Dalton Transactions

ROYAL SOCIETY OF CHEMISTRY

COMMUNICATION

View Article Online
View Journal | View Issue

Cite this: *Dalton Trans.*, 2020, **49**, 603

Received 27th November 2019,
Accepted 13th December 2019

DOI: 10.1039/c9dt04555d

rsc.li/dalton

Isolation of heterometallic cerium(III) complexes with a multidentate nitrogen–phosphorus ligand†

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Heterometallic complexes play an important role in catalysis and activation of small molecules due to the synergistic effects from different metals. Here we report a straightforward strategy to construct a series of heterobimetallic complexes of bromine bridged cerium(III)-alkali metal or group 9 metals using a multidentate nitrogen–phosphorus ligand.

Rare-earth metal containing heterometallic clusters are of great interest because of their multimetallic synergistic effects in organic catalysis[1] and activation of small molecules.[2] Cerium plays an especially unique role in the rare-earth chemistry due to its stable +4 oxidation state and the Ce(III/IV) redox-couple,[3] and has been widely investigated in materials science,[4] organic synthesis,[5] and industrial catalysis.[6] A general method for the synthesis of cerium(III) heterometallic clusters was reported by the reactions of $Ce(NO_3)_3{\cdot}6H_2O$ with metal acetates, nitrites or polyoxometalates (POMs).[7] Leung and co-workers reported the synthesis of cerium(IV) heterometallic clusters with Re, Mo, V, Os, or Mn employing a Kläui tripodal ligand $[Co(\eta^5\text{-}C_5H_5)\{P(O)(OEt)_2\}_3]^-$.[8] Schelter and co-workers reported the construction of Ce(III)/Ce(IV) heterometallic clusters with (*S*)-binolate ligand and explored their oxidation, electronic, and catalytic performances.[9] Recently, Nippe and co-workers reported the preparation of a novel complex with an unsupported Ce–Fe bond by the reaction of a $PyCp_2^{2-}$-stabilized cerium complex with $K[FeCp(CO)_2]$.[10] However, heterometallic clusters with cerium and other transition metals such as Rh and Ir remain under developed due to the absence of an efficient synthetic strategy.

The development of new ligands is an important issue in synthetic organometallic chemistry, which plays a key role in the construction of heterometallic clusters.[11] Multidentate ligands are typically used to construct heterometallic clusters or to stabilize metal–metal bonds. For example, Thomas group has demonstrated that the species with transition metal–metal multiple bonds could be linked by a phosphinoamide ligand framework (Chart 1, **A**).[12] The Arnold group found that the phosphine-substituted phenol ligand (Chart 1, **B**) could be useful to synthesize species with uranium–metal bonds.[13] Lu and co-workers isolated a series of complexes with metal–metal bond and employing a tripodal ligand with three NCH_2P units (Chart 1, **C**).[14] The ligand with NCH_2P units could also be used to synthesize heterometallic complexes with LM → Sc (LM = Ni, Pd, Pt) dative bond.[15] Recently, our group also developed a straightforward method for the construction of heterometallic clusters with multiple U–M bonds by employing a multidentate ligand with three rigid N–P units (Chart 1, **D**).[16]

Herein, we report a new multidentate ligand with two rigid N–P units (compound **1**), which could be used to synthesize hetereometallic clusters containing cerium(III) and alkali metal or group 9 metals. This study not only offers a new ligand for the construction of heterometallic cluster with rare-earth metals but also allows investigation of the potential application of cerium-containing heterometallic cluster in metalla-photocatalysis.

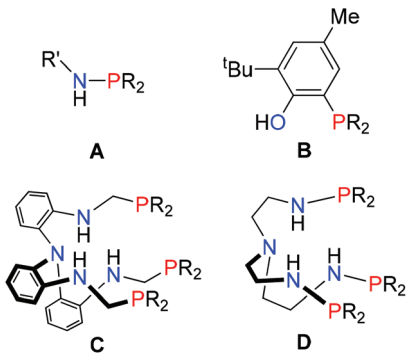

Chart 1 Representative ligands for the construction of heterometallic species.

