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PAPER

Metallomacrocycles as ligands: synthesis and characterisation of aluminium-bridged bisglyoximate complexes of palladium and iron†

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Dialuminiummacrocycles based on bisglyoximate moieties were prepared and their coordination chemistry with Fe^{II} and Pd^{II} was investigated. The bridging aluminium centers were supported by several types of tetradentate diphenoxide diamine ligands. The nature of the ancillary ligands bound to aluminium was found to affect the overall geometry and symmetry of the metallomacrocycles. Enantiopure, chiral diphenoxide ligands based on the (*R,R*)-*trans*-1,2-diaminocyclohexane backbone afforded cleanly one metallomacrocyclic isomer. The size and electronic properties of remote substituents on aluminium-bound ligands affected the binding mode and electronic properties of the central iron. A structurally characterized iron complex shows trigonal prismatic coordination mode, with phenoxide bridges between iron and aluminium. Increasing the size of the phenoxide substituents led to square bipyramidal coordination at iron. Employing *p*-NO₂- instead of *p*-*t*Bu-substituted phenoxide as supporting ligands for aluminium caused a 0.27 V positive shift of the Fe^{III}/Fe^{II} reduction potential. These results indicate that the present synthetic approach can be applied to a variety of metallomacrocycles based on bisglyoximate motifs to affect the chemistry at the central metal.

Introduction

Metallomacrocycles have been studied for a variety of applications including the synthesis of extended solids, catalysis, selective binding of ions and sensing.^{1–18} Rational selection of metal precursors and ligands has afforded metallomacrocycles with diverse shape and size. Incorporation of binding sites for additional metals into the metallomacrocycles typically relies on the ability of coordinating atoms to bridge between the macrocycle metals and the incoming metals. Such systems, known as metallacrowns, have been extensively studied.^{2,3,19} An alternative approach to coordinating additional metals involves orthogonal metal-binding atoms on the organic units of the macrocycles. Systems with monodentate phosphine, phenanthroline, phenol or diimine donors capable of binding diverse transition metals are known.^{20–24}

Transition metal complexes supported by bisglyoximate moieties exhibit the interesting ability to bind metal centres in a coordination environment similar to biologically relevant macrocycles. Iron bisglyoximate complexes have chemistry reminiscent of heme species.^{25,26} The reactivity of cobalt bisglyoximate complexes was investigated in the context of vitamin B12

chemistry^{27,28} and, recently, in the context of catalytic proton reduction to dihydrogen.^{29–34} The large majority of these species display proton or boron bridges between the oxygen atoms. Boron-bridged variants are generally constructed from the preformed, proton-bridged, metal-bisglyoximate species.^{35–38} Metallomacrocycles consisting of two glyoximate ligands and bridges other than hydrogen or boron are rare, but examples are known with aluminium, gallium, indium or copper moieties.^{39,40} Additionally there are several examples of cryptands consisting of tris-glyoximate moieties with the oxygen donors bound to antimony, tin, iron, manganese, or chromium.^{41–47} Given the utilization of macrocycles for many applications including biomimetic chemistry, catalysis, and solar fuels, facile synthetic access to diverse metallomacrocycles is of interest as a complementary strategy for tuning of the electronic and steric environment of coordinated metal centers. We report herein on the synthesis of metallomacrocycles based on aluminium bridged bisglyoximate frameworks and their coordination chemistry with iron and palladium. The described approach allows for facile binding of a central metal to preformed dialuminiummacrocycles. The effects of the ancillary ligands bound to aluminium in tuning the properties of the metallomacrocyclic complexes are reported.

