
- A. Sisak, A. Sironi, M. Moret, C. Zucchi, F. Ghelfi and G. Palyi, *J. Chem. Soc., Chem. Commun.*, 1991, **3**, 176–178.
- A. C. Filippou, E. Herdtweck, H. Alt and J. Guido, *J. Organomet. Chem.*, 1988, **355**, 437–447.
- S. A. Benyunes and P. A. Chaloner, *J. Organomet. Chem.*, 1988, **341**, C50–C52.
- G. Erker, R. Lecht, J. L. Petersen and H. Boennemann, *Organometallics*, 1987, **6**, 1962–1967.
- D. W. Macomber and R. D. Rogers, *Organometallics*, 1985, **4**, 1485–1487.
- D. J. Doonan, J. E. Parks and A. L. Balch, *J. Am. Chem. Soc.*, 1976, **98**, 2129–2134.
- E. O. Fischer, F. R. Kreissl, E. Winkler and C. G. Kreiter, *Chem. Ber.*, 1972, **105**, 588–598.
- C. te Grotenhuis, N. van den Heuvel, J. I. van der Vlugt and B. de Bruin, *Angew. Chem., Int. Ed.*, 2018, **57**, 140–145.
- B. G. Das, A. Chirila, M. Tromp, J. N. H. Reek and B. de Bruin, *J. Am. Chem. Soc.*, 2016, **138**, 8968–8975.
- Y. Wang, X. Wen, X. Cui, L. Wojtas and X. P. Zhang, *J. Am. Chem. Soc.*, 2017, **139**, 1049–1052.
- J. V. Ruppel, X. Cui, X. Xu and X. P. Zhang, *Org. Chem. Front.*, 2014, **1**, 515–520.
- A. Grass, D. Wannipurage, R. L. Lord and S. Groysman, *Coord. Chem. Rev.*, 2019, **400**, 1–16.
- J. A. Bellow, M. Yousif and S. Groysman, *Comments Inorg. Chem.*, 2015, **36**, 92–122.
- J. A. Bellow, S. A. Stoian, J. Van Tol, A. Ozarowski, R. L. Lord and S. Groysman, *J. Am. Chem. Soc.*, 2016, **138**, 5531–5534.
- J. A. Bellow, D. Fang, N. Kovacevic, P. D. Martin, J. Shearer, G. A. Cisneros and S. Groysman, *Chem. – Eur. J.*, 2013, **19**, 12225–12228.
- J. A. Bellow, M. Yousif, D. Fang, E. G. Kratz, G. A. Cisneros and S. Groysman, *Inorg. Chem.*, 2015, **54**, 5624–5633.
- A. Grass, N. S. Dewey, R. L. Lord and S. Groysman, *Organometallics*, 2019, **38**, 962–972.
- A. Grass, S. A. Stoian, R. L. Lord and S. Groysman, *Chem. Commun.*, 2019, **55**, 8458–8461.
- S. H. Vosko, L. Wilk and M. Nusair, *Can. J. Phys.*, 1980, **58**, 1200–1211.
- C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1988, **37**, 785–789.
- A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648–5652.
- P. J. Stephens, F. J. Devlin, C. F. Chabalowski and M. J. Frisch, *J. Phys. Chem.*, 1994, **98**, 11623–11627.
- P. A. Leach, S. J. Geib, S. J. Corella, G. F. Garnock and N. J. Cooper, *J. Am. Chem. Soc.*, 1994, **116**, 8566–8574.
- Y. Okhi, A. Murata, M. Imada and K. Tatsumi, *Inorg. Chem.*, 2009, **48**, 4271–4273.
- J. Bauer, H. Braunschweig, C. Hörl, K. Radacki and J. Wahler, *Chem. – Eur. J.*, 2013, **19**, 13396–13401.
- N. J. Hartmann, G. Wu and T. W. Hayton, *Organometallics*, 2017, **36**, 1765–1769.
- D. Buchholz, B. Gloaguen, J.-L. Fillaut, M. Cotrait and D. Astruc, *Chem. – Eur. J.*, 1995, **1**, 374–381.
- P. Lu and Y. Wang, *Chem. Soc. Rev.*, 2012, **41**, 5687–5705.
- L. L. Cao, J. Zhou, Z. W. Quo and D. W. Stephan, *Angew. Chem., Int. Ed.*, 2019, **58**, 18487–18491.
- M. Alajarin, A. Vidal and M.-M. Ortin, *Org. Biomol. Chem.*, 2003, **1**, 4282–4292.