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Rhenium Calix[4]arenes: Precursors to Novel Imaging and Cancer Therapy Agents

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Dedicated to the memory of Dr. Ginny Annison

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Interaction of $[ReOCl_3(PPh_3)_2]$ with *tert*-butylcalix[4]-areneH$_4$, Cax(OH)$_4$, in the presence of MO*t*Bu (M = Na, K), or MH, under anaerobic conditions affords the isostructural rhenium(V) oxo complexes $[Re(O)(PPh_3)Cax(O)_4M(NCMe)_2]\cdot 4MeCN$ [M = Na, (**1**); K, (**2**)] containing an alkali-metal cation within an elliptical ligand conformation. In the presence of air, the same reaction affords dioxo rhenium(VII) complexes of the form $[Re(O)_2Cax(O)_4M(NCMe)_2]$ [M = Na, ·ca. 2.8MeCN (**3**); K, ·3MeCN (**4**)]. Prolonged heating also led to the isolation of the first examples of rhenium–rhenium bonding supported by calixarene ligands, viz. $[ReCax(O)_4M(NCMe)_2(\mu\text{-}O)]_2\cdot 4MeCN$ [M = Na, (**5**); K, (**6**)], and in one case to $\{ReCax(O)_4K(NCMe)_2[\mu\text{-}OK(NCMe)_2]\}_2Cax(O)_2(OH)_2\cdot 7MeCN$ (**7**). The use of **2** as starting material led to the isolation of the complex $\{[Re(O)Cax(O)_4K(NCMe)_2]_2(\mu\text{-}O)\}\cdot 2MeCN$ (**8**). Given the diversity and complexity of the products arising from these "oxo" reactions, attention was switched to the isoelectronic organoimido [NR] group, and given its synthetic utility, the *tert*-butylimido group [N*t*Bu] was chosen as our entry point. Reaction of $[Re(NtBu)_2Cl_3]$ with Cax(OH)$_4$ in a 1:1 ratio afforded the orange $[Re(NtBu)_2ClCax(O)_2(OH)_2]\cdot MeCN$ (**9**), containing both a linear and a bent imido group. Increasing the amount of Cax(OH)$_4$ (2:3 ratio) afforded both **9** together with the dark red complex $[Re(NtBu)Cax(O)_4Cax(O)(OH)_3]\cdot 6MeCN$ (**10**), which contains both mono- and tetra-dentate calixarene ligands. In the presence of adventitious oxygen, the complex $\{[Re(NtBu)Cax(O)_4]_2(\mu\text{-}O)\}\cdot 3MeCN$ (**11**) was formed. To favour monomeric complex formation, the lithium salt of the monomethoxycalix[4]arene, namely Cax(OLi)$_3$(OMe), was treated with $[Re(NtBu)_2Cl_3]$ affording the mono- and bisacetonitrile-ligated species $[Re(NtBu)_2Cax(O)_4Li(NCMe)_2][Re(NtBu)_2Cax(O)_4Li(NCMe)]\cdot MeCN$ (**12**). To avoid the lithium incorporation of **12**, Cax(OH)$_3$(OMe) was treated with $[Re(NtBu)_3(OSiMe_3)]$ affording $[Re(NtBu)_2Cax(O)_3(OMe)]$ (**13**), for which the methoxy ether group protudes into the calixarene cavity. The compounds **1**–**13** have been structurally characterised by single-crystal X-ray diffraction (synchrotron radiation was used for **4**, **6**, **7**, **9**, **11**–**13**).

Introduction

The advent of readily available technetium imaging agents, such as technetium-^{99}m sestambi (Cardiolite®) have revolutionised the imaging of many disease states including cancer and heart disease.[1,2] ^{99}Tc is a γ-emitter making it an ideal imaging agent but limiting its therapeutic use. In contrast, the 3rd row congener, rhenium, has two isotopes ^{186}Re ($t_{1/2}$ = 90 h) and ^{188}Re ($t_{1/2}$ = 17 h) which are β-emitters and are thus suited for use as therapeutics.[3] Indeed the availability of in-house ^{188}W/^{188}Re generators has led to an increase in the development of ^{188}Re-labelled radiopharmaceuticals. The similarities in the chemistry of technetium and rhenium, for example their atomic size and lipophilicity, enable chemical methodologies developed for the preparation of technetium chelates to be applied to their rhenium analogues (and vice versa).

One of the major challenges in the development of therapeutic radiopharmaceuticals is to ensure a localised radiation effect through targeting to a specific organ or indeed cell type. To-date, two approaches have been developed for the targeting of rhenium to a site of action. Firstly, the metal ion can be directly co-ordinated to a receptor ligand, for example by complexation with hydroxyethylidene diphosphonate for the imaging of bone metastases.[4] However this approach may result in a change in the properties

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of a ligand and thus a reduction in the affinity of binding. In contrast, a more adaptable approach is the use of a linker between the unmodified targeting group and the metal chelation site[5] e. g. folate-based systems for the treatment of ovarian tumours in which the folate receptor is over expressed[6] or systems based on RGD ligands with potential for activity in malignant melanomas.[7]

Crucial to the design and development of this novel type of agent is the development of new chelating scaffolds for rhenium. Our approach presented herein focuses on the development of chelating systems for rhenium based on the use of calixarenes as scaffolds/carrier molecules. Such a strategy has shown promise for targeted radiotherapy using ^{188}Re-labelled porphyrin derivatives.[8]

Calixarene molecules are renowned for their strong chelating properties. They are readily available either commercially or via standard aqueous syntheses.[9] Their ability to bind to transition metals is well-documented, particularly at their lower-rim (phenolic edge).[10] In such systems, the calix[4]arene molecule usually binds in a tetradentate fashion and retains a cone-like conformation. These molecules provide a robust, but inert support and offer considerable variation in the substituent groups that can be attached. Calixarenes are capable of forming bonds to biomolecules, which, it is proposed, enhance the selectivity of the calixarene for predetermined receptors located on the surface of the cancer cells.[11] More recently, non-peptido calixarenes have also shown promising anti-tumour activity.[12] Reinhoudt and co-workers have isolated a rhenium(V) Schiff-base complex by metallation of an upper-rim ligand and recognised the potential of rhenium calixarenes as radiopharmaceuticals. The methodology was extended to include an N_2S_2 complex readily generated from rhenium(V) gluconate, which showed good solubility in phosphate-buffered saline solution.[13] Other studies using calixarenes as chelates to either lanthanide cations or Ac^{3+} have demonstrated stability in aqueous solution,[14] whilst 4-sulfonic calix[4]arenes have been used to probe pore properties of volume regulated anion channels in endothelial cells.[15]

Most relevant to our present contribution is the work of Ishii, who reported that treatment of *p*-*tert*-butylcalix[4]areneH$_4$, Cax(OH)$_4$, with *n*-butyllithium (3 equiv.) and subsequent treatment with [PPh$_4$][ReOCl$_4$] affords the rhenium(VI) anion [ReCl(O)Cax(O)$_4$]$^-$. Oxidation with excess Ag$_2$O furnishes the dioxo rhenium(VII) complex [Re(O)$_2$-Cax(O)$_4$]$^-$, which has been structurally characterised as its PPN salt.[16]

