Calix[6] and [8]arene complexes of vanadium

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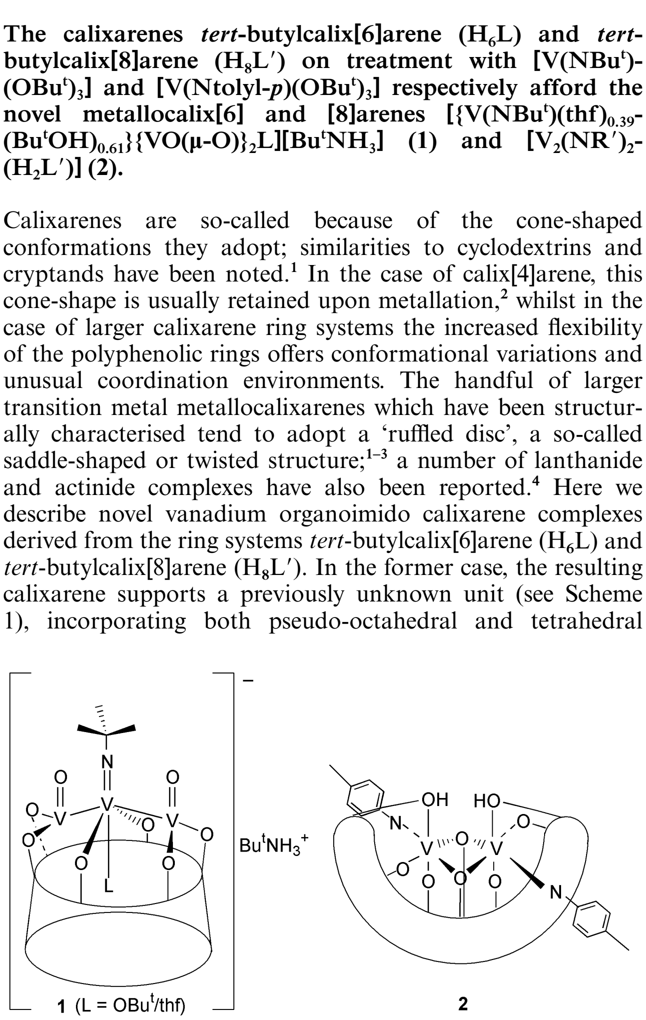
The calixarenes *tert*-butylcalix[6]arene (H_6L) and *tert*-butylcalix[8]arene (H_8L') on treatment with [V(NBu^t)(OBu^t)$_3$] and [V(Ntolyl-*p*)(OBu^t)$_3$] respectively afford the novel metallocalix[6] and [8]arenes [{V(NBu^t)(thf)$_{0.39}$(Bu^{t}OH)$_{0.61}$}{VO(μ-O)}$_2$L][Bu^{t}NH$_3$] (1) and [V$_2$(NR′)$_2$(H$_2$L′)] (2).

Calixarenes are so-called because of the cone-shaped conformations they adopt; similarities to cyclodextrins and cryptands have been noted.[1] In the case of calix[4]arene, this cone-shape is usually retained upon metallation,[2] whilst in the case of larger calixarene ring systems the increased flexibility of the polyphenolic rings offers conformational variations and unusual coordination environments. The handful of larger transition metal metallocalixarenes which have been structurally characterised tend to adopt a 'ruffled disc', a so-called saddle-shaped or twisted structure;[1–3] a number of lanthanide and actinide complexes have also been reported.[4] Here we describe novel vanadium organoimido calixarene complexes derived from the ring systems *tert*-butylcalix[6]arene (H_6L) and *tert*-butylcalix[8]arene (H_8L'). In the former case, the resulting calixarene supports a previously unknown unit (see Scheme 1), incorporating both pseudo-octahedral and tetrahedral vanadium environments supported on an unusually constrained ring, whilst the latter exhibits a twisted calixarene conformation. A number of vanadium(III) complexes of calix[4]arenes have recently been reported.[5]



1 (L = OBu^t/thf)

