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Reactivity of gold and copper acetylide with a secondary borane

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Gold(I) triphenylphosphine phenylacetylide reacts with bis(1-methyl-*ortho*-carboranyl)borane to give a hydroboration product that is best described as an η^2-1-borataallene gold complex. Contrarily, the analogous reaction with the copper acetylide undergoes transmetalation to furnish an alkynylborate with the $CuPPh_3^+$ moiety bound to the alkyne and a hydride bridging boron to copper. The compounds were analyzed by single crystal X-ray diffraction and DFT computations that rationalize the unusual bonding arrangements.

The hydroboration reaction is a versatile synthetic tool to introduce functionalization on unsaturated carbon–carbon bonds with anti-Markovnikov selectivity.[1] The boryl group in hydroboration products is a convenient handle that can be oxidized to a variety of functional groups or used as a building block for coupling reactions.[2] Borane (BH_3) is an effective hydroboration reagent, however, it bears three reactive B–H bonds, thus secondary boranes offer more control with the reactivity of the borane tuned by the two other substituents on boron.[3] Secondary boranes featuring chelating π-donors increase stability but reduce reactivity that typically necessitates a catalyst.[4] Electron withdrawing groups increase the electrophilicity at boron and enhance hydroboration reactivity.[5] Fluoroaryl groups have been very effective and recently, it has been demonstrated that *ortho*-carborane substituents give rise to potent organoborane Lewis acids.[6]

The first catalyzed hydroboration reactions were with rhodium and since then, other late transition metals have become prominent.[7] In recent years, gold and copper catalysts have demonstrated high efficacy in the hydroboration of alkynes.[8] In copper catalyzed hydroborations of terminal alkynes, copper acetylide species are proposed intermediates in the catalytic cycle.[9] Despite this, direct stoichiometric reactions between gold or copper acetylides and secondary boranes have not been reported. In fact, the only stoichiometric reaction reported of a metal acetylide with a secondary borane is that of a bis(imino)-pyridine ligated cobalt(II) acetylide with HBPin that furnished *E* and *Z* 1,1-hydroboration products, where the hydrogen and boryl group are on the same carbon (Fig. 1).[10] In addition to the hydroboration catalysis, it is known that electron rich metal centers proximal to main group Lewis acidic centers, including tricoordinate boranes, readily engage in Z-type interactions.[11] In this work, we investigate the reactivity of a gold and copper acetylide with the extremely potent hydroboration reagent, bis(1-methyl-*ortho*-carboranyl)borane ($HB^{Me}oCb_2$, ^{Me}oCb = 1-methyl-*ortho*-carborane)[12] to determine whether typical hydroboration reactivity occurs, Z-type bonding, or a different outcome.

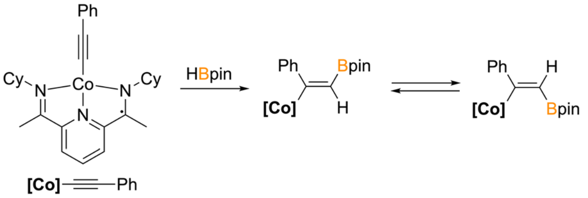

Fig. 1 Reported Co(II) phenylacetylide hydroboration with HBPin.

The equimolar reaction of $Ph_3PAuCCPh$ and $HB^{Me}oCb_2$ in toluene at 23 °C was monitored by NMR spectroscopy (Fig. 2). After 30 minutes, a $^{11}B\{^1H\}$ NMR resonance was observed at

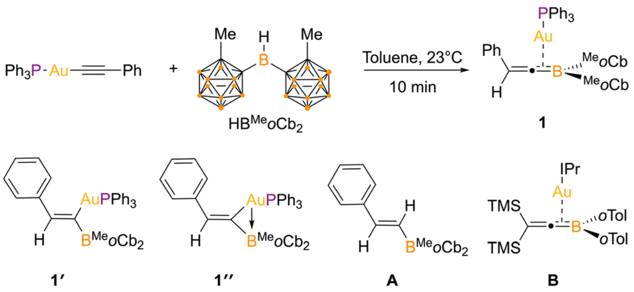

Fig. 2 Synthesis of **1** with different structural representations (**1′** and **1″**), reported syn-1,2-hydoboration product of phenylacetylene (**A**) and the only known 1-borataallene metal complex (**B**, IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene).

