ChemComm

COMMUNICATION

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Cite this: *Chem. Commun.*, 2023, **59**, 9618

Received 20th June 2023,
Accepted 13th July 2023

DOI: 10.1039/d3cc02943c

rsc.li/chemcomm

Slip to π Ru: structural distortions due to metal-iminoxolene π bonding†

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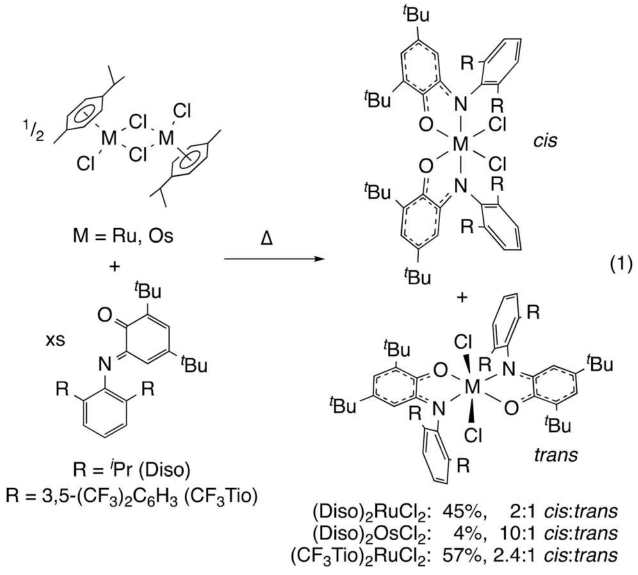
Both pseudo-octahedral and pseudo-square pyramidal bis-iminoxolene complexes *trans*-(Diso)$_2$RuCl$_2$ and *trans*-(Diso)$_2$Ru(PPh$_3$) are structurally distorted, with the ruthenium atom slipping off the twofold axis of the idealized coordination polyhedra. These distortions take place because they allow or enhance π interactions between ruthenium and the iminoxolene π orbitals.

Inorganic chemistry is dominated by high-symmetry coordination polyhedra: tetrahedral and square planar geometries for four-coordination, trigonal bipyramidal and square pyramidal geometries for five-coordination, and octahedra for six-coordination. For coordination compounds, a significant part of this preference originates in the large ionic contribution to the overall bonding: in a purely ionic system, the lowest-energy arrangement will involve a centrally located positive metal ion surrounded by symmetrically distributed negative ligands. When the σ bonding to the ligands becomes more covalent, such as in metal alkyls or hydrides, unusual coordination geometries can result.[1] A canonical example of this phenomenon is WX$_6$, which is octahedral for X = F[2] or Cl[3] but exhibits a C_{3v}-symmetric, distorted trigonal prismatic geometry for X = CH$_3$.[4] Pi bonding effects can cause geometric distortions as well, an example being (ONO)$_2$M (M = Ru, Os; ONO = N[2-O-3,5-^{t}Bu$_2$C$_6$H$_2$]$_2$), where avoidance of metal–ligand π* interactions drives the structures towards a trigonal prismatic geometry.[5] Here we describe even more striking structural distortions, driven by improving the quality of π bonding between iminoxolene ligands and ruthenium or osmium.

The sterically hindered iminoquinone *N*-(2,6-diisopropylphenyl)-3,5-di-*tert*-butyl-*o*-iminobenzoquinone (Diso)[6] reacts with {(*p*-cymene)RuCl$_2$}$_2$ to give a mixture of *cis*- and *trans*-(Diso)$_2$RuCl$_2$, which can be separated by column chromatography on silica gel (eq. 1). The osmium analogues can be prepared analogously, though yields are lower, and *trans*-(Diso)$_2$OsCl$_2$ is formed in only trace amounts and could not be completely separated from paramagnetic impurities. *Cis*-(Diso)$_2$RuCl$_2$ and *trans*-(Diso)$_2$RuCl$_2$ interconvert only extremely slowly (∼5% conversion after 22 d at 55 °C), and comparison of the initial rates of interconversion allow one to estimate $K_{eq} \approx 0.4$ for the *cis*→*trans* conversion at 55 °C.