2

Scheme 1

The reaction of H_6L with two equivalents of [V(NBu^t)(OBu^t)$_3$] in refluxing toluene, affords after work-up (extraction into thf), yellow-brown prisms of the trimetallated product [{V(NBu^t)(thf)$_{0.39}$(Bu^{t}OH)$_{0.61}$}{VO(μ-O)}$_2$L][Bu^{t}NH$_3$] (**1**)† in low yield, for which solution NMR spectra are complex, six distinct ArCH_2 signals are observed.‡ Single crystals of **1** were grown from acetonitrile at −20 °C. The crystals were too weakly diffracting to give reasonable structural details using a conventional sealed-tube source, so Synchrotron radiation§ at Daresbury Laboratory Station 9.8 was used. The molecular structure (three molecules of solvent are incorporated per molecule of the complex) is shown in Fig. 1 and reveals a uniquely constrained conformation adopted with severe twisting needed to accommodate the three vanadium centres. The vast majority of VO species possess square pyramidal or octahedral geometries at vanadium, hence the tetrahedral (C_{3v}) geometries of V(1) and V(3) were quite unexpected. Indeed, to our knowledge **1** represents the first occurrence of this structural motif, and its presence is doubtless due to the conformational constraints imposed by the calix[6]arene ring. The net result of this alignment is that both the V=O groups and the imido group are all above the plane of the calix[6]arene ring and point approximately in the same direction; the oxo groups O(8) and O(10) are also involved in H-bonding to the [Bu^{t}NH$_3$]$^+$ cation.†[5] Nevertheless, the V=O bonds are short (*ca.* 1.62 Å) and there is a strong V=O stretching band in the IR at 970 cm^{-1}. Interestingly, the central pseudo-octahedral vanadium atom V(2) binds a thf or Bu^{t}OH molecule *trans* to the linear *tert*-butylimido group in preference to the solvent MeCN. Any mechanism for the formation of **1** has to account for the loss of a NBu^t group from V(1) and V(3) and for the presence of the bridging oxygens O(7) and O(9). It is possible that oxygen could be extracted from either diethyl ether or thf[7] or even, given that the reaction is non-stoichiometric, a second calix[6]areneH$_6$ molecule, or possibly it is the result of adventitious water. In any case, it is most likely that the NBu^t groups are removed as *tert*-butylamine (one of which is then protonated).

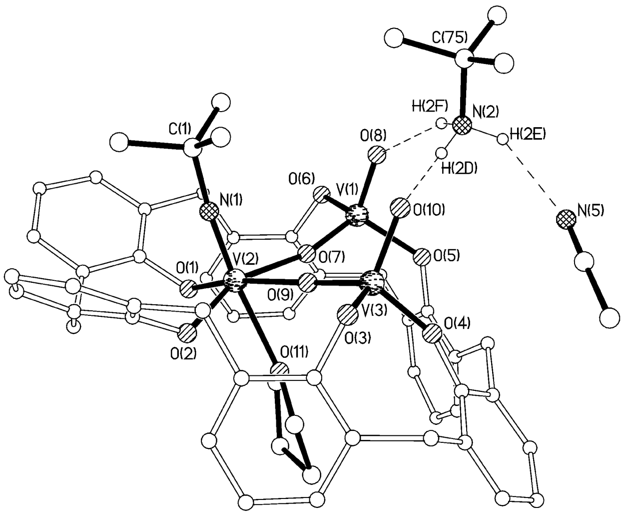


Fig. 1 Structure of **1** showing H-bonding interaction between cation and anion. Calixarene Bu^t groups, partially occupied Bu^{t}OH and most H-atoms omitted for clarity. Selected bond lengths (Å) and angles (°) are: V(1)–O(8) 1.6166(18), V(1)–O(7) 1.6554(17), V(1)–O(6) 1.8119(17), V(1)–O(5) 1.8146(18), V(2)–N(1) 1.646(2), V(2)–O(1) 1.8539(16), V(2)–O(2) 1.8546(16), V(2)–O(7) 2.0469(17), V(2)–O(9) 2.0541(19), V(2)–O(11) 2.253(2); V(2)–N(1)–C(1) 173.2(2). Geometry around V(3) is similar to that around V(1).

