









Cite this: *Chem. Commun.*, 2019, 55, 9641

Received 16th April 2019,  
Accepted 16th July 2019

DOI: 10.1039/c9cc02960e

rsc.li/chemcomm

# Synthesis and reactivity of asymmetric Cr(I) dinitrogen complexes supported by cyclopentadienyl–phosphine ligands†

Jiapeng Li,  Jianhao Yin,  Gao-Xiang Wang,  Zhu-Bao Yin,   
Wen-Xiong Zhang \* and Zhenfeng Xi \*

**Asymmetric trinuclear and dinuclear Cr(I) dinitrogen complexes bearing cyclopentadienyl–phosphine ligands were synthesized via reduction of their corresponding Cr(III) chloride complexes in the presence of N<sub>2</sub>. Oxidative addition reactions of single, double and triple bonds are found to take place on the low-valent Cr(I) centre.**

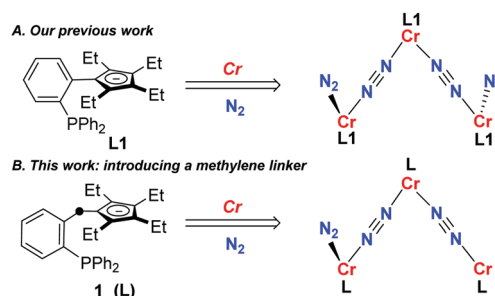
Dinitrogen activation with transition metals has been studied for decades.<sup>1</sup> Since the first dinitrogen complex was discovered in 1965,<sup>2</sup> dinitrogen complexes have been reported for a wide variety of transition metals.<sup>3</sup> Especially, It has been intensively investigated at Mo and W centers.<sup>4,5</sup> However, compared with Mo and W congeners, only a limited number of Cr dinitrogen complexes are known and most of them contain labile N<sub>2</sub> ligands.<sup>6</sup> Recently, we have reported a chromium hydrazido complex from N<sub>2</sub> functionalization,<sup>7</sup> which is supported by our designed cyclopentadienyl–phosphine ligands (L1, Scheme 1).<sup>8</sup> Inspired by this work, we further designed another cyclopentadienyl–phosphine ligand which features a methylene group between the cyclopentadienyl and the phenyl ring (1, Scheme 1) and extended our exploration of structure and reactivity on its corresponding Cr dinitrogen complexes.

Herein, we report the synthesis and characterization of unusual asymmetric Cr(I) dinitrogen complexes bearing the cyclopentadienyl–phosphine ligand (1), which demonstrates that small changes in ligand design can result in dramatic changes in N<sub>2</sub> coordination and reactivity.<sup>9</sup> Reaction chemistry of these asymmetric Cr(I) dinitrogen complexes revealed that oxidative addition reactions on low-valent Cr(I) centers could be achieved to produce their corresponding mononuclear Cr(III) complexes accompanied by the loss of N<sub>2</sub> ligands. Further, the

reaction of the Cr(I) dinitrogen complex with PhSiH<sub>3</sub> could realize the activation of Si–H bond, generating a mixed-valence dinuclear Cr dinitrogen complex.

The ligand 1 and its precursor can be readily prepared (for details, please see ESI†).<sup>10</sup> Reaction of 1 with CrCl<sub>2</sub> in THF at room temperature for 12 h generated chromium chloride complexes 2 in good isolated yields (Scheme 2). Complexes 2a–c were characterized by single-crystal X-ray structural analysis (for structural information of 2a–c, please see ESI†). Complexes 2a–c have solution magnetic moments of 3.1 ± 0.1 μ<sub>B</sub>, 3.2 ± 0.1 μ<sub>B</sub> and 3.0 ± 0.1 μ<sub>B</sub> (measured by Evans' method<sup>11</sup>) in C<sub>6</sub>D<sub>6</sub> at 296 K, respectively, which are in alignment with the spin-only value (*S* = 1). Magnetic susceptibility measurements at variable temperature with a superconducting quantum inference device (SQUID) show that the effective magnetic moment of 2c at room temperature (μ<sub>eff</sub> ≈ 3.5 μ<sub>B</sub>) is higher than the spin-only value (2.8 μ<sub>B</sub>) expected for an *S* = 1 state, suggesting an unquenched orbital momentum contribution (for details, please see ESI†).<sup>12</sup>