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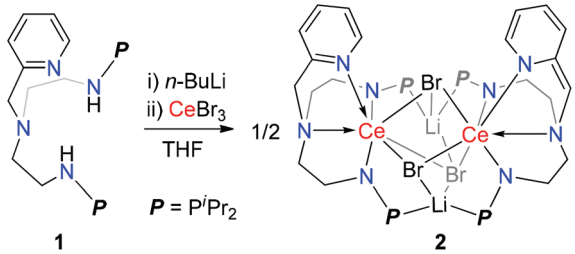
†Electronic supplementary information (ESI) available. CCDC 1940013 and 1940015–1940017. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c9dt04555d

The multidentate N–P ligand, compound **1**, was readily synthesized by the reaction of (2-C_5H_4N)$CH_2N(CH_2CH_2NH_2)_2$ with two equivalents of *i*-Pr_2PCl in the presence of excess Et_3N (see ESI† for details).[17] Treatment of compound **1** with two equivalents of *n*-BuLi at −30 °C and further stirring at room temperature (RT) in tetrahydrofuran (THF) for 2 h, followed by the addition of one equivalent of $CeBr_3$ and stirring at RT overnight formed a red solution, from which complex **2** was isolated as a red solid in 76% yield (Scheme 1). The ^{1}H NMR spectrum of complex **2** shows paramagnetically shifted resonances in the range from +21.06 to −12.38 ppm, which is typical of Ce(III) complexes.[9] Moreover, the $^{31}P\{^1H\}$ NMR spectrum of **2** consists of two resonances at 49.2 and 33.0 ppm (see Fig. S8 and S9 in the ESI†).

The molecular structure of complex **2** was confirmed by single-crystal X-ray diffraction.[18] As shown in Fig. 1, complex **2** is an unsymmetrical dimer, in which each cerium center is coordinated to three μ-Br atoms and four N atoms, adopting a distorted pentagonal bipyramidal geometry. This structural feature is also consistent with the complicated ^{1}H NMR spectrum of complex **2**. The bond lengths of Ce1–N1 (2.348(2) Å) and Ce1–N2 (2.370(3) Å) are shorter than those of Ce1–N4 (2.613(2) Å), which are consistent with the Ce–N bond lengths observed in $[Ce\{N(CH_2CH_2NSiMe_2tBu)_3\}_2(\mu\text{-}Br)]$[19] and $[CeN\{C_6H_4CH_2(2\text{-}tBuNO)\}_3Br]$.[20] The bond length of Ce1–N3 (2.645(3) Å) is slightly longer than that of Ce1–N4, reflecting a weak coordination of the pyridyl nitrogen atom with the cerium center. The Ce2–N_{amido} and Ce2–N_{amine} bond lengths are comparable to those of Ce1–N_{amido} and Ce1–N_{amine}, whereas the bond length of Ce2–N7 (2.483(3) Å) is significantly shorter than that of Ce1–N3 (2.645(3) Å). In addition, the bond length of C15–C16 (1.348(4) Å) is also shorter than the bond length of C5–C6 (1.511(4) Å), which suggests that the benzylic position (C15) of this pyridine was deprotonated and C15–C16 is a double bond. This result is consistent with the short bond length of Ce2–N7. The Ce–Br bond lengths (3.1249(4)–3.2903(4) Å) in complex **2** are longer than the terminal Ce–Br bond lengths of 2.912(5)/2.885(2) and 2.874(2)–2.912(2) Å observed in $[CeBr_2\{N(SiMe_3)_2\}(THF)_2]$ and $[CeBr_3THF_4]$,[21,22] which is largely due to their bridging nature and the Li coordination effect. There is need for more base to afford complex **2** logically. However, the yield of complex **2** was reduced when we tried the reaction of compound **1** with 2.5 equivalents of *n*-BuLi. Moreover, an attempt to synthesize the C5 deprotonated product from compound **1** was also unsucessful.

