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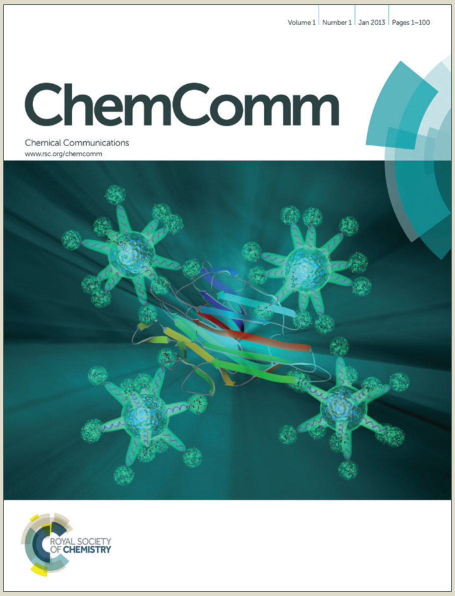

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Octahedral to trigonal prismatic distortion driven by subjacent orbital π antibonding interactions and modulated by ligand redox noninnocence

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$Ru(ONO)_2$ and $Os(ONO)_2$ distort from octahedral towards trigonal prismatic geometry in order to relieve π antibonding due to donation from the second-highest ligand orbital to the metal. Increasing oxidation of the ONO ligand suppresses distortion by increasing σ* interactions in the trigonal prism.

The geometries of the vast majority of six-coordinate complexes of the transition metals are well-described as octahedral. When alternative geometries, such as trigonal prismatic, are observed, it is indicative of either constraints imposed by the ligand[1] or unusual electronic features of the complex.[2] As a celebrated example of the latter, early metal alkyls and hydrides,[3] as well as compounds with other ligands such as thiolates that also form highly covalent bonds,[4] are often non-octahedral in order to maximize overlap with the metal *s* and *d* orbitals.[5] As metal-ligand bonding becomes more ionic or involves π bonds,[6] or as *d* electron counts increase,[7] these predilections are overruled and octahedral structures are again observed.

The ONO ligand (Fig. 1), with its highly electronegative O and N donor atoms and its propensity to be a π donor, particularly in early metal complexes where it is generally in a reduced oxidation state, would thus appear to fall squarely into a class of ligand that should favor octahedral geometry in its six-coordinate complexes. This expectation is buttressed by its geometric structure, where its consecutive 5-membered chelate rings with all ligand atoms sp^2-hybridized predispose it to adopt a *mer* geometry in an octahedron and appear ill-suited to the curvature that would be required for tridentate coordination in a trigonal prism. This expectation is confirmed experimentally, as all thirteen structurally characterized homoleptic bis-ONO complexes of transition metals (neutral species from Ti-Zn[8,9] plus Mo[9] and W[10], and cationic Mn[11] and Co[12]) are octahedral, with perpendicular ONO planes.

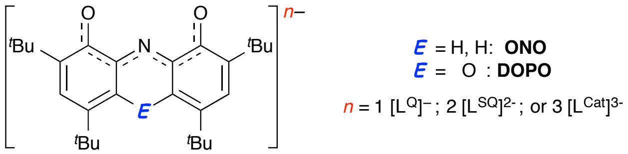
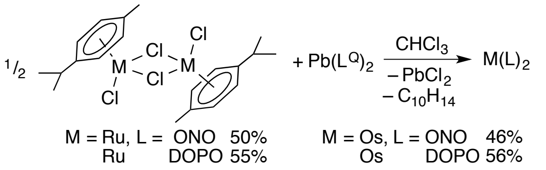


Fig. 1. Structures and oxidation states of the ONO and DOPO ligands.

Not so $Ru(ONO)_2$ and $Os(ONO)_2$! These compounds are readily prepared by treating $\{(p\text{-cymene})MCl_2\}_2$ with $Pb(ONO^Q)_2$[13] at room temperature (eq 1) to abstract chloride.[9,13b,14] The complexes containing the DOPO ligand[15] (Fig. 1) are prepared analogously using $Pb(DOPO^Q)_2$[9] at 60 ºC, and all four compounds are isolated as crystalline, diamagnetic, highly coloured, air-stable solids.



