

(μ -1,2-Dimethoxyethane- κ^2 O:O')-bis[(1,2-dimethoxyethane- κ^2 O,O')-tris(1,1,1,5,5,5-hexafluoro-4-oxopent-2-en-2-olato- κ^2 O,O')cerium(III)]

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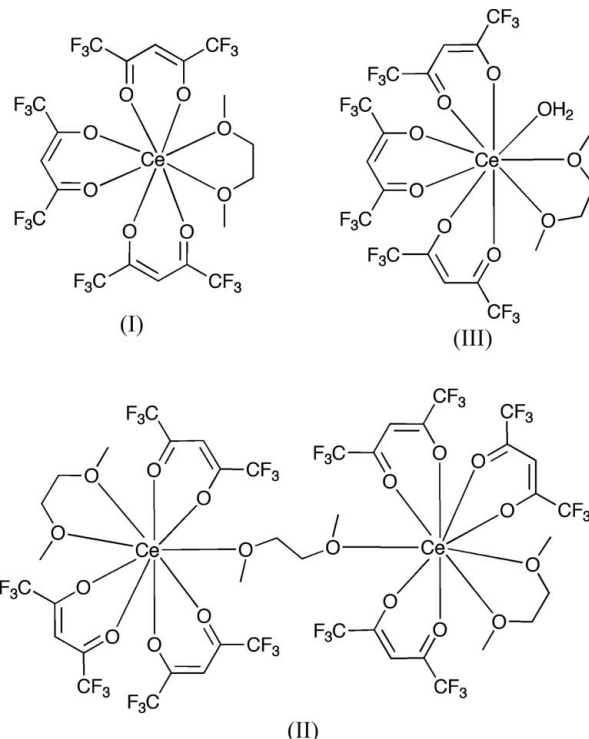
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A previous analysis [Fatila *et al.* (2012). *Dalton Trans.* **41**, 1352–1362] of the title complex, [Ce₂(C₅HF₆O₂)₆(C₄H₁₀O₂)₃], had identified it as Ce(hfac)₃(dme)_{1.5} according to the ¹H NMR integration [hfac = 1,1,1,5,5,5-hexafluoroacetylacetonate (1,1,1,5,5,5-hexafluoro-4-oxopent-2-en-2-olate) and dme = 1,2-dimethoxyethane]; however, it was not possible to determine the coordination environment unambiguously. The structural data presented here reveal that the complex is a binuclear species located on a crystallographic inversion center. Each Ce^{III} ion is coordinated to three hfac ligands, one bidentate dme ligand and one monodentate (bridging) dme ligand, thus giving a coordination number of nine (CN = 9) to each Ce^{III} ion. The atoms of the bridging dme ligand are unequally disordered over two sets of sites. In addition, in two of the –CF₃ groups, the F atoms are rotationally disordered over two sets of sites. This is the first crystal structure of a binuclear lanthanide β -diketonate with a bridging dme ligand.

Comment

Metal–organic chemical vapor deposition (MOCVD) is an important technique for the production of thin-film devices (Krumdieck, 2009; Jones *et al.*, 2004; Jones, 2002). The quality of an MOCVD process is dependent on the precursor materials. As such, the development of useful MOCVD precursors is a large and rapidly growing field of research (Carpentier, 2010; Jones & Chalker, 2003; Hubert-Pfalzgraf & Guillon, 1998). Currently in use are the so-called ‘second-generation’ MOCVD precursors which combine fluorinated β -diketonates and coordinated polyethers in the design of anhydrous monomeric metal complexes. Main group, *d*- and *f*-block metal precursors have been developed according to this general formula (Condorelli *et al.*, 2007; Malandrino & Fragalà, 2006; Binnemans, 2005).

The improvement of techniques and precursor materials for the deposition of ceria (CeO₂) is an ongoing area of study owing to the broad spectrum of uses for ceria films, such as anode materials in solid-oxide fuel cells, in magneto-optical devices and as a dielectric material in metal oxide semiconductors (CMOS) (Barreca *et al.*, 2003, 2006; Lo Nigro *et al.*, 2001). It is predictable, then, that second-generation MOCVD cerium precursors are of interest, particularly since volatile complexes of both Ce^{III} and Ce^{IV} are equally viable for the deposition of ceria (Lo Nigro *et al.*, 2003, 2005; Pollard *et al.*, 2000; McAleese *et al.*, 1996).