Reduction of 2a,b with 1 equivalent of KC<sub>8</sub> in THF under N<sub>2</sub> gave a dark brown solution, from which the Cr(I)–N<sub>2</sub> complexes 3 (3a: R = Ph, 3b: R = <sup>i</sup>Pr) were obtained in 67% and 68% isolated yields as brown powder, respectively (Scheme 3). Although single crystals suitable for X-ray structural analysis could not be obtained for the reduction product from 2c with KC<sub>8</sub> in THF under N<sub>2</sub>, its IR spectrum (see Fig. S6 in ESI†) is very similar to



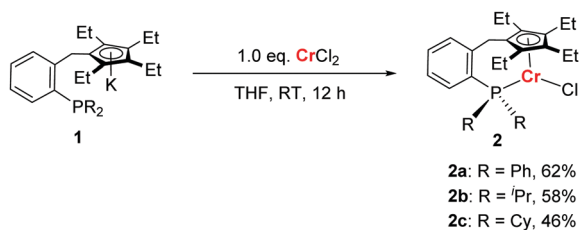
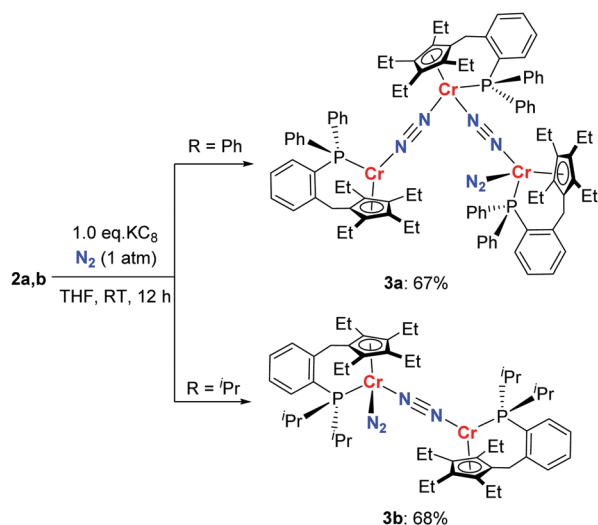
**Scheme 1** (A) Our previous synthesis of symmetric dinitrogen complexes. (B) Synthesis of asymmetric dinitrogen complexes.

Beijing National Laboratory for Molecular Sciences (BNLMS), Key Laboratory of Bioorganic Chemistry and Molecular Engineering of Ministry of Education, College of Chemistry, Peking University, Beijing 100871, China.

E-mail: wx\_zhang@pku.edu.cn, zfxi@pku.edu.cn

† Electronic supplementary information (ESI) available. CCDC 1860867, 1860868, 1860875–1860877, 1903190, 1907372–1907376. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c9cc02960e

‡ These authors contributed equally to this work.

Scheme 2 Synthesis of chromium complexes **2**.Scheme 3 Reduction of **2a,b** to afford dinitrogen complexes **3**.

that of dinitrogen complex **3b**. Complexes **3a** and **3b** have solution magnetic moments of  $5.2 \pm 0.1 \mu_B$  and  $4.2 \pm 0.1 \mu_B$  at 296 K, respectively, which are consistent with the DFT calculation results (for details, please see ESI†).

The molecular structures of **3a** and **3b** were characterized by single-crystal X-ray structural analysis (Fig. 1 and 2). Notably, compared with our previously reported trinuclear Cr(I) dinitrogen complex,<sup>7</sup> **3a** shows a novel asymmetric trinuclear structure when a methylene linker is added between the phenyl ring and

