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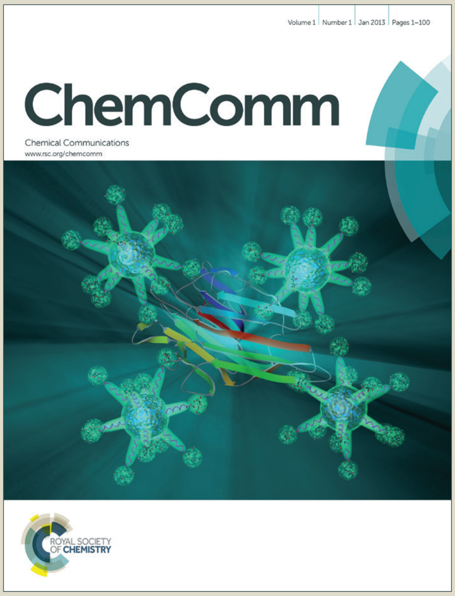

Volume 1 | Number 1 | Jan 2013 | Pages 1–100

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Cite this: DOI: 10.1039/c0xx00000x

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ARTICLE TYPE

Thyminate(2–)-bridged cyclic tetranuclear rhodium(III) complexes formed by a template of a sodium, calcium or lanthanoid ion†

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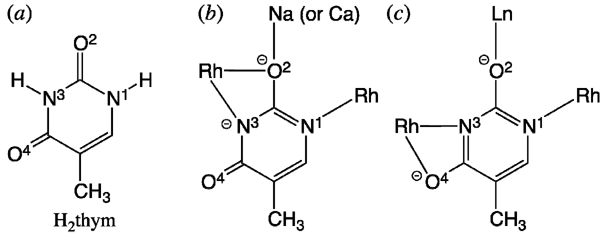
Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

In the thyminate(2–)-bridged tetranuclear Cp*Rh^{III} complexes incorporating a Na$^+$, Ca^{2+} or Ln^{3+} cation, a homochiral aggregation of four Rh^{III} centres was achieved to form metallacalix[4]arene-type clusters. The thyminate(2–) bridged two Rh^{III} and the third metal ion with a μ_3-$1\kappa N^1$:$2\kappa^2 N^3,O^2$:$3\kappa O^2$ mode in the Na$^+$ and Ca^{2+} complexes, while in the Ln^{3+} analogues it exhibited a different bridging mode, μ_3-$1\kappa N^1$:$2\kappa^2 N^3,O^4$:$3\kappa O^2$.

Cyclic polynuclear metal complexes bridged by suitable ligands are often termed metallamacrocycles,[1,2] metallacrowns[3–5] or metallacalix[*n*]arenes,[6–9] and have recently attracted considerable attention. In particular, those complexes consisting of half-sandwich organometallic fragments[10–14] have been widely studied, not only because of their structural versatility,[10,11,15,16] but also because of their potential application for selective capture of a specific molecule or pair of ions,[11–13,17] biomolecular sensing,[18] chiral recognition[19] and as stereospecific catalysts.[20] To develop such functional compounds, the design and selection of bridging ligands are particularly important. Severin et al. used a 2,3-dihydroxypyridine and its derivatives,[1,2,12–15] while Jin et al. utilized pyridyl-β-diketonates,[10,11] and the group of Oro, Carmona and Joo adopted chiral amino acids.[20,21] Adenine, guanine (i.e., purine-based nucleobases) and their derivatives were used to construct tetranuclear Cp*M^{III} (Cp* = η^5-C_5Me_5; M = Rh or Ir) and (arene)Ru^{II} complexes by Yamanari et al.,[16,19,22] Fish et al.[18] and Sheldrick et al.[23] Thymine (H_2thym: Scheme 1*a*), uracil and cytosine are the complementary pyrimidine-based nucleobases, and their anions have also been utilized to build cyclic polynuclear Pd^{II} and Pt^{II} complexes with fascinating molecular structures by Lippert et al.[6,7,24] and other groups.[9,25] However, to the best of our knowledge, there are no papers describing cyclic polynuclear complexes with half-sandwich organometallic fragments and the pyrimidine-based nucleobase anions. In this communication, we report cyclic tetranuclear Cp*Rh^{III} complexes bridged by thyminate(2–) (thym^{2-}) anions.