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The *cis* compounds display only a single, *cis*-α isomer in solution by NMR spectroscopy (Fig. S6 and S8, ESI†). Judging by the solid-state structures, the observed isomer has the nitrogen atoms mutually *trans* (Fig. 1a and Fig. S1, ESI†), as expected on steric grounds. The analogous osmium compound with smaller *N*-phenyliminoxolenes, (^{H}ap)$_2$OsCl$_2$, crystallizes as the *cis*-α compound with mutually *trans* oxygens, though multiple *cis* stereoisomers of this compound are observed in solution.[7]

Iminoxolene ligands can be viewed as having three possible formal oxidation states, ranging from the neutral iminoquinone

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† Electronic supplementary information (ESI) available: Synthetic, crystallographic, and computational details, spectral characterization of compounds, VT NMR data. CCDC 2270327–2270334. For ESI and crystallographic data in CIF or other electronic format see DOI: https://doi.org/10.1039/d3cc02943c

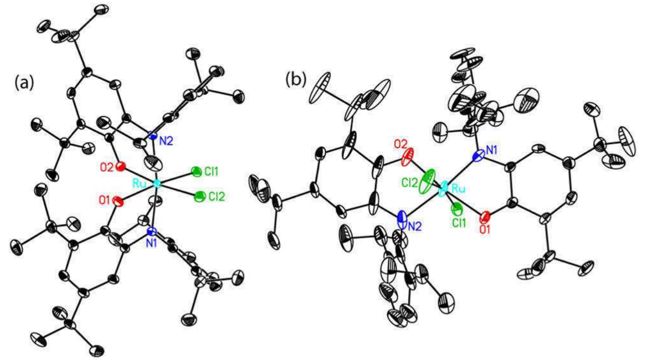


Fig. 1 Thermal ellipsoid plots of (a) *cis*-(Diso)$_2$RuCl$_2$ and (b) *trans*-(Diso)$_2$RuCl$_2$. Hydrogen atoms are omitted for clarity. Only one orientation of disordered iminoxolene ring 2 in the *trans* compound is shown.

through the radical anion iminosemiquinonate to the dianionic amidophenoxide,[8] depending on the occupancy of the key ligand π orbital, the so-called redox-active orbital or RAO (LUMO of the iminoquinone, SOMO of the iminosemiquinone, HOMO of the amidophenoxide). In complexes of Ru and Os, where the metal orbitals are close in energy to the RAO, the metal–ligand bonding becomes highly covalent and a molecular orbital analysis of the bonding is often more illuminating than an attempt to assign ligand oxidation states. In this vein, the bonding in (^{H}ap)$_2$OsCl$_2$ and a *cis*-β bis(iminoxolene)dichloroosmium complex[9] have been described in terms of the formation of two strong osmium-iminoxolene π bonds. The distribution of electron density in the π bonding orbital (on the metal *vs.* the ligand) can be assessed from the intraligand bond distances, which can be read out in the form of a "metrical oxidation state" (MOS).[10] The MOS of *cis*-(Diso)$_2$OsCl$_2$ (−1.11(4)) is similar to values in previously characterized bis(iminoxolene)dichloroosmium complexes and consistent with a bonding orbital that is quite covalent but has slightly more ligand than metal character.[9] No bis(iminoxolene)dichlororuthenium compounds have been reported previously, but the MOS value of *cis*-(Diso)$_2$RuCl$_2$ (−0.78(4)) is similar to that of a dichlororuthenium complex with one iminoxolene and one benzenediimide (MOS = −0.74(9)),[11] and shows the expected shift in the bonding orbital to one that has slightly more ruthenium than ligand character.[9]