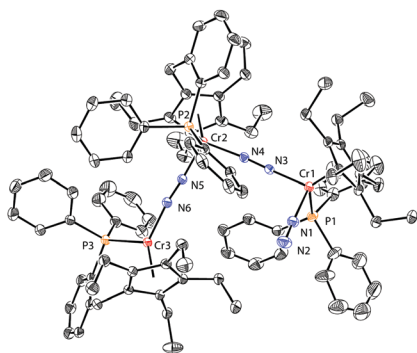


Fig. 1 Molecular structure of complex **3a** with thermal ellipsoids at 30% probability. H atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Cr1–N1 1.855(3), Cr1–N3 1.815(2), Cr2–N4 1.877(2), Cr2–N5 1.799(3), Cr3–N6 1.873(3), N1–N2 1.127(4), N3–N4 1.162(3), N5–N6 1.176(4), N3–Cr1–N1 93.54(11), N4–Cr2–N5 98.07(11), N6–Cr3–P3 108.00(8).

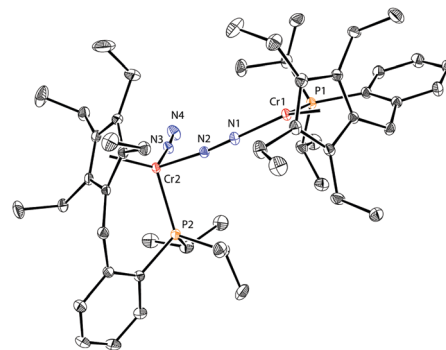


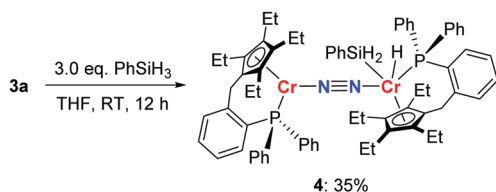
Fig. 2 Molecular structure of complex **3b** with thermal ellipsoids at 30% probability. H atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Cr1–N1 1.890(7), Cr2–N2 1.778(4), Cr2–N3 1.875(4), N1–N2 1.184(1), N3–N4 1.124(3), N1–Cr1–P1 95.72(4), N2–Cr2–N3 93.61(5).

the cyclopentadienyl ring in the ligand framework. As shown in Fig. 1, the three Cr centers are bridged by two end-on  $\text{N}_2$  ligands and the N(5)–Cr(2)–N(4) angle is 98.07 degree. The Cr(1) center coordinates a terminal  $\text{N}_2$  ligand while the Cr(3) center does not. From the space-filling model of **3a** derived from the crystal structure, the Cr(3) center is surrounded closely by the ligand and there is no vacancy for  $\text{N}_2$  binding. When changing the phenyl groups on the phosphorus center into isopropyl groups, another asymmetric dinuclear dinitrogen complex **3b** was generated, probably due to the increase of steric hindrance on the phosphorus center. As shown in Fig. 2, the two Cr centers of **3b** are bridged by an end-on  $\text{N}_2$  ligand. There is only one terminal  $\text{N}_2$  ligand binding at the Cr(2) center. The N–N bond lengths of the bridging  $\text{N}_2$  ligands in **3a** and **3b** are in the range of 1.162 to 1.184 Å, which are longer than those in terminal  $\text{N}_2$  ligands (1.127 Å for **3a**, 1.124 Å for **3b**).

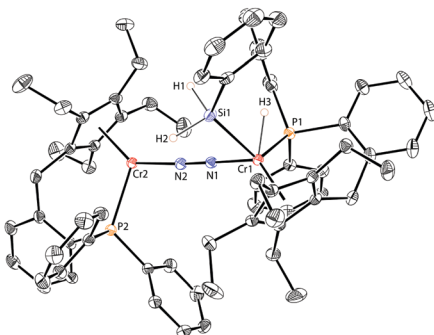
The IR spectra of **3a** and **3b** show strong vibration peaks ( $1752 \text{ cm}^{-1}$ ,  $1933 \text{ cm}^{-1}$  for **3a**;  $1748 \text{ cm}^{-1}$ ,  $1957 \text{ cm}^{-1}$  for **3b**) assignable to the bridging and terminal dinitrogen ligands, respectively. No remarkable differences were observed between the solution and the solid-state IR spectra of **3a** and **3b**, indicating that terminal  $\text{N}_2$  ligands are stable at room temperature. In contrast to symmetric dinitrogen-bridged complexes, such asymmetric trinuclear (**3a**) or dinuclear (**3b**) dinitrogen complexes are very rare.<sup>13</sup>