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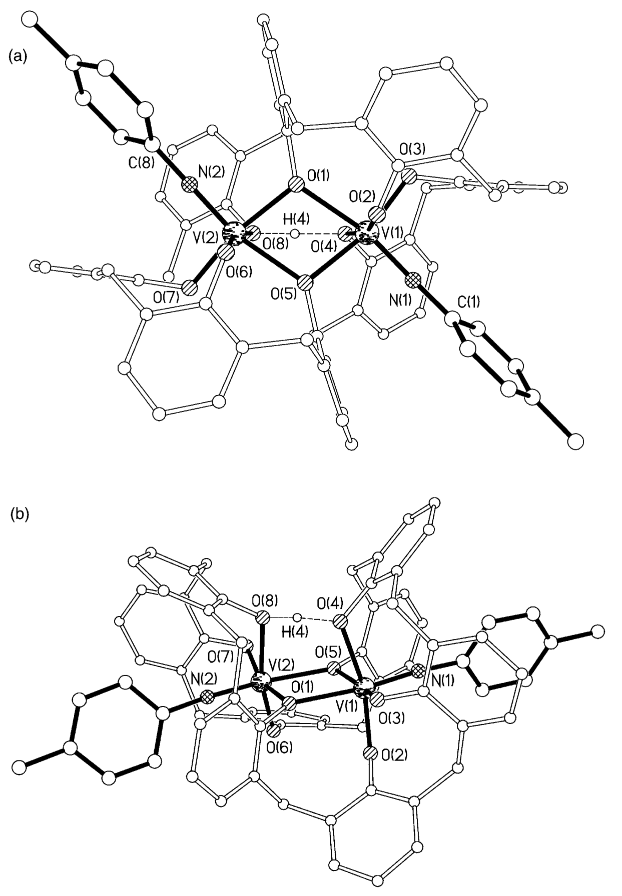

Fig. 2 (a) Structure of **2** looking onto the $V_2(\mu\text{-}O)_2$ plane with the O···H···O linkage below. Calixarene Bu^t groups and most H-atoms omitted for clarity. Selected bond lengths (Å) and angles (°) are: V(1)–N(1) 1.669(3), V(1)–O(3) 1.855(2), V(1)–O(2) 1.890(2), V(1)–O(5) 2.002(2), V(1)–O(4) 2.057(2), V(1)–O(1) 2.156(2); V(1)–N(1)–C(1) 175.0(3). Geometry around V(2) is similar to that around V(1). (b) Side view of **2** highlighting the unusual twist in the Bu^tcalix-8-arene ligand. Calixarene Bu^t groups and most H atoms omitted for clarity.

Treatment of $[V(Ntolyl\text{-}p)(OBu^t)_3]$[8] with 0.5 equivalents of (H_8L') in refluxing toluene affords, after work-up, the dimetallocalix[8]arene complex $[V_2(NR')_2(H_2L')]$ (**2**) as large dark needles† in good yield (*ca.* 70%). Complex **2** is presumed to form *via* displacement of six *tert*-butoxide ligands in an analogous fashion to the reactions of $Mo(NAr)_2(OBu^t)_2$ ($Ar = C_6H_3Pr^i_2$-2,6) with H_8L.[9] Crystals of **2** suitable for an X-ray determination¶ were grown from acetonitrile at −20 °C; they incorporate 4.5 molecules of solvent per molecule of the complex. The molecular structure is shown in Fig. 2(a) and (b) and reveals the way in which the *tert*-butylcalix[8]arene ring twists to produce a local confacial bioctahedral environment with asymmetric 'phenoxide' bridges about the two six-coordinate vanadium centres. A consequence of the bridging phenoxides and the twist adopted by the calixarene ring is the absence of any vacant coordination sites for the metal to bind solvent molecules in this case. The calixarene conformation is similar to that observed for $Na[(Bu^t calix[8]arene)\{Ti(OPr^i)\}_2]$.[3b]