More suprising are the structures, and even the existence, of the *trans* isomers. In a *trans* octahedral complex, one combination of the iminoxolene RAOs would have ungerade symmetry and would have no overlap with any metal d orbitals, meaning that only one metal-iminoxolene π bond could form, in contrast to the two π bonds possible in the *cis* isomer. (Diso)$_2$RuCl$_2$ does form a stable *trans* isomer, but it distorts substantially from a regular octahedral structure (Fig. 1b). The simplest way to view the structure is that the ligating atoms remain in an octahedron, but that the ruthenium has slipped off-center in the plane of the iminoxolenes perpendicular to the line connecting the centers of the iminoxolenes. This results in short distances to the nitrogen of one Diso ligand and the oxygen of the other (Ru–N1 = 1.949(3) Å, Ru–O2 = 1.966(3) Å), with the other distances (Ru–N2 = 2.064(4) Å, Ru–O1 = 2.079(2) Å) over 0.1 Å longer. The structure of (Diso)$_2$RuCl$_2$ is disordered, but the disorder does not appear to be relevant to the structural distortion, which is also observed in the ordered structure of *trans*-(CF$_3$Tio)$_2$RuCl$_2$, containing an iminoxolene ligand with a *N*-2,6-bis(3,5-bis(trifluoromethyl)phenyl)phenyl group (see ESI† for synthetic and structural information), and is reproduced in DFT calculations on *trans*-(ap)$_2$RuCl$_2$ (ap = *o*-C$_6$H$_4$(NH)O).

This distortion is thus undoubtedly electronic rather than steric in origin. The fact that the MOS values of the iminoxolene rings are not significantly different from those of the *cis* isomers (Os, −1.03(8); Ru, −0.72(7)) suggests that the distortion has allowed a significant π interaction with the in-phase RAO combination, as loss of a π bond would be expected to substantially change the observed MOS values (*e.g.*, by about 0.4 units for Os).[9] Theoretical calculations support the notion that this distortion is driven by enhancement of π bonding upon lowering the symmetry from C_{2h} to C_s (Fig. 2). In the presence of the inversion center, the ligand RAO combination of *u* symmetry and the metal dπ orbital are very close in energy and have two electrons between the two orbitals. Slipping the metal off-center therefore represents a pseudo-Jahn–Teller distortion[12] which results in formation of a π bonding and π antibonding combination and a calculated stabilization in free energy of 14.3 kcal mol^{-1} for *trans*-(ap)$_2$RuCl$_2$ and 15.1 kcal mol^{-1} for the Os analogue.

The equilibrium structures of *trans*-(Diso)$_2$MCl$_2$ are thus unsymmetrical and should show inequivalent iminoxolene ligands. At temperatures down to the freezing point of CD$_2$Cl$_2$, NMR spectra are consistent with C_{2h} symmetry, indicating that the barrier to "wagging" the metal from side to side in the complex is very low. Changing the solvent to 80% CF$_2$Cl$_2$/20% CDFCl$_2$ allows access to temperatures down to 100 K, and at

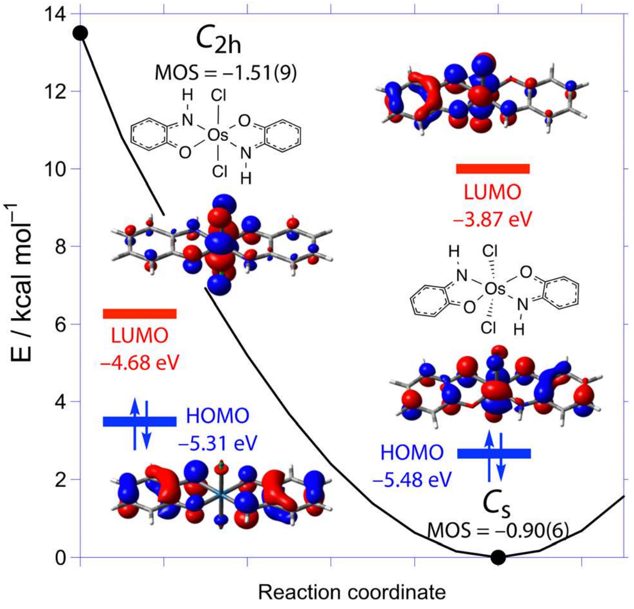


Fig. 2 Calculated orbital interactions and total energies in *trans*-(ap)$_2$OsCl$_2$ constrained to C_{2h} symmetry (left) and in its minimum-energy C_s structure. Energies of the Kohn–Sham orbitals are from DFT (B3LYP, SDD basis for Os, 6-31G* basis for other atoms).