The reaction of $[(Cp^*Rh)_2(\mu\text{-}OH)_3]OH$[26] and H_2thym in a 1:2 mole ratio in MeOH, followed by addition of $NaPF_6$, $NaBF_4$ or $NaNO_3$, gave orange crystalline solids of **1**, **2** or **3**, respectively. Recrystallization of the products **1** and **2** from MeOH/Et_2O and that of **3** from MeCN/$^i Pr_2O$ afforded orange crystals of **1**•Et_2O•MeOH (with $NaPF_6$), **2**•Et_2O•MeOH•H_2O (with $NaBF_4$) and **3**•3MeCN•H_2O (with $NaNO_3$). X-ray structural analysis of these crystals (Table S1†) revealed that they are composed of a cyclic tetranuclear Cp*Rh^{III} unit containing four bridging thym^{2-} ligands, as shown in Fig. 1 (and Fig. S1†). The thym^{2-} anion was bound to the first Rh^{III} ion via the N^1 atom in a monodentate mode and to the second Rh^{III} ion through the N^3 and O^2 atoms forming a four-membered chelate ring (Scheme 1*b*). Because the thym^{2-} bridge was unsymmetric, each Rh centre with a Cp* ligand became asymmetric. The four Rh centres in the cyclic tetranuclear unit were homochiral; this conformation gave the $(Cp^*Rh)_4(\mu\text{-}thym)_4$ unit as a truncated square-pyramidal structure or a metallacalix[4]arene arrangement. Similar tetranuclear complexes with half-sandwich organometallic fragments and nucleobase-derived or -related ligands have been reported previously; e.g., $[\{(p\text{-}cymene)Ru\}_4(\mu\text{-}ade)_4]^{4+}$ (Hade = adenine), $[(Cp^*Ir)_4(\mu\text{-}ade\ or\ Hgua)_4]^{4+}$ (H_2gua = guanine),[23] $[(Cp^*Rh)_4(\mu\text{-}H_{0.5}put)_4]^{2+}$ (Hput = 6-purinethione),[16] $[(Cp^*Rh)_4(\mu\text{-}ima)_4]$ (H_2ima = 4-imidazolecarboxylic acid)[14] and $[(Cp^*Ir)_4(\mu\text{-}pyac)_4]^{4+}$ (Hpyac = 1-(4-pyridyl)butane-1,3-dione).[10] However, these complexes were aggregated heterochirally (i.e., an *ACAC* conformation). In contrast, the related cyclic trinuclear complexes achieved homochiral aggregation forming metallacalix[3]arene structures, where an interesting inclusion phenomenon of a LiF ion pair was observed.[2,12,13] Complexes **1**–**3** are the first examples of homochiral aggregation in nucleobase-bridged cyclic tetranuclear Cp*Rh^{III} complexes.



Scheme 1 (*a*) Thymine (H_2thym) with the atom-numbering scheme used in this paper, and bridging modes of thym^{2-} found in (*b*) complexes **1**–**4** and (*c*) complexes **5**–**8**.

In all of the complexes **1**–**3**, a Na$^+$ cation was incorporated in the hydrophilic open site of the metallacalix[4]arene core through co-ordination by the O^2 atoms of the bridging thym^{2-} ligands (Fig. 1*a* and Scheme 2*a*). Thus, the total bridging mode of thym^{2-} to two Rh and one Na centres can be expressed as μ_3-$1\kappa N^1$:$2\kappa^2 N^3,O^2$:$3\kappa O^2$ (Scheme 1*b*). Together with the Na$^+$ cation,

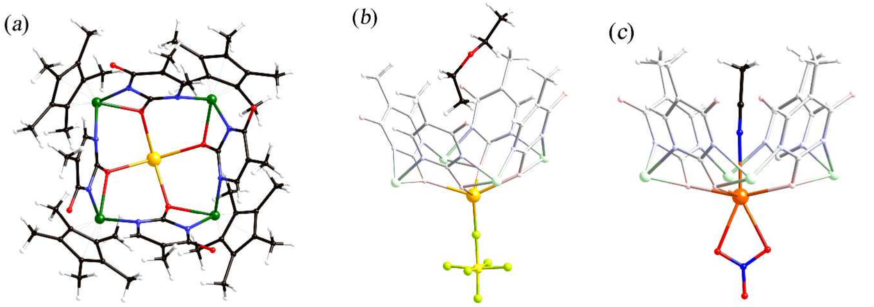
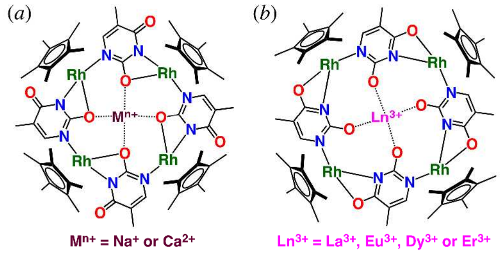