(1)

The solid-state structure of $Ru(ONO)_2$ (Fig. 2) shows modest, but clearly significant, deviations from the expected octahedral geometry. In particular, the N1-Ru-N2 angle (162.05(12)º) is noticeably nonlinear, and one of the intraligand O-M-O angles (O2-Ru-O4) is appreciably expanded from that expected for *cis* ligands in an octahedron (106.50(9)º vs. 92.1(25)º avg for other $M(ONO)_2$). These distortions reduce the symmetry from D_2 to C_2, and as a result the two aryloxide rings within each ONO ligand are chemically inequivalent, which can be seen structurally in, for example, significantly different Ru–O distances (2.023(6) vs. 1.988(8) Å).

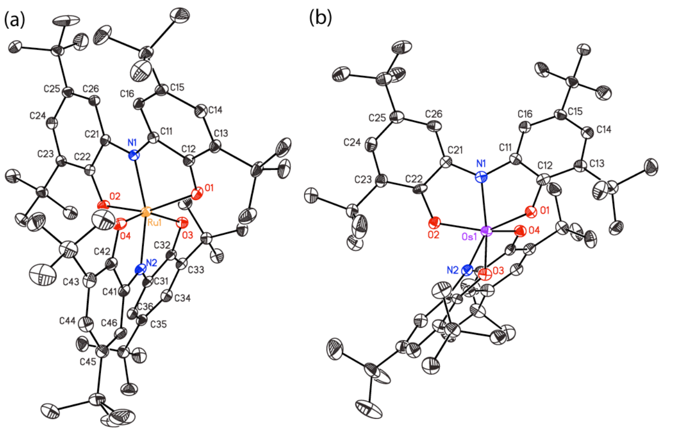


Fig. 2. Thermal ellipsoid plots of the metal complexes in (a) $Ru(ONO)_2{\bullet}CHCl_3{\bullet}1.31\ CH_3CN$ and (b) $Os(ONO)_2{\bullet}2\ CHCl_3$. Hydrogen atoms are omitted for clarity, and only one of two crystallographically inequivalent complexes in each structure is shown.

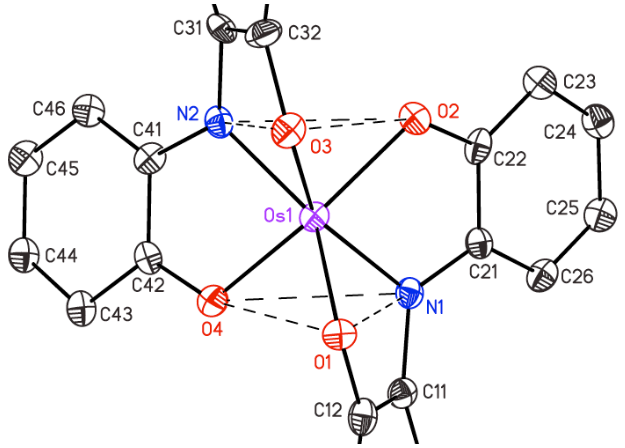


Fig. 3. Thermal ellipsoid plot of the core of $Os(ONO)_2$, with hydrogens, ^{t}Bu groups, and most of rings 1 and 3 omitted. Dashed lines illustrate the trigonal faces of the approximately trigonal prismatic geometry.