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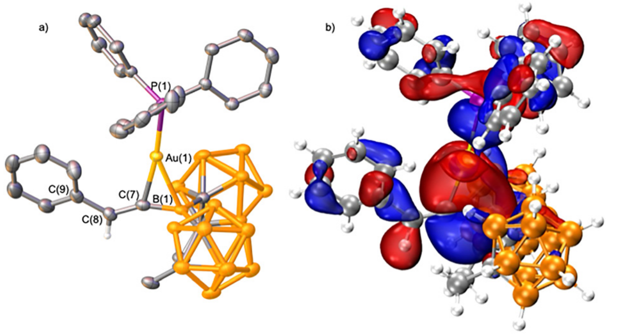

Fig. 3 (a) X-ray diffraction structure of **1**. Selected bond lengths (Å) and angles (°): Au(1)–B(1) 2.430(4), Au(1)–C(7) 2.135(4), B(1)–C(7) 1.469(6), C(7)–C(8) 1.331(5), P(1)–Au(1)–C(7) 171.24(10), C(7)–C(8)–B(1) 155.2(4). (b) HOMO−1 of **1**.

25.0 ppm, shifted upfield from $HB^{Me}oCb_2$ (70.9 ppm) and in the ^{31}P NMR spectrum, a resonance at 41.7 ppm is observed, shifted slightly from $Ph_3PAuCCPh$ (44.7 ppm) with complete consumption of the two starting materials. Upon work up, the new species was isolated in 57% yield. X-ray diffraction of crystals grown from vapor diffusion of *n*-pentane into a concentrated toluene solution revealed a product consistent with a *syn*-1,2-hydroboration reaction with the substituents introduced according to the polarity of the acetylide. The boryl group is introduced on the α-carbon of $Ph_3PAuCCPh$ and the hydrogen to the β-carbon (**1**, Fig. 3a).

Close analysis of the structure reveal that the structure of **1** deviates from an idealized vinyl borane from a *syn*-1,2-hydroboration (**1′**). While the bond distance between the formerly acetylide carbons, C(7) to C(8), is 1.331(5) Å and consistent with a double bond, the C(7) to B(1) bond length is shorter than a single bond at 1.497(9) Å, lying in the range of a borataalkene.[13a] However, the C(8)-C(7)-B(1) bond angle of 155.2(4)° is considerably perturbed from an idealized trigonal planar geometry at C(7). Comparing this angle in **1** to the analogous complex with a proton in place of gold, *E*-PhHC = $CHB^{Me}oCb_2$ (**A**: 128.8(6)°) reveals considerable expansion. Based on these metrical parameters, two other bonding descriptors were considered that would impact this angle, a vinyl borane that features a gold to boron *Z*-type interaction (**1″**) and an η^2-coordinated 1-boratallene gold complex. The Au–B distance of 2.436(1) Å is in the range of both a Z-type (2.26 to 2.59 Å) or an η^2-boratalkene interaction (2.29 to 2.42 Å).[11g,13]

DFT analysis reveals a gold to carbon Wiberg bond index (WBI) less than unity of 0.68 and from gold to boron at 0.41. The B(1) to C(7) WBI is 1.29, considerably higher than that of the analogous complex with a proton in place of gold (**A**, WBI = 0.91). Combined with a WBI of 1.81 for the C═C bond, these results indicate the best descriptor is a Au-borataallene complex. The gold center interacts stronger with the central carbon atom of the borataallene fragment than the boron [Au–B = 2.436(1) Å and Au–C = 2.135(4) Å], in line with the polarized nature of Au-borataalkene systems.[14] The NPA charge at B(1) is positive at 0.651, attributed to the electron withdrawing power of the carborane substituents. The central carbon, C(7) has an NPA charge of −0.530, consistent with the polarization of a borataalkene while the gold atom bears a positive charge of 0.454, in line with boratalkene π-complexation to $AuPPh_3^+$. Analysis of the frontier orbitals revealed the HOMO−1 features a bonding interaction between the gold center and the BC π-bond (Fig. 3b).