The organoimido ligands are clearly acting as multiply-bonded four-electron donors [*e.g.* V(1)–N(1) = 1.669(3) Å, V(1)–N(1)–C(1) = 175.0(3)°, V(2)–N(2) = 1.667(3) Å, V(2)–N(2)–C(8) = 175.0(3)°]. As in other imido-alkoxides,[8] the V–O bonds *trans* to the imido groups [V(1)–O(1) = 2.156(2) Å, V(2)–O(5) = 2.163(2) Å] are substantially longer than others bonded to the metal [1.855(2)–2.104(2) Å], whilst the long V–O bonds to O(4) [2.057(2) Å] and O(8) [2.104(2) Å] are thought to be phenolic (δ = 17.4—only one O*H* observed). The variation in the V–O bond length can thus be explained if **2** is formally regarded as possessing a 16 electron configuration with the further electron density provided by the strongly π-donating aryloxide groups O(2) and O(3) *cis* to the *p*-tolylimido group.

Unfortunately the severe twist of the macrocycle renders the internal V–O–C angles useless when determining phenolic hydrogen positions. However, a proton H(4) was located in the difference maps and included in the refinement; a second extra proton is included in the formula but was not located. The latter is thought to have partial occupancy (50 : 50%) on O(4) and O(8) with an exchange rate too fast to be observed on the NMR time-scale. The V–V internuclear distance (3.334 Å) is clearly too long for any bonding interaction between the two vanadium centres. The ^{51}V NMR of **2** displays a broad (fwhm *ca.* 2800 Hz) low field resonance at δ +588 (relative to external $VOCl_3$–CD_3CN); ^{51}V chemical shifts for (*p*-tolylimido)vanadium(V) complexes have been observed over the range δ +1050 to −654 (relative to $VOCl_3$–$CDCl_3$).[9]

Preliminary experiments‖ show that **2** can, in the presence of dimethylaluminium chloride, Me_2AlCl (DMAC) polymerise ethylene at room temperature with an activity of 50 g $mmol^{-1}$ h^{-1} bar^{-1}. In the presence of methylaluminoxane (MAO), the activity is somewhat reduced (*ca.* 8 g $mmol^{-1}$ h^{-1} bar^{-1}); such co-catalyst effects have been noted in other early transition metal catalytic systems.[10] The only previous metallocalixarene-based ethylene polymerisation studies we are aware of have been on proximally bridged *p*-*tert*-butylcalix[4]arene derivatives complexed with titanium(IV).[11]

In conclusion, it is clear that the availability of metallocalixarenes such as **1** and **2** highlights the potential for stabilising unusual and, in the case of **1**, hitherto unknown metal coordination enviroments. Other large ring vanadium calixarene systems will be reported separately.

Acknowledgements

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Notes and references

† Elemental analysis data, for **1**·$2CH_3CN$: Calc. for $C_{82}H_{112.62}O_{12}N_3V_3$: C, 66.3; H, 7.6; N, 2.8%. Found: C, 65.9; H, 7.4; N, 2.5%. For **2**·$1.5CH_3CN$: Calc. for $C_{105}H_{124.5}O_8N_{3.5}V_2$: C, 75.7; H, 7.5; N, 2.9%. Found: C, 74.7; H, 7.6; N, 2.2%.

Selected spectroscopic data for **1**: IR ν(OH) 3369 cm^{-1}; ν(V=O) 970 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz, 298 K): δ 4.68–4.60 (3 × d, 3H, $^2J_{HH}$ 13.5 Hz, CH_2), 4.45 (d, 1H, $^2J_{HH}$ 16.8 Hz, CH_2), 4.18 (d, 1H, $^2J_{HH}$ 16.4 Hz, CH_2), 4.11 (d, 1H, $^2J_{HH}$ 13.2 Hz, CH_2)—all *endo* calix CH_2—3.47–3.30 (4 × d, 4H, $^2J_{HH}$ 13.6 Hz, CH_2), 3.13 (d, 1H, $^2J_{HH}$ 13.2 Hz, CH_2), 2.96 (d, 1H, $^2J_{HH}$ 13.1 Hz, CH_2)–all *exo* calix CH_2.