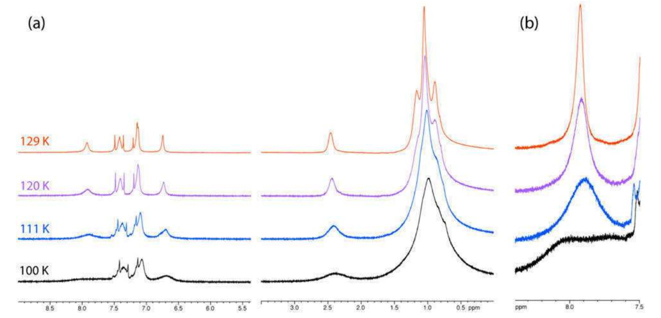
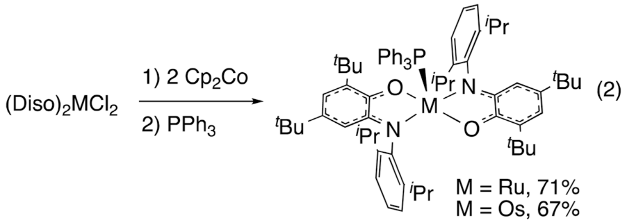


Fig. 3 ^1H NMR spectra of *trans*-$(Diso)_2RuCl_2$ in 80% CF_2Cl_2/20% $CDFCl_2$ (400 MHz). (a) Full spectrum. (b) Downfield region, showing the decoalescence of the iminoxolene resonance at δ 7.9 ppm.

these low temperatures decoalescence of one of the iminoxolene aromatic resonances is observed (Fig. 3), allowing one to estimate the barriers for interconversion of the two ligands to be $\Delta G^{\ddagger}_{298K} = 6.8(17)$ kcal mol^{-1} for Os and 9.4(6) kcal mol^{-1} for Ru (Fig. S50, ESI†). DFT calculations indicate that the interconversion likely takes place through C_2-symmetric transition states that retain some π bonding with the in-phase combination of ligand redox-active RAOs and are lower-energy than the C_{2h} structures. The observed barriers thus represent lower bounds for the energetic benefit of π bonding to this RAO combination, and the experimental data are in reasonable agreement with the calculated ΔG° for the $C_s \rightarrow C_2$ transformation (5.3 kcal mol^{-1} for Ru, 8.7 kcal mol^{-1} for Os).

Reduction of the *cis*-dichloride complexes, followed by addition of triphenylphosphine, allows isolation of five-coordinate $(Diso)_2M(PPh_3)$ (M = Ru, Os, eq. 2). X-ray crystallography of the two isostructural compounds (Fig. 4 and Fig. S5, ESI†) shows that they have approximately square pyramidal structures, with MOS values for the iminoxolene ligands that are, as expected, more negative than those shown by the dichloride complexes (Ru, avg MOS = −1.40(9); Os, avg. MOS = −1.57(10)). These values are similar to those of known six-coordinate $(iminoxolene)_2ML_2$ compounds (*e.g.*, M = Ru, L_2 = bpy, MOS = −1.44(4) avg;[13] M = Os, L = PPh_3, MOS = −1.59(9)[14]).



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Strikingly, the triphenylphosphine complexes are also distorted in a similar way to $(Diso)_2MCl_2$, with the metal-phosphorus bond canted off the approximate twofold axis of the $(iminoxolene)_2M$ fragment in the cleft between the two iminoxolenes. The metal atom is located closer to one edge of the iminoxolenes, with Ru–N1 0.052(2) Å shorter than Ru–N2 and Ru–O2 0.0651(18) Å shorter than Ru–O1. The distortion is thus qualitatively similar to, though quantitatively about half the magnitude of, that shown in *trans*-$(Diso)_2RuCl_2$.