In the literature, borataallene structures are rare. There have been four 1-borataallenes reported with two being this year and only one 2-boratallene.[15] Regarding borataallene metal complexes, only one exists, a gold 1-borataallene complex reported by Yamashita and co-workers (**B**) that features *ortho*-tolyl groups on boron, two trimethylsilyl groups on the allenic carbon, and the IPr carbene on gold (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene).[16] Their method of preparation involved reacting IPrAu-B(*o*-toyl)$_2$ with bis(trimethylsilyl)acetylene. The solid-state structures of **1** and **B** are similar with the pertinent Au–B, Au–C, B–C, and C–C distances close to or within error of measurement of each other [Au–B = 2.430(4) *vs.* 2.441(4) Å, Au–C = 2.135(4) *vs.* 2.164(4) Å, B–C = 1.469(6) *vs.* 1.509(6) Å, and C–C = 1.331(5) *vs.* 1.338(5) Å] despite featuring very different substituents on the allenic carbon and boron atoms as well as a different ancillary ligand on gold. Interestingly, neither **1** or **B** were generated from the free 1-borataallene and are distinct synthetic routes.

Treatment of $Ph_3PCuCCPh$ with $HB^{Me}oCb_2$ in toluene at 23 °C and examining the $^{11}B\{^1H\}$ NMR spectrum after 30 minutes revealed a resonance upfield from the cluster boron region at −18.5 ppm, very different than the boryl resonance for **1** at 25.0 ppm (Fig. 4). This peak became a doublet in the ^{11}B NMR spectrum, consistent with the hydride retained on boron. The ^{31}P NMR resonance is at −1.4 ppm, slightly shifted from $Ph_3PCuCCPh$ at −4.6 ppm. Obtaining a single crystal X-ray diffraction structure reveals the product as the copper-alkyne π-complex, **2**, with the $HB^{Me}oCb_2$ moiety covalently bound to the α-carbon (Fig. 5). The borane underwent transmetalation with copper to furnish the borate functionalized alkyne and $CuPPh_3^+$ migrated to the alkyne. In the ^1H NMR spectrum, the hydrogen in the B–H–Cu unit is in the region of the carborane cluster B–H atoms. Conducting the reaction with $DB^{Me}oCb_2$ and analyzing the ^2H NMR spectrum reveals a peak at 2.38 ppm corresponding to the bridging deuteride.[17] To determine if **2** would isomerize to give a hydroboration product, the toluene solution of **2** was stirred for 16 h at 23 °C but no change was observed by ^{31}P or ^{11}B NMR spectroscopy. Heating at 80 °C for 72 hours gave an indiscernible mixture.

The CC bond in **2** is 1.218(2) Å and the FT-IR CC stretching frequency is 2211 cm^{-1}, both in the range of alkynes (CC bond lengths range 1.20 to 1.22 Å and FT-IR frequencies lie between 2100 and 2260 cm^{-1}). The copper atom is equidistant to the two

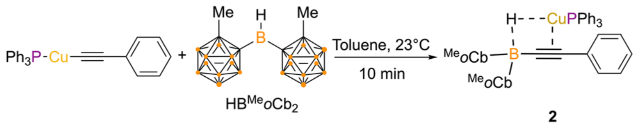

Fig. 4 Synthesis of **2**.