The eight-coordinate Ce(hfac)₃(dme) complex [hfac = 1,1,1,5,5,5-hexafluoroacetylacetonate (1,1,1,5,5,5-hexafluoro-4-oxopent-2-en-2-olate) and dme = 1,2-dimethoxyethane], (I) (see Scheme), is an example of a second-generation MOCVD cerium precursor. The first publication claiming the synthesis of (I) presents characterization data that do not quite fit the proposed structural formula (Pollard *et al.*, 2000). We have since isolated and fully characterized (I), including its single-crystal X-ray structure (Fatila *et al.*, 2012). Interestingly, during the course of our study, we discovered that the initial product recovered from our synthesis, prior to the sublimation that generates (I), has the formula Ce(hfac)₃(dme)_{1.5}. However, in the absence of crystallographic data, we could not determine definitively if this represents solvation of (I) with a half molar equivalent of dme, or a cocrystallization of (I) and a complex with the formula Ce(hfac)₃(dme)₂, or a binuclear complex with a bridging dme ligand. We present here the single-crystal X-ray structure of this Ce(hfac)₃(dme)_{1.5} complex demonstrating that it is, in fact, the binuclear [Ce(hfac)₃(dme)]₂(μ -dme) complex, (II) (Fig. 1).

Yellow needles of (II), prepared by precipitation from cold anhydrous hexane, formed in the monoclinic space group

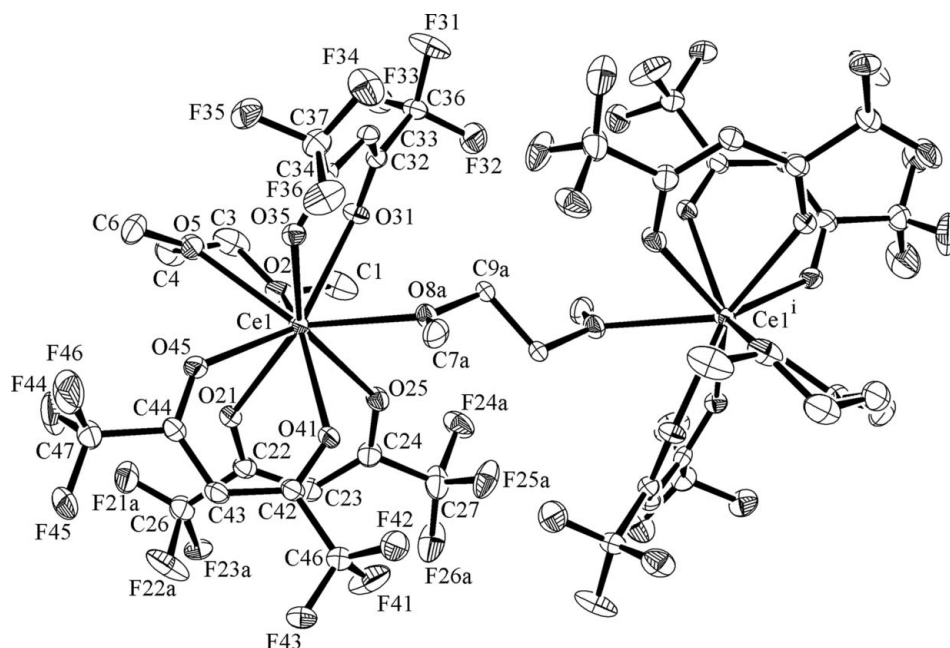


Figure 1

The molecular structure of (II). H atoms have been omitted and the disorder is not shown. Displacement ellipsoids are drawn at the 25% probability level. [Symmetry code: (i) $-x + 1, -y + 1, -z + 1$.]

$P2_1/n$. The title complex lies on an inversion center with the unique Ce^{III} ion chelated by three bidentate hfac ligands and one bidentate dme ligand. A bridging dme ligand connects the two symmetry-related Ce^{III} ions completing the coordination number nine ($\text{CN} = 9$) for each. The bridging dme ligand is in the *anti* conformation. It is worth noting that there is disorder with respect to the atom positions of the bridging dme ligand resulting from the two possible ways in which the 'Z' shape of the *anti* conformation can be achieved (Fig. 2). There is also disorder with respect to the positions of some of the F atoms.