Results and Discussion

Oxo Chemistry

We have found that the reaction of Cax(OH)$_4$ and [ReOCl$_3$(PPh$_3$)$_2$] in the presence of the base MO*t*Bu or MH (M = Na, K) affords green/yellow blocks of the oxo rhenium(V) salts [Re(O)(PPh$_3$)Cax(O)$_4$M(NCMe)$_2$]·4MeCN [M = Na, (**1**); K, (**2**)] containing an alkali-metal cation within an elliptical ligand conformation (Figure 1). Selected bond lengths and angles for **1** and **2** are given in Table 1, with crystallographic data presented in Tables 11, 12 and 13. The compounds are isostructural and, in each, a triphenylphosphane ligand remains bound to the rhenium(V) centre [Re–P 2.4390(9) (for **1**) and 2.4432(10) for **2** Å]. The Re=O bond lengths for **1** [1.698(2) Å] and **2** [1.696(2) Å] are consummate with those reported elsewhere for Re=O.[16–18] The IR spectrum of **1** (and **2**) contains a strong *v*Re=O stretch vibration at 1019 cm^{-1} (1020 cm^{-1} for **2**). The ^{1}H

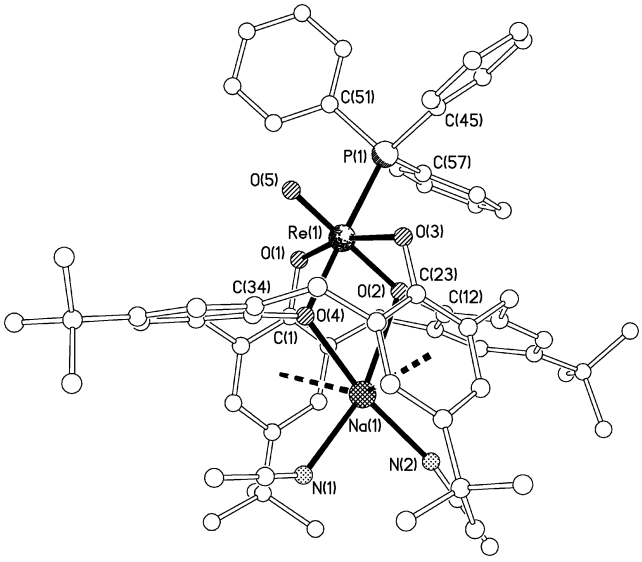
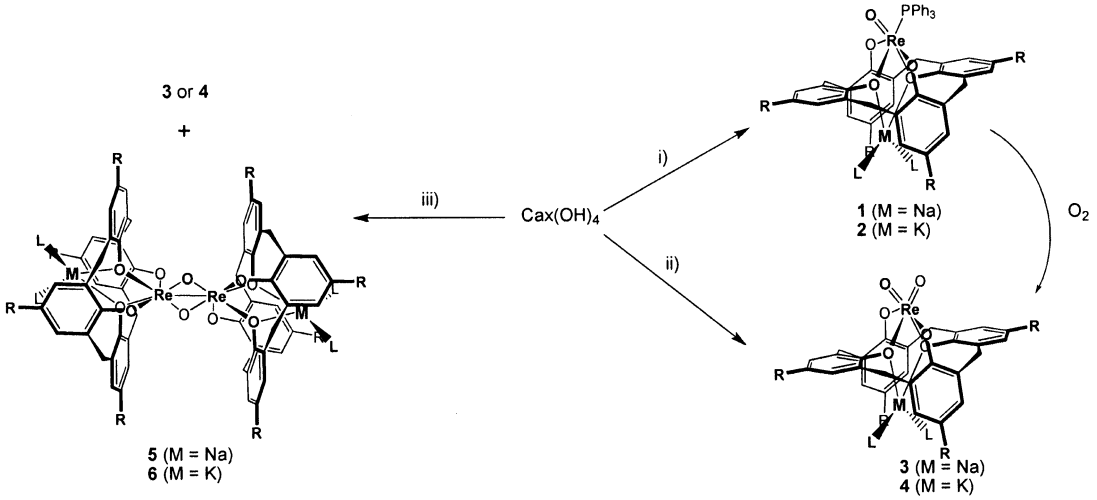


Figure 1. Molecular structure of **1** (complex **2** is isostructural). H atoms and MeCNs of crystallisation omitted for clarity.

Table 1. Molecular dimensions in **1** and **2** [Å/°].

	1	**2**
Re(1)–O(1)	2.048(2)	2.054(2)
Re(1)–O(2)	1.938(2)	1.925(2)
Re(1)–O(3)	2.060(2)	2.068(2)
Re(1)–O(4)	2.069(2)	2.065(2)
Re(1)–O(5)	1.698(2)	1.696(2)
Re(1)–P(1)	2.4390(9)	2.4432(10)
Re(1)···Na/K(1)	3.5346(16)	3.8335(9)
Na/K(1)–O(2)	2.591(3)	2.867(2)
Na/K(1)–O(4)	2.309(3)	2.595(2)
Na/K(1)–N(1)	2.396(4)	2.784(4)
Na/K(1)–N(2)	2.375(4)	2.705(5)
O(1)–Re(1)–O(2)	81.76(9)	81.88(9)
O(1)–Re(1)–O(3)	163.54(9)	163.05(9)
O(1)–Re(1)–P(1)	90.47(7)	90.74(7)
O(2)–Re(1)–O(4)	84.39(9)	85.83(9)
O(5)–Re(1)–P(1)	88.20(9)	90.90(7)
Re(1)–O(2)–Na/K(1)	101.64(10)	104.52(9)
Re(1)–O(4)–Na/K(1)	107.55(10)	110.19(10)
O(2)–Na/K(1)–O(4)	66.39(9)	59.45(7)
N(1)–Na/K(1)–N(2)	92.54(15)	92.89(16)



Scheme 1. Synthesis of complexes **1**–**4**, and **5** and **6**. Reagents and conditions: (i) (a) MO*t*Bu, toluene, 30 min; (b) $[ReOCl_3(PPh_3)_2]$. (ii) $[ReOCl_3(PPh_3)_2]$, toluene, 12 h. (iii) (a) $[ReOCl_3(PPh_3)_2]$ + MO*t*Bu, CH_2Cl_2, –78 °C, 4 h; (b) $Cax(OH)_4$, toluene, reflux, 12 h; (c) MeCN. L = MeCN, R = *t*Bu.

NMR spectra of **1** and **2** each contain four methylene doublets as well as three peaks due to *tert*-butyl groups in a 1:1:2 ratio.

Treatment of **1** or **2** with O_2 affords the red/brown rhenium(VII) dioxo complexes $[Re(O)_2Cax(O)_4M(NCMe)_2]$ [M = Na, ·2.8MeCN (**3**); K, ·3MeCN (**4**)] (Scheme 1). The structures of **3** and **4** (Figure 2) resemble that of the dioxo complex reported by Ishii, viz. pseudooctahedral rhenium bound by two *cis*-oxo groups and four phenolate calixarene oxygen atoms. Selected bond lengths and angles for **3** and **4** are given in Table 2. The Re=O bond lengths here [1.697(6) and 1.710(5) Å for **3**; 1.718(2) and 1.724(2) Å for **4**] are in general slightly longer than those observed in **1** and **2**. The ^1H NMR spectra of **3** and **4** (two methylene doublets and two *tert*-butyl peaks) differ from those of **1** and **2** due to the C_{2v} symmetry of the dioxo complexes.

