ChemComm

Cite this: *Chem. Commun.*, 2011, **47**, 3123–3125

www.rsc.org/chemcomm

COMMUNICATION

Synthesis and structural characterization of tris(2-oxo-1-*tert*-butylimidazolyl) and tris(2-oxo-1-methylbenzimidazolyl)hydroborato complexes: a new class of tripodal oxygen donor ligand†

Ahmed Al-Harbi, Wesley Sattler, Aaron Sattler and Gerard Parkin*

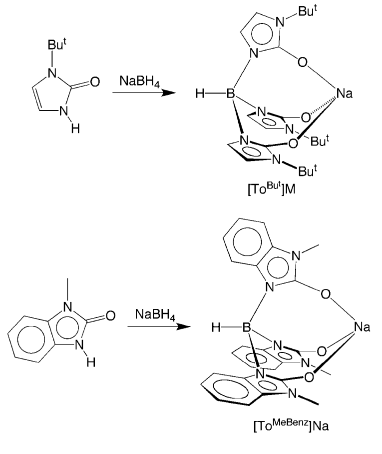
Received 18th September 2010, Accepted 10th December 2010
DOI: 10.1039/c0cc03943h

A new class of tripodal L_2X ligands that feature three oxygen donors, namely the tris(2-oxo-1-*tert*-butylimidazolyl) and tris-(2-oxo-1-methylbenzimidazolyl)hydroborato ligands, $[To^{Bu^t}]$ and $[To^{MeBenz}]$, has been synthesized *via* the reactions of $NaBH_4$ with the respective imidazolone. Structural and spectroscopic studies indicate that both $[To^{Bu^t}]$ and $[To^{MeBenz}]$ are significantly more sterically demanding but less electron donating than the related $[O_3]$ donor ligand, $[CpCo\{P(O)(OEt)_2\}_3]$.

C_3 symmetric tripodal ligands that belong to the L_2X Covalent Bond Classification[1] have received considerable attention due to their ability to tailor the steric and electronic properties of a metal center. For example, a series of C_3 symmetric L_2X tripodal ligands that feature a variety of donor arrays, including $[C_3]$,[2] $[N_3]$,[3–5] $[O_3]$,[6] $[P_3]$,[7] $[S_3]$,[8,9] and $[Se_3]$,[10] are available, thereby providing an effective means to modulate reactivity of metal complexes. Of these, the tris(pyrazolyl)hydroborato $[N_3]$ donor ligand system, $[Tp^R]$,[3,4] has been studied the most extensively. By comparison, C_3 symmetric $[O_3]$ donors are less common, with those belonging to the L_2X class being effectively dominated by the $[CpCo\{P(O)(OR)_2\}_3]$ ligand system.[6,11] Despite the formal analogy between $[Tp^R]$ and $[CpCo\{P(O)(OR)_2\}_3]$ ligands, however, an important distinction pertains to their steric demands. Specifically, whereas substitution at the 3-position of the pyrazolyl group provides an effective method to manipulate the steric environment around the metal center, the locations of the R substituents of $[CpCo\{P(O)(OR)_2\}_3]$ are such that they do not create a sterically demanding binding pocket. An L_2X $[O_3]$ donor ligand that is more sterically demanding than $[CpCo\{P(O)(OR)_2\}_3]$ would, therefore, provide a means for developing the coordination chemistry of metal centers in an oxygen rich environment. For example, such ligands have the potential for mimicking molecular species that are grafted to oxide surfaces *via* three oxygen atoms, as illustrated by the binding of zirconium hydride, alkoxide and acetylacetonate moieties to silica surfaces.[12] Therefore, we report here the synthesis of a new class of sterically demanding C_3 symmetric $[O_3]$ donor ligands.

Previous studies have demonstrated that the tris(2-mercapto-1-R-imidazolyl)hydroborato ligand system, $[Tm^R]$, provides an $[S_3]$ donor array that is capable of supporting a variety of metal centers.[8] By analogy, we rationalized that a related system based on oxoimidazolyl groups would provide a correspondingly useful $[O_3]$ donor ligand. Therefore, adopting the procedure used for the synthesis of $[Tm^R]$ ligands,[8] 1-*tert*-butylimidazolone reacts with $NaBH_4$ to yield the tris(2-oxo-1-*tert*-butylimidazolyl)-hydroborato compound $[To^{Bu^t}]Na$ (Scheme 1).[13] Furthermore, the tris(2-oxo-1-methylbenzimidazolyl)hydroborato derivative, $[To^{MeBenz}]Na$, can be obtained similarly (Scheme 1).