Results and discussion

In order to assemble metallomacrocycles capable of chelating a variety of metals, a strategy to link two dioximate ligands was employed. Aluminium precursors supported by tetradentate

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ligands capable of affording two open *cis* coordination sites were selected. Diphenoxide diamines have been used as ancillary ligands for olefin polymerization precisely due to the availability of two *cis* coordination sites.^{48–50} Furthermore, the synthesis of these ligands is modular and allows for steric and electronic variation as well as changes in the linkages between the donor atoms. Methylaluminium species were prepared *in situ* by a modification of literature procedures and used as precursors for protonolysis reactions with glyoximes (Scheme 1).^{51,52}

Treatment of acenaphthenequinonedioxime (glyoxime **b**, Scheme 1), which is sparingly soluble in THF, with **2** led to a homogeneous mixture indicating that a reaction occurred. The ¹H NMR spectrum in C₆D₆ contains signals corresponding to both the phenoxide ligand and the dioximato backbone. Additionally, a peak slightly downfield of 14 ppm indicated protonation of two of the nitrogen atoms of the glyoximato moiety. A single crystal X-ray diffraction (XRD) study reveals the dialuminium-bridged bisglyoximato macrocycle with pseudo-*C*₂ symmetry (Fig. 1, top). The two aluminium centres are six-coordinate with the glyoximato oxygens bound in *cis* geometry, as enforced by the diphenoxide diamine ligands. The dihedral angle between the two diimino moieties is *ca.* 89°. The metal centres are located 7.29 Å apart and are oriented *syn* relative to the plane defined by the four imine nitrogens.

The metallomacrocycle in **3b** consists of 14 atoms. NMR analysis of compound **3b** reveals that the methyl groups *ortho* to the phenoxide oxygen and the N(CH₃)₂ groups display single peaks, respectively (room temperature). The CH protons at the 2 and 7 positions of the naphthalene moiety display different signals in NMR spectra. These data support an average structure that has *C*_{2h} symmetry (Scheme 1), suggesting a fast fluxional process that exchanges the methyl groups on the NMR time scale, but preserves the *C*₂ axis. Attempts to synthesise a variant of **3b** with *tert*-butyl substituents in the positions *ortho* and *para* with respect to oxygen generated a mixture of products. Nevertheless, a single crystal suitable for XRD was isolated and

analyzed. The solid-state structure (Fig. 1, bottom) reveals coplanar arrangement of the glyoximato moieties and an overall *pseudo-C*_{2h} symmetry. The Al–Al distance is 7.54 Å and the metals centres are found *anti* with respect to the glyoximato plane. The change in geometry compared to **3** is likely due to the bulky *tert*-butyl substituents that do not allow the phenoxides to move close to one another. The solution NMR spectroscopic behaviour and the two solid state structures discussed above suggest that the conformation of the macrocycle is dynamic and can be affected by the steric environment defined by the ancillary ligands bound to aluminium.

With metallomacrocycle **3b** in hand, two independent procedures were designed to bind a palladium center to the macrocycle. One approach involved the *in situ* synthesis of an H-bridged palladium bisdioximato complex by treatment of Pd(OAc)₂ with acenaphthenequinonedioxime, followed by addition of methyl aluminium species **2** to generate **5b-Pd** (Route B, Scheme 1). Route B first templates the two dioximato ligands around palladium followed by completion of the metallomacrocycle upon alkane elimination with the methyl aluminium species. Recrystallisation yielded a mixture of two species in a 10 : 1 ratio. XRD studies were performed on two types of crystals obtained from the mixture and revealed two conformers (Fig. 2). In both species, the oximato moieties are roughly coplanar affording square planar coordination about palladium. The two conformers differ in the location of the aluminium centers, *anti* or *syn* with respect to the plane of the four imine nitrogens. These solid-state structures indicate that although the two dioximato moieties are not coplanar in the free metallomacrocycle (**3b**), the central metal can alter the conformation of the macrocycle to afford square planar coordination. ¹H NMR spectroscopy shows only one singlet, at room temperature, for the methyl groups *ortho* to the phenoxide oxygen and the N(CH₃)₂, respectively. Variable temperature ¹H NMR spectroscopy revealed broadening of these peaks but no decoalescence down to –90 °C. This spectroscopic behavior is indicative of a fast

Scheme 1 Synthesis of metal complexes supported by aluminiummacrocycles.