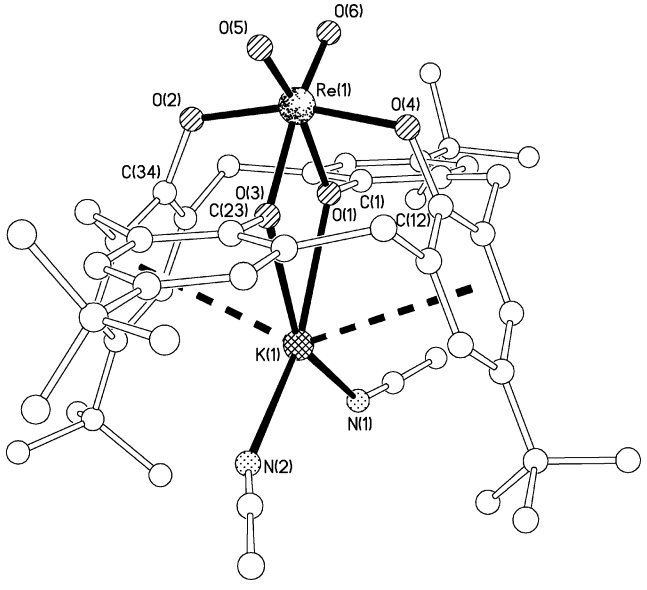


Figure 2. Molecular structure of **4** (complex **3** is very similar). H atoms and MeCNs of crystallisation omitted for clarity.

Table 2. Molecular dimensions in **3** and **4** [Å/°].

	3	**4**
Re(1)–O(1)	2.041(5)	2.017(2)
Re(1)–O(2)	1.908(6)	1.948(2)
Re(1)–O(3)	2.050(5)	2.018(2)
Re(1)–O(4)	1.921(6)	1.946(2)
Re(1)–O(5)	1.697(6)	1.724(2)
Re(1)–O(6)	1.710(5)	1.718(2)
Re(1)···Na/K(1)	3.620(3)	3.9724(9)
Na/K(1)–O(1)	2.326(6)	2.654(2)
Na/K(1)–O(3)	2.326(6)	2.653(2)
Na/K(1)–N(1)	2.358(12)	2.799(5)
Na/K(1)–N(2)	2.370(11)	2.792(5)
O(1)–Re(1)–O(2)	83.4(2)	83.53(9)
O(1)–Re(1)–O(3)	73.3(2)	73.89(8)
O(2)–Re(1)–O(4)	163.5(2)	163.26(9)
O(2)–Re(1)–O(6)	95.0(2)	94.84(11)
O(5)–Re(1)–O(6)	103.4(3)	103.41(12)
Re(1)–O(1)–Na/K(1)	111.8(2)	115.86(9)
Re(1)–O(3)–Na/K(1)	111.5(2)	115.84(9)
O(1)–Na/K(1)–O(3)	63.36(19)	54.38(6)
N(1)–Na/K(1)–N(2)	104.3(5)	117.94(17)

Interestingly, when the order of addition is changed such that $[ReOCl_3(PPh_3)_2]$ and [MO*t*Bu] are combined prior to addition of $Cax(OH)_4$,[19] subsequent prolonged heating in toluene results predominantly in the formation of either **3** or **4** together with a second minor dark red/purple product, shown by single-crystal X-ray diffraction using X-ray synchrotron radiation[20] to be the metal-metal-bonded dimers $[ReCax(O)_4M(NCMe)_2(\mu\text{-}O)]_2$ [M = Na, ·4MeCN (**5**); K,

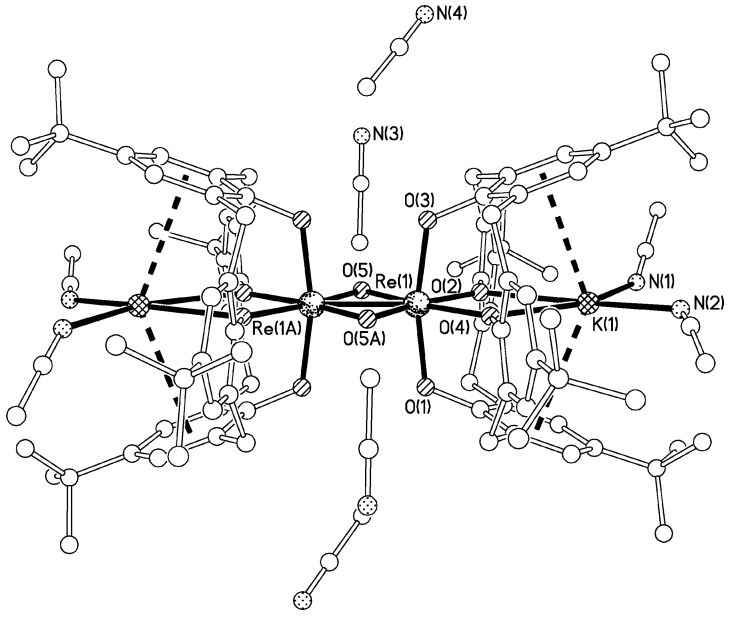
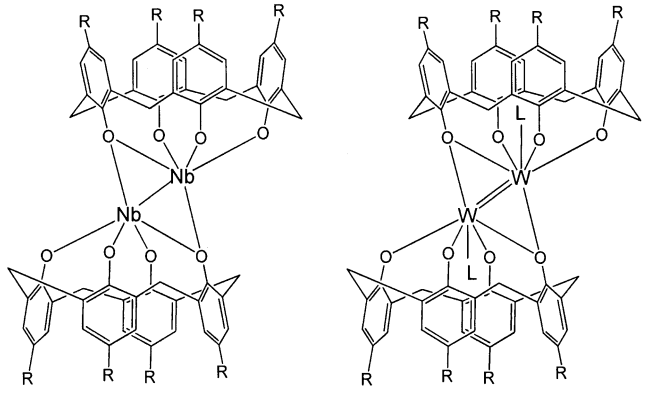


Figure 3. Molecular structure of **6** (complex **5** is isostructural). H atoms omitted for clarity.

·4MeCN (**6**)], respectively (see Figure 3 and Table 3). The complexes **5** and **6** are the first examples of rhenium–rhenium bonding supported by calixarene ligands; metal-metal-bonded calix[4]arene species have been reviewed by Cotton, and by Floriani and Floriani-Moro.[21] Interestingly, in the absence of excess alkali-metal cation, metal-metal-bonded calixarenes are usually bridged by an oxygen atom of a phenolic group of each calixarene (Scheme 2).[21b] This is not the case for **5** and **6**. The structures **5** and **6** are isostructural and the molecules sit about an inversion centre, with the two pseudooctahedral rhenium centres linked by μ_2-oxo bridges and a Re–Re bond [2.3906(8) (**5**) and 2.3913(4) (**6**) Å], distances consistent with a bond order of ca. 2.5. The angles subtended at O(5) and O(5A) by the rhenium atoms [75.8(2) (**5**) and 75.70(12)° (**6**)] are significantly contracted from 90°, a consequence of satisfying the Re–Re bonding. The Re–O(5/5A)$_{bridge}$ distances are in the range 1.941(7)–1.950(7) Å. In the IR spectrum, bands at ca. 647 cm^{-1} are tentatively assigned to the *v*Re–O–Re stretch vibration. The calixarene ligands of both **5** and **6** contain an alkali-metal cation within an elliptical ligand conformation, for example in **5** the Na^+ to ring centroid distances are Na(1)–C(1)/C(6) ring: 2.968 Å and Na(1)–C(23)/C(28) ring: 3.224 Å. ^{1}H NMR spectra for **5** and **6** are broad, however, crude reaction mixtures of **3**/**5** and **4**/**6** show no evidence of any paramagnetic species by EPR.