The steric and electronic properties of the $[To^{Bu^t}]$ and $[To^{MeBenz}]$ ligands have been assessed by analysis of the rhenium carbonyl compounds, $[To^{Bu^t}]Re(CO)_3$ and $[To^{MeBenz}]Re(CO)_3$, obtained *via* treatment of $Re(CO)_5Br$ with $[To^{Bu^t}]Na$ and $[To^{MeBenz}]Na$, respectively. Significantly, comparison of the crystallographic cone angles (Θ)[14] of $[To^{Bu^t}]Re(CO)_3$ (229°), $[To^{MeBenz}]Re(CO)_3$ (196°) and $[CpCo\{P(O)(OEt)_2\}_3]Re(CO)_3$ (174°) indicates that the $[To^{Bu^t}]$ and $[To^{MeBenz}]$ ligands are substantially more sterically demanding than is the related $[O_3]$ donor ligand, $[CpCo\{P(O)(OEt)_2\}_3]$. Furthermore, comparison of the cone angles of pairs of $[To^R]Re(CO)_3$ and $[Tm^R]Re(CO)_3$ compounds, namely (i) $[To^{Bu^t}]Re(CO)_3$ (229°) and $[Tm^{Bu^t}]Re(CO)_3$ (213°),[15] and (ii) $[To^{MeBenz}]Re(CO)_3$ (196°) and $[Tm^{MeBenz}]Re(CO)_3$ (189°), demonstrates that the $[To^R]$ ligands are also more sterically demanding than are the corresponding $[Tm^R]$ sulfur donor ligands, a



Scheme 1

Department of Chemistry, Columbia University, New York, New York 10027, USA. E-mail: parkin@columbia.edu

† Electronic supplementary information (ESI) available: Experimental details. CCDC 794058–794071. For ESI and crystallographic data in CIF or other electronic format see DOI 10.1039/c0cc03943h

Table 1 Cone angles and electron donating properties of various L_2X ligands as evaluated by ν_{CO} values (in CH_2Cl_2) for $[L_2X]Re(CO)_3$ derivatives

$[L_2X]$	ν_{CO}/cm^{-1}	$\Theta/°$
$[To^{Bu^t}]$	2018, 1887	229
$[Tm^{Bu^t}]^a$	2008, 1880	213
$[To^{MeBenz}]$	2026, 1894	196
$[Tm^{MeBenz}]$	2014, 1895	189
$[Tm^{Me}]$	2007, 1888	191 and 183^b
$[CpCo\{P(O)(OEt)_2\}_3]$	2015, 1880	174

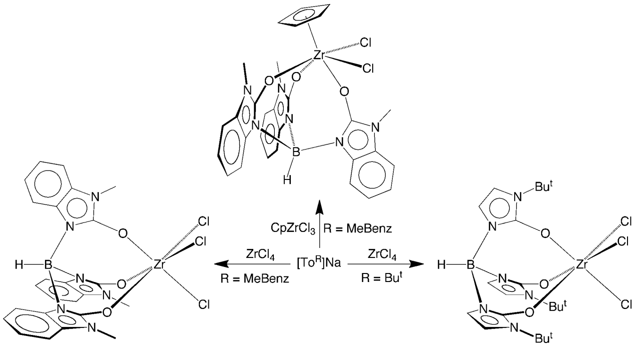
[a] Ref. 15. [b] Values for two crystallographically independent molecules (CSD# QUSNOH).

consequence of the fact that the Re–O bonds are *ca.* 0.35 Å shorter than the Re–S bonds.

The electronic nature of the $[To^{Bu^t}]$ and $[To^{MeBenz}]$ ligands has been evaluated by IR spectroscopic studies on $[To^R]Re(CO)_3$.[16] Specifically, comparison of the ν_{CO} stretching frequencies of $[To^R]Re(CO)_3$ and $[CpCo\{P(O)(OEt)_2\}_3]Re(CO)_3$ indicates that the metal centers of $[To^R]Re(CO)_3$ are less electron rich than that of $[CpCo\{P(O)(OEt)_2\}_3]Re(CO)_3$ (Table 1). Furthermore, comparison of the ν_{CO} stretching frequencies of $[To^R]Re(CO)_3$ with those of $[Tm^R]Re(CO)_3$ indicates that the $[To^R]$ oxygen ligand is less electron donating than the corresponding $[Tm^R]$ sulfur ligand.