In $Os(ONO)_2$ the distortions that are subtle in the ruthenium compound become gross (Fig. 2b). The ONO ligands are markedly folded, with intraligand O-Os-O angles of 124(3)º avg. Out of over 50 reported structurally characterized ONO compounds, only $Pb(ONO)_2$[13] and $(ONO)ReO(PPh_3)$[14] show similar degrees of ligand nonplanarity. The geometry at the metal center in $Os(ONO)_2$ is far from octahedral, with N1-Os-N2 = 128.54(19), 133.33(19)º and O2-Os-O4 = 146.57(16), 140.68(16)º for the two inequivalent molecules in the crystal. Instead, the overall structure is well-described as a trigonal prism (Fig. 3), with deviations from the idealized angles of 131.8º plausibly attributed to geometric constraints of the ligands. This structure is retained in solution, with ^{1}H NMR spectra in CD_2Cl_2 showing resonances due to an unsymmetrical ligand at low temperature with $\Delta G^{\ddagger}$ (298 K) = 11.0(7) kcal mol^{-1} for ligand symmetrization (see ESI). This value is in good agreement with the calculated ΔG° = 10.5 kcal mol^{-1} between optimized C_2-symmetric and constrained D_2-symmetric $Os(ONO)_2$ (DFT, B3LYP, 6-31G*/SDD for Os, see ESI for more details).

The distortions from octahedral toward trigonal prismatic geometry in the group 8 complexes cannot be due to steric or geometric constraints of the ONO ligand, given the abundance of octahedral $M(ONO)_2$ complexes, and the formation of octahedral Ru and Os complexes of a tridentate NOS chelate with the same backbone.[16] The group 8 metals are among the more electronegative metals whose $M(ONO)_2$ complexes have been described, and one might imagine that the metal-ligand bonds are now covalent enough that the preference for non-octahedral geometries seen in covalent species of the early transition metals might come into play. This hypothesis is implausible for several reasons. First, known examples of ruthenium and osmium complexes with oxygen and nitrogen ligands, for example the neutral osmium and ruthenium tris(catecholates)[17] and tris(amidophenolates),[18] are usually octahedral. Second, distortions away from octahedral geometry in, e.g., the metal hexamethyls become *less* pronounced as one goes to the right in the periodic table, whereas $W(ONO)_2$ is clearly octahedral (in contrast to its thio analogue, where covalency is the likely structural driver).[10] Finally, DFT calculations, which reproduce the mild and serious distortions of $Ru(ONO)_2$ and $Os(ONO)_2$, respectively, do not support this explanation. In particular, $[Re(ONO)_2]^+$, where the metal-ligand bond polarity should be similar to $Os(ONO)_2$, is calculated to be octahedral (D_2-symmetric), like the isoelectronic $W(ONO)_2$. Anionic $[Re(ONO)_2]^-$ is calculated to be even more distorted than isoelectronic $Os(ONO)_2$. Thus, it would appear that it is the electron configuration, rather than the covalency of the σ-bonding, that is germane to the structural preferences of the complex.

If the σ bonding is not critical, the reason behind the distortion might lie with π bonding. Metal-ligand π bonding will be dominated by the highest-lying ligand π orbital, which is mostly on nitrogen with in-phase contributions from both oxygens and is carbon-heteroatom antibonding.[19] In an octahedral complex, the two ligand combinations interact with two of the *d*π orbitals (d_{xz} and d_{yz}, with the N atoms along the *z* axis), while the third *d*π orbital, d_{xy}, is nonbonding with respect to the ligand HOMOs.[9] In low-spin group 8 ML_2 complexes, one would expect the metal-ligand π bonding orbitals, as well as the d_{xy} orbital, to be filled, while the metal-ligand π* orbitals would be empty.

At first glance, this would appear to be a stable orbital arrangement. The catch is that the d_{xy} orbital, while nonbonding with respect to the ligand HOMO, is strongly antibonding with respect to the *second-highest* ligand orbital, where the two oxygen *p* orbitals are out of phase with each other in a phenoxide-like nonbonding combination (Fig. 4a, shown for $[Re(ONO)_2]^-$ constrained to be D_2-symmetric). This π* interaction of the filled metal *d* orbital with the subjacent ligand π orbital is largely relieved upon distortion to a trigonal prismatic structure (Fig. 4b). In this geometry, the oxygen *p*π orbitals are all oriented roughly perpendicular to the pseudo-C_3 axis of the trigonal prism and so have little or no overlap with the d_{z^2} orbital. This behavior can be seen in a Walsh diagram for $[Re(ONO)_2]^-$ (Fig. 5), where the energy of this orbital is minimized at the N-Re-N angle of an ideal trigonal prism, while the two Re-N π bonding orbitals, in the aggregate, are relatively insensitive to changes along this coordinate, leading to an overall energy that closely tracks the energy of the HOMO. This explanation is consistent with the observation that $Os(DOPO)_2$ and $Ru(DOPO)_2$ are octahedral (by crystallography and DFT, see ESI),