Next we explored the reaction chemistry of dinitrogen complex **3a** towards some organic small molecules. For example, addition of 3.0 eq. of phenylsilane to a THF solution of **3a** at room temperature resulted in the formation of mixed-valence dinuclear Cr dinitrogen complex **4** in 35% isolated yield, which features chromium in +I and +III formal oxidation states (Scheme 4). Complex **4** has a solution magnetic moment of  $3.3 \pm 0.1 \mu_B$  at 296 K.

The molecular structure of **4** was characterized by single-crystal X-ray structural analysis. As shown in Fig. 3, one Cr center in **4** remains +I formal oxidation state, while another Cr center is oxidized into +III valence *via* the oxidative addition reaction with phenylsilane. The Si(1)–H(3) distance of 1.90 Å indicates that the bonding interaction between Si(1) and H(3) is very weak, in which the H(3) can be regarded as a hydride



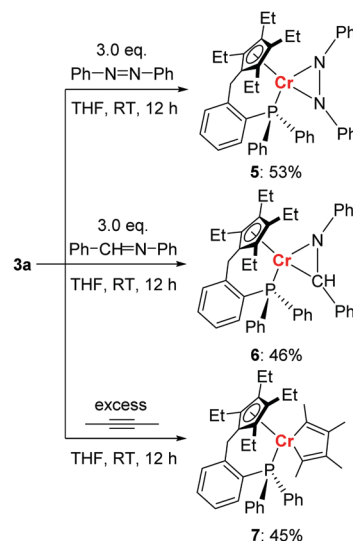
**Scheme 4** Oxidative addition reaction of **3a** with  $\text{PhSiH}_3$  to afford dinitrogen complex **4**.



**Fig. 3** Molecular structure of complex **4** with thermal ellipsoids at 30% probability. H atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Cr1–P1 2.292(2), Cr1–N1 1.774(7), Cr1–Si1 2.359(0), N1–N2 1.175(2), P1–Cr1–N1 89.67(5), P1–Cr1–Si1 118.40(2), Cr1–N1–N2 177.81(15).

ligand,<sup>14</sup> instead of a bridging hydride ligand featuring the Si–H distances around 1.60 Å.<sup>15a–c</sup> As for the characterization of hydride in complex **4**, Cr–H or Cr–D stretch cannot be identified in the IR spectrum due to their weak signals, however, the doublet at  $-5.6$  ppm might be assigned to the hydride, which disappeared if it was substituted by the deuteride in the reaction between complex **3a** and  $\text{PhSiD}_3$ . Furthermore,  $^2\text{H(D)}$  NMR spectrum showed that the signal at  $-3.3$  ppm should be assigned to the deuteride in the product obtained from the reaction between **3a** and  $\text{PhSiD}_3$  (for details, see ESI†). The N–N bond length of the bridging  $\text{N}_2$  ligand is 1.175 Å. Its IR spectrum shows one strong vibration peak at  $1761\text{ cm}^{-1}$ , assignable to the bridging dinitrogen ligand. These lengths and IR values are comparable to those of bridging  $\text{N}_2$  ligands in **3a** and **3b**. Complexes bearing both a hydride and a silyl ligand, generated through oxidative addition of Si–H bonds to various transition metals, are a type of important intermediates in hydrosilylation reactions.<sup>15</sup> To the best of our knowledge, this is the first structurally characterized chromium dinitrogen complex possessing this phenylsilyl and hydride structural motif.