While the latter trend is in accord with the greater electronegativity of oxygen, it is pertinent to note that π-donor effects could exert an opposite effect. For example, the ν(NO) stretching frequencies of related alkoxide and thiolate complexes, namely $W(EBu^t)_3(NO)(py)$[17] and $[Tp^{Me_2}]Mo(NO)(ER)X$,[18] are lower for E = O than for the corresponding E = S derivative, a difference that was ascribed to alkoxide being a better π-donor ligand. π-Donor effects have also been invoked to rationalize why $[Tm^R]$ ligands are generally more strongly electron donating than $[Tp^R]$ ligands;[10,19–21] however, on the basis that the ν_{CO} stretching frequencies of $[To^R]Re(CO)_3$ are greater than those for the corresponding $[Tm^R]Re(CO)_3$ derivatives, it appears that π-donation is not a dominant distinguishing feature in this system. It is also worth noting that annulation of the imidazole ring has an impact on the electron donor properties of the $[To^R]$ and $[Tm^R]$ ligands. Thus, $[To^{MeBenz}]$ and $[Tm^{MeBenz}]$ are less electron donating than $[To^{Bu^t}]$ and $[Tm^{Me}]$, respectively (Table 1).

We are particularly interested in the application of $[To^R]$ ligands to early transition metal chemistry on the basis that these ligands could allow access to counterparts of bent metallocenes that feature an oxygen rich environment. In this regard, the zirconium compounds $[To^{Bu^t}]ZrCl_3$ and $[To^{MeBenz}]ZrCl_3$ may be obtained *via* the reactions of $ZrCl_4$ with $[To^{Bu^t}]Na$ and $[To^{MeBenz}]Na$, respectively (Scheme 2). The molecular structures of $[To^{Bu^t}]ZrCl_3$ and $[To^{MeBenz}]ZrCl_3$ have been determined by X-ray diffraction, as illustrated in Fig. 1 for the former compound, which clearly indicates the similarity with the half-sandwich compound, $CpZrCl_3$. Furthermore, the hybrid complex $Cp[To^{MeBenz}]ZrCl_2$ (Fig. 2) may be obtained *via* the reaction of $[To^{MeBenz}]Na$ with $CpZrCl_3$ (Scheme 2).



Scheme 2

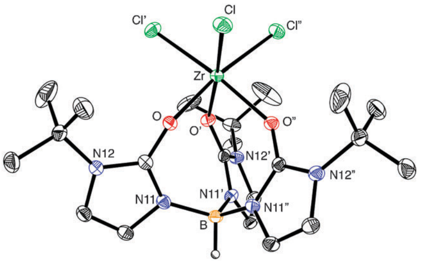


Fig. 1 Molecular structure of $[To^{Bu^t}]ZrCl_3$.

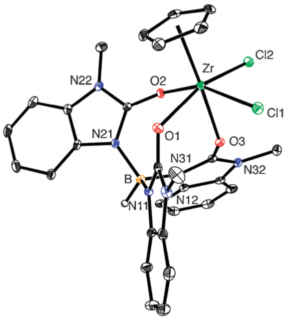


Fig. 2 Molecular structure of $Cp[To^{MeBenz}]ZrCl_2$.

The ability to isolate $Cp[To^{MeBenz}]ZrCl_2$ is noteworthy because the corresponding reaction of $CpZrCl_3$ with $[CpCo\{P(O)(OEt)_2\}_3]Na$ does not yield $Cp[CpCo\{P(O)(OEt)_2\}_3]ZrCl_2$, but rather results in preferential displacement of the cyclopentadienyl ligand and the formation of $[CpCo\{P(O)(OEt)_2\}_3]ZrCl_3$.[22] As such, it is evident that the $[To^{MeBenz}]$ ligand provides a means to obtain a sought-after zirconocene analogue in which one of the cyclopentadienyl ligands is replaced with an $[O_3]$ donor array. In support of this analogy, the geometry of $Cp[To^{MeBenz}]ZrCl_2$ bears a close resemblance to that of the bent metallocene, Cp_2ZrCl_2.[23] For example, the Cp_{cent}–Zr–B angle of $Cp[To^{MeBenz}]ZrCl_2$ (130.5°) is similar to the Cp_{cent}–Zr–Cp_{cent} angle of Cp_2ZrCl_2 (129.2°),[23a] as are the Cl–Zr–Cl bond angles of 93.9° and 97.0°, respectively.