Fig. 1 Solid-state structures of **3b** (top) and *tert*-butyl-substituted variant (**3b^{tBu}**) (bottom). Hydrogen atoms and solvent molecules have been omitted for clarity; thermal ellipsoids are displayed at 50% probability.

exchange between the *syn* and *anti* conformers, or a *pseudo*- C_{2h} structure in solution. An alternative synthetic pathway to **5b-Pd** involved a reaction between isolated metallomacrocyclic **3b** and $\text{Pd}(\text{OAc})_2$ (Scheme 1, Route A). Based on ^1H NMR spectroscopy, the product is identical by the two independent syntheses. The minor species observed by spectroscopy was assigned as a diastereomer (*vide infra*).

The Pd^{II} centre in **5b-Pd** enforces the square planar geometry upon binding of the macrocycle. To investigate the binding mode of the aluminiummacrocyclic to metal centres that can access six-coordinate geometry, Fe^{II} complexes were synthesized. Via synthetic route B, previously reported iron

Fig. 2 Solid-state structures of **5b-Pd** conformers. Hydrogen atoms and solvent molecules have been omitted for clarity; thermal ellipsoids are displayed at 50% probability.

diglyoximato complex (**4a-Fe**),^{26,53} was treated with methylaluminium species **3a** in THF. Precursor **4a-Fe** is sparingly soluble in THF, but slowly dissolved as the reaction proceeded to generate a bright purple solution. Purification by fractional precipitation afforded the isolation of a red-purple solid. Using route A, treatment of **3a** with base followed by FeCl_2 and pyridine allows the isolation of a red-purple solid with spectroscopic properties identical to the product obtained from route B. The ^1H NMR spectrum of the red-purple residue in C_6D_6 shows a single major peak for each of the three types of methyl groups, NMe_2 , *para*- CH_3 and *ortho*- CH_3 . Additionally, two coordinated pyridines are present (by integration of ^1H NMR peaks). Similar to the palladium complex above (**5b-Pd**), these spectroscopic data suggest a C_{2h} structure (or fast exchange) with two pyridines bound along the C_2 axis. ESI-MS data shows a peak at $m/z = 1452.7$ that is consistent with assignment of the product as **5a-Fe**.

Attempts to grow X-ray quality single crystals of **5a-Fe** resulted in yellow crystals from a red-purple solution in THF layered with hexanes. An XRD study of this material revealed an unexpected binding for the macrocycle (**5a-Fe-O-bridge**, Fig. 3 and eqn (1)). The iron centre is six-coordinate, with a trigonal prismatic geometry. The iron ligands are two phenoxide oxygens bridging between iron and aluminium and the four oxime moieties. The conformation of the metallomacrocyclic bound to iron is reminiscent of the structure of **3b** with the two dioximato planes departing from coplanarity with a dihedral angle of 63° .

Fig. 3 Solid-state structure of **5a-Fe-O-bridge**. Hydrogen atoms and solvent molecules have been omitted for clarity; thermal ellipsoids are displayed at the 50% probability.

Fig. 4 UV-Vis spectra at 70 μM of complexes **5a-Fe-O-bridge** (black), **5a-Fe** (blue), **5a^{tBu}-Fe** (green) and **5a-Fe** plus excess pyridine (2 mM, red).

Compound **5a-Fe-O-bridge** was prepared free of pyridine by trituration of **5a-Fe** with toluene several times. **5a-Fe-O-bridge** shows a paramagnetic ^1H NMR spectrum with broad peaks between 1 and 14 ppm. Further studies were performed to elucidate the behaviour of **5a-Fe** and **5a-Fe-O-bridge** in solution. An NMR sample of **5a-Fe** in CD_2Cl_2 displayed the diamagnetic peaks as described above, but also some paramagnetic peaks consistent with the presence of **5a-Fe-O-bridge**. Addition of excess pyridine led to an increase of the diamagnetic peaks assigned to **5a-Fe**.

Compound **5a-Fe** was dissolved in benzene and analyzed by UV-Vis spectroscopy (Fig. 4). Two absorptions, at 461 and 548 nm were observed. Addition of pyridine led to an increase in the intensity of the band at 548 nm and decrease of the band at 461 nm. The 548 nm band is in the range previously reported for iron bisglyoximate complexes, with coplanar oximes.^{26,54,55} The observed spectral shift in the presence of pyridine is consistent with an equilibrium between **5a-Fe** and **5a-Fe-O-bridge** plus free pyridine.