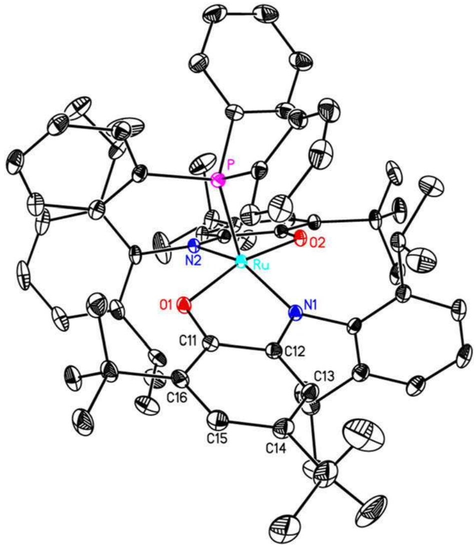

Fig. 4 Thermal ellipsoid plot of $(Diso)_2Ru(PPh_3)\cdot 2\ CH_2Cl_2$, with hydrogen atoms and lattice solvent omitted for clarity.

The distortion is undoubtedly driven by electronic factors, as it is observed computationally in unhindered $(ap)_2M(PMe_3)$. The distortion must depend on the relatively low energy of the *A*-symmetry M–P σ^* orbital (largely d_{z^2}), since octahedral complexes such as $(^Hap)_2Os(PPh_3)_2$ are undistorted.[14] The critical filled orbital appears to be the *B*-symmetry d_{yz} orbital, which is nonbonding with respect to the ligand RAO combinations but is high in energy due to an antibonding interaction with the appropriate combination of the lower-energy iminoxolene π donor orbital, the so-called subjacent orbital (SJO).[5] Shifting the metal atom towards one edge of the bis(iminoxolene) plane allows these two orbitals to mix and thus stabilizes the filled orbital (Fig. 5). While the structural distortion is appreciable, the energetic stabilization appears to be small. The equilibrium C_1 structure is calculated to be less than 1 kcal mol^{-1} lower in energy than a structure with enforced C_2 symmetry of the $(ap)_2MP$ core.

The effects of the slipped structure of $(Diso)_2M(PPh_3)$ can be observed by ^1H NMR spectroscopy, which at low temperature in CD_2Cl_2 confirms a C_1-symmetric structure for $(Diso)_2M(PPh_3)$, with inequivalent iminoxolene ligands as well as inequivalent phenyl groups on the PPh_3 ligand (Fig. S48 and S49, ESI†). Iminoxolene exchange takes place in the temperature range of 267 K–313 K (Fig. S51, ESI†). The exchange process involves both rocking the ruthenium back and forth as well as partial rotation of the triphenylphosphine, as can be seen in the fact that phenyl ring interchange in the PPh_3 group takes place concurrently with iminoxolene exchange. The magnitudes of the observed barriers ($\Delta G^{\ddagger}_{298K} = 13.1(15)$ kcal mol^{-1} for Ru, 14.3(6) kcal mol^{-1} for Os) are doubtless principally due to the steric cost of moving the PPh_3 phenyl groups past the isopropyl groups of the Diso ligands. However, these effects should be very similar for the Ru and Os congeners, which are essentially isosteric, whereas any bonding effects should be larger for the third-row element Os. The approximately 7-fold faster rates

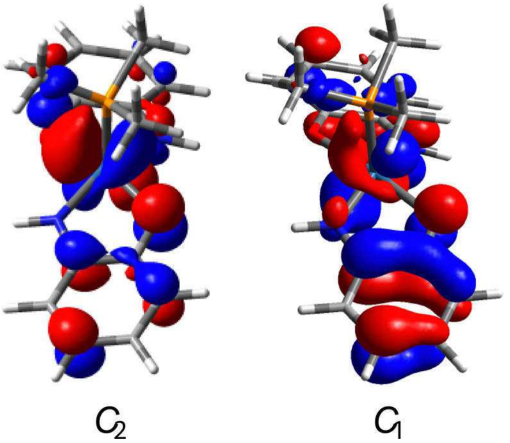

Fig. 5 Filled metal d_{yz}-iminoxolene SJO π* orbital in $(ap)_2Os(PMe_3)$ with the $(ap)_2OsP$ core constrained to have C_2 symmetry (left) or at its equilibrium C_1 geometry (right).