Selected spectroscopic data for **2**: ^1H NMR (CD_3CN, 400 MHz, 298 K): δ 17.36 (s, OH, 1H), 7.30 (d, 2H, $^4J_{HH}$ 2.4 Hz), 7.19 (d, 2H, $^4J_{HH}$ 2.4 Hz), 7.13 (d, 2H, $^4J_{HH}$ 2.6 Hz), 7.06 (d, 2H, $^4J_{HH}$ 2.4 Hz), 7.03 (d, 2H, $^4J_{HH}$ 2.5 Hz), 6.77 (d, 2H, $^4J_{HH}$ 2.6 Hz), 6.68 (d, 2H, $^4J_{HH}$ 3.1 Hz), 6.36 (d, 2H, $^4J_{HH}$ 2.2 Hz)—all aromatic calixarene hydrogens—6.13 (d, 4H, $^2J_{HH}$ 8.1 Hz), 5.93 (d, 2H, $^2J_{HH}$ 12.8 Hz), 5.79 (d, 2H, $^2J_{HH}$ 11.1 Hz)—all $C_6H_4CH_3$—4.98 (d, 4H, $^2J_{HH}$ 8.2 Hz), 4.81 (d, 2H, $^2J_{HH}$ 13.6 Hz), 4.71 (d, 2H, $^2J_{HH}$ 11.4 Hz)—all *endo* calix CH_2—3.29 (d, 2H, $^2J_{HH}$ 11.2 Hz), 3.22 (d, 2H, $^2J_{HH}$ 12.6 Hz), 3.20 (d, 2H, $^2J_{HH}$ 11.4 Hz), 2.86 (d, 2H, $^2J_{HH}$ 13.9 Hz)—all *exo*-calix CH_2—2.18 (s, 3H, $C_6H_4CH_3$), 1.97 (s, 3H, $C_6H_4CH_3$), 1.25 (s, 18H, CMe_3), 1.17 (s, 18H, CMe_3), 1.10 (s, 18H, CMe_3), 0.96 (s, 18H, CMe_3). One phenolic proton not observed. ^{51}V NMR (CD_3CN): δ 588.46; $\Delta_{1/2}$ 2800 Hz.

‡ There is no sign of any electron density close to O(8) or O(10) suggestive of protonation and consequently a neutral tri-vanadium complex. Moreover, electron density is seen in three positions around N(2)—the Bu^tNH_3 cation. We cannot however completely rule out the possibility that this cation arises *via* protonation of *tert*-butanol. A search of the Cambridge Crystallographic Database and the EPSRC's Chemical Database Service at Daresbury (see refs. 6*a*,*b*) revealed a number of complexes involving protonated alcohols have been structurally characterised (representative examples given in refs. 6*c*–*f*).

§ Crystal data for **1**·$3CH_3CN$: $[C_4H_{12}N][C_{74}H_{95.6}NO_{11}V_3]\cdot 3CH_3CN)_3$, brown crystal, 0.78 × 0.19 × 0.16 mm, $M = 1525.3$, monoclinic, space group $P2_1/c$, $a = 23.2373(11)$, $b = 14.7206(7)$, $c = 26.6427(13)$ Å, $\beta = 114.503(2)°$, $U = 8292.8(7)$ Å^3, $Z = 4$, $D_c = 1.222$ g cm^{-3}, μ(Mo-Kα) = 0.390 mm^{-1}, $T = 160$ K. 48390 reflections (18205 unique, $2\theta_{max} = 54.3°$, $R_{int} = 0.0934$) were collected on a Bruker AXS SMART 1K CCD area detector diffractometer using synchrotron radiation

($\lambda = 0.6879$ Å) at Daresbury SRS Station 9.8.[12] Data were corrected semi-empirically for absorption. Structure solution by direct methods, refinement by full-matrix least-squares on F^2 values. Non-H atoms refined anisotropically. Three calixarene Bu^t groups were disordered over two sets of positions refined with restraints. The solvent molecule coordinated at V(2) was refined as disordered thf and Bu^{t}OH (0.39 : 0.61). H atoms were constrained. Final $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{\frac{1}{2}} = 0.1213$ for 1058 parameters, conventional $R = 0.0520$ $[F^2 > 4\sigma(F^2)]$. Final difference synthesis within ±0.64 e Å^{-3}.