Fig. 5 Effect of the ancillary ligand of aluminium on the symmetry of the metallomacrocyclic.

The structural change from **5a-Fe** and **5a-Fe-O-bridge** is accompanied by a spin change from diamagnetic to paramagnetic and a change in the electronic absorption spectrum (Fig. 4). The change in the iron coordination geometry from square bipyramid to trigonal prism is expected to lead to a smaller d-d splitting because none of the d orbitals have all lobes pointing to ligands.^{56,57} Consequently a high-spin species was generated. The band at 548 nm (**5a-Fe**) is consistent with a d- π^* charge transfer, as previously assigned.^{54,55,58} The observed shift to higher energy is likely due to an increase in the energy of the glyoxime π^* orbital due to more direct interactions with d orbitals.

Analysis of the solid-state structure of **5a-Fe-O-bridge** shows that the two bridging phenoxides are spatially close to each other. In order to disfavour phenoxide bridges and facilitate intermolecular binding of ligands, a bulkier phenoxide was utilized. A variant with *tert*-butyl instead of methyl groups in the *para* position vs. the phenoxide oxygens was employed. Species **5a^{tBu}-Fe** was prepared analogously to **5a-Fe** and investigated by UV-Vis spectroscopy (Fig. 4). Without added pyridine the peak at 548 nm, corresponding to the d- π^* transition in **5a^{tBu}-Fe**, is almost as intense as the 548 nm peak of **5a-Fe** upon addition of excess pyridine. This indicates that the increased steric bulk on the ligand periphery affects the coordination environment at the iron centre, disfavouring the formation of phenoxide bridges (eqn (1)).

The geometry of the ancillary ligand bound to the aluminium centre affects the overall symmetry of the metallomacrocyclic. A tripodal $\text{N}(\text{O}_2\text{N})$ ligand generates an aluminium precursor of pseudo- C_s symmetry (**2**, Scheme 1). Since two aluminium centres are part of the metallomacrocyclic, the symmetry can be *pseudo-C_{2v}* or *pseudo-C_{2h}* (approximating the macrocycle as planar) dependent on the relative orientation of the $\text{Al}[\text{N}(\text{O}_2\text{N})]$ moiety (Fig. 5). If the four donors of the diphenoxide diamine ligands are linked in a linear fashion $(\text{NO})_2$, the resulting aluminium complexes display *pseudo-C₂*-symmetry rendering the metal centres chiral. Again, depending on the stereochemistry at

aluminium, two types of macrocycles are possible, with *pseudo-D₂* or *pseudo-C_{2h}* symmetry. It was envisioned that the stereochemistry at aluminium could be set by a chiral centre in the ligand backbone, such as defined by a *trans*-1,2-diaminocyclohexane moiety. Control of the stereochemistry by the ancillary ligand was expected to favour the chiral, *pseudo-D₂* structure.

To examine the stereochemistry of complexes with *C₂* symmetric ancillary ligands on aluminium, precursors **7** and **10** supported by linear diphenoxide diamine ligands were prepared using 1,2-ethylenediamine or (*R,R*)-*trans*-1,2-diaminocyclohexane backbones (Scheme 2). Attempts to prepare iron complexes ligated by aluminiummacrocycles with ethylenediamine backbones resulted in a mixture of diamagnetic products likely due to the formation of both *pseudo-D₂* and *pseudo-C_{2h}* structures. Nevertheless, one isomer can be enriched by precipitation. Since NMR spectroscopy does not allow for determination of the symmetry of the isolated product, an XRD study was performed and showed a *pseudo-D₂* structure in the solid-state (**8^{tBu}**). The iron coordination environment is *pseudo*-octahedral, with the phenoxide oxygens coordinated only to aluminium (Fig. 6). This geometry at iron is consistent with the sharp, diamagnetic NMR spectra, and the vibrant purple colour. Since a variant with methyl groups in the position *para* to the phenoxide oxygen was not prepared, it is not clear if the macrocycle binding mode is a consequence of the bulky substituent or the steric demands of the linear ligand set bound to aluminium. The metallomacrocycle appears to be larger than boron or hydrogen linked versions.^{59,60} The O1–O3 and O2–O4 distances in **8^{tBu}** are *ca.* 0.4 Å larger than the corresponding ones in difluoroborate and proton linked iron diglyoximate species (average 2.90 vs. 2.57 and 2.52 Å respectively).^{59,60} This ring expansion is due to the larger aluminium centre. Ruffling of the metalocycle is observed and contrasts with the flat geometry observed for bisglyoximate complexes bridged by protons or boron moieties. This distortion could be due to *C₂*-twists caused by the aluminium centres or the larger size of the macrocycle.