Fig. 1 (*a*) A perspective view of the $[(Cp^*Rh)_4(\mu\text{-thym})_4Na]^+$ moiety in **1**•Et_2O•MeOH. Side views of (*b*) the $Rh_4(\mu\text{-thym})_4(NaPF_6)$ and Et_2O moieties in **1**•Et_2O•MeOH and (*c*) the $Rh_4(\mu\text{-thym})_4Ca(NO_3)(MeCN)$ moiety in **4**•$9H_2O$, emphasizing the inclusion and/or co-ordination structure of the clusters (Cp* ligands are omitted for clarity). Colour code: Rh, green; Ca, reddish orange; P, yellow; Na, yellowish orange; F, yellowish green; O, red; N, blue; C, black; H, white.



Scheme 2 Schematic drawings of (*a*) $[(Cp^*Rh)_4(\mu\text{-thym})_4M]^{n+}$ (M^{n+} = Na^+ or Ca^{2+}) and (*b*) $[(Cp^*Rh)_4(\mu\text{-thym})_4Ln]^{3+}$ (Ln = La, Eu, Dy or Er).

the cluster can be viewed as a bowl-like structure. The incorporated Na^+ cation is further co-ordinated by a F atom of the PF_6^- or BF_4^- anions (in **1** or **2**[27]) from the outside of the bowl (Fig. 1*b*). In complex **3**, a NO_3^- anion was co-ordinated to the Na^+ in a κ^2*O,O'* mode.[27] The Na–O bond lengths in **1**, **2** and **3** vary widely because of the co-ordinated anion in the range 2.38–2.50 Å. Furthermore, in the hydrophobic inner space of the metallacalix[4]arene a Et_2O or a MeCN molecule was included, as shown in Fig. 1*b* (and Fig. S1†).

The molecular structure of $[(Cp^*Rh)_4(\mu\text{-thym})_4Na]^+$ was retained in solution, as confirmed by ESI-mass spectrometry and ^1H NMR spectroscopy. The ESI-mass spectrum (positive ion mode) of **1** (and that of **2**) in MeOH (Figs. S2†) exhibited a main signal at *m*/*z* = 1471 corresponding to $[Cp^*_4Rh_4(thym)_4Na]^+$. The ^1H NMR spectrum of **1** in CD_3OD (Fig. S3†) showed three singlet resonances for Cp*, thym-CH_3 and thym-C^6–H in the integration ratio of 15:3:1. Using these observations, the formation of the cyclic tetramer was monitored by ^1H NMR spectroscopy. A mixture of $[(Cp^*Rh)_2(\mu\text{-}OH)_3]OH$ and H_2thym in a 1:2 mole ratio in CD_3OD showed at least four resonances for the Cp* protons (Fig. S4*a*†), indicating the existence of a number of reaction products (and the starting complex). When an excess amount of $NaPF_6$ was added to the mixture, these resonances disappeared, and a singlet Cp* resonance corresponding to complex **1** quantitatively grew (Fig. S4*b*†). In addition, the ESI-mass spectrum of a mixture of $[(Cp^*Rh)_2(\mu\text{-}OH)_3]OH$, H_2thym (2 equiv) and (excess) $NaPF_6$ in MeOH similarly showed a peak at *m*/*z* = 1471. Thus, it is concluded that the tetranuclear $[(Cp^*Rh)_4(thym)_4Na]^+$ complex was quantitatively formed by a template of Na^+ cation, although the isolated yields of **1**–**3** were relatively low.