¶ Crystal data for **2**·4.5CH$_3$CN: $C_{102}H_{120}N_2O_8V_2\cdot(CH_3CN)_{4.5}$, black crystal, 0.70 × 0.24 × 0.18 mm, $M = 1788.8$, monoclinic, space group $P2_1/n$, $a = 12.1377(5)$, $b = 32.0853(13)$, $c = 28.7935(12)$ Å, $\beta = 100.040(2)°$, $U = 11041.7(8)$ Å^3, $Z = 4$, $D_c = 1.076$ g cm^{-3}, μ(Mo-Kα) = 0.223 mm^{-1}, $T = 160$ K. 57353 reflections (19453 unique, $2\theta_{max} = 50.0°$, $R_{int} = 0.0493$) were collected on a Bruker AXS SMART 1K CCD area detector using Mo-Kα radiation ($\lambda = 0.71073$ Å) and data were corrected for absorption. Methods as above. H-atoms constrained except for H(4) with freely refined coordinates. Three calixarene Bu^t groups disordered over two sets of positions; MeCN solvent molecules rather disordered and diffuse, refined with restraints. $wR2 = 0.1824$ (1327 parameters), $R = 0.0668$. Final difference synthesis within ±1.42 e Å^{-3}. Programs used: SHELXTL[13] for structure solution and refinement and molecular graphics, Bruker AXS SMART (control), and SAINT (integration) and local programs.[14] CCDC reference numbers 155488 and 155489. See http://www.rsc.org/suppdata/dt/b0/b010248m/ for crystallographic data in CIF or other electronic format.

|| 1 bar ethylene Schlenk test carried out in toluene (40 cm^3) at 25 °C over 60 min, reaction quenched with dilute HCl (40 cm^3) and the solid PE (polyethylene) washed with methanol (50 cm^3) and dried in a vacuum oven at 40 °C.

1 C. D. Gutsche, *Acc. Chem. Res.*, 1983, **16**, 161.

2 (*a*) D. M. Roundhill, *Prog. Inorg. Chem.*, 1995, **43**, 533; (*b*) C. Wieser, C. B. Dieleman and D. Matt, *Coord. Chem. Rev.*, 1997, **165**, 93.

3 (*a*) M. Fan, H. Zhang and M. Lattman, *Chem. Commun.*, 1998, 99; (*b*) F. J. Parlevliet, A. Olivier, W. G. J. de Lange, P. C. J. Kamer, H. Kooijman, A. L. Spek and P. W. N. M. van Leeuwen, *Chem. Commun.*, 1996, 583; (*c*) S. G. Bott, A. W. Coleman and J. L. Atwood, *J. Chem. Soc., Chem. Commun.*, 1986, 610; (*d*) G. E. Hofmeister, F. E. Halm and S. F. Pedersen, *J. Am. Chem. Soc.*, 1989, **111**, 2318; (*e*) G. E. Hofmeister, E. Alvarado, J. A. Leary, D. I. Yoon and S. F. Pedersen, *J. Am. Chem. Soc.*, 1990, **112**, 8843; (*f*) V. C. Gibson, C. Redshaw, W. Clegg and M. R. J. Elsegood, *J. Chem. Soc., Chem. Commun.*, 1995, 2371; (*g*) F. J. Parlevliet, M. A. Zuideveld, C. Kiener, H. Kooijman, A. L. Spek, P. C. J. Kamer and P. W. N. M. van Leeuwen, *Organometallics*, 1999, **18**, 3394; (*h*) S. Blanchard, M.-N. Rager, A. F. Duprat and O. Reinaud, *New J. Chem.*, 1998, **22**, 1143; (*i*) L. Le Clainche, M. Giorgi and O. Reinaud, *Inorg. Chem.*, 2000, **39**, 3436; (*j*) C. D. Andreeti, G. Calestani and F. Ugozzoli, *J. Inclusion Phenom.*, 1987, **5**, 123.