Fortunately, upon the reaction of complex **2** with wet Et_2O at RT for 48 h, the protonated product, complex **3**, was isolated in 45% yield as a yellow crystalline solid (Scheme 2). The ^{1}H NMR spectrum of complex **3** also exhibits paramagnetically shifted resonances in the range from +18.40 to −7.60 ppm (Fig. S10†). The $^{31}P\{^1H\}$ NMR signals were observed at 169.4 and 69.6 ppm (Fig. S11†). The structure of complex **3** was confirmed by single-crystal X-ray diffraction (Fig. 2). The cerium centers in dimer **3** also adopt distorted pentagonal bipyramidal geometry, in which each cerium atom is coordinated by four N atoms and three bridged-Br atoms. The four Ce–N_{amido} bond lengths (range from 2.329(3) to 2.427(4) Å) are shorter than the two Ce–N_{amine} (2.665(4) and 2.664(4) Å) and two Ce–$N_{pyridyl}$ (2.696(4) and 2.688(4) Å) bond lengths, indicating the protonation of the benzylic position (C15) to regenerate the pyridyl unit. The formation of complex **3** may be caused by traces of water in the Et_2O. Complexes **2** and **3** represent a rare example of a heterometallic cluster with rare-earth metal cerium and main-group metals.

With complex **2** in hand, we tried to synthesize heterometallic clusters with other transition metals. Treatment of **2** with one equivalent of $[Rh(COD)Cl]_2$ at 90 °C in toluene for 2 h



Scheme 1 The synthesis of complex **2**.

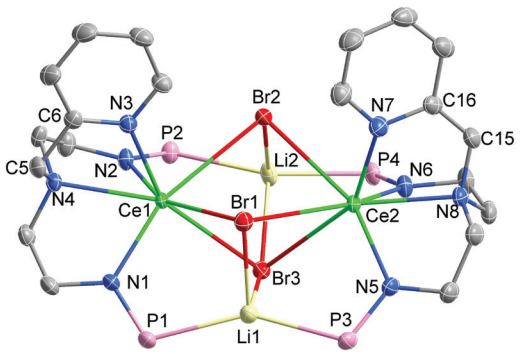
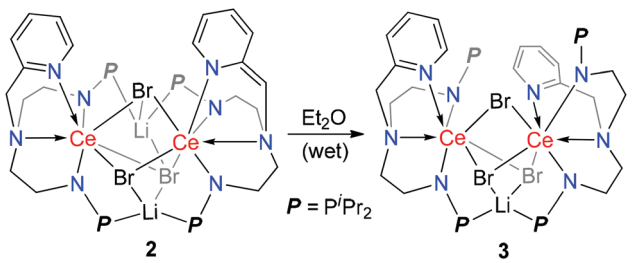


Fig. 1 Molecular structure of complex **2** (thermal ellipsoids shown at 40% probability). Hydrogen atoms and isopropyl moieties in P^iPr_2 are omitted for clarity. Selected bond distances (Å): Ce1–N1 2.348(2), Ce1–N2 2.370(3), Ce1–N3 2.645(3), Ce1–N4 2.613(2), Ce1–Br1 3.1249(4), Ce1–Br2 3.1516(3), Ce1–Br3 3.1539(3), Ce2–N5 2.380(2), Ce2–N6 2.393(3), Ce2–N7 2.483(3), Ce2–N8 2.584(2), Ce2–Br1 3.2034(4), Ce2–Br2 3.1300(3), Ce2–Br3 3.2903(4), C5–C6 1.511(4), C15–C16 1.348(4).



Scheme 2 The synthesis of complex **3**.