Despite the similarity between the structures of Cp_2ZrCl_2 and $Cp[To^{MeBenz}]ZrCl_2$, an interesting difference is that the latter is chiral due to the propeller-like twist of the $[To^{MeBenz}]$ ligand.[24] ^1H NMR spectroscopy demonstrates, however, that the two enantiomers interconvert rapidly in solution at −73 °C, a behavior which is very different to that of the mercapto counterpart, $Cp[Tm^{Me}]ZrCl_2$, for which enantiomer interconversion is not observed on the NMR time scale at 70 °C.[25,26]

Enantiomer interconversion within $Cp[To^{MeBenz}]ZrCl_2$ can be achieved by either a concerted "inversion" at each oxygen atom or by a mechanism in which one of the arms dissociates to facilitate the isomerization.[27] If the interconversion for Cp[To$^{\mathrm{MeBenz}}$]ZrCl$_2$ and Cp[Tm$^{\mathrm{Me}}$]ZrCl$_2$ were to proceed *via* a common mechanism, the observation of a more facile process for the [O$_3$] ligand would be consistent with a mechanism that involves direct "inversion" at the chalcogen, since barriers to inversion are typically lower for second row rather than third row elements.[28] In this regard, calculations on [Tm$^{\mathrm{H}}$]ZnCl and [Tm$^{\mathrm{H}}$]Mn(CO)$_3$ predict an increase in M–S–C bond angle upon accessing the transition state in which the [Tm$^{\mathrm{H}}$] ligand has local C_{3v} symmetry,[27b] and so the tendency of two-coordinate oxygen to adopt larger bond angles than sulfur would be expected to facilitate the concerted isomerization process. Supporting this suggestion, the Zr–O–C angles for Cp[To$^{\mathrm{MeBenz}}$]ZrCl$_2$ [132°–137°] are significantly greater than the Zr–S–C angles for Cp[Tm$^{\mathrm{Me}}$]ZrCl$_2$ [107°–114°].[25] It is, therefore, evident that [To$^{\mathrm{R}}$] ligands are more flexible than [Tm$^{\mathrm{R}}$] ligands.

In addition to its application to zirconium chemistry, [To$^{\mathrm{MeBenz}}$]Na has also been used to synthesize derivatives of less oxophilic metals such as zinc, cobalt and iron. Thus, [To$^{\mathrm{MeBenz}}$]Na reacts with (i) ZnI$_2$ to give tetrahedral [To$^{\mathrm{MeBenz}}$]ZnI and (ii) CoCl$_2$ and FeCl$_2$ to give octahedral [To$^{\mathrm{MeBenz}}$]$_2$Co and [To$^{\mathrm{MeBenz}}$]$_2$Fe, respectively. The molecular structures of [To$^{\mathrm{MeBenz}}$]ZnI and [To$^{\mathrm{MeBenz}}$]$_2$M (M = Fe, Co) have been determined by X-ray diffraction. In each case, the [To$^{\mathrm{MeBenz}}$] ligand adopts a κ^3-coordination mode that resembles the coordination mode of the [Tm$^{\mathrm{Me}}$] ligands in similar compounds, *e.g.* [Tm$^{\mathrm{Me}}$]ZnI[29] and [Tm$^{\mathrm{Me}}$]$_2$Fe.[30] The formation of [To$^{\mathrm{MeBenz}}$]$_2$Co, however, is particularly noteworthy because (i) the [Tm$^{\mathrm{Me}}$]$_2$Co counterpart has not been isolated[31,32] and (ii) [Tm$^{\mathrm{Ph}}$]$_2$Co adopts a type of structure that is totally different to that of [To$^{\mathrm{MeBenz}}$]$_2$Co. Specifically, while both [To$^{\mathrm{MeBenz}}$]$_2$Fe and [To$^{\mathrm{MeBenz}}$]$_2$Co adopt octahedral structures with κ^3-O$_3$ coordination of the ligand, [Tm$^{\mathrm{Ph}}$]$_2$Fe and [Tm$^{\mathrm{Ph}}$]$_2$Co exhibit coordination *via* only two of the sulfur donors of each ligand, with the coordination sphere being completed by interaction with the two B–H groups.[33]