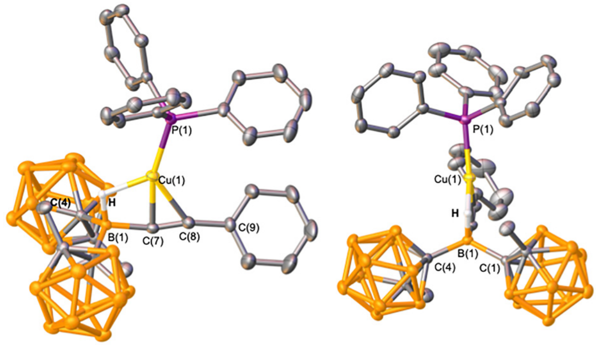

Fig. 5 Two views of the X-ray diffraction structure of **2**. Selected bond lengths (Å) and angles (°): Cu(1)–C(7) 2.0037(14), Cu(1)–C(8) 2.0083(16), C(7)–C(8) 1.218(2), C(7)–B(1) 1.590(2), C(8)–C(7)–B(1) 165.11(15), C(7)–C(8)–C(9) 165.37(18), C(4)–B(1)–C(1) 122.73(12), C(1)–B(1)–C(7) 108.36(11), C(4)–B(1)–C(7) 112.02(12).

carbon atoms [Cu(1)–C(1) 2.0037(14) Å and Cu(1)–C(2) 2.0083(16) Å] and the bond angles about the two alkyne carbon atoms are close to linear [C(8)–C(7)–B(1) 165.11(15)° and C(7)–C(8)–C(9) 165.37(18)°]. The sum of the C–B–C bond angles about B(1) is 343.11(18)°, consistent with a distorted tetrahedral environment with a hydride bound to boron. In the mass spectrum, a peak was observed in the cation mode for $CuPPh_3^+$ (*m/z* = 325.0185) and in the negative mode for the alkynylborate fragment (*m/z* = 427.4581).

The isolated species **2** resembles cobalt hydride alkyne π-complexes that have been proposed as catalytic intermediates in cobalt-mediated alkyne hydroboration reactions with HBPin by Chirik as well as by Grutzmacher and Hu.[10,18] Their cobalt complex reacted with an equivalent of terminal alkyne to release the vinyl borane hydroboration product and regenerate the metal acetylide. Given this, **2** was subjected to stoichiometric reactions with terminal alkynes (phenylacetylene and trimethylsilyl acetylene) and heated in toluene to 80 °C for 16 h, however no reaction was observed. The high hydride affinity of the bis(1-methyl-*ortho*-carboranyl)boryl unit rationalizes the trapping of **2**.[6h] The mechanism to form **2** could be *via* a hydroboration sequence involving metalate shift of the $CuPPh_3$ moiety or through a direct transmetalation. Copper acetylides are more susceptible to transmetalation than gold acetylides, that may be the root of the differing reactivity.[19]

The Cu–C WBIs approach 0.5 that is in line with π-complexation and reveal a slightly stronger bond to the borate functionalized carbon of the alkyne [C(7)–Cu = 0.41, C(8)–Cu = 0.33]. The computed NPA charges show significant cationic charge on copper (+0.83) and slight negative charges on the alkyne carbon atoms, with the borate carbon being higher in magnitude [C(7) (−0.29) and C(8) (−0.07)]. Regarding the hydride, the B–H interaction is computed to be much stronger than the Cu–H interaction (WBI = 0.69 *vs.* 0.20) but consistent with the bridged hydride. The NPA on the central boron atom is +0.19, attributed to the strong electron withdrawing ability of the carborane substituents and the "hydride" is 0.00, indicative of the contacts to copper and boron.

This work demonstrates that $HB^{Me}oCb_2$ reacts with $Ph_3PAuCCPh$ and $Ph_3PCuCCPh$ to give two distinct products. The gold complex is best described as an η^2-coordinated 1-boratallene gold complex while the copper species is an alkynylborate complexed to $CuPPh_3^+$ *via* the alkyne. The former is a rare example of a 1-boratallene or a borataalkene unit complexed to gold. The copper species features a bridging hydride between boron and the metal that is reminiscent of proposed intermediates in metal catalyzed hydroborations. The resilient B-H interaction is attributed to the high hydride affinity of the bis(*ortho*-carboranyl)boryl moiety and provides insight into unique reactivity of secondary boranes with CC triply bonded species.