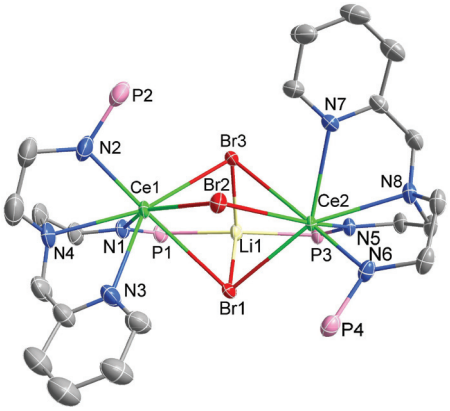
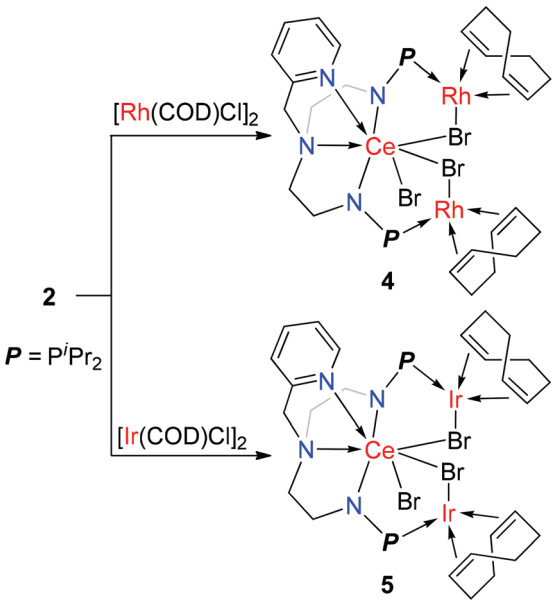


Fig. 2 Molecular structure of complex **3** (thermal ellipsoids shown at 40% probability). Hydrogen atoms and isopropyl moieties in P^iPr_2 are omitted for clarity. Selected bond distances (Å): Ce1–N1 2.427(4), Ce1–N2 2.330(4), Ce1–N3 2.696(4), Ce1–N4 2.665(4), Ce1–Br1 3.2733(5), Ce1–Br2 3.0797(5), Ce1–Br3 3.0620(5), Ce2–N5 2.402(3), Ce2–N6 2.329(3), Ce2–N7 2.688(4), Ce2–N8 2.664(4), Ce2–Br1 3.0941(5), Ce2–Br2 3.0727(5), Ce2–Br3 3.2923(5).

afforded complex **4**, which was isolated as a yellow crystalline solid in 28% yield (Scheme 3). Complex **4** shows two doublets with characteristic $^1J_{P-Rh}$ coupling constants of 149.4 Hz and 155.4 Hz in the $^{31}P\{^1H\}$ NMR spectrum (Fig. S13†). Under the similar conditions, complex **2** could also react with one equivalent of $[Ir(COD)Cl]_2$ to generate complex **5** in 34% crystalline yield (Scheme 3). The resonances in ^1H NMR spectra of complexes **4** and **5** were difficult to assigned due to their low solubility and the paramagnetism of Ce(III). Therefore, the purities of the bulk samples of **4** and **5** were further confirmed by elemental analysis and powder X-ray diffraction (Fig. S16 and S17†).



Scheme 3 Reactions of **2** with $[M(COD)Cl]_2$ (M = Rh, Ir).

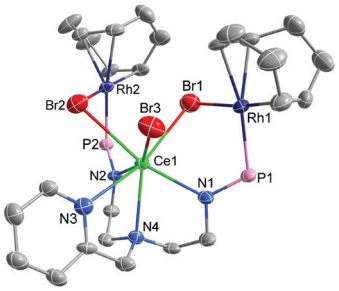


Fig. 3 Molecular structure of complex **4** (thermal ellipsoids shown at 40% probability). Hydrogen atoms and isopropyl moieties in P^iPr_2 are omitted for clarity. Selected bond distances (Å): Ce1–N1 2.453(8), Ce1–N2 2.466(7), Ce1–N3 2.676(8), Ce1–N4 2.630(7), Ce1–Br1 2.9139(14), Ce1–Br2 3.0509(14), Ce1–Br3 2.9448(13), Rh1–Br1 2.4891(17), Rh1–P1 2.350(2), Rh2–Br2 2.4787(13), Rh2–P2 2.338(2).