Utilization of enantiopure (*R,R*)-*trans*-1,2-diaminocyclohexane backbones results in significantly cleaner reactions for the synthesis of iron complexes ligated by aluminiummacrocycles, **12^{tBu}** and **12^{NO₂}** (¹H NMR spectroscopy, Scheme 2). To gain insight into the coordination environment at aluminium, complexes **10^{tBu}**, **11^{tBu}** and **12^{tBu}** were investigated by ²⁷Al NMR spectroscopy. Complex **10^{tBu}** displays a broad peak at *ca.* 74 ppm consistent with a five coordinate aluminium

center.^{52,61–63} Complexes **11^{tBu}** and **12^{tBu}** show peaks that are significantly shifted from **10^{tBu}**, at 14 and 12 ppm, respectively. These are consistent with a hexacoordinate environment at aluminium.^{61–63} The ²⁷Al NMR spectroscopy data agree with

Fig. 6 Solid state structures of **8^{tBu}** and **11^{NO₂}**. Hydrogen atoms and solvent molecules have been omitted for clarity; thermal ellipsoids are displayed at the 50% probability.

Scheme 2 Synthesis of iron complexes supported by aluminiummacrocycles with *C₂*-symmetric ancillary ligands.

Fig. 7 Cyclic voltammograms of complexes **12^{tBu}** (red) and **12^{NO2}** (blue) (1 mM in 1 : 1 DCM : MeCN solution, 0.1 M *n*Bu₄ClO₄, 0.01 M AgNO₃ reference electrode, platinum working electrode, platinum wire counter electrode, referenced to [FeCp₂]^{+/0}/FeCp₂).

the solid-state structures of related complexes.^{52,61–63} These indicate that upon formation of the dialuminiummacrocycles, the aluminium centers are coordinated to two glyoximate oxygen in addition to the tetradentate diphenoxide ancillary ligand. Ligand variants with *para*-NO₂ and *para*-*tert*-butyl substitution were employed for the phenoxides. An XRD study of complex **12^{NO2}** revealed a *pseudo-D*₂ structure. Similar to complex **8^{tBu}** supported by the ethylenediamine backbone, **12^{NO2}** shows ruffling of the macrocycle. The control of the overall symmetry of the metallomacrocycle by the ancillary ligand on aluminium is notable as it affords enantiopure macrocycles.^{18,64}

Remote substituents on the phenoxide rings were found to affect the coordination environment around the central iron, likely due to steric interactions (*vide supra*). To complement those findings, complexes **12^{tBu}** and **12^{NO2}** allow for studies of the electronic effect of different aluminium-bound phenoxides on the redox properties of the iron centre. Cyclic voltammetry of **12^{tBu}** (Fig. 7) shows waves between 0.5 and 1 V vs. [FeCp₂]^{+/0}/FeCp₂, which are assigned to phenoxide based redox events. Metal-bound trialkyl phenoxides were reported previously to have reduction potentials in the above range.^{65,66} Complex **12^{NO2}** displays a positive shift of these potentials consistent with the presence of electron withdrawing nitro groups that disfavour ligand oxidation. Complexes **11^{tBu}** and **11^{NO2}** (see ESI[†]), without an iron centre, show irreversible features at potentials similar to **12^{tBu}** and **12^{NO2}**, respectively, supporting the assignment of these redox events as ligand-based. The redox event at −0.34 V for **12^{tBu}** was assigned to the Fe^{III}/Fe^{II} couple. This is 0.32 V more negative compared to proton-bridged iron diglyoximate species (−0.02 V vs. [FeCp₂]^{+/0}/FeCp₂). It is not clear if this is a consequence of increasing electron density at iron when six-coordinate aluminium bridges are present or of the larger macrocycle size with aluminium.⁶⁷ The presence of four *para*-NO₂ groups in **12^{NO2}** led to a Fe^{III}/Fe^{II} couple at −0.07 V. The significant 0.27 V shift of the Fe^{III}/Fe^{II} reduction potential compared to **12^{tBu}** supports the notion that the redox properties of the central atom can be affected by remote substituents at the periphery of the macrocycle.