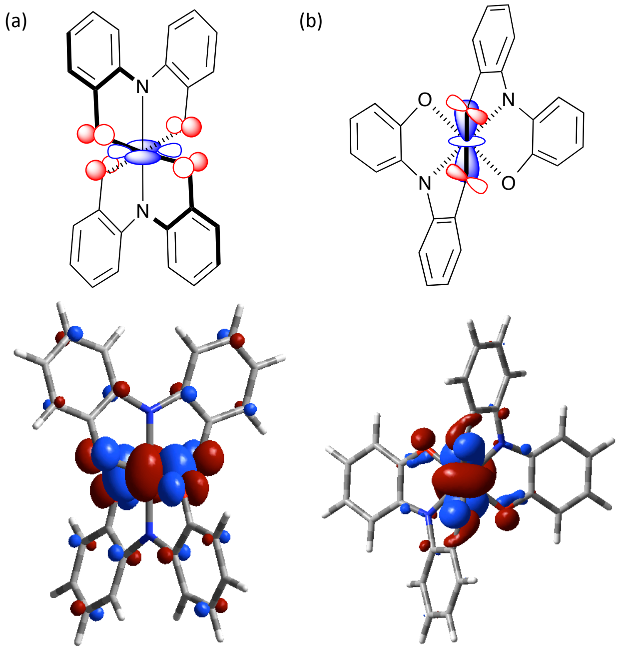


Fig. 4. (a) HOMO of octahedral M(ONO)$_2$ (D_2 symmetry). **(b)** HOMO of trigonal prismatic M(ONO)$_2$ (C_2 symmetry). Top: schematic; bottom: calculated Kohn-Sham orbitals for [Re(ONO)$_2$]$^-$ (B3LYP, 6-31G* except SDD for Re).

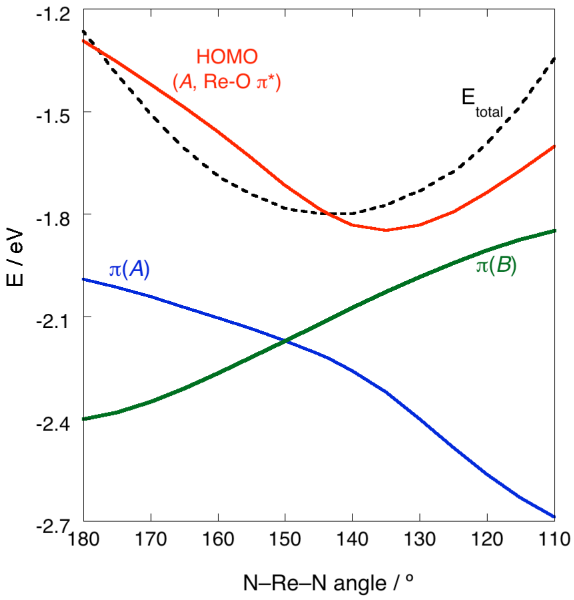


Fig. 5. Walsh diagram for C_2-symmetric [Re(ONO)$_2$]$^-$ showing the energies of the HOMO and the two main metal-ONO π bonding orbitals (of A and B symmetry) as a function of the N-Re-N angle. The offset of the total calculated energy (dashed line) is arbitrary, but it is shown on the same energy scale.

as the elongation of the metal-oxygen bonds[9,15b] by ~0.08 Å would be expected to attenuate the metal-oxygen π^* interaction, though the greater rigidity of the DOPO ligand probably plays a more important role in preventing distortion to a prismatic geometry. Tellingly, cyclic voltammetry (see ESI) shows that in octahedral M(DOPO)$_2$, the osmium complex is 95 mV more easily oxidized than ruthenium, consistent with the usual periodic trends for a metal-based oxidation.