The solid-state structure of **4** was confirmed by single-crystal X-ray diffraction (Fig. 3). The most important structural feature of complex **4** is that the rare-earth metal (Ce) and two transition metals (Rh) are bridged by two Br atoms. Complex **4** represents the first example of a heterometallic cluster containing both Ce and Rh.[23] The bond angles of Ce1–Br1–Rh1 and Ce1–Br2–Rh2 are 91.36(5)° and 91.02(4)°, respectively. The bond lengths of Ce1–N1 (2.453(8) Å) and Ce1–N2 (2.466(7) Å) are significantly shorter than those of Ce1–N3 (2.676(8) Å) and Ce1–N4 (2.630(7) Å). The Ce–Br bond lengths (2.9139(14)–3.0509(14) Å) are shorter than those observed in complex **3**. The Rh–P bond lengths of 2.350(2) and 2.338(2) Å are similar to those previously reported.[24]

The structural features of complex **5** were also revealed by X-ray diffraction (Fig. 4). It is also a heterometallic cluster with one rare-earth cerium and two transition metals (Ir). The bond distances of Ce1–N1 (2.445(7) Å) and Ce1–N2 (2.447(7) Å) in complex **5** are very close to that observed in complex **4**, and are also shorter than the bond lengths of Ce1–N3 (2.671(7) Å) and Ce1–N4 (2.624(7) Å). We attempted to synthesize heterometallic cluster with direct Ce–M bonds by the reduction of complexes **4** and **5** but were unsuccessful.

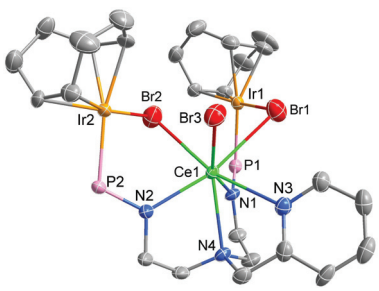


Fig. 4 Molecular structure of complex **5** (thermal ellipsoids shown at 40% probability). Hydrogen atoms and isopropyl moieties in P^iPr_2 are omitted for clarity. Selected bond distances: Ce1–N1 2.445(7), Ce1–N2 2.447(7), Ce1–N3 2.671(7), Ce1–N4 2.624(7), Ce1–Br1 3.0742(14), Ce1–Br2 2.9215(14), Ce1–Br3 2.9440(12), Ir1–Br1 2.4547(13), Ir1–P1 2.343(2), Ir2–Br2 2.4432(14), Ir2–P2 2.340(2).

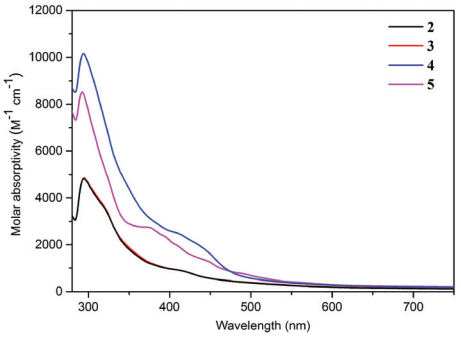


Fig. 5 UV–Visible electronic absorption spectra of heterobimetallic clusters **2** (black), **3** (red), **4** (blue), and **5** (magenta) recorded in THF at RT.

The ultraviolet–visible (UV–Vis) absorption spectra of **2**, **3**, **4**, and **5** were recorded in THF at RT (Fig. 5). All the heterobimetallic complexes showed strong absorption in the region from 300 to 500 nm, in which shoulder peaks of **2**, **3**, **4**, and **5** were found at about 295 nm and the molar absorption coefficients of **4** (ε = ~10 151 M^{-1} cm^{-1}) and **5** (ε = ~8522 M^{-1} cm^{-1}) were significantly higher than those of **2** and **3** (ε = ~4837 and 4857 M^{-1} cm^{-1}).