Conclusions

In summary, metallomacrocycles consisting of dialuminium diglyoximate frameworks were synthesized and utilized as ligands for palladium and iron. These palladium and iron complexes were also prepared independently by first binding two glyoximate units to a central metal followed by reaction with alkyl aluminium precursors. The overall symmetry of the products is affected by the ancillary ligands bound to aluminium. Utilization of enantiopure, C₂-symmetric backbones facilitates the formation of a single, chiral isomer. The steric bulk of remote substituents was found to affect the conformation of the free metallomacrocycles as well as the coordination geometry around the central metal. In case of iron, complexes with trigonal prismatic and square bipyramidal coordination modes were characterized. Additionally, the electronic properties of the substituents on ligands bound to aluminium significantly influence the reduction potentials of the central metal. The present synthetic strategies and properties suggest that metallomacrocycles with a variety of ancillary ligands can be prepared and designed to affect chemistry at the central atom both sterically and electronically.

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Notes and references

- R. Chakrabarty, P. S. Mukherjee and P. J. Stang, *Chem. Rev.*, 2011, **111**, 6810–6918.
- V. L. Pecoraro, A. J. Stemmler, B. R. Gibney, J. J. Bodwin, H. Wang, J. W. Kampf and A. Barwinski, in *Prog. Inorg. Chem.*, 2007, John Wiley & Sons, Inc., pp. 83–177.
- G. Mezei, C. M. Zaleski and V. L. Pecoraro, *Chem. Rev.*, 2007, **107**, 4933–5003.
- F. A. Cotton, C. Lin and C. A. Murillo, *Proc. Natl. Acad. Sci. U. S. A.*, 2002, **99**, 4810–4813.
- F. A. Cotton, C. Lin and C. A. Murillo, *Acc. Chem. Res.*, 2001, **34**, 759–771.
- R. S. Forgan, J.-P. Sauvage and J. F. Stoddart, *Chem. Rev.*, 2011, **111**, 5434–5464.
- N. C. Gianneschi, M. S. Masar and C. A. Mirkin, *Acc. Chem. Res.*, 2005, **38**, 825–837.
- C. G. Oliveri, P. A. Ulmann, M. J. Wiester and C. A. Mirkin, *Acc. Chem. Res.*, 2008, **41**, 1618–1629.
- M. J. Wiester, P. A. Ulmann and C. A. Mirkin, *Angew. Chem., Int. Ed.*, 2011, **50**, 114–137.
- M. Fujita, *Chem. Soc. Rev.*, 1998, **27**, 417–425.
- M. Fujita, M. Tominaga, A. Hori and B. Therrien, *Acc. Chem. Res.*, 2005, **38**, 369–378.
- J. Meeuwissen and J. N. H. Reek, *Nat. Chem.*, 2010, **2**, 615–621.
- R. Q. Snurr, J. T. Hupp and S. T. Nguyen, *AIChE J.*, 2004, **50**, 1090–1095.
- C. Piguet, G. Bernardinelli and G. Hopfgartner, *Chem. Rev.*, 1997, **97**, 2005–2062.
- S. De, K. Mahata and M. Schmittel, *Chem. Soc. Rev.*, 2010, **39**, 1555–1575.
- P. H. Dinolfo and J. T. Hupp, *Chem. Mater.*, 2001, **13**, 3113–3125.