We have also examined the efficiency of the other alkali metal ions as a template for cyclic polynuclear rhodium clusters. In the case of $LiBF_4$, the ESI-mass spectrum of the mixture exhibited two main signals at *m*/*z* = 1087 and 1093, corresponding to $[(Cp^*Rh)_3(thym)_3H]^+$ and $[(Cp^*Rh)_3(thym)_3Li]^+$, respectively (Fig. S5†). However, the ^1H NMR spectrum showed several Cp* resonances, and no crystalline product could be isolated from the reaction mixture. In the case of KPF_6, the ESI-mass spectrum exhibited signals corresponding to $[(Cp^*Rh)_4(thym)_4Na]^+$ (*m*/*z* = 1471) and $[(Cp^*Rh)_4(thym)_4K]^+$ (*m*/*z* = 1487), although the latter has a considerably weaker intensity (another intense signal was observed at *m*/*z* = 1639 corresponding to $[(Cp^*Rh)_4(thym)_4Na + NaPF_6]^+$) (Fig. S6†). This suggests that the Na^+ adduct is much more favourable than the K^+ analogue.

The difference in stability of the Li^+-, Na^+- and K^+-incorporated compounds would be caused by the ionic radii of the cations, as in the case of crown ethers and calix[*n*]arenes. In the next experiment, therefore, other metal ions with a similar ionic radius (but different cationic charge) were examined: e.g., Na^+(5) 100, Ca^{2+}(6) 100, Eu^{3+}(8) 107 and Dy^{3+}(7) 97 pm.[28]

When an excess amount of $Ca(NO_3)_2$•$4H_2O$ was added to a mixture of $[(Cp^*Rh)_2(\mu\text{-}OH)_3]OH$ and H_2thym (2 equiv) in MeOH, an orange crystalline product was obtained by evaporation of the solvent, followed by extraction with CH_2Cl_2. Recrystallization of the crude product from MeCN/$^iPr_2O$ afforded orange prismatic crystals (**4**•$9H_2O$). X-ray analysis confirmed that the crystal consists of the Ca^{2+}-incorporated tetranuclear $(Cp^*Rh)_4(\mu\text{-thym})_4$ complex (Fig. S7†). The thym^{2-} ligand showed the same bridging mode, μ_3-$1\kappa N^1$:$2\kappa^2 N^3,O^2$:$3\kappa O^2$, as those in complexes of **1**–**3**. Also, a homochiral aggregation was achieved. The Ca^{2+} ion was co-ordinated by four O^2 atoms of the bridging thym^{2-} ligands, two O atoms of the chelating NO_3^- anion, and a N atom of MeCN located inside the bowl-like structure (Fig. 1*c*). In the crystal, together with the cationic cluster of $[(Cp^*Rh)_4(\mu\text{-thym})_4Ca(NO_3)(MeCN)]^+$, there are disordered counter anions of NO_3^- or OH^- and water molecules of crystallization. Compared with the $Na(NO_3)$-incorporated complex **3**, the Rh–O(O^2) bonds in **4** (av. 2.272 Å) are remarkably longer (av. 2.206 Å in **3**), while the Ca–O bonds in **4** (av. 2.366 Å) are slightly shorter than the Na–O bonds in **3** (av. 2.422 Å). These differences are caused by the higher ionic charge of Ca^{2+} than Na^+. A more pronounced difference in the structural parameters between these complexes is the *trans*-positioned O–M–O bond angles; in the Na^+ complex (**3**) the O–

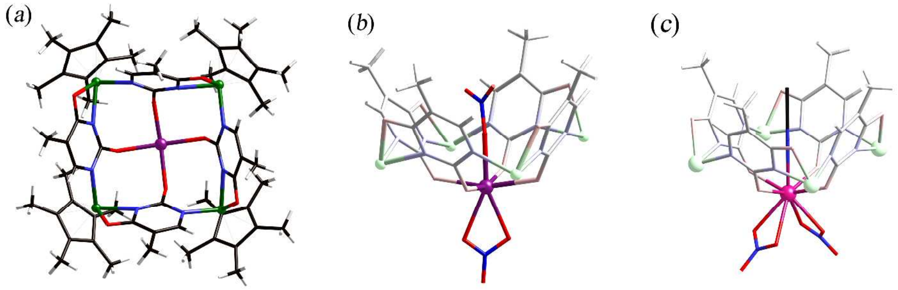


Fig. 2 (*a*) A perspective view of the $[(Cp^*Rh)_4(\mu\text{-thym})_4Dy]^{3+}$ moiety in **7**•H_2thym•MeOH. Side views of (*b*) the $Rh_4(\mu\text{-thym})_4Dy(NO_3)_2$ moiety in **7**•H_2thym•MeOH and (*c*) the $Rh_4(\mu\text{-thym})_4Eu(NO_3)_2(MeCN)$ moiety in **6**•$2H_2O$, emphasizing the co-ordination around the Dy^{III} and Eu^{III} centres, respectively. Colour code: Dy, purple; Eu, bright pink; Rh, green; O, red; N, blue; C, black; H, white.