Conclusions

In summary, a series of novel heterobimetallic complexes containing a rare-earth metal (Ce) and an alkali metal (Li) or transition metals (Rh and Ir) were constructed based on a novel hexadentate N_4P_2 ligand with two rigid N–P units. This study offers an effective ligand for the construction of heterometallic clusters with different metals, and thus provides new opportunities for the investigation of the potential applications of these heterometallic clusters. Studies on the reactivity and catalysis of these heterobimetallic clusters and the construction of heterometallic clusters with direct metal–metal bonds based on novel N–P ligands are currently under investigation.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This research was supported by the National Natural Science Foundation of China (Grant No. 21772088), the Training Program of the Major Research plan of the National Natural Science Foundation of China (Grant No. 91961116), the Young Elite Scientist Sponsorship Program of China Association of Science and Technology, the program of Jiangsu Specially-Appointed Professor, and Shuangchuang Talent Plan of Jiangsu Province.

Notes and references

1 (*a*) *Molecular Metal-Metal Bonds*, ed. S. T. Liddle, Wiley-VCH, Weinheim, Germany, 2015; (*b*) H. Sasai, T. Arai, Y. Satow, K. N. Houk and M. Shibasaki, *J. Am. Chem. Soc.*, 1995, **117**, 6194–6198; (*c*) M. Shibasaki and N. Yoshikawa, *Chem. Rev.*, 2002, **102**, 2187–2210; (*d*) M. Shibasaki, M. Kanai, S. Matsunaga and N. Kumagai, *Acc. Chem. Res.*, 2009, **42**, 1117–1127; (*e*) L. Wang, C. Xu, Q. Han, X. Tang, P. Zhou, R. Zhang, G. Gao, B. Xu, W. Qin and W. Liu, *Chem. Commun.*, 2018, **54**, 2212–2215.

2 (*a*) T. Shima and Z. Hou, Molecular Rare Earth Hydride Clusters, ed. Z. Zheng, in *Recent Development in Clusters of Rare Earths and Actinides: Chemistry and Materials*, 2016, vol 173, pp. 315–335; (*b*) Y. Takenaka, T. Shima, J. Baldamusand and Z. Hou, *Angew. Chem., Int. Ed.*, 2009, **48**, 7888–7891.

3 R. Anwander, M. Dolg and F. T. Edelmann, *Chem. Soc. Rev.*, 2017, **46**, 6697–6709.

4 X. Qin, X. Liu, W. Huang, M. Bettinelli and X. Liu, *Chem. Rev.*, 2017, **117**, 4488–4527.

5 (*a*) H. Yin, P. J. Carroll, J. M. Anna and E. J. Schelter, *J. Am. Chem. Soc.*, 2015, **137**, 9234–9237; (*b*) H. Yin, P. J. Carroll, B. C. Manor, J. M. Anna and E. J. Schelter, *J. Am. Chem. Soc.*, 2016, **138**, 5984–5991; (*c*) J.-J. Guo, A. Hu, Y. Chen, J. Sun, H. Tang and Z. Zuo, *Angew. Chem., Int. Ed.*, 2016, **55**, 15319–15322; (*d*) H. Yin, Y. Jin, J. E. Hertzog, K. C. Mullane, P. J. Carroll, B. C. Manor, J. M. Anna and E. J. Schelter, *J. Am. Chem. Soc.*, 2016, **138**, 16266–16273; (*e*) A. Hu, J.-J. Guo, H. Pan and Z. Zuo, *Science*, 2018, **361**, 668–672; (*f*) A. Hu, J.-J. Guo, H. Pan, H. Tang, Z. Gao and Z. Zuo, *J. Am. Chem. Soc.*, 2018, **140**, 1612–1616; (*g*) Y. Qiao, Q. Yang and E. J. Schelter, *Angew. Chem., Int. Ed.*, 2018, **57**, 10999–11003.

6 (*a*) A. Trovarelli, C. de Leitenburg, M. Boaro and G. Dolcetti, *Catal. Today*, 1999, **50**, 353–367; (*b*) D. Duprez and C. Descorme, *Catal. Sci. Ser.*, 2002, **2**, 243–280; (*c*) W. C. Chueh, C. Falter, M. Abbott, D. Scipio, P. Furler, S. M. Haile and A. Steinfeld, *Science*, 2010, **330**, 1797–1801.