In summary, a new class of tripodal L$_2$X ligands that feature three oxygen donors, namely [To$^{\mathrm{Bu^t}}$] and [To$^{\mathrm{MeBenz}}$], has been synthesized *via* the respective reactions of NaBH$_4$ with 1-*tert*-butylimidazolone and 1-methyl-2-benzimidazolinone. These ligands are substantially more sterically demanding than related [O$_3$] donor ligands and offer potential for providing counterparts of metallocenes in an oxygen rich environment.

We thank the U. S. Department of Energy, Office of Basic Energy Sciences (DE-FG02-93ER14339) and the National Science Foundation (CHE-0749674) for support of this research. A.A.-H. thanks the government of Saudi Arabia for a scholarship.

Notes and references

1 (*a*) M. L. H. Green, *J. Organomet. Chem.*, 1995, **500**, 127–148; (*b*) G. Parkin, in *Comprehensive Organometallic Chemistry III*, ed. R. H. Crabtree and D. M. P. Mingos, Elsevier, Oxford, 2006, vol. 1, ch. 1.01.

2 I. Nieto, F. Cervantes-Lee and J. M. Smith, *Chem. Commun.*, 2005, 3811–3813.

3 (*a*) *Scorpionates—The Coordination Chemistry of Polypyrazolylborate Ligands*, S. Trofimenko, Imperial College Press, London, 1999; (*b*) *Scorpionates II: Chelating Borate Ligands*, C. Pettinari, Imperial College Press, London, 2008.

4 C. Santini, M. Pellei, G. G. Lobbia and G. Papini, *Mini-Reviews in Organic Chemistry*, 2010, **7**, 84.

5 F. Armbruster, I. Fernández and F. Breher, *Dalton Trans.*, 2009, 5612.

6 (*a*) W. Kläui, H. O. Asbahr, G. Schramm and U. Englert, *Chem. Ber.*, 1997, **130**, 1223–1229; (*b*) W.-H. Leung, Q.-F. Zhang and X.-Y. Yi, *Coord. Chem. Rev.*, 2007, **251**, 2266; (*c*) W. Kläui, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 627.

7 (*a*) A. A. Barney, A. F. Heyduk and D. G. Nocera, *Chem. Commun.*, 1999, 2379; (*b*) J. C. Peters, J. D. Feldman and T. D. Tilley, *J. Am. Chem. Soc.*, 1999, **121**, 9871.

8 (*a*) M. D. Spicer and J. Reglinski, *Eur. J. Inorg. Chem.*, 2009, 1553; (*b*) G. Parkin, *New J. Chem.*, 2007, **31**, 1996; (*c*) J. M. Smith, *Comments Inorg. Chem.*, 2008, **29**, 189.

9 C. G. Riordan, *Coord. Chem. Rev.*, 2010, **254**, 1815.

10 (*a*) M. Minoura, V. K. Landry, J. G. Melnick, K. Pang, L. Marchiò and G. Parkin, *Chem. Commun.*, 2006, 3990; (*b*) V. K. Landry, K. Pang, S. M. Quan and G. Parkin, *Dalton Trans.*, 2007, 820.

11 The tris(phthalimidyl)hydroborato ligand has been reported. However, since there is no structural verification of either the ligand or its complexes, the true nature of these compounds remains unknown. See: S. A. A. Zaidi, M. Jaria and Z. A. Siddiqi, *Synth. React. Inorg., Met.-Org., Nano-Met. Chem.*, 1986, **16**, 1067.

12 (*a*) V. Salinier, J. M. Corker, F. Lefebvre, F. Bayard, V. Dufaud and J. M. Basset, *Adv. Synth. Catal.*, 2009, **351**, 2155; (*b*) V. Salinier, G. P. Niccolai, V. Dufaud and J. M. Basset, *Adv. Synth. Catal.*, 2009, **351**, 2168.