R. A. T. carried out the synthetic experiments and the single crystal X-ray diffraction analyses. K. A. F. and K. L. S. performed the DFT calculations and composed the related text. C. D. M. conceived and supervised the project. R. A. T. and C. D. M. wrote the manuscript with edits from K. A. F. and K. L. S.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article have been included as part of the supplementary information (SI). Supplementary information: experimental procedures, NMR spectra, computational details, and X-ray crystallographic data. See DOI: https://doi.org/10.1039/d5cc06957b.

CCDC 2491533 and 2491534 contain the supplementary crystallographic data for this paper.[20a,b]

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References

1 (*a*) H. C. Brown, R. Liotta and C. G. Scouten, *J. Am. Chem. Soc.*, 1976, **98**, 5297–5301; (*b*) H. C. Brown, R. Liotta and L. Brener, *J. Am. Chem. Soc.*, 1977, **99**, 3427–3432; (*c*) G. Zweifel and H. C. Brown, *Org. React.*, 1963, **13**, 1–54; (*d*) G. Wilkinson, F. G. A. Stone and E. W. Abel, *Comprehensive organometallic chemistry: the synthesis, reactions, and structures of organometallic compounds*, Pergamon Press, 1982; (*e*) H. C. Brown, in *Advances in Organometallic Chemistry*, ed. F. G. A. Stone and R. West, Academic Press, 1973, vol. 11, pp. 1–20; (*f*) H. C. Brown, *Science*, 1980, **210**, 485–492.

2 (*a*) A. Suzuki, *Angew. Chem., Int. Ed.*, 2011, **50**, 6722–6737; (*b*) J. X. Qiao and P. Y. S. Lam, *Synthesis*, 2011, 829–856; (*c*) R. Martin and S. L. Buchwald, *Acc. Chem. Res.*, 2008, **41**, 1461–1473.

3 (*a*) T. Clark and P. V. R. Schleyer, *J. Organomet. Chem.*, 1978, **156**, 191–202; (*b*) J. M. Clay and E. Vedejs, *J. Am. Chem. Soc.*, 2005, **127**, 5766–5767.

4 (*a*) D. P. Zobernig, B. Stöger, L. F. Veiros and K. Kirchner, *ACS Catal.*, 2024, **14**, 12385–12391; (*b*) H. Braunschweig, R. D. Dewhurst and A. Schneider, *Chem. Rev.*, 2010, **110**, 3924–3957; (*c*) G. A. Chotana, B. A. Vanchura II, M. K. Tse, R. J. Staples, J. Robert, E. Maleczka and M. R. Smith III, *Chem. Commun.*, 2009, 5731–5733; (*d*) B. A. Vanchura II, S. M. Preshlock, P. C. Roosen, V. A. Kallepalli, R. J. Staples, J. R. E. Maleczka, D. A. Singleton and M. R. Smith III, *Chem. Commun.*, 2010, **46**, 7724–7726; (*e*) M. R. Smith III, R. Bisht, C. Haldar, G. Pandey, J. E. Dannatt, B. Ghaffari, R. E. Jr. Maleczka and B. Chattopadhyay, *ACS Catal.*, 2018, **8**, 6216–6223.

5 (*a*) S. Ranasinghe, Y. Li, M. E. Andrews, M. O. Akram, R. A. Thornton and C. D. Martin, *Chem. Commun.*, 2025, **61**, 10182–10185; (*b*) D. J. Parks, R. E. von, H. Spence and W. E. Piers, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 809–811.