The geometry of the coordination about each Ce^{III} ion is a slightly distorted monocapped square antiprism wherein the capping position O atom (O2) belongs to the bidentate coordinated dme ligand, not the bridging dme ligand. This connectivity describes a polyhedron with nine vertices, 20 edges and 13 faces, known as a Johnson solid J10 or a gyroelongated square pyramid (Fig. 3).

The Ce—O bond lengths are summarized in Table 1, where they are also compared with bond lengths observed in the eight-coordinate species, (I), and the nine-coordinate hydrate $\text{Ce}(\text{hfac})_3(\text{dme})(\text{H}_2\text{O})$ complex, (III) (see Scheme). It should be noted that, although (III) is also a monocapped square antiprism, the capping O atom is assigned to water, not dme (Fatila *et al.*, 2012).

The crystal structures of complexes in which dme acts as a bridging ligand are not uncommon for cations of alkali metals (Li, Na, K and Rb) [Cambridge Structural Database (CSD; Allen, 2002) refcodes IMADAC (Beck *et al.*, 2010), OJEKIY (Hsu & Liang, 2010), XAHZOX (Wong *et al.*, 2010), CIMTAU and CIMTEY (Maudez *et al.*, 2007), VEPJAC (Wang *et al.*, 2006) and QEXWAR (Neander *et al.*, 2000)]. There are also a few examples of such structures with cations of alkaline earth metals [Mg (INARIZ; Kriek *et al.*, 2010) and Ca (FEGRIT;

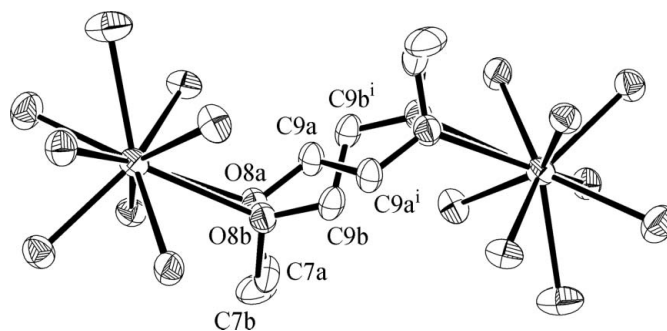


Figure 2

The structure of complex (II), highlighting the disorder with respect to the bridging dme ligand atom positions. The chelating hfac and dme ligands are represented by their O-atom positions. H atoms have been omitted. All displacement ellipsoids are drawn at the 50% probability level. [Symmetry code: (i) $-x + 1, -y + 1, -z + 1$.]

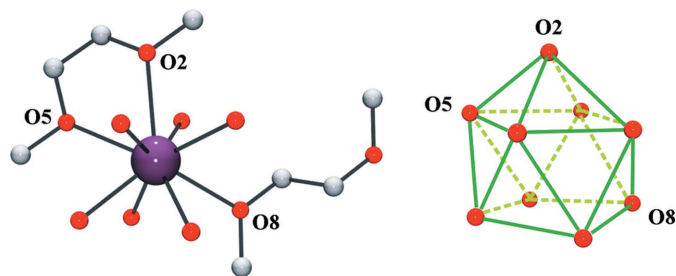


Figure 3

Left: ball-and-stick representation of the monocapped square antiprism coordination geometry about the Ce^{III} ion (purple in the electronic version of the paper); all O atoms (red) are shown. C atoms (gray) of the dme ligands are included. C atoms of the hfac ligands, all H atoms and all F atoms have been omitted. Right: O-atom positions only, with the J10 polyhedron they describe drawn with solid lines (green).

Becker *et al.*, 2004)], transition metals [Mo (PAHNIW; Parsons *et al.*, 2004) and Pd (MOBQEZ; Lohner *et al.*, 2002)] and main group metals [Al (SAMLAT; Saied *et al.*, 1998) and In (ZADCOW; Carta *et al.*, 1995)]. Structures of this nature incorporating lanthanide ions are limited to six reported examples: [Ln(NCS)₃(dme)₂(μ-dme)_{0.5}]₂ [Ln = Eu (CUYLIS), Dy (CUYLOY) and Er (CUYLUE); Bakker *et al.*, 2010], [Nd₂(OCH-*i*-Pr₂)₆(μ-dme)]_n (HANJEL; Barnhart *et al.*, 1993), [YbI₂(dme)₂]₂(μ-dme) (HOXYAU; Gröb *et al.*, 2000) and [Nd(3,5-di-*t*-butylpyrazolato)(μ-dme)]_n (TUMJIU; Cosgriff *et al.*, 1996). The present results for complex (II) are the first reported of this nature involving Ce, and the first potential MOCVD precursor with this structure.