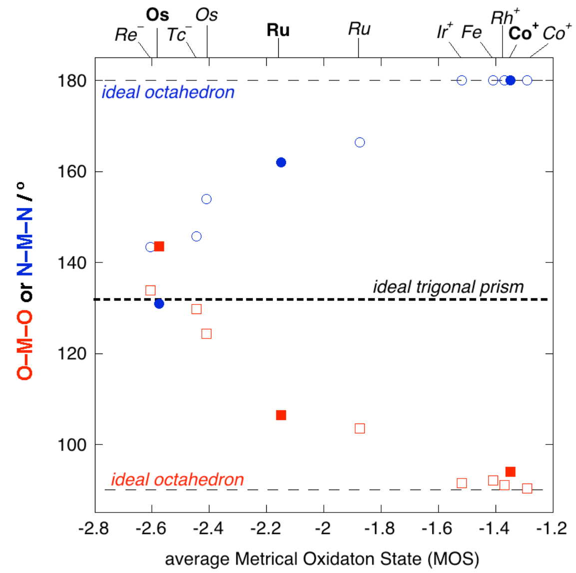


Fig. 6. Variation of largest interligand O-M-O angle (red squares) and N-M-N angle (blue circles) with metrical oxidation state of the ligands in a series of complexes isoelectronic with Os(ONO)$_2$. Calculated values (DFT, B3LYP, 6-31G* except SDD for $4d$ and $5d$ metals, singlet states) are given by open symbols and labeled in italics; experimental data are given with solid symbols and labeled in boldface. Experimental data for [Co(ONO)$_2$]$^+$ are from ref. 12.

In contrast, Os(ONO)$_2$ is 300 mV more *difficult* to oxidize than Ru(ONO)$_2$, supporting the notion that the distortion strongly stabilizes the HOMO of the compound.

The degree of distortion toward trigonal prismatic varies considerably among complexes isoelectronic to Os(ONO)$_2$. Os(ONO)$_2$ is much more distorted than Ru(ONO)$_2$, while [Ir(ONO)$_2$]$^+$ (computationally) and [Co(ONO)$_2$]$^+$ (both experimentally[12] and computationally) are nearly ideal octahedra. Qualitatively, this means that the more octahedral complexes correspond to those with less reduced ONO ligands. Quantitatively, the degree of reduction of the ligand can be judged by the C–N, C–O, and C–C bond distances in the ligand, which can be correlated with literature values to determine an apparent "metrical oxidation state" (MOS).[9,20] There is an excellent correlation with the degree of ligand reduction and the degree of distortion (Fig. 6). In all of these compounds, the M-N π bonding orbitals are filled and the M-N π^* orbitals are empty. As the electronegativity of the metal increases, the character of the M-N π orbital shifts from mostly ligand-centered (ONO$^{\mathrm{Cat}}$-like, MOS approaching –3) to mostly metal-centered (ONO$^{\mathrm{Q}}$-like, MOS approaching –1). As the metal character of this orbital increases, so too does its σ^* character due to interactions with the ligand σ lone pairs (E' symmetry in an ideal trigonal prism). In other words, as the metal character of these orbitals increases, they increasingly resemble d_{xy} and $d_{x^2-y^2}$ orbitals, whose σ^* character in a trigonal prism is responsible for the strong preference for octahedral over trigonal prismatic geometry in, e.g., low-spin d^6 complexes.[21]

Similar subjacent orbital effects may also be germane to other complexes of π-donor noninnocent ligand complexes of the middle transition metals. For example, Ru(3,5-^{t}Bu$_2$Cat)$_3$ is stereochemically rigid while Os(3,5-^{t}Bu$_2$Cat)$_3$ is fluxional, undergoing facile trigonal twists.[17b] In this case, the A_2-symmetric combination of the strongly π-donating catecholate orbital is nonbonding in both the octahedron and the trigonal prism, but the subjacent catecholate orbital forms a combination which is A_1-symmetric in the D_3 symmetry of the octahedral complex and is antibonding with respect to the filled d_{z^2} orbital. This antibonding interaction is relieved in the trigonal prism (where the subjacent ligand combination is A_1'' and strictly nonbonding), stabilizing it. The effect is expected to be larger for Os than Ru because of the same differences in degree of ligand oxidation seen in $Os(ONO)_2$ and $Ru(ONO)_2$.