Na–O angle averages 142.8°, while the corresponding O–Ca–O angle of **4** averages 158.7°. In compound **4**, the Ca atom is displaced by 0.436(2) Å from the least-squares plane defined by the four O^2(thym) atoms, but the Na atom in compound **3** is displaced more (av. 0.772 Å) from the O^2 plane (Table S3†).

Similar reactions of the Cp*Rh precursor and H_2thym in the presence of $Ln(NO_3)_3$•$6H_2O$ (Ln = La, Eu, Dy or Er) in MeOH were also examined. Crude orange products with the composition of $(Cp^*Rh)_4(thym)_4Ln(NO_3)_3$ (**5**, **6**, **7** and **8** for the La, Eu, Dy and Er adducts, respectively) were obtained and recrystallized from MeCN (for **5** and **6**) or MeOH (for **7** and **8**) by vapour diffusion of Et_2O, affording orange prismatic crystals.

X-ray crystallographic analysis revealed that complexes **7** and **8** crystallized in the monoclinic space group $P2_1/c$ with $Z = 4$, together with a free H_2thym and a MeOH molecule of crystallization. The molecular structures of the Dy^{3+}-incorporated cyclic tetrarhodium complex cations in **7**•H_2thym•MeOH are illustrated in Fig. 2*a* and Scheme 2*b*. It is notable that the co-ordination mode of $thym^{2-}$ in these complexes is different from that in the Na^+ and Ca^{2+} complexes **1**–**4**. Besides the monodentate N^1-co-ordination to the first Rh^{III} and the O^2-co-ordination to the Dy^{III} or Er^{III} (= Ln^{III}), the N^3 and O^4 atoms bind to the second Rh^{III} centre forming a four-membered chelate ring: μ_3-1κN^1:2κ$^2N^3$,O^4:3κO^2 mode (Scheme 1*c*). The central Ln^{III} atom has two NO_3^- anions having different co-ordination modes; one is in the κ^2*O,O*'-mode bound from the outside of the bowl-like $Rh_4(\mu\text{-thym})_4Ln$ core, and the other has a monodentate κ*O*-mode located in the space of the bowl (Fig. 2*b*). Thus, the Ln^{III} centre in **7** and **8** has seven-co-ordination geometry. In the crystals, the neutral H_2thym molecule is hydrogen-bonded to one of the bridging $thym^{2-}$ ligands and a counter NO_3^- anion (Fig. S8†).

The La^{3+}- and Eu^{3+}-incorporated complexes (**5** and **6**, respectively) crystallized, together with two water molecules of crystallization, in the orthorhombic space group $P2_12_12$ with $Z = 2$. The La^{III} or Eu^{III} (= Ln^{III}) atom was located on a crystallographic C_2 axis. There is half of a cyclic $(Cp^*Rh)_4(\mu\text{-thym})_4Ln$ core in an asymmetric unit, but a different orientation of the tetramer was overlapped. That is, enantiomeric tetramers aggregated homochirally are co-crystallized randomly in a non-centrosymmetric space group. The molecular structures of the Eu^{3+}-incorporated cyclic tetramers in **6**•$2H_2O$ are shown in Fig. S9†. The $thym^{2-}$ ligands show the same bridging mode as that found in complexes **7** and **8**. The Ln^{III} centre is co-ordinated by an acetonitrile molecule located on the C_2 axis inside the bowl. Also, two symmetry-related NO_3^- anions are bound to the Ln^{III} centre in the κ^2*O,O'* mode outside the bowl. Thus, the Ln^{III} cation is described as having nine-co-ordination geometry (Fig. 2*c*).