6 (*a*) L. Xiang, J. Wang, A. Matler and Q. Ye, *Chem. Sci.*, 2024, **15**, 17944–17949; (*b*) K. Vashisth, S. Dutta, M. O. Akram and C. D. Martin, *Dalton Trans.*, 2023, **52**, 9639–9645; (*c*) X. Tan, X. Wang, Z. H. Li and H. Wang, *J. Am. Chem. Soc.*, 2022, **144**, 23286–23291; (*d*) L. Xiang, A. Matler, L. Tan and Q. Ye, *Dalton Trans.*, 2024, **53**, 11655–11658; (*e*) K. M. Lee, J. O. Huh, T. Kim, Y. Do and M. H. Lee, *Dalton Trans.*, 2011, **40**, 11758–11764; (*f*) J. O. Huh, H. Kim, K. M. Lee, Y. S. Lee, Y. Do and M. H. Lee, *Chem. Commun.*, 2010, **46**, 1138–1140; (*g*) K. C. Song, H. Kim, K. M. Lee, Y. S. Lee, Y. Do and M. H. Lee, *Dalton Trans.*, 2013, **42**, 2351–2354; (*h*) M. O. Akram, C. D. Martin and J. L. Dutton, *Inorg. Chem.*, 2023, **62**, 13495–13504; (*i*) M. O. Akram, J. R. Tidwell, J. L. Dutton and C. D. Martin, *Angew. Chem., Int. Ed.*, 2022, **61**, e202212073; (*j*) V. Nori, F. Pesciaioli, A. Sinibaldi, G. Giorgianni and A. Carlone, *Catalysts*, 2021, **12**, 5; (*k*) J. Wang, L. Xiang, X. Liu, A. Matler, Z. Lin and Q. Ye, *Chem. Sci.*, 2024, **15**(13), 4839–4845; (*l*) C. Zhang, X. Liu, J. Wang and Q. Ye, *Angew. Chem., Int. Ed.*, 2022, **61**, 36; (*m*) C. Zhang, J. Wang, W. Su, Z. Lin and Q. Ye, *J. Am. Chem. Soc.*, 2021, **143**, 8552–8558; (*n*) L. Xiang, J. Wang, I. Krummenacher, K. Radacki, H. Braunschweig, Z. Lin and Q. Ye, *Chem. – Eur. J.*, 2023, **29**, e202301270; (*o*) J. Kahlert, L. Böhling, A. Brockhinke, H.-G. Stammler, B. Neumann, L. M. Rendina, P. J. Low, L. Weber and M. A. Fox, *Dalton Trans.*, 2015, **44**, 9766–9781; (*p*) S. Yruegas, J. C. Axtell, K. O. Kirlikovali, A. M. Spokoyny and C. D. Martin, *Chem. Commun.*, 2019, **55**, 2892–2895; (*q*) M. Diab, K. Jaiswal, D. Bawari and R. Dobrovetsky, *Isr. J. Chem.*, 2023, **63**, e202300010; (*r*) C. Zhang, J. Wang, Z. Lin and Q. Ye, *Inorg. Chem.*, 2022, **61**(45), 18275–18284; (*s*) L. Xiang, J. Wang, I. Krummenacher, K. Radacki, H. Braunschweig, Z. Lin and Q. Ye, *Chem. – Eur. J.*, 2023, **29**, e202301270; (*t*) H. Wang and Z. Xie, *Organometallics*, 2021, **40**(22), 3819–3824; (*u*) C. Dai, Y. Huang and J. Zhu, *Organometallics*, 2022, **41**(12), 1480–1487; (*v*) M. Faizan, D. Behera, M. Chakraborty and R. Pawar, *ChemPhysChem*, 2024, **25**, e202400647; (*w*) L. Zhang and Z. Xie, *Chem. Sci.*, 2021, **12**, 1745–1749; (*x*) M. Zhong, J. Zhang and Z. Xie, *Chem. Sci.*, 2024, **15**, 18048–18051.

7 (*a*) S. J. Geier, C. M. Vogels, J. A. Melanson and S. A. Westcott, *Chem. Soc. Rev.*, 2022, **51**, 8877–8922; (*b*) M. Haberberger and S. Enthaler, *Chem. – Asian J.*, 2013, **8**, 50–54; (*c*) H. Wadepohl, U. Arnold, U. Kohl, H. Pritzkow and A. Wolf, *J. Chem. Soc. Dalton Trans.*, 2000, **20**, 3554–3565; (*d*) K. Burgess and M. J. Ohlmeyer, *Chem. Rev.*, 1991, **91**, 1179–1191; (*e*) D. Männig and H. Nöth, *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 878–879.