Table 3. Molecular dimensions in **5** and **6** [Å/°].

	5	**6**
Re(1)–O(1)	1.937(6)	1.954(3)
Re(1)–O(2)	1.999(6)	1.990(3)
Re(1)–O(3)	1.942(6)	1.948(3)
Re(1)–O(4)	2.008(7)	1.994(3)
Re(1)–O(5)	1.941(7)	1.949(3)
Re(1)–O(5A)	1.950(7)	1.948(3)
Re(1)···Re(1A)	2.3906(8)	2.3913(4)
Re(1)···Na/K(1)	3.535(4)	3.9042(12)
O(2)–Na/K(1)	2.310(8)	2.659(4)
O(4)–Na/K(1)	2.329(8)	2.676(3)
Na/K(1)–N(1)	2.403(12)	2.808(6)
Na/K(1)–N(2)	2.377(14)	2.712(12)
O(1)–Re(1)–O(3)	167.0(3)	166.94(13)
O(2)–Re(1)–O(4)	76.3(3)	77.89(13)
O(3)–Re(1)–O(4)	85.5(2)	85.34(13)
O(3)–Re(1)–O(5A)	94.9(3)	94.24(13)
O(5)–Re(1)–O(5A)	104.2(2)	104.30(12)
Re(1)–O(2)–Na/K(1)	110.1(3)	113.47(14)
Re(1)–O(4)–Na/K(1)	109.0(3)	112.63(13)
O(2)–Na/K(1)–O(4)	64.5(3)	56.01(10)
N(1)–Na/K(1)–N(2)	100.8(4)	107.9(4)
Re(1)–O(5)–Re(1A)	75.8(2)	75.70(12)



Scheme 2. R = *t*Bu; L = *t*BuCN.

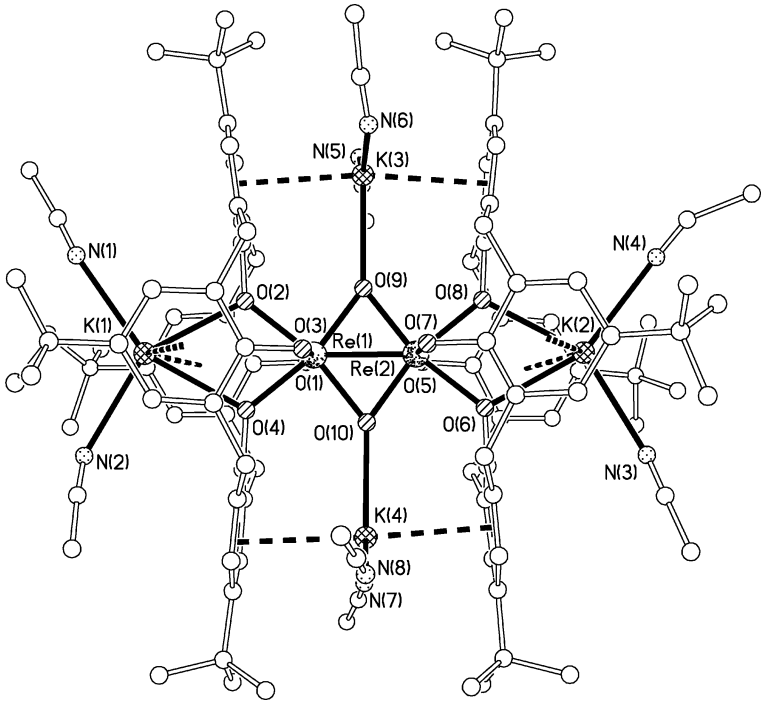


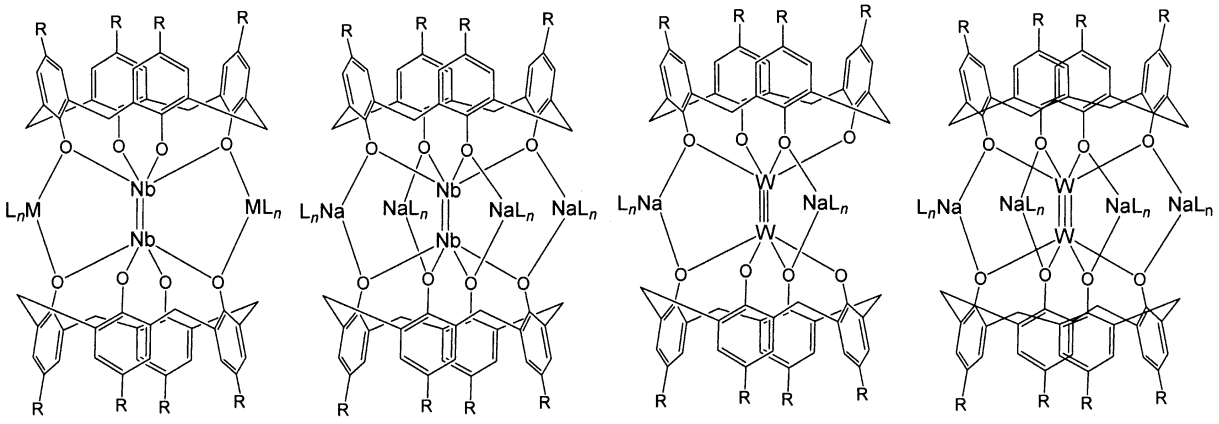
Figure 4. Molecular structure of **7**. H atoms and MeCNs of crystallisation omitted for clarity.

Given that the way the reagents are combined can lead to differing products, we decided to explore also the effect of all three reagents reacting simultaneously in a one-pot reaction. Following work-up, very small red prisms formed in low yield which were suitable for a single-crystal X-ray diffraction study using synchrotron radiation. The product was identified solely by crystallography as $\{ReCax(O)_4K(NCMe)_2[\mu\text{-}OK(NCMe)_2]\}_2Cax(O)_2(OH)_2 \cdot 7MeCN$ (**7**), in which potassium ions, as well as residing in calixarene cavities, are also found to bind to oxo bridges whilst simultaneously being involved in π-interactions with calixarene arene rings (see Figure 4 and Table 4). The overall result for the rhenium-containing portion is a net 2^+ charge, and this is off-set by a co-crystallised calix[4]arene ligand which is doubly deprotonated, i.e. $[Cax(O)_2(OH)_2]^{2-}$. The K^+-to-C_6 ring distances are shorter for the K^+ ions bridging between the rings spanning the Re–Re bond [2.909–2.960 Å], than those inside each pinched calixarene ring [3.131–3.219 Å]. A number of metallocalix[4]arene complexes of niobium and tungsten possessing double (Nb), triple (W) and quadruple (W) metal–metal bonding have been structurally characterised in which similar alkali-metal ion (Li^+, Na^+ or K^+) bridging has been identified (Scheme 3).[21b] The Re–Re bond length [2.3589(6) Å] is slightly shorter than those found in **5** and **6**. The Re_2 cations pack in alternate layers with the co-crystallised calix[4]arene anions residing in the voids.