The surprising deviations of $Os(ONO)_2$ and $Ru(ONO)_2$ from octahedral geometry have three important implications. First, a novel electronic driving force for octahedral to trigonal prismatic distortion, namely the avoidance of π* interactions in the trigonal prism, has been identified. Second, even the subjacent orbitals, which are often neglected in π-donor ligands, can cause energetically significant π* interactions. Finally, these interactions are modulated by the nature of the principal π interaction between the ONO ligand and the metal. As the metal-ligand π bonding orbitals shift from ligand-centered to metal-centered, and hence the ligand becomes more oxidized, these orbitals become more σ antibonding in the trigonal prism and restore the geometric preference to octahedral. Importantly, this balance is a *continuous* function of the orbital character, not a matter of a change in discrete oxidation state. In these highly covalent molecules, assignment of a specific integer oxidation state is an often futile exercise, but the smooth changes possible in the nature of the metal-ligand bonding still exercise palpable effects.

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Notes and references

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Electronic Supplementary Information (ESI) available: Synthetic and spectroscopic characterization of compounds, details of X-ray crystallography of $M(ONO)_2$ and $M(DOPO)_2$ (M = Ru, Os), optical spectroscopy, cyclic voltammetry, variable-temperature ^1H NMR of $Os(ONO)_2$ and details of theoretical calculations. CCDC 1001300-1001303. See DOI: 10.1039/c000000x/