8 (*a*) D. Hemming, R. Fritzemeier, S. A. Westcott, W. L. Santos and P. G. Steel, *Chem. Soc. Rev.*, 2018, **47**, 7477–7494; (*b*) M. Zhong, Y. Gagné, T. O. Hope, X. Pannecoucke, M. Frenette, P. Jubault and T. Poisson, *Angew. Chem.*, 2021, **133**, 14619–14624; (*c*) I. G. R. Juliani Costa, P. R. Batista, M. T. de Oliveira and A. A. C. Braga, *ACS Org. Inorg. Au*, 2025, **5**, 181–193; (*d*) Q. Wang, S. E. Motika, N. G. Akhmedov, J. L. Petersen and X. Shi, *Angew. Chem., Int. Ed*, 2014, **53**, 5418–5422; (*e*) G. Wang, Y. Wang, Z. Li, H. Li, M. Yu, M. Pang and X. Zhao, *Org. Lett.*, 2022, **24**, 9425–9430.

9 (*a*) E. A. Romero, R. Jazzar and G. Bertrand, *J. Organomet. Chem.*, 2017, **829**, 11–13; (*b*) X. Liu, W. Ming, A. Friedrich, F. Kerner and T. B. Marder, *Angew. Chem., Int. Ed.*, 2020, **59**, 304–309; (*c*) Y. Gao, Z. Q. Wu and K. M. Engle, *Org. Lett.*, 2020, **22**(13), 5235–5239.

10 J. V. Obligacion, J. M. Neely, A. N. Yazdani, I. Pappas and P. J. Chirik, *J. Am. Chem. Soc.*, 2015, **137**, 5855–5858.

11 (*a*) A. Amgoune and D. Bourissou, *Chem. Commun.*, 2010, **47**, 859–871; (*b*) H. Braunschweig and R. D. Dewhurst, *Dalton Trans.*, 2010, **40**, 549–558; (*c*) J. S. Jones and F. P. Gabbaï, *Acc. Chem. Res.*, 2016, **49**, 857–867; J. S. Jones, C. R. Wade and F. P. Gabbaï, *Angew. Chem., Int. Ed.*, 2014, **53**, 8876–8879; (*d*) H. Braunschweig and M. Colling, *Coord. Chem. Rev.*, 2001, **223**, 1–51; (*e*) W. Huynh, J. W. Taylor, W. H. Harman and M. P. Conley, *Dalton Trans.*, 2021, **50**, 14855–14863; (*f*) J. W. Taylor, A. McSkimming, M.-E. Moret and W. H. Harman, *Angew. Chem., Int. Ed.*, 2017, **56**, 10413–10417; (*g*) H. Kameo and H. Nakazawa, *Chem. – Asian J.*, 2013, **8**, 1720–1734; (*h*) F. Krämer, M. Radius, H. Berberich, I. Fernández and F. Breher, *Chem. Commun.*, 2022, **58**, 3905–3908; (*i*) F.-G. Fontaine, J. Boudreau and M.-H. Thibault, *Eur. J. Inorg. Chem.*, 2008, 5439–5454; (*j*) C. R. Wade, B. L. Murphy, S. Bedajna and F. P. Gabbaï, *Organometallics*, 2024, **43**, 1785–1788; Y.-H. Lo and F. P. Gabbaï, *Angew. Chem., Int. Ed.*, 2019, **58**, 10194–10197; (*k*) D. You, H. Yang, S. Sen and F. P. Gabbaï, *J. Am. Chem. Soc.*, 2018, **140**, 9644–9651; (*l*) G. Bouhadir and D. Bourissou, *Chem. Soc. Rev.*, 2016, **45**, 1065–1079; (*m*) G. Bouhadir and D. Bourissou, *Chem. Soc. Rev.*, 2016, **45**, 1065–1079.