Table 4. Molecular dimensions in **7** [Å/°].

Re(1)···Re(2)	2.3589(6)		
Re(1)–O(1)	1.976(6)	Re(2)–O(5)	1.972(6)
Re(1)–O(2)	2.012(6)	Re(2)–O(6)	2.010(6)
Re(1)–O(3)	1.987(6)	Re(2)–O(7)	1.992(6)
Re(1)–O(4)	2.000(6)	Re(2)–O(8)	1.993(6)
Re(1)–O(9)	1.928(6)	Re(2)–O(9)	1.948(6)
Re(1)–O(10)	1.973(6)	Re(2)–O(10)	1.940(6)
Re(1)···K(1)	3.889(3)	Re(2)···K(2)	3.879(3)
O(2)–K(1)	2.602(7)	O(6)–K(2)	2.627(7)
O(4)–K(1)	2.675(7)	O(8)–K(2)	2.637(6)
K(1)–N(1)	2.748(15)	K(2)–N(3)	2.774(11)
K(1)–N(2)	2.736(17)	K(2)–N(4)	2.83(2)
O(9)–K(3)	2.645(6)	O(10)–K(4)	2.632(7)
K(3)–N(5)	2.836(10)	K(4)–N(7)	2.913(16)
K(3)–N(6)	2.728(14)	K(4)–N(8)	2.900(14)
O(1)–Re(1)–O(3)	167.9(3)	O(5)–Re(2)–O(7)	168.1(3)
O(1)–Re(1)–O(4)	85.7(3)	O(5)–Re(2)–O(8)	83.8(2)
O(1)–Re(1)–O(10)	93.8(3)	O(5)–Re(2)–O(9)	93.6(2)
O(2)–Re(1)–O(4)	77.3(2)	O(6)–Re(2)–O(8)	77.3(2)
O(9)–Re(1)–O(10)	105.2(3)	O(9)–Re(2)–O(10)	105.7(3)
Re(1)–O(2)–K(1)	114.3(2)	Re(2)–O(6)–K(2)	112.9(3)
Re(1)–O(4)–K(1)	111.7(2)	Re(2)–O(8)–K(2)	113.1(2)
O(2)–K(1)–O(4)	56.66(19)	O(6)–K(2)–O(8)	56.74(19)
N(1)–K(1)–N(2)	114.3(7)	N(3)–K(2)–N(4)	112.5(6)
Re(1)–O(9)–Re(2)	75.0(2)	Re(1)–O(10)–Re(2)	74.1(2)
Re(1)–O(9)–K(3)	143.2(3)	Re(1)–O(10)–K(4)	141.0(3)
Re(2)–O(9)–K(3)	141.8(3)	Re(2)–O(10)–K(4)	144.5(3)
O(9)–K(3)–N(5)	109.0(3)	O(10)–K(4)–N(7)	107.5(5)
O(9)–K(3)–N(6)	103.6(4)	O(10)–K(4)–N(8)	110.3(3)
N(5)–K(3)–N(6)	147.4(5)	N(7)–K(4)–N(8)	142.2(6)

The use of $[Re(O)(PPh_3)Cax(O)_4M(NCMe)_2]$ (**2**) as starting material gave, following prolonged heating in toluene and recrystallisation from acetonitrile, large dark crystals of $\{[Re(O)Cax(O)_4K(NCMe)_2]_2(\mu\text{-}O)\}$ (**8**). The molecular structure is shown in Figure 5 (bond lengths and angles are given in Table 5) and reveals a centrosymmetric complex with a linear oxo bridge providing the centre of symmetry;



Scheme 3. R = *t*Bu; M = Li, Na, K; L_n = solvent (THF, DME or pyridine).

a band at ca. 695 cm^{-1} is tentatively assigned to this stretch vibration in the IR spectrum, with a strong band for the *v*Re=O stretch vibration at 1028 cm^{-1}. The geometry at each rhenium is reminiscent of that found in **4**, whereby the octahedral geometry is completed by the bridging (*cis*) oxo group. As expected, the rhenium–oxo bond length [Re(1)–O(5)] to the bridging oxo group [1.85885(10) Å] is somewhat longer than that observed to the terminal oxo group [1.6949(17) Å]. The calix[4]arene, as in **4**, is similarly pinched by the incorporation of the potassium cation in each cavity.

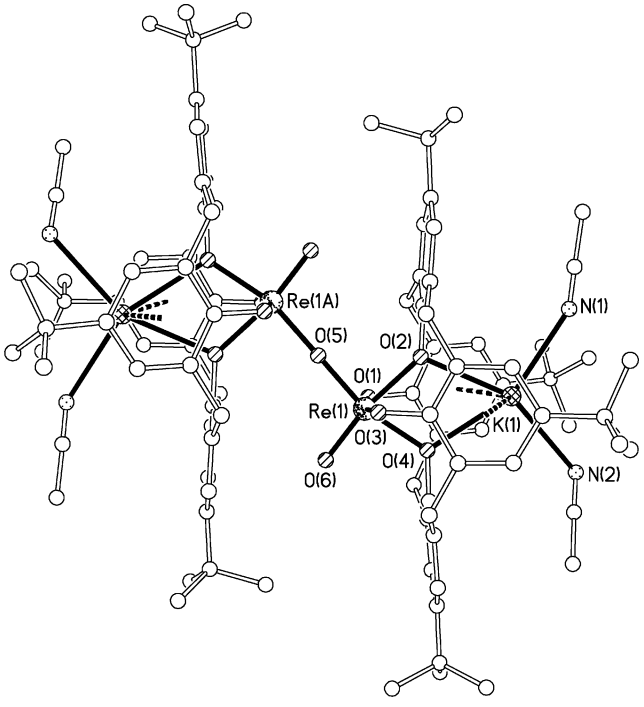


Figure 5. Molecular structure of **8**. H atoms and MeCNs of crystallisation omitted for clarity.

Table 5. Molecular dimensions in **8** [Å/°].