($\Delta\Delta G^{\ddagger}$ = 1.1 kcal mol^{-1}) observed for the Ru compound over the observed temperature range affords a rough experimental estimate of the magnitude of the electronic contribution to stabilization of the C_1 structure.

In conclusion, the bis(iminoxolene) complexes *trans*-$(Diso)_2MCl_2$ and $(Diso)_2M(PPh_3)$ show marked structural distortions in which the metal atom has slipped considerably along the groove between the iminoxolene ligands, away from the centers of the idealized coordination polyhedra. These distortions cannot be explained by steric effects or electrostatic considerations, which must always favor a more symmetrical structure. Nor are they endemic to all bis-iminoxolene group 8 compounds, as *cis*-$(Diso)_2MCl_2$ and *trans*-$(^{H}ap)_2Os(PPh_3)_2$ adopt highly symmetric structures. Instead, the metal slippage is fostered by the particular π bonding needs in the given compounds. The inability to form a second π bond between the metal and the ligand RAO in symmetric *trans*-$(Diso)_2MCl_2$ strongly drives distortion from a C_{2h} to a C_s structure. The presence of a metal-SJO π* interaction in $(Diso)_2M(PPh_3)$ likewise causes the molecule to distort from a C_2 to a C_1 structure, though the energetic benefit here is much smaller than that in the dichloride. Both of these examples indicate that the covalent metal-iminoxolene π interactions can be important drivers of structure in metal complexes.

This work was supported by the US National Science Foundation (grant CHE-1955933). We thank Dr Allen G. Oliver for his assistance with the X-ray crystallography.

Conflicts of interest

There are no conflicts to declare.

References

1 (*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.
2 T. Drews, J. Supel, A. Hagenbach and K. Seppelt, *Inorg. Chem.*, 2006, **45**, 3782–3788.
3 (*a*) R. V. G. Ewens and M. W. Lister, *Trans. Faraday Soc.*, 1938, **34**, 1358–1362; (*b*) J. A. A. Ketelaar and G. W. van Oosterhout, *Recl. Trav. Chim. Pays-Bas*, 1943, **62**, 197–200; (*c*) J. C. Taylor and P. W. Wilson, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.*, 1974, **30**, 1216–1220; (*d*) F. A. Cotton, P. A. Kibala and R. B. W. Sandor, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1989, **45**, 1287–1289; (*e*) L. Pusztai and R. L. McGreevy, *J. Chem. Phys.*, 2006, **125**, 044508.
4 K. Seppelt and V. Pfennig, *Science*, 1996, **271**, 626–628.
5 J. Cipressi and S. N. Brown, *Chem. Commun.*, 2014, **50**, 7956–7959.
6 G. A. Abakumov, N. O. Druzhkov, Y. A. Kurskii and A. S. Shavyrin, *Russ. Chem. Bull.*, 2003, **52**, 712–717.
7 J. Gianino, A. N. Erickson, S. J. Markovitz and S. N. Brown, *Dalton Trans.*, 2020, **49**, 8504–8515.
8 D. L. J. Broere, R. Plessius and J. I. van der Vlugt, *Chem. Soc. Rev.*, 2015, **44**, 6886–6915.
9 J. Gianino and S. N. Brown, *Dalton Trans.*, 2020, **49**, 7015–7027.
10 S. N. Brown, *Inorg. Chem.*, 2012, **51**, 1251–1260.
11 K. N. Mitra, S.-M. Peng and S. Goswami, *Chem. Commun.*, 1998, 1685–1686.
12 T. A. Albright, J. K. Burdett and M.-H. Whangbo, *Orbital Interactions in Chemistry*, John Wiley & Sons, Hoboken, NJ, 2nd edn, 2013, p. 136.
13 D. Das, T. K. Mondal, A. D. Chowdhury, F. Weisser, D. Schweinfurth, B. Sarkar, S. M. Mobin, F. A. Urbanos, R. Jimenez-Aparicio and G. K. Lahiri, *Dalton Trans.*, 2011, **40**, 8377–8390.
14 A. N. Erickson, J. Gianino, S. J. Markovitz and S. N. Brown, *Inorg. Chem.*, 2021, **60**, 4004–4014.