The reactions of **3a** with azobenzene, benzylideneaniline and 2-butyne took similar oxidative addition pathway, in which the Cr centers were oxidized from +I to +III valence, along with the loss of  $\text{N}_2$  ligands to generate mononuclear  $\text{Cr(III)}$  complexes **5–7** (Scheme 5). Complexes **5–7** were obtained in 53%, 46% and 45% isolated yields, respectively. They have solution magnetic moments of  $3.6 \pm 0.1\ \mu_{\text{B}}$ ,  $3.8 \pm 0.1\ \mu_{\text{B}}$  and  $3.7 \pm 0.1\ \mu_{\text{B}}$  at 296 K, respectively, which are consistent with chromium in the +III oxidation state.<sup>6f</sup> Magnetic susceptibility measurements at

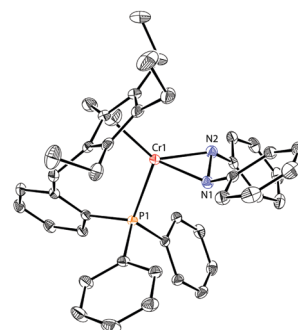


**Scheme 5** Oxidative addition reaction of **3a** to afford complexes **5–7**.

variable temperature by SQUID show that the effective magnetic moment of **5** at room temperature ( $\mu_{\text{eff}} \approx 4.5\ \mu_{\text{B}}$ ) is higher than the spin-only value ( $3.9\ \mu_{\text{B}}$ ) expected for an  $S = 3/2$  state, suggesting an unquenched orbital momentum contribution (for details, please see ESI†).

The molecular structures of **5–7** were characterized by single-crystal X-ray structural analysis (for details see ESI†). The ORTEP drawing of **5** is shown in Fig. 4. Two N atoms are coordinated to the Cr center affording the three-membered metallacycle. Both N(1) and N(2) were found to be located at similar distances from the chromium at distances of 1.945 Å and 1.942 Å, respectively. The N–N distance of the azobenzene was elongated to 1.434 Å, indicating the N–N single bond character. As shown in Fig. 5, complex **7** is a chromacyclopentadiene,<sup>16</sup> which results from reductive coupling of two 2-butyne bound to chromium.

In summary, novel asymmetric chromium(i) dinitrogen complexes have been realized and their reaction chemistry has been demonstrated with phenylsilane and some unsaturated organic compounds. These examples show the potential utilities



**Fig. 4** ORTEP drawing of **5** with 30% thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Cr1–N1 1.944(9), Cr1–N2 1.942(3), Cr1–P1 2.430(2), N1–N2 1.434(2), N1–Cr1–P1 94.50(5), N2–Cr1–N1 43.30(6), N2–N1–Cr1 68.25(9).

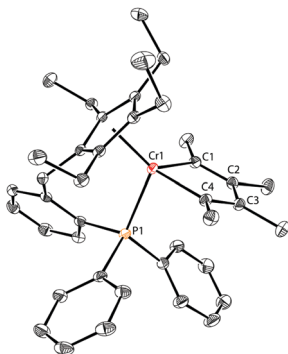


Fig. 5 ORTEP drawing of **7** with 30% thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Cr1–C1 2.051(1), Cr1–P1 2.406(1), C1–C2 1.354(3), C2–C3 1.483(3), C1–Cr1–C4 83.02(8), P1–Cr1–C1 90.73(6), Cr1–C1–C2 111.22(14).

of low valence Cr(I) dinitrogen complexes as synthons for activation of some organic small molecules by the Cr(I) centers.

This work was supported by the National Natural Science Foundation of China (No. 21690061, 21725201), and Beijing National Laboratory for Molecular Sciences (BNLMS). The calculation part was supported by **High-Performance Computing Platform of Peking University**. We thank Mr Botao Wu and Dr Yinshan Meng (Dalian University of Technology) for their help in computational calculations and SQUID tests.

## Conflicts of interest

There are no conflicts to declare.