Re(1)–O(1)	1.9967(16)
Re(1)–O(2)	2.0035(15)
Re(1)–O(3)	2.0064(16)
Re(1)–O(4)	1.9878(15)
Re(1)–O(5)	1.85885(10)
Re(1)–O(6)	1.6949(17)
Re(1)···K(1)	3.8982(5)
K(1)–O(2)	2.6373(16)
K(1)–O(4)	2.6386(17)
K(1)–N(1)	2.749(3)
K(1)–N(2)	2.816(3)
O(1)–Re(1)–O(2)	83.23(6)
O(1)–Re(1)–O(3)	165.80(7)
O(1)–Re(1)–O(5)	89.84(5)
O(1)–Re(1)–O(2)	101.60(6)
O(2)–Re(1)–O(4)	76.40(6)
Re(1)–O(2)–K(1)	113.58(6)
Re(1)–O(4)–K(1)	114.09(7)
O(2)–K(1)–O(4)	55.79(5)
N(1)–K(1)–N(2)	106.98(11)
Re(1)···Re(1A)	3.7177(2)
Re(1)–O(1)–Re(1A)	180.0

Imido Chemistry

Given the complexity of these "oxo" reactions, we turned our attention to the isoelectronic organoimido group. For technetium, organoimido [Tc=NAr], hydrazido(2–) [Tc=NNR_2] and diazenide [Tc–N=NAr] complexes are attracting growing attention.[2] This is principally because selectivity may be further enhanced by means of fixation to a suitable biologically active fragment, and with this in mind we note that rhenium complexes bearing highly functionalised imido substituents (structural analogues of the anti-cancer drug chlorambucil) have been prepared.[22] We note however, that calixarene-containing organoimido complexes of rhenium have not previously been reported.[23]

We have focussed our initial studies on *tert*-butylimido species, [N*t*Bu], because such species are likely to be pivatol to our future chemistry in that they are known to readily

undergo imido exchange reactions. This synthetic procedure has been shown to be quite general and has been used to exchange *tert*-butyl groups for aryl groups for a variety of metals from titanium through to iridium.[24] Indeed, this exchange reaction has also been extended to include hydrazido(2–) ligands.[25]

Reaction of $[Re(N\textit{t}Bu)_2Cl_3]$ with $Cax(OH)_4$ in a 1:1 ratio afforded, upon recrystallisation from acetonitrile, the orange complex $[Re(N\textit{t}Bu)_2ClCax(O)_2(OH)_2]\cdot MeCN$ (**9**) in ca. 55% yield. The structure of **9** shown in Figure 6, Scheme 4 (selected bond lengths and angles are given in Table 6), as determined by synchrotron radiation, reveals a distorted trigonal-bipyramidal rhenium centre. The calix[4]-arene acts as a chelate ligand, binding through only O(1) and O(2) (bite angle ca. 81°); the latter is also involved in intramolecular H-bonding, acting as an H-bond acceptor from a hydrogen atom on one of the two remaining calixarene phenolic groups. The two *cis* imido groups are very different, with that involving N(1) being best described as bent [Re(1)–N(1)–C(45) 143.7(2)°], whilst the other is near linear [Re(1)–N(2)–C(49) 170.5(2)°]. The Re–Cl bond length is 2.3687(8) Å. There is one molecule of acetonitrile associated with the complex and this resides within the $Cax(O)_2(OH)_2$ cavity.

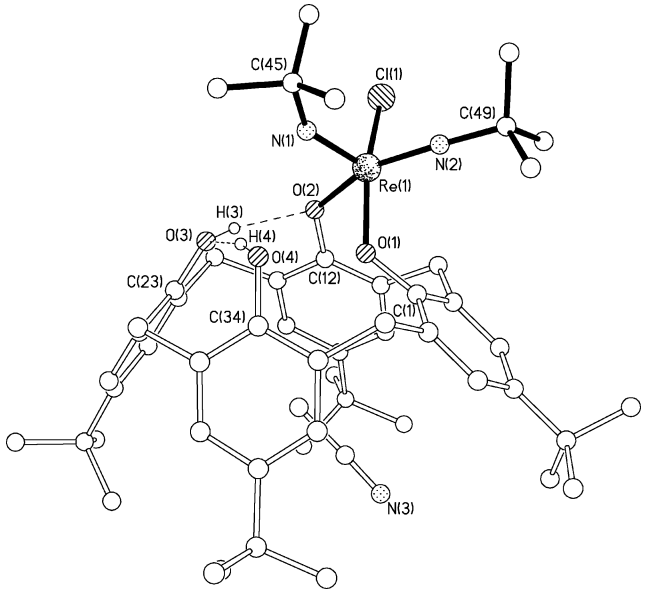
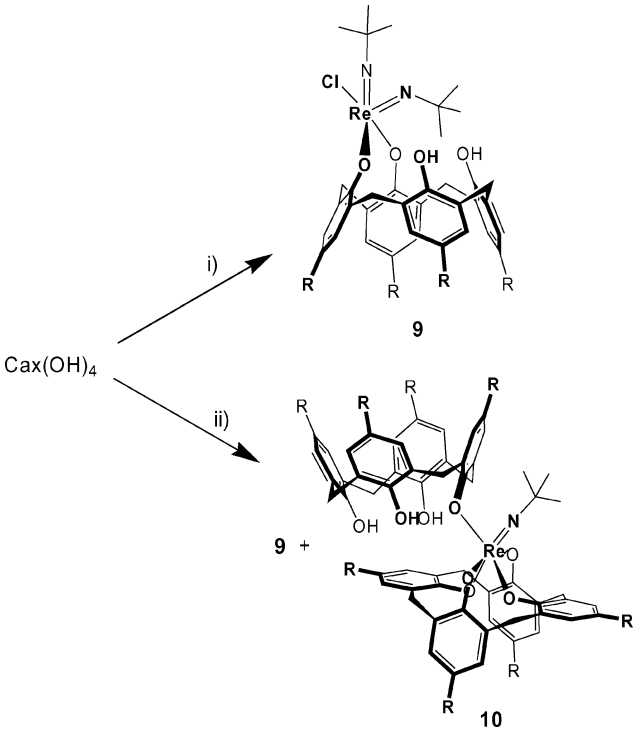


Figure 6. Molecular structure of **9**. Most H atoms omitted for clarity.



Scheme 4. Synthesis of complexes **9** and **10**. Reagents and conditions: (i) $Cax(OH)_4$, $[Re(N\textit{t}Bu)_2Cl_3]$, toluene, reflux, 12 h. (ii) 3 $Cax(OH)_4$, 2 $[Re(N\textit{t}Bu)_2Cl_3]$, toluene, reflux, 12 h.

Table 6. Molecular dimensions in **9** [Å/°].

Re(1)–O(1)	1.9421(19)
Re(1)–O(2)	1.9895(19)
Re(1)–N(1)	1.736(2)
Re(1)–N(2)	1.726(2)
Re(1)–Cl(1)	2.3687(8)
O(1)–Re(1)–O(2)	80.98(8)
N(1)–Re(1)–O(1)	100.41(10)
N(1)–Re(1)–O(2)	98.73(10)
N(2)–Re(1)–O(1)	96.07(10)
N(2)–Re(1)–O(2)	153.67(11)
N(1)–Re(1)–N(2)	107.51(12)
N(1)–Re(1)–Cl(1)	102.03(8)
N(2)–Re(1)–Cl(1)	89.48(9)
O(1)–Re(1)–Cl(1)	154.05(6)
O(2)–Re(1)–Cl(1)	82.88(6)

Hydrogen bonds

D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	<(DHA)
O(3)–H(3)···O(2)	0.84	2.04	2.864(3)	164.9
O(4)–H(4)···O(3)	0.84	1.93	2.749(3)	164.2

On increasing the amount of $Cax(OH)_4$ in this reaction, orange **9** is obtained along with dark red $[Re(N\textit{t}Bu)Cax(O)_4Cax(O)(OH)_3]\cdot 6MeCN$ (**10**) (see Scheme 4). Crops of analytically pure **10** can be obtained by further concentration and cooling of the mother liquor; total yield of **10** is 42%. Analytically pure **9** can be obtained by washing the mixture with cold hexane. In **10**, the rhenium centre is pseudooctahedral and is coordinated by two very different calix[4]arene ligands (Figure 7 and Table 7). One is fully deprotonated, i.e. $Cax(O)_4$, binding in a tetradentate fashion to rhenium, and surprisingly, given the absence of alkali-metal cations, adopts an elliptical conformation. The kink observed at O(1) is reminiscent of the situation found in the complexes $[V(X)Cax(O)_3(OMe)]$ (X = O, N*p*tolyl) and $[MoO_2Cax(OMe)_2(O)_2]$.[26,27] The second calix[4]arene is monodentate and retains the cone conformation, and there is intramolecular H-bonding involving the remaining phenolic groups. A linear imido group [Re(1)–N(1)–C(89) 178.4(2)°] completes the coordination at rhenium.