Experimental

CeCl₃ and Hhfac were purchased from Alfa Aesar and monoglyme was purchased from Acros. All reagents were used as received. CeCl₃ was converted to its Ce(hfac)₃(H₂O)₃ adduct according to a slightly modified literature method (Richardson *et al.*, 1968). Modifications include dissolving the CeCl₃ starting material in a solution (pH = 7–8) of aqueous Hhfac deprotonated with Na₂CO₃, following which the solution was extracted with Et₂O three times and washed with saturated KCl(aq). The organic phase was concentrated to a yellow oil which was then dissolved in hexanes. Evaporation of the hexanes yielded a yellow solid with an IR spectrum consistent with literature values for Ln(hfac)₃(H₂O)₃, where Ln = La–Nd (Richardson *et al.*, 1968) (m.p. 370–373 K).

Elemental analyses were performed by MHW Laboratories in Phoenix, AZ. All ¹H NMR spectra were collected on a Bruker 400 Avance spectrometer at ambient temperature. Solvents were dried using an LC Technology Solvent Purification System with standard molecular sieves of size 3 Å.

Excess monoglyme (1.1 ml, 11 mmol) was added to a slurry of Ce(hfac)₃(H₂O)₃ (2.0546 g, 2.5200 mmol) in hexanes (100 ml). The resulting yellow solution was stirred for 2 h at room temperature, then concentrated to a yellow–orange oil which crystallized into yellow–orange microcrystals upon introduction to a glove-box (Ar atmosphere) (crude yield 2.2156 g, 98%). Crystallographic quality yellow needles were obtained by dissolving the yellow–orange microcrystalline material in a minimum amount of anhydrous hexane under an inert atmosphere and cooling to 253 K for 2 d. A yellow block was cut from a needle and mounted for crystallographic data

Table 1

Ce–O bond lengths (Å) for (I), (II) and (III).

(I) and (III) are from Fatila *et al.* (2012) and (II) is this work. For (III), values are given as molecule 1/molecule 2.

	(I)	(II)	(III)
Temperature	150 K	147 K	150 K
Ce–O _{hfac}	2.434 (5) 2.435 (4) 2.439 (5) 2.446 (5) 2.447 (5) 2.466 (4)	2.461 (2) 2.466 (2) 2.468 (2) 2.477 (2) 2.483 (2) 2.491 (2)	2.495 (4)/2.453 (4) 2.454 (5)/2.499 (3) 2.487 (3)/2.499 (4) 2.496 (3)/2.503 (3) 2.506 (4)/2.499 (3) 2.515 (4)/2.492 (4)
Ce–O _{dme}	2.531 (5) 2.566 (5)	2.578 (3) 2.657 (3) ^a 2.552 (8)/2.796 (19) ^b	2.570 (5)/2.566 (4) 2.608 (4)/2.611 (4)
Ce–O _{water}			2.595 (4)/2.601 (4)

Notes: (a) capping O atom; (b) bridging dme ligand.

collection. IR (Nujol, NaCl, cm⁻¹): 3146 (w), 1651 (*ms, br*), 1609 (*mw*), 1559 (*m*), 1533 (*m*), 1496 (*ms*), 1348 (*w*), 1254 (*s*), 1207 (*s*), 1146 (*s*), 1094 (*ms*), 1056 (*m*), 1023 (*mw*), 1008 (*mw*), 949 (*w*), 910 (*mw*), 863 (*mw*), 834 (*mw*), 800 (*m*), 769 (*w*), 740 (*mw*), 722 (*w*), 660 (*m*), 583 (*s*). ¹H NMR [400 MHz, (CD₃)₂CO, 25.2 mg in 1.0054 g of *d*₆-acetone]: δ 11.54 (*s*, 6H, CH of hfac), 3.52 (*s*, 12H, CH₂ of monoglyme), 3.35 (*s*, 18H, CH₃ of monoglyme). ¹H NMR (400 MHz, CD₂Cl₂, 25.7 mg in 1.0356 g of CD₂Cl₂): δ 14.19 (*s*, 6H, CH of hfac), –1.17 (*s*, 12H, CH₂ of monoglyme), –3.42 (*s*, 18H, CH₃ of monoglyme). ¹H NMR (400 MHz, CDCl₃, 14.2 mg in 1.1296 g of CDCl₃): δ 14.26 (*s*, 6H, CH of hfac), –1.15 (*s*, 12H, CH₂ of monoglyme), –3.61 (*s*, 18H, CH₃ of monoglyme). Analysis calculated for C₂₁H₁₈CeF₁₈O₉: C 28.14, H 2.02%; found: C 28.27, H 2.16%.