4 (*a*) J. M. Harrowfield, M. I. Ogden, W. R. Richmond and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1991, 2153; (*b*) J. M. Harrowfield, M. I. Ogden and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1991, 2625; (*c*) P. Thuéry, M. Nierlich, M. I. Ogden and J. M. Harrowfield, *Supramol. Chem.*, 1998, **9**, 297; (*d*) L. M. Engelhardt, B. M. Furphy, J. M. Harrowfield, D. L. Kepert, A. H. White and F. R. Wilner, *Aust. J. Chem.*, 1988, **41**, 1465; (*e*) J. M. Harrowfield, M. I. Ogden and A. H. White, *Aust. J. Chem.*, 1991, **44**, 1237; (*f*) J. M. Harrowfield, M. I. Ogden and A. H. White, *Aust. J. Chem.*, 1991, **44**, 1249; (*g*) B. M. Furphy, J. M. Harrowfield, D. L. Kepert, B. W. Skelton, A. H. White and F. R. Wilner, *Inorg. Chem.*, 1987, **26**, 4231; (*h*) P. Thuéry, N. Keller, M. Lance, J. D. Vigner and M. Nierlich, *Acta Crystallogr., Sect. C*, 1995, **51**, 1570.

5 B. Castellano, E. Solari, C. Floriani and R. Scopelliti, *Inorg. Chem.*, 1999, **38**, 3406.

6 (*a*) The United Kingdom Chemical Database Service, D. A. Fletcher, R. F. McMeeking and D. Parkin, *J. Chem. Inf. Comput. Sci.*, 1996, **36**, 746; (*b*) 3D Search and Research using the Cambridge Structural Database, F. H. Allen and O. Kennard, *Chem. Des. Automat. News*, 1993, **8**, 1; F. H. Allen and O. Kennard, *Chem. Des. Automat. News*, 1993, **8**, 31; (*c*) K. Krogmann, A. Kiem, R. Stahl and H. P. Pfeger, *Mol. Cryst. Liq. Cryst.*, 1985, **120**, 401; (*d*) R. Minkwitz and S. Reinemann, *Z. Anorg. Allg. Chem.*, 1999, **625**, 121; (*e*) W. S. Sheldrick and R. Exner, *J. Organomet. Chem.*, 1990, **386**, 375; (*f*) M. B. Hursthouse, J. Newton, P. R. Page and I. Villax, *Polyhedron*, 1988, **7**, 2087.

7 L. G. Hubert-Pfalzgraf, M. Tsunoda and G. Le Borgne, *J. Chem. Soc., Dalton Trans.*, 1988, 533.

8 D. D. Devore, J. D. Lichtenhan, F. Takusagawa and E. A. Maatta, *J. Am. Chem. Soc.*, 1987, **109**, 7408.

9 V. C. Gibson, C. Redshaw, W. Clegg and M. R. J. Elsegood, *J. Chem. Soc., Chem. Commun.*, 1995, 2371.

10 V. C. Gibson, P. J. Maddox, C. Newton, C. Redshaw, G. A. Solan, A. J. P. White and D. J. Williams, *Chem. Commun.*, 1998, 1651.

11 O. V. Ozerov, N. P. Rath and F. T. Ladipo, *J. Organomet. Chem.*, 1999, **586**, 223.

12 W. Clegg, M. R. J. Elsegood, S. J. Teat, C. Redshaw and V. C. Gibson, *J. Chem. Soc., Dalton Trans.*, 1998, 3037.

13 G. M. Sheldrick, *SHELXTL user manual*, version 5, Bruker AXS Inc., Madison, WI, 1994.

14 SMART and SAINT software for CCD diffractometers, Bruker AXS Inc., Madison, WI, 1994.