12 M. O. Akram, J. Tidwell, J. L. Dutton and C. D. Martin, *Angew. Chem., Int. Ed.*, 2023, **62**, e202307040.

13 (*a*) M. Eaton, Y. Zhang and S.-Y. Liu, *Chem. Soc. Rev.*, 2024, **53**, 1915–1935; (*b*) Y. Li, Y.-H. Shen, A. M. Esper, J. R. Tidwell, A. S. Veige and C. D. Martin, *Dalton Trans.*, 2023, **52**, 668–674; (*c*) A. Simonneau, F. Jaroschik, D. Lesage, M. Karanik, R. Guillot, M. Malacria, J.-C. Tabet, J.-P. Goddard, L. Fensterbank, V. Gandon and Y. Gimbert, *Chem. Sci.*, 2011, **2**, 2417–2422; (*d*) S. Bontemps, G. Bouhadir, K. Miqueu and D. Bourissou, *J. Am. Chem. Soc.*, 2006, **128**, 12056–12057; (*e*) A. Ueno, K. Watanabe, C. G. Daniliuc, G. Kehr and G. Erker, *Chem. Commun.*, 2019, **55**, 4367–4370; (*f*) D. W. Stephan and G. Erker, *Angew. Chem., Int. Ed.*, 2015, **54**, 6400–6441.

14 (*a*) N. A. Phillips, R. Y. Kong, A. J. P. White and M. R. Crimmin, *Angew. Chem., Int. Ed.*, 2021, **60**, 12013–12019; (*b*) T. A. Bartholome, A. Kaur, D. J. D. Wilson, J. L. Dutton and C. D. Martin, *Angew. Chem., Int. Ed.*, 2020, **59**, 11470; (*c*) G. K. Wisofsky, K. Rojales, X. Su, T. A. Bartholome, A. Molino, A. Kaur, D. J. D. Wilson, J. L. Dutton and C. D. Martin, *Inorg. Chem.*, 2021, **60**(24), 18981–18989.

15 (*a*) M. O. Akram, K. A. French, K. L. Shuford and C. D. Martin, *J. Am. Chem. Soc.*, 2025, **147**, 33120–33126; (*b*) M. Pilz, J. Allwohn, P. Willershausen, W. Massa and A. Berndt, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 1030–1032; (*c*) R. Bertermann, H. Braunschweig, C. K. L. Brown, A. Damme, R. D. Dewhurst, C. Hörl, T. Kramer, I. Krummenacher, B. Pfaffinger and K. Radacki, *Chem. Commun.*, 2014, **50**, 97–99; (*d*) C. Kojima, K.-H. Lee, Z. Lin and M. Yamashita, *J. Am. Chem. Soc.*, 2016, **138**, 6662–6669.

16 A. Suzuki, L. Wu, Z. Lin and M. Yamashita, *Angew. Chem., Int. Ed.*, 2021, **60**, 21007–21013.

17 A. Begum, M. O. Akram and C. D. Martin, *Dalton Trans.*, 2025, **54**, 5664–5667.

18 J. Wen, Y. Huang, Y. Zhang, H. Grützmacher and P. Hu, *Nat. Commun.*, 2024, **15**, 2208.

19 (*a*) S. Díez-González, *Adv. Organomet. Chem.*, 2016, **66**, 93–146; (*b*) B. Ranieri, I. Escofet and A. M. Echavarren, *Org. Biomol. Chem.*, 2015, **13**(26), 7103–7118; (*c*) I. Meana, P. Espinet and A. C. Albéniz, *Organometallics*, 2014, **33**(1), 1–7; (*d*) L. Zhang, W. Zhang, D. Li, R. Yang and Z. Xia, *iScience*, 2023, **27**(1), 108531; (*e*) D. V. Partyka, M. Zeller, A. D. Hunter and T. G. Gray, *Angew. Chem., Int. Ed.*, 2006, **45**, 8188–8191.

20 (*a*) CCDC 2491533: Experimental Crystal Structure Determination, 2025, DOI: 10.5517/ccdc.csd.cc2pmn11; (*b*) CCDC 2491534: Experimental Crystal Structure Determination, 2025, DOI: 10.5517/ccdc.csd.cc2pmn22.