Crystal data

[Ce ₂ (C ₅ HF ₆ O ₂) ₆ (C ₄ H ₁₀ O ₂) ₃]	V = 3131.9 (11) Å ³
M _r = 1792.95	Z = 2
Monoclinic, P2 ₁ /n	Mo Kα radiation
a = 9.1135 (18) Å	μ = 1.61 mm ⁻¹
b = 13.818 (3) Å	T = 147 K
c = 24.971 (5) Å	0.22 × 0.22 × 0.20 mm
β = 95.16 (3)°	

Data collection

Nonius KappaCCD diffractometer	32118 measured reflections
Absorption correction: multi-scan (SORTAV; Blessing, 1995)	6407 independent reflections
T _{min} = 0.667, T _{max} = 0.729	5262 reflections with I > 2σ(I)
	R _{int} = 0.044

Refinement

R[F ² > 2σ(F ²)] = 0.035	227 restraints
wR(F ²) = 0.065	H-atom parameters constrained
S = 1.08	Δρ _{max} = 0.78 e Å ⁻³
6407 reflections	Δρ _{min} = –0.48 e Å ⁻³
517 parameters	

The bridging dme ligand was disordered over two sites across the inversion center. The occupancies were refined initially then ultimately fixed at 0.69:0.31. The geometries of the two sites of the bridging dme ligand were restrained to be similar. In addition, atoms O8a and O8b were constrained to have identical anisotropic displacement parameters. Two of the –CF₃ groups were disordered and both were modeled anisotropically with site-occupation factors of the alternate orientations at 0.64:0.36. For each disordered –CF₃ group, the C–F bond lengths were restrained to be similar. H atoms were positioned geometrically and refined using a riding model, with C–H = 0.98 (methyl), 0.99 (methylene) or 0.95 Å (aromatic) and with U_{iso}(H) = 1.5U_{eq}(C) for methyl groups and 1.2U_{eq}(C) otherwise.

Data collection: COLLECT (Nonius, 2002); cell refinement: DENZO-SMN (Otwinowski & Minor, 1997); data reduction: DENZO-SMN; program(s) used to solve structure: SHELXTL (Sheldrick, 2008); program(s) used to refine structure: SHELXTL; molecular graphics: PLATON (Spek, 2009); software used to prepare material for publication: SHELXTL.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG3244). Services for accessing these data are described at the back of the journal.