1 P. Comba, *Coord. Chem. Rev.*, 1993, **123**, 1-48.
2 K. Seppelt, *Acc. Chem. Res.*, 2003, **36**, 147-153.
3 (a) P. M. Morse and G. S. Girolami, *J. Am. Chem. Soc.*, 1989, **111**, 4114-4116. (b) K. Seppelt and V. Pfennig, *Science*, 1996, **271**, 626-628. (c) S. Kleinhenz, M. Schubert and K. Seppelt, *Chem. Ber.*, 1997, **130**, 903-906. (d) S. Kleinhenz, V. Pfennig and K. Seppelt, *Chem. Eur. J.*, 1998, **4**, 1687-1691. (e) B. Roessler and K. Seppelt, *Angew. Chem. Int. Ed.*, 2000, **39**, 1259-1261. (f) X. Wang and L. Andrews, *J. Am. Chem. Soc.*, 2002, **124**, 5636-5637.
4 (a) S.-M. Koo, R. Bergero, A. Salifoglou and D. Coucouvanis, *Inorg. Chem.*, 1990, **29**, 4844-4846. (b) J. C. Friese, A. Krol, C. Puke, K. Kirschbaum and D. M. Giolando, *Inorg. Chem.*, 2000, **39**, 1496-1500.
5 (a) C. R. Landis, T. Cleveland and T. K. Firman, *J. Am. Chem. Soc.*, 1995, **117**, 1859-1860. (b) C. A. Bayse and M. B. Hall, *Inorg. Chim. Acta*, 1997, **259**, 179-184. (c) C. R. Landis, T. K. Firman, D. M. Root and T. Cleveland, *J. Am. Chem. Soc.*, 1998, **120**, 1842-1854. (d) M. Kaupp, *Chem. Eur. J.*, 1998, **4**, 1678-1686. (e) C. A. Bayse and M. B. Hall, *J. Am. Chem. Soc.*, 1999, **121**, 1348-1358.
6 M. Kaupp, *Angew. Chem. Int. Ed.*, 2001, **40**, 3534-3565.
7 E. Cremades, J. Echeverría and S. Alvarez, *Chem. Eur. J.*, 2010, **16**, 10380-10396.
8 (a) Ti, V: S. Bruni, A. Caneschi, F. Cariati, C. Delfs, A. Dei and D. Gatteschi, *J. Am. Chem. Soc.*, 1994, **116**, 1388-1394. (b) Mn, Co: S. K. Larsen and C. G. Pierpont, *J. Am. Chem. Soc.*, 1988, **110**, 1827-1832. (c) Fe, Ni: C. L. Simpson, S. R. Boone and C. G. Pierpont, *Inorg. Chem.*, 1989, **28**, 4379-4385. (d) Cu: G. Speier, J. Csihony, A. M. Whalen and C. G. Pierpont, *Inorg. Chem.*, 1996, **35**, 3519-3524. (e) Zn: P. Chaudhuri, M. Hess, K. Hildenbrand, E. Bill, T. Weyhermüller and K. Wieghardt, *Inorg. Chem.*, 1999, **38**, 2781-2790.
9 L. G. Ranis, K. Werellapatha, N. J. Pietrini, B. A. Bunker and S. N. Brown, submitted.
10 D. W. Shaffer, G. Szigethy, J. W. Ziller and A. F. Heyduk, *Inorg. Chem.*, 2013, **52**, 2110-2118.
11 D. Ruiz-Molina, K. Wurst, D. N. Hendrickson, C. Rovira and J. Veciana, *Adv. Funct. Mater.*, 2002, **12**, 347-351.
12 D. Ruiz-Molina, J. Veciana, K. Wurst, D. N. Hendrickson and C. Rovira, *Inorg. Chem.*, 2000, **39**, 617-619.
13 (a) B. R. McGarvey, A. Ozarowski, Z. Tian and D. G. Tuck, *Can. J. Chem.*, 1995, **73**, 1213-1222. (b) S. Shekar and S. N. Brown, *Organometallics*, 2013, **32**, 556-564.
14 D. D. Wright and S. N. Brown, *Inorg. Chem.*, 2013, **52**, 7831-7833.
15 (a) V. I. Simakov, Y. Y. Gorbanev, T. E. Ivakhnenko, V. G. Zaletov, K. A. Lyssenko, Z. A. Starikova, E. P. Ivakhnenko and V. I. Minkin, *Russ. Chem. Bull.*, 2009, **58**, 1361-1370. (b) E. P. Ivakhnenko, A. G. Starikov, V. I. Minkin, K. A. Lyssenko, M. Y. Antipin, V. I. Simakov, M. S. Korobov, G. S. Borodkin and P. A. Knyazev, *Inorg. Chem.*, 2011, **50**, 7022-7032.
16 R. Hübner, B. Sarkar, J. Fiedler, S. Záliš and W. Kaim, *Eur. J. Inorg. Chem.*, 2012, 3569-3576.
17 (a) M. B. Hursthouse, T. Fram, L. New, W. P. Griffith and A. J. Nielson, *Trans. Met. Chem.*, 1978, **3**, 255-256. (b) S. Bhattacharya, S. R. Boone, G. A. Fox and C. G. Pierpont, *J. Am. Chem. Soc.*, 1990, **112**, 1088-1096.
18 (a) D. Das, A. K. Das, B. Sarkar, T. K. Mondal, S. M. Mobin, J. Fiedler, S. Zális, F. A. Urbanos, R. Jiménez-Aparicio, W. Kaim and G. K. Lahiri, *Inorg. Chem.*, 2009, **48**, 11853-11864. (b) A. K. Das, R. Hübner, B. Sarkar, J. Fiedler, S. Záliš, G. K. Lahiri and W. Kaim, *Dalton Trans.*, 2012, **41**, 8913-8921.
19 T. Ren, *Inorg. Chim. Acta*, 1995, **229**, 195-202.
20 S. Brown, *Inorg. Chem.*, 2012, **51**, 1251-1260.
21 R. Hoffman, J. M. Howell and A. R. Rossi, *J. Am. Chem. Soc.*, 1976, **98**, 2484-2492.