- 17 J. R. Nitschke, *Acc. Chem. Res.*, 2007, **40**, 103–112.
- 18 S. J. Lee and W. Lin, *Acc. Chem. Res.*, 2008, **41**, 521–537.
- 19 M. S. Lah and V. L. Pecoraro, *J. Am. Chem. Soc.*, 1989, **111**, 7258–7259.
- 20 D. Li, R. Li, Z. Qi, X. Feng, J. Cai and X. Shi, *Inorg. Chem. Commun.*, 2001, **4**, 483–485.
- 21 T. Mizuta, T. Aotani, Y. Imamura, K. Kubo and K. Miyoshi, *Organometallics*, 2008, **27**, 2457–2463.
- 22 S. Ghosh, R. Chakrabarty and P. S. Mukherjee, *Inorg. Chem.*, 2009, **48**, 549–556.
- 23 H. Rauter, E. C. Hillgeris, A. Erxleben and B. Lippert, *J. Am. Chem. Soc.*, 1994, **116**, 616–624.
- 24 M. J. E. Resendiz, J. C. Noveron, H. Disteldorf, S. Fischer and P. J. Stang, *Org. Lett.*, 2004, **6**, 651–653.
- 25 J. F. Drake and R. J. P. Williams, *Nature*, 1958, **182**, 1084.
- 26 L. Vaska and T. Yamaji, *J. Am. Chem. Soc.*, 1971, **93**, 6673–6674.
- 27 G. N. Schrauzer, *Acc. Chem. Res.*, 1968, **1**, 97–103.
- 28 G. N. Schrauzer and J. Kohnle, *Chem. Ber.*, 1964, 97.
- 29 P. Connolly and J. H. Espenson, *Inorg. Chem.*, 1986, **25**, 2684–2688.
- 30 X. Hu, B. M. Cossairt, B. S. Brunschwig, N. S. Lewis and J. C. Peters, *Chem. Commun.*, 2005, 4723–4725.
- 31 M. Razavet, V. Artero and M. Fontecave, *Inorg. Chem.*, 2005, **44**, 4786–4795.
- 32 C. Baffert, V. Artero and M. Fontecave, *Inorg. Chem.*, 2007, **46**, 1817–1824.
- 33 J. L. Dempsey, B. S. Brunschwig, J. R. Winkler and H. B. Gray, *Acc. Chem. Res.*, 2009, **42**, 1995–2004.
- 34 J. L. Dempsey, J. R. Winkler and H. B. Gray, *J. Am. Chem. Soc.*, 2010, **132**, 16774–16776.
- 35 X. Hu, B. S. Brunschwig and J. C. Peters, *J. Am. Chem. Soc.*, 2007, **129**, 8988–8998.
- 36 D. V. Stynes, I. Vernik and F. Zobi, *Coord. Chem. Rev.*, 2002, **233**, 273–287.
- 37 D. V. Stynes, D. B. Leznoff and D. G. A. Harshani de Silva, *Inorg. Chem.*, 1993, **32**, 3989–3990.
- 38 D. W. Thompson and D. V. Stynes, *Inorg. Chem.*, 1990, **29**, 3815–3822.
- 39 U. Kohler, H. D. Hausen and J. Weidlein, *J. Organomet. Chem.*, 1984, **272**, 337–350.
- 40 C. H. Li, R.-J. Wang, H.-Z. Kou and Y. Li, *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2003, **59**, m608–m610.
- 41 P. Chaudhuri, M. Winter, P. Fleischhauer, W. Haase, U. Florke and H.-J. Haupt, *J. Chem. Soc., Chem. Commun.*, 1990, 1728–1730.
- 42 F. Birkelbach, U. Flörke, H.-J. Haupt, C. Butzlaff, A. X. Trautwein, K. Wieghardt and P. Chaudhuri, *Inorg. Chem.*, 1998, **37**, 2000–2008.
- 43 F. Birkelbach, T. Weyhermüller, M. Lengen, M. Gerdan, A. X. Trautwein, K. Wieghardt and P. Chaudhuri, *J. Chem. Soc., Dalton Trans.*, 1997, 4529–4538.