Carrying out this reaction in the presence of adventitious oxygen led to an oxo-bridged complex $\{[Re(N\textit{t}Bu)Cax(O)_4]_2(\mu\text{-}O)\}$ (**11**) (Figure 8, Table 8) which can be consid-

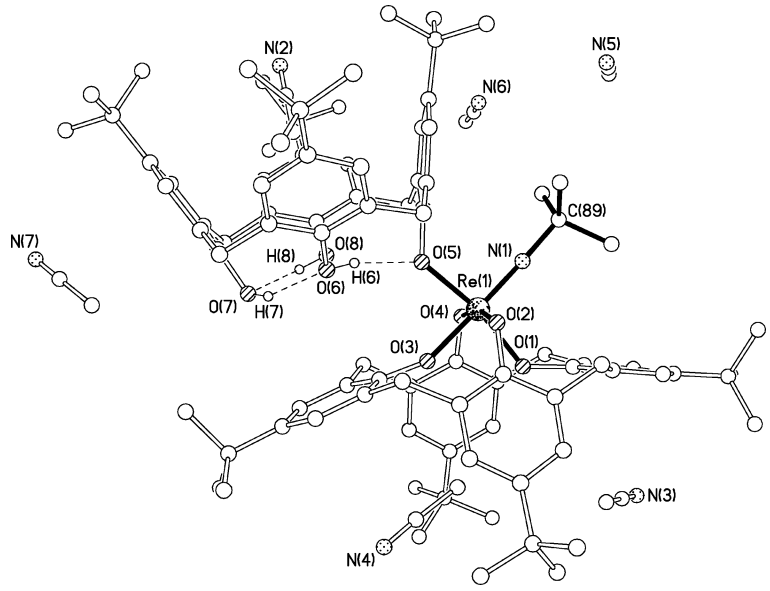


Figure 7. Molecular structure of **10**. Most H atoms omitted for clarity.

Table 7. Molecular dimensions in **10** [Å/°].

Re(1)–O(1)	1.9365(19)			
Re(1)–O(2)	1.948(2)			
Re(1)–O(3)	1.9047(19)			
Re(1)–O(4)	1.9448(19)			
Re(1)–O(5)	1.9524(19)			
Re(1)–N(1)	1.729(2)			
O(1)–Re(1)–O(3)	83.88(8)			
O(2)–Re(1)–O(3)	84.75(8)			
O(2)–Re(1)–O(4)	164.29(8)			
O(2)–Re(1)–O(5)	93.56(8)			
N(1)–Re(1)–O(5)	94.54(10)			
Hydrogen bonds				
D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	<(DHA)
O(6)–H(6)···O(5)	0.84	2.14	2.968(3)	169.0
O(7)–H(7)···O(6)	0.84	1.93	2.697(3)	151.1
O(8)–H(8)···O(7)	0.84	1.91	2.697(3)	155.5

ered to be an imido analogue of **8** (minus the alkali metals). Crystals of **11** suitable for a structure determination using synchrotron radiation were obtained from a saturated acetonitrile solution at ambient temperature. Each rhenium centre is distorted octahedral, coordinated by the four oxygen atoms of a splayed-out $Cax(O)_4$ ligand, a linear *tert*-butylimido group [Re–N–C 168.3(3) and 171.8(3)°], and linked together by a bent Re(1)–O(9)–Re(2) [152.31(19)°] bridge; Re(1/2)–O(9) distances 1.904(3) and 1.910(3) Å, respectively. In the IR spectrum, a band at 722 cm^{-1} is tentatively assigned to the *v*Re–O–Re stretch vibration. For adjacent molecules of **11**, the calixarenes align in a slipped cup-to-cup fashion, with each cup being filled by a *t*Bu group of the facing $Cax(O)_4$ ligand and a disordered acetonitrile molecule. Overall, for each Re_2 unit, there are three acetonitrile molecules, two of which are disordered.

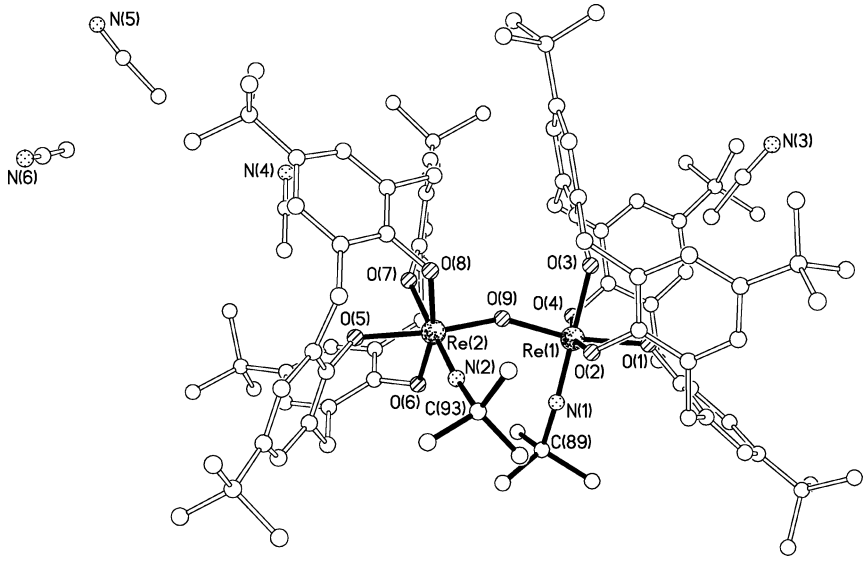
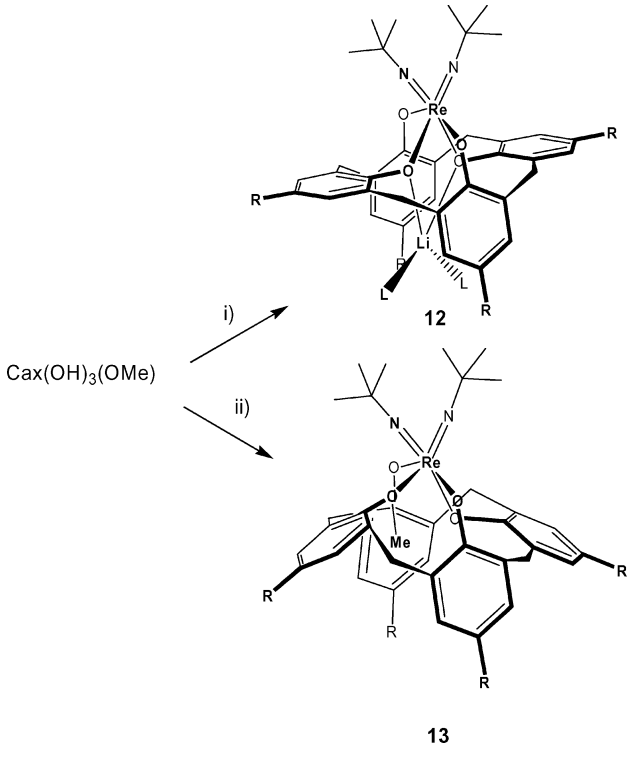


Figure 8. Molecular structure of **11**. H atoms omitted for clarity.