7 (*a*) G. B. Deacon, C. M. Forsyth and M. Forsyth, *Z. Anorg. Allg. Chem.*, 2003, **629**, 1472–1474; (*b*) J.-P. Costes, F. Dahan, G. Novitchi, V. Arion, S. Shova and J. Lipkowski, *Eur. J. Inorg. Chem.*, 2004, 1530–1537; (*c*) H. L. C. Feltham, S. Dhers, M. Rouzières, R. Clérac, A. K. Powell and S. Brooker, *Inorg. Chem. Front.*, 2015, **2**, 982–990; (*d*) B. Artetxe, S. Reinoso, L. San Felices, L. Lezama, J. M. Gutiérrez-Zorrilla, C. Vicent, F. Haso and T. Liu, *Chem. – Eur. J.*, 2016, **22**, 4616–4625; (*e*) J. Liu, J. Yu, Q. Han, Y. Wen, L. Chen and J. Zhao, *Dalton Trans.*, 2016, **45**, 16471–16484; (*f*) L. Wang, J.-C. Ma, W.-K. Dong, L.-C. Zhu and Y. Zhang, *Z. Anorg. Allg. Chem.*, 2016, **642**, 834–839; (*g*) S. A. Güngör and M. Kose, *J. Mol. Struct.*, 2017, **1150**, 274–278; (*h*) A. E. Thuijs, X.-G. Li, Y.-P. Wang, K. A. Abboud, X.-G. Zhang, H.-P. Cheng and G. Christou, *Nat. Commun.*, 2017, **8**, 500.

8 (*a*) X.-Y. Yi, G.-C. Wang, H.-F. Ip, W.-Y. W, L. Chen, H. H.-Y. Sung, I. D. Williams and W.-H. Leung, *Eur. J. Inorg. Chem.*, 2014, **35**, 6097–6103; (*b*) K.-L. Wong, Y.-Mi. So, G.-C. Wang, H. H.-Y. Sung, I. D. Williams and W.-H. Leung, *Dalton Trans.*, 2016, **45**, 8770–8876.

9 (*a*) J. R. Robinson, P. J. Carroll, P. J. Walsh and E. J. Schelter, *Angew. Chem., Int. Ed.*, 2012, **51**, 10159–10163; (*b*) J. R. Robinson, Z. Gordon, C. H. Booth, P. J. Carroll, P. J. Walsh and E. J. Schelter, *J. Am. Chem. Soc.*, 2013, **135**, 19016–19024; (*c*) J. R. Robinson, Y. Qiao, J. Gu, P. J. Carroll, P. J. Walsh and E. J. Schelter, *Chem. Sci.*, 2016, **7**, 4537–4547.

10 C. P. Burns, X. Yang, S. Sung, J. D. Wofford, N. S. Bhuvanesh, M. B. Hall and M. Nippe, *Chem. Commun.*, 2018, **54**, 10893–10896.

11 (*a*) M. Stradiotto and R. J. Lundgren, *Ligand Design in Metal Chemistry*, Wiley, Chichester, 2016; (*b*) P. Braunstein, *J. Organomet. Chem.*, 2004, **689**, 3953–3967; (*c*) G. Wu, I. J. Hewitt, S. Mameri, Y. Lan, R. Clérac, C. E. Anson, S. Qiu and A. K. Powell, *Inorg. Chem.*, 2007, **46**, 7229–7231; (*d*) K. Liu, W. Shi and P. Cheng, *Coord. Chem. Rev.*, 2015, **289–290**, 74–122.

12 (*a*) B. P. Greenwood, G. T. Rowe, C.-H. Chen, B. M. Foxman and C. M. Thomas, *J. Am. Chem. Soc.*, 2010, **132**, 44–45; (*b*) J. P. Krogman, B. M. Foxman and C. M. Thomas, *J. Am. Chem. Soc.*, 2011, **133**, 14582–14585; (*c*) R. Mathialagan, S. Kuppuswamy, A. T. De Denko, M. W. Bezpalko, B. M. Foxman and C. M. Thomas, *Inorg. Chem.*, 2013, **52**, 701–706; (*d*) B. Wu, K. M. Gramigna, M. W. Bezpalko, B. M. Foxman and C. M. Thomas, *Inorg. Chem.*, 2015, **54**, 10909–10917; (*e*) G. Culcu, D. A. Iovan, J. P. Krogman, M. J. T. Wilding, M. W. Bezpalko, B. M. Foxman and C. M. Thomas, *J. Am. Chem. Soc.*, 2017, **139**, 9627–9636; (*f*) K. M. Gramigna, D. A. Dickie, B. M. Foxman and C. M. Thomas, *ACS Catal.*, 2019, **9**, 3153–3164.