13 X-Ray diffraction indicates that [To$^{\mathrm{Bu^t}}$]Na is dinuclear in the solid state.

14 T. E. Müller and D. M. P. Mingos, *Transition Met. Chem.*, 1995, **20**, 533.

15 K. Yurkerwich and G. Parkin, unpublished results.

16 For compilations of IR spectroscopic data on (L$_2$X)Re(CO)$_3$ and (L$_2$X)Mn(CO)$_3$ compounds, see ref. 10*b*, references therein and: (*a*) R. Garcia, A. Paulo and I. Santos, *Inorg. Chim. Acta*, 2009, **362**, 4315; (*b*) L. A. Graham, A. R. Fout, K. R. Kuehne, J. L. White, B. Mookherji, F. M. Marks, G. P. A. Yap, L. N. Zakharov, A. L. Rheingold and D. Rabinovich, *Dalton Trans.*, 2005, 171.

17 M. H. Chisholm, E. R. Davidson, J. C. Huffman and K. B. Quinlan, *J. Am. Chem. Soc.*, 2001, **123**, 9652.

18 J. A. McCleverty, *Chem. Soc. Rev.*, 1983, **12**, 331.

19 (*a*) M. Schwalbe, P. C. Andrikopoulos, D. R. Armstrong, J. Reglinski and M. D. Spicer, *Eur. J. Inorg. Chem.*, 2007, 1351; (*b*) M. Garner, M. A. Lehmann, J. Reglinski and M. D. Spicer, *Organometallics*, 2001, **20**, 5233.

20 L. A. Graham, A. R. Fout, K. R. Kuehne, J. L. White, B. Mookherji, F. M. Marks, G. P. A. Yap, L. N. Zakharov, A. L. Rheingold and D. Rabinovich, *Dalton Trans.*, 2005, 171.

21 R. Garcia, A. Paulo and I. Santos, *Inorg. Chim. Acta*, 2009, **362**, 4315.

22 T. R. Ward, S. Duclos, B. Therrien and K. Schenk, *Organometallics*, 1998, **17**, 2490.

23 (*a*) T. Repo, M. Klinga, I. Mutikainen, Y. C. Su, M. Leskelä and M. Polamo, *Acta Chem. Scand.*, 1996, **50**, 1116; (*b*) J. Y. Corey, X.-H. Zhu, L. Brammer and N. P. Rath, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1995, **51**, 565.

24 K. Mislow, D. Gust, P. Finocchiaro and R. J. Boettcher, *Top. Curr. Chem.*, 1974, **47**, 1.

25 D. Buccella, A. Shultz, J. G. Melnick, F. Konopka and G. Parkin, *Organometallics*, 2006, **25**, 5496.

26 Differences in barriers to enantiomer interconversion due to geometrical changes at sulfur and oxygen have been observed previously. See, for example: P. Ghosh and G. Parkin, *Chem. Commun.*, 1998, 413.

27 (*a*) M. R. St.-J. Foreman, A. F. Hill, A. J. P. White and D. J. Williams, *Organometallics*, 2003, **22**, 3831; (*b*) P. J. Bailey, A. Dawson, C. McCormack, S. A. Moggach, I. D. H. Oswald, S. Parsons, D. W. H. Rankin and A. Turner, *Inorg. Chem.*, 2005, **44**, 8884.

28 Alternatively, if isomerization were to require dissociation of one of the arms, it is likely that the barrier would be greater for the [O$_3$] ligand, assuming that the Zr–O bonds are stronger than the corresponding Zr–S bonds.

29 I. Cassidy, M. Garner, A. R. Kennedy, G. B. S. Potts, J. Reglinski, P. A. Slavin and M. D. Spicer, *Eur. J. Inorg. Chem.*, 2002, 1235.

30 M. Garner, K. Lewinski, A. Pattek-Janczyk, J. Reglinski, B. Sieklucka, M. D. Spicer and M. Szaleniec, *Dalton Trans.*, 2003, 1181.

31 C. A. Dodds, M. A. Lehmann, J. F. Ojo, J. Reglinski and M. D. Spicer, *Inorg. Chem.*, 2004, **43**, 4927.

32 S. Senda, Y. Ohki, T. Hirayama, D. Toda, J.-L. Chen, T. Matsumoto, H. Kawaguchi and K. Tatsumi, *Inorg. Chem.*, 2006, **45**, 9914.

33 C. Kimblin, D. G. Churchill, B. M. Bridgewater, J. N. Girard, D. A. Quarless and G. Parkin, *Polyhedron*, 2001, **20**, 1891.