The different co-ordination geometries around the Ln^{III} centre between the early (La^{III} and Eu^{III}) and the late (Dy^{III} and Er^{III}) lanthanoids would be caused by the difference in ionic radii of the Ln^{3+}. Larger La^{3+} and Eu^{3+} ions cannot match the cavity size formed by the $Rh_4(\mu\text{-thym})_4$ cycle, while smaller Dy^{3+} and Er^{3+} ions fit better into the cavity, as parameterized by the deviation of the Ln^{III} center from the least-squares plane defined by the four O^2 atoms of the bridging $thym^{2-}$ ligands and the mutually *trans* O^2–Ln–O^2 bond angles (Table S2†). The La^{III} and Eu^{III} centres hanging out from the four O^2 planes have a large open space to be bonded by two nitrate anions in the κ^2*O,O'* mode from the outside of the bowl. In contrast, the flattened Dy^{III} and Er^{III} centres cannot bind two NO_3^- anions in the κ^2*O,O'* mode, but are surrounded by a NO_3^--κ^2*O,O'* and a NO_3^--κ*O* from the outside and inside of the bowl.

The Ca^{2+}- and Ln^{3+}-incorporated tetranuclear Cp*Rh clusters also maintained their molecular structures in methanol solution. The ^{1}H NMR spectra of **4** and **5** showed a single set of resonances indicating a high (C_4) symmetry for the dissolved complexes. The ESI-mass spectrum of **4** in MeOH showed a signal corresponding to $[(Cp^*Rh)_4(thym)_4Ca]^{2+}$ at m/z = 1550. The spectrum of **5** in MeCN gave intense signals at m/z = 824.5 and 1711, which are assigned to $[(Cp^*Rh)_4(thym)_4La(NO_3)]^{2+}$ and $[(Cp^*Rh)_4(thym)_4La(NO_3)_2]^+$, respectively. The other Ln^{3+}-incorporated complexes showed similar ESI-mass spectra, exhibiting two signals corresponding to the $Ln(NO_3)^{2+}$ and $Ln(NO_3)_2^+$ species (Figs. S9–S13†).

In summary, cyclic tetranuclear Cp^*Rh^{III} complexes bridged by $thym^{2-}$ anions were obtained by the reaction of $[(Cp^*Rh)_2(\mu\text{-}OH)_3]OH$ and 2 equiv of H_2thym in the presence of Na(NO_3, PF_6 or BF_4), $Ca(NO_3)_2$ or $Ln(NO_3)_3$ (Ln = La, Eu, Dy or Er). The cations Na^+, Ca^{2+} and Ln^{3+} (M^{n+}) acted as a template to achieve homochiral aggregations of four Cp*Rh(thym) moieties through the co-ordination by the O^2 atom of $thym^{2-}$. This aggregation resulted in a truncated square-pyramidal structure for the $Rh_4(\mu\text{-thym})_4M^{n+}$ cluster, which may also be described as a M^{n+}-incorporated metallacalix[4]arene. The cluster binds at least one anion (PF_6^-, BF_4^- or NO_3^-) to the central M^{n+} cation from the outside of the bowl-like core. In the case of Na^+ complexes (**1**–

3), the frustum (or metallacalix[4]arene) includes a solvent molecule (Et_2O or CH_3CN) in the hydrophobic inner space, but an acetonitrile molecule located in the inner cavity is co-ordinated to the central M^{n+} cation in the Ca^{2+}, La^{3+} and Eu^{3+} complexes (**4**–**6**). It is most striking that both in the Na^+ and Ca^{2+} complexes the ligand, $thym^{2-}$, has a $\mu_3\text{-}1\kappa N^1{:}2\kappa^2 N^3,O^2{:}3\kappa O^2$ bridging mode, while in the Ln^{3+} complexes it showed a different mode: $\mu_3\text{-}1\kappa N^1{:}2\kappa^2 N^3,O^4{:}3\kappa O^2$.

This work was financially supported by a Grant-in-Aid for Scientific Research No. 25410070 from the Ministry of Education, Culture, Sports, Science, and Technology, Japan.

Notes and references

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† Electronic Supplementary Information (ESI) available: details of syntheses, tables of crystallographic information and selected structural parameters, perspective drawings of the complexes, ^{1}H NMR and ESI-mass spectra of the complexes. CCDC reference numbers: 1033776–1033783. See DOI: 10.1039/b000000x/

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