13 (*a*) J. A. Hlina, J. R. Pankhurst, N. Kaltsoyannis and P. L. Arnold, *J. Am. Chem. Soc.*, 2016, **138**, 3333–3345; (*b*) J. A. Hlina, J. A. L. Wells, J. R. Pankhurst, J. B. Love and P. L. Arnold, *Dalton Trans.*, 2017, **46**, 5540–5545.

14 (*a*) L. J. Clouston, R. B. Siedschlag, P. A. Rudd, N. Planas, S. Hu, A. D. Miller, L. Gagliardi and C. C. Lu, *J. Am. Chem. Soc.*, 2013, **135**, 13142–13148; (*b*) P. A. Rudd, S. Liu, N. Planas, E. Bill, L. Gagliardi and C. C. Lu, *Angew. Chem., Int. Ed.*, 2013, **52**, 4449–4452; (*c*) A. L. Ward, W. W. Lukens, C. C. Lu and J. Arnold, *J. Am. Chem. Soc.*, 2014, **136**, 3647–3654; (*d*) R. J. Eisenhart, L. J. Clouston and C. C. Lu, *Acc. Chem. Res.*, 2015, **48**, 2885–2894; (*e*) R. B. Siedschlag, V. Bernales, K. D. Vogiatzis, N. Planas, L. J. Clouston, E. Bill, L. Gagliardi and C. C. Lu, *J. Am. Chem. Soc.*, 2015, **137**, 4638–4641.

15 (*a*) J. Du, Z. Huang, Y. Zhang, S. Wang, S. Zhou, H. Fang and P. Cui, *Chem. – Eur. J.*, 2019, **25**, 10149–10155; (*b*) P. Cui, C. Xiong, J. Du, Z. Huang, S. Xie, H. Wang, S. Zhou, H. Fang and S. Wang, *Dalton Trans.*, 2020, **49**, 124–130.

16 (*a*) G. Feng, M. Zhang, D. Shao, X. Wang, S. Wang, L. Maron and C. Zhu, *Nat. Chem.*, 2019, **11**, 248–253; (*b*) G. Feng, M. Zhang, P. Wang, S. Wang, L. Maron and C. Zhu, *Proc. Natl. Acad. Sci. U. S. A.*, 2019, **116**, 17654–17658.

17 M. J. Sgro and D. W. Stephan, *Angew. Chem., Int. Ed.*, 2012, **51**, 11343–11345.

18 CCDC 1940013 (**2**), 1940015 (**3**), 1940016 (**4**), 1940017 (**5**)† contain the supplementary crystallographic data for this paper.

19 C. Morton, N. W. Alcock, M. R. Lees, I. J. Munslow, C. J. Sanders and P. Scott, *J. Am. Chem. Soc.*, 1999, **121**, 11255–11256.

20 J. A. Bogart, C. A. Lippincott, P. J. Carroll, C. H. Booth and E. J. Schelter, *Chem. – Eur. J.*, 2015, **21**, 17850–17859.

21 P. B. Hitchcock, A. G. Hulkes and M. F. Lappert, *Inorg. Chem.*, 2004, **43**, 1031–1038.

22 S. T. Liddle and P. L. Arnold, *Organometallics*, 2005, **24**, 2597–2605.

23 Based on a search of the Cambridge Structural Database, CSD (version 5.38, February, 2017).

24 J. T. Moore, N. E. Smith and C. C. Lu, *Dalton Trans.*, 2017, **46**, 5689–5701.