References

- Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.
- Bakker, J. M., Deacon, G. B., Forsyth, C. M., Junk, P. C. & Wiecko, M. (2010). *Eur. J. Inorg. Chem.* pp. 2813–2825.
- Barnhart, D. M., Clark, D. L., Huffman, J. C., Vincent, R. L. & Watkin, J. G. (1993). *Inorg. Chem.* **32**, 4077–4083.
- Barrea, D., Gasparotto, A., Maccato, C., Maragno, C. & Tondello, E. (2006). *Langmuir*, **22**, 8639–8641.
- Barreca, D., Gasparotto, A., Tondello, E., Sada, C., Polizzi, S. & Benedetti, A. (2003). *Chem. Vap. Deposition*, **9**, 199–206.
- Beck, J. F., Neshat, A. & Schmidt, J. A. R. (2010). *Eur. J. Inorg. Chem.* pp. 5146–5155.
- Becker, G., Niemeyer, M., Mundt, O., Schwarz, W., Westerhausen, M., Ossberger, M. W., Mayer, P., Nöth, H., Zhong, Z., Dijkstra, P. J. & Feijen, J. (2004). *Z. Anorg. Allg. Chem.* **630**, 2605–2621.
- Binnemans, K. (2005). *Handbook on the Physics and Chemistry of Rare Earths*, Vol. 35, edited by K. A. Gschneider Jr, J.-C. G. Bünzli & V. K. Pecharsky, ch. 225, pp. 107–272. Amsterdam: Elsevier.
- Blessing, R. H. (1995). *Acta Cryst.* **A51**, 33–38.
- Carpentier, J.-F. (2010). *Dalton Trans.* **39**, 37–48.
- Carta, G., Benetollo, F., Sitran, S., Rossetto, G., Braga, F. & Zanella, P. (1995). *Polyhedron*, **14**, 1923–1928.
- Condorelli, G. G., Malandrino, G. & Fragalà, I. L. (2007). *Coord. Chem. Rev.* **251**, 1931–1950.
- Cosgriff, J. E., Deacon, G. B., Fallon, G. D., Gatehouse, B. M., Schumann, H. & Weimann, R. (1996). *Chem. Ber.* **129**, 953–958.
- Fatila, E. M., Hetherington, E. E., Jennings, M., Lough, A. J. & Preuss, K. E. (2012). *Dalton Trans.* **41**, 1352–1362.
- Gröb, T., Seybert, G., Massa, W. & Dehnicke, K. (2000). *Z. Anorg. Allg. Chem.* **626**, 349–353.
- Hsu, Y.-L. & Liang, L.-C. (2010). *Organometallics*, **29**, 6201–6208.
- Hubert-Pfalzgraf, L. G. & Guillon, H. (1998). *Appl. Organomet. Chem.* **12**, 221–236.
- Jones, A. C. (2002). *J. Mater. Chem.* **12**, 2576–2590.
- Jones, A. C., Aspinall, H. C., Chalker, P. R., Potter, R. J., Kukli, K., Rahtu, A., Ritala, M. & Leskelä, M. (2004). *J. Mater. Chem.* **14**, 3101–3112.
- Jones, A. C. & Chalker, P. R. (2003). *J. Phys. D Appl. Phys.* **36**, R80–R95.
- Kriek, S., Görls, H. & Westerhausen, M. (2010). *Organometallics*, **29**, 6790–6800.
- Krumdieck, S. P. (2009). *ECS Trans.* **25**, 1209–1219.
- Lohner, P., Fischer, J. & Pfeffer, M. (2002). *Inorg. Chim. Acta*, **330**, 220–228.
- Lo Nigro, R., Malandrino, G. & Fragalà, I. L. (2001). *Chem. Mater.* **13**, 4402–4404.
- Lo Nigro, R., Toro, R., Malandrino, G. & Fragalà, I. L. (2003). *Chem. Mater.* **15**, 1434–1440.
- Lo Nigro, R., Toro, R., Malandrino, G. & Fragalà, I. L. (2005). *J. Mater. Chem.* **15**, 2328–2337.
- McAleese, J., Darr, J. A. & Steele, B. C. (1996). *Chem. Vap. Deposition*, **2**, 244–247.
- Malandrino, G. & Fragalà, I. L. (2006). *Coord. Chem. Rev.* **250**, 1605–1620.
- Maudez, W., Meuwly, M. & Fromm, K. A. (2007). *Chem. Eur. J.* **13**, 8302–8316.
- Neander, S., Behrens, U. & Olbrich, F. (2000). *J. Organomet. Chem.* **604**, 59–67.
- Nonius (2002). *COLLECT*. Nonius BV, Delft, The Netherlands.
- Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
- Parsons, S., Liu, X., Yellowlees, L. & Wood, P. (2004). Private communication (refcode PAHNIW). CCDC, Cambridge, England.
- Pollard, K. D., Jenkins, H. A. & Puddephatt, R. J. (2000). *Chem. Mater.* **12**, 701–710.
- Richardson, M. F., Wagner, W. F. & Sands, D. E. (1968). *J. Inorg. Nucl. Chem.* **30**, 1275–1289.
- Saied, O., Simard, M. & Wuest, J. D. (1998). *Organometallics*, **17**, 1128–1133.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.
- Wang, J., Gurevich, Y., Botoshansky, M. & Eisen, M. S. (2006). *J. Am. Chem. Soc.* **128**, 9350–9351.
- Wong, E. W. Y., Walsby, C. J., Storr, T. & Leznoff, D. B. (2010). *Inorg. Chem.* **49**, 3343–3350.