## Notes and references

- (a) N. Stucke, B. M. Flöser, T. Weyrich and F. Tuczek, *Eur. J. Inorg. Chem.*, 2018, 1337–1355; (b) J. Li, J. Yin, C. Yu, W.-X. Zhang and Z. Xi, *Acta Chim. Sin.*, 2017, 75, 733–743; (c) N. S. Sickerman, K. Tanifuji, Y. Hu and M. W. Ribbe, *Chem. – Eur. J.*, 2017, 23, 12425–12432; (d) R. J. Burford, A. Yeo and M. D. Fryzuk, *Coord. Chem. Rev.*, 2017, 334, 84–99; (e) R. J. Burford and M. D. Fryzuk, *Nat. Rev. Chem.*, 2017, 1, 0026; (f) M. J. Bezdek and P. J. Chirik, *Angew. Chem., Int. Ed.*, 2016, 55, 7892–7896; (g) I. Ćorić and P. L. Holland, *J. Am. Chem. Soc.*, 2016, 138, 7200–7211; (h) N. Lehnert and J. C. Peters, *Inorg. Chem.*, 2015, 54, 9229–9233; (i) S. F. McWilliams and P. L. Holland, *Acc. Chem. Res.*, 2015, 48, 2059–2065; (j) C. Köthe and C. Limberg, *Z. Anorg. Allg. Chem.*, 2015, 641, 18–30.
- A. D. Allen and C. V. Senoff, *Chem. Commun.*, 1965, 621–622.
- (a) J. Higuchi, S. Kuriyama, A. Eizawa, K. Arashiba, K. Nakajima and Y. Nishibayashi, *Dalton Trans.*, 2018, 47, 1117–1121; (b) T. M. Buscagan, P. H. Oyala and J. C. Peters, *Angew. Chem., Int. Ed.*, 2017, 56, 6921–6926; (c) P. J. Hill, L. R. Doyle, A. D. Crawford, W. K. Myers and A. E. Ashley, *J. Am. Chem. Soc.*, 2016, 138, 13521–13524; (d) Y. Gao, G. Li and L. Deng, *J. Am. Chem. Soc.*, 2018, 140, 2239–2250; (e) T. Suzuki, K. Fujimoto, Y. Takemoto, Y. Wasada-Tsutsui, T. Ozawa, T. Inomata, M. D. Fryzuk and H. Masuda, *ACS Catal.*, 2018, 8, 3011–3015; (f) Y. Sekiguchi, K. Arashiba, H. Tanaka, A. Eizawa, K. Nakajima, K. Yoshizawa and Y. Nishibayashi, *Angew. Chem., Int. Ed.*, 2018, 57, 9064–9068; (g) L. R. Doyle, A. J. Woolees, L. C. Jenkins, F. Tuna, E. J. L. McInnes and S. T. Liddle, *Angew. Chem., Int. Ed.*, 2018, 57, 6314–6318; (h) S. Pfirrmann, C. Limberg, C. Herwig, R. Stöber and B. Ziemer, *Angew. Chem., Int. Ed.*, 2009, 48, 3357–3361.
- (a) A. Eizawa, K. Arashiba, H. Tanaka, S. Kuriyama, Y. Matsuo, K. Nakajima, K. Yoshizawa and Y. Nishibayashi, *Nat. Commun.*, 2017, 8, 14874–14885; (b) L. A. Wickramasinghe, T. Ogawa, R. R. Schrock and P. Müller, *J. Am. Chem. Soc.*, 2017, 139, 9132–9135; (c) S. Kuriyama, K. Arashiba, K. Nakajima, H. Tanaka, N. Kamaru, K. Yoshizawa and Y. Nishibayashi, *J. Am. Chem. Soc.*, 2014, 136, 9719–9731; (d) K. Arashiba, Y. Miyake and Y. Nishibayashi, *Nat. Chem.*, 2011, 3, 120–125; (e) D. V. Yandulov and R. R. Schrock, *Science*, 2003, 301, 76–78; (f) K. Komori, H. Oshita, Y. Mizobe and M. Hidai, *J. Am. Chem. Soc.*, 1989, 111, 1939–1940.