- 44 D. Burdinski, E. Bill, F. Birkelbach, K. Wieghardt and P. Chaudhuri, *Inorg. Chem.*, 2001, **40**, 1160–1166.
- 45 D. Burdinski, F. Birkelbach, T. Weyhermüller, U. Flörke, H.-J. Haupt, M. Lengen, A. X. Trautwein, E. Bill, K. Wieghardt and P. Chaudhuri, *Inorg. Chem.*, 1998, **37**, 1009–1020.
- 46 Y. Z. Voloshin, O. A. Varzatskii, A. S. Belov, Z. A. Starikova, A. V. Dolganov and T. V. Magdesieva, *Polyhedron*, 2008, **27**, 325–334.
- 47 Y. Z. Voloshin, O. A. Varzatskii, A. V. Palchik, N. G. Strizhakova, I. I. Vorontsov, M. Y. Antipin, D. I. Kochubey and B. N. Novgorodov, *New J. Chem.*, 2003, **27**, 1148–1155.
- 48 E. Y. Tshuva, I. Goldberg and M. Kol, *J. Am. Chem. Soc.*, 2000, **122**, 10706–10707.
- 49 A. Yeor, I. Goldberg, M. Shuster and M. Kol, *J. Am. Chem. Soc.*, 2006, **128**, 13062–13063.
- 50 E. Y. Tshuva, S. Groysman, I. Goldberg, M. Kol and Z. Goldschmidt, *Organometallics*, 2002, **21**, 662–670.
- 51 C.-T. Chen, C.-A. Huang and B.-H. Huang, *Dalton Trans.*, 2003, 3799–3803.
- 52 H. Du, A. H. Velders, P. J. Dijkstra, J. Sun, Z. Zhong, X. Chen and J. Feijen, *Chem.–Eur. J.*, 2009, **15**, 9836–9845.
- 53 I. W. Pang and D. V. Stynes, *Inorg. Chem.*, 1977, **16**, 590–594.
- 54 B. A. Jillot and R. J. P. Williams, *J. Chem. Soc.*, 1958, 462–467.
- 55 N. Sanders and P. Day, *J. Chem. Soc. A*, 1969, 2303–2308.
- 56 R. Hoffmann, J. M. Howell and A. R. Rossi, *J. Am. Chem. Soc.*, 1976, **98**, 2484–2492.
- 57 E. Cremades, J. Echeverria and S. Alvarez, *Chem.–Eur. J.*, 2010, **16**, 10380–10396.
- 58 Y. Yamano, I. Masuda and K. Shinra, *Bull. Chem. Soc. Jpn.*, 1971, **44**, 1581–1585.
- 59 I. Vernik and D. V. Stynes, *Inorg. Chem.*, 1996, **35**, 6210–6220.
- 60 A. A. Dvorkin, Y. A. Simonov, T. I. Malinovskii, I. I. Bulgak and D. G. Batir, *Proc. Natl. Acad. Sci. U. S. S. R.*, 1997, **234**, 1372.
- 61 R. Benn, A. Ruffin, H. Lehmkuhl, E. Janssen and C. Krüger, *Angew. Chem., Int. Ed. Engl.*, 1983, **22**, 779–780.
- 62 J. W. Akitt, *Prog. Nucl. Magn. Reson. Spectrosc.*, 1989, **21**, 1–149.
- 63 J. H. Wengrovius, M. F. Garbaskas, E. A. Williams, R. C. Goint, P. E. Donahue and J. F. Smith, *J. Am. Chem. Soc.*, 1986, **108**, 982–989.
- 64 B. Olenyuk, J. A. Whiteford and P. J. Stang, *J. Am. Chem. Soc.*, 1996, **118**, 8221–8230.
- 65 D. Lionetti, A. J. Medvecz, V. Ugrinova, M. Quiroz-Guzman, B. C. Noll and S. N. Brown, *Inorg. Chem.*, 2010, **49**, 4687–4697.
- 66 B. Adam, E. Bill, E. Bothe, B. Goerd, G. Haselhorst, K. Hildenbrand, A. Sokolowski, S. Steenzen, T. Weyhermüller and K. Wieghardt, *Chem.–Eur. J.*, 1997, **3**, 308–319.
- 67 R. R. Gagne and D. M. Ingle, *Inorg. Chem.*, 1981, **20**, 420–425.