- (a) B. M. Hoffman, D. Lukoyanov, Z.-Y. Yang, D. R. Dean and L. C. Seefeldt, *Chem. Rev.*, 2014, 114, 4041; (b) T. Spatzal, M. Aksoyoglu, L. Zhang, S. L. A. Andrade, E. Schleicher, S. Weber, D. C. Rees and O. Einsle, *Science*, 2011, 334, 940; (c) K. M. Lancaster, M. Roemelt, P. Ettenhuber, Y. Hu, M. W. Ribbe, F. Neese, U. Bergmann and S. DeBeer, *Science*, 2011, 334, 974.
- (a) A. J. Kendall, S. I. Johnson, R. M. Bullock and M. T. Mock, *J. Am. Chem. Soc.*, 2018, 140, 2528–2536; (b) J. D. Egbert, M. O'Hagan, E. S. Wiedner, R. M. Bullock, N. A. Piro, W. S. Kassel and M. T. Mock, *Chem. Commun.*, 2016, 52, 9343–9346; (c) E. S. Akturk, G. P. A. Yap and K. H. Theopold, *Chem. Commun.*, 2015, 51, 15402–15405; (d) M. T. Mock, S. Chen, M. O'Hagan, R. Rousseau, W. G. Dougherty, W. S. Kassel and R. M. Bullock, *J. Am. Chem. Soc.*, 2013, 135, 11493–11496; (e) M. T. Mock, S. Chen, R. Rousseau, M. J. O'Hagan, W. G. Dougherty, W. S. Kassel, D. L. DuBois and R. M. Bullock, *Chem. Commun.*, 2011, 47, 12212–12214; (f) W. H. Monillas, G. P. A. Yap and K. H. Theopold, *Inorg. Chim. Acta*, 2011, 369, 103–119.
- J. Yin, J. Li, G.-X. Wang, Z.-B. Yin, W.-X. Zhang and Z. Xi, *J. Am. Chem. Soc.*, 2019, 141, 4241–4247.
- (a) G.-X. Wang, J. Yin, J. Li, Z.-B. Yin, W.-X. Zhang and Z. Xi, *Inorg. Chem. Front.*, 2019, 6, 428–433; (b) J. Yin, Q. Ye, W. Hao, S. Du, Y. Gu, W.-X. Zhang and Z. Xi, *Org. Lett.*, 2017, 19, 138–141; (c) W. Hao, H. Wang, Q. Ye, W.-X. Zhang and Z. Xi, *Org. Lett.*, 2015, 17, 5674–5677.
- M. D. Fryzuk, *Chem. Commun.*, 2013, 49, 4866–4868.
- (a) W. Geng, W.-X. Zhang, W. Hao and Z. Xi, *J. Am. Chem. Soc.*, 2012, 134, 20230–20233; (b) Z. Xi, Q. Song, J. Chen, H. Guan and P. Li, *Angew. Chem., Int. Ed.*, 2001, 40, 1913–1916; (c) Z. Xi and P. Li, *Angew. Chem., Int. Ed.*, 2000, 39, 2950–2952.
- (a) D. F. Evans, *J. Chem. Soc.*, 1959, 2003–2005; (b) S. K. Sur, *J. Magn. Reson.*, 1989, 82, 169–173.
- (a) M. H. Voges, C. Rømming and M. Tilset, *Organometallics*, 1999, 18, 529–533; (b) B. J. Thomas, S. K. Noh, G. K. Schulte, S. C. Sendlinger and K. H. Theopold, *J. Am. Chem. Soc.*, 1991, 113, 893–902.
- D. G. Gusev, F. M. Dolgushin and M. Y. Antipin, *Organometallics*, 2000, 19, 3429–3434.
- B. R. Jagirdar, R. Palmer, K. J. Klabunde and L. J. Radonovich, *Inorg. Chem.*, 1995, 34, 278–283.
- (a) R. C. Handford, P. W. Smith and T. D. Tilley, *Organometallics*, 2018, 37, 4077–4085; (b) P. W. Smith and T. D. Tilley, *J. Am. Chem. Soc.*, 2018, 140, 3880–3883; (c) U. Schubert, J. Müller and H. G. Alt, *Organometallics*, 1987, 6, 469–472; (d) J. L. Speier, *Adv. Organomet. Chem.*, 1979, 17, 407–447.
- (a) W. Ma, C. Yu, T. Chen, L. Xu, W.-X. Zhang and Z. Xi, *Chem. Soc. Rev.*, 2017, 46, 1160–1192; (b) W. H. Monillas, J. F. Young, G. P. A. Yap and K. H. Theopold, *Dalton Trans.*, 2013, 42, 9198–9210.