Table 8. Molecular dimensions in **11** [Å/°].

Re(1)–O(1)	1.944(3)	Re(2)–O(5)	1.948(3)
Re(1)–O(2)	1.949(3)	Re(2)–O(6)	1.955(3)
Re(1)–O(3)	1.924(3)	Re(2)–O(7)	1.923(3)
Re(1)–O(4)	1.947(3)	Re(2)–O(8)	1.949(3)
Re(1)–N(1)	1.734(4)	Re(2)–N(2)	1.739(4)
Re(1)–O(9)	1.904(3)	Re(2)–O(9)	1.910(3)
O(1)–Re(1)–O(3)		82.13(12)	
O(2)–Re(1)–O(4)		164.51(12)	
O(3)–Re(1)–O(4)		84.39(12)	
O(4)–Re(1)–O(9)		100.75(13)	
N(1)–Re(1)–O(9)		95.87(15)	
Re(1)–O(9)–Re(2)		152.31(19)	
O(5)–Re(2)–O(7)		81.03(12)	
O(6)–Re(2)–O(8)		165.08(12)	
O(7)–Re(2)–O(8)		84.52(12)	
O(8)–Re(2)–O(9)		99.34(13)	
N(2)–Re(2)–O(9)		96.29(15)	

In an attempt to favour monomeric complex formation, $Cax(OLi)_3(OMe)$ was treated with $[Re(N\textit{t}Bu)_2Cl_3]$ (Scheme 5) affording, after work-up, small yellow prisms in good yield (ca. 60%). An X-ray synchrotron study reveals (Figure 9, Table 9) a 50:50 mixture of mono- and bis-ligated acetonitrile species, such that the correct formula is best represented as $[Re(N\textit{t}Bu)_2Cax(O)_4Li(NCMe)_2][Re(N\textit{t}Bu)_2Cax(O)_4Li(NCMe)]\cdot 2MeCN$ (**12**). The rhenium centres are pseudooctahedral and are bound by linear *cis* imido groups [Re–N–C ca. 169°] and by a $Cax(O)_4$ ligand possessing an elliptical conformation; each acetonitrile-ligated lithium centre resides in a $Cax(O)_4$ cavity. Such Lewis acid assisted cleavage of the ether calixarene functionality has been noted previously by Floriani.[28]



Scheme 5. Synthesis of complexes **12** and **13**. Reagents and conditions: (i) (a) *n*BuLi, diethyl ether, –78 °C, 6 h; (b) $[Re(N\textit{t}Bu)_2Cl_3]$, toluene, reflux, 6 h, crystallisation from MeCN. (ii) $[Re(N\textit{t}Bu)_3(OSiMe_3)]$, toluene, reflux, 12 h; crystallisation from MeCN.

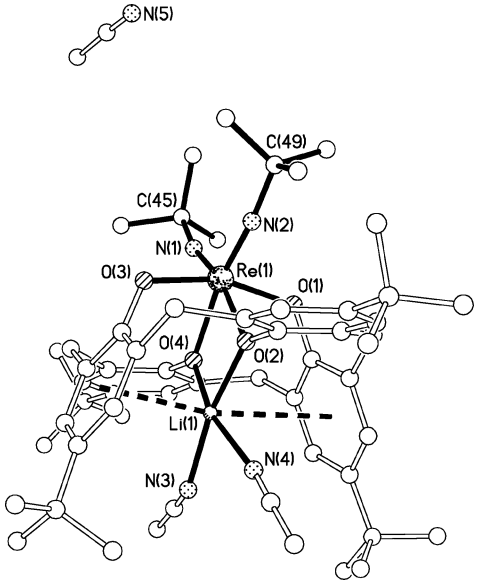


Figure 9. Molecular structure of **12**. Bis(acetonitrile) structure only is shown. H atoms omitted for clarity.

Table 9. Molecular dimensions in **12** [Å/°].

Re(1)–O(1)	2.0177(16)
Re(1)–O(2)	2.0834(16)
Re(1)–O(3)	2.0053(16)
Re(1)–O(4)	2.0784(15)
Re(1)–N(1)	1.738(2)
Re(1)–N(2)	1.740(2)
Re(1)···Li(1)	3.167(5)
O(2)–Li(1)	1.904(5)
O(4)–Li(1)	1.910(6)
Li(1)–N(3)	2.040(6)
Li(1)–N(4)	2.194(8)
O(1)–Re(1)–O(2)	82.76(7)
O(1)–Re(1)–O(3)	161.41(7)
O(2)–Re(1)–O(4)	70.78(6)
O(1)–Re(1)–N(2)	96.06(8)
N(1)–Re(1)–N(2)	105.28(10)
Li(1)–O(2)–Re(1)	105.05(18)
Li(1)–O(4)–Re(1)	105.04(15)
O(2)–Li(1)–O(4)	78.4(2)
N(3)–Li(1)–N(4)	85.8(3)

To avoid lithium incorporation, $Cax(OH)_3(OMe)$ was treated with $[Re(N\textit{t}Bu)_3(OSiMe_3)]$ affording after work-up, orange prisms in good yield (ca. 70%) (Scheme 5). The structure (Figure 10, Table 10), as determined by synchrotron radiation, reveals the complex $[Re(N\textit{t}Bu)_2Cax(O)_3(OMe)]$ (**13**), which contains a pseudooctahedral rhenium centre bound to a fully deprotonated $Cax(O)_3(OMe)$ adopting a conformation with the rings bound by O(1) and O(3) severely splayed out and those bound at O(2) and O(4) in the usual cone "down" position. The conformation displayed here by **13** is somewhat more distorted from cone than that of the *cis,paco*-2′ (or 1′) observed by Radius[27] for the complex $[MoO_2Cax(OMe)_2(O)_2]$, and is better de-

scribed as an elliptical cone similar to those observed in **1**–**8**. This perhaps explains the difference in the ^{1}H NMR spectroscopic data for **13** vs. the Radius complexes, with a far more complex methylene region in **13**, together with the lack of a large shift for any endohedrally coordinated ether group (δ_{OMe} = 0.78 (3 H) and 4.55 (3 H) ppm for $[MoO_2Cax(OMe)_2(O)_2]$ cf. 3.79 ppm in **13**). The coordination at rhenium is completed by two imido groups, with that to N(1) more closely approaching linearity [Re(1)–N(1)–C(46) 173.34(12)° cf. Re(1)–N(2)–C(50) 159.92(12)°]. There is no solvent of crystallisation, however, zig-zag stacks of **13** form along *a* in an anti-parallel fashion. In the IR spectra of **12** and **13**, bands at ca. 1304 cm^{-1} are assigned to the *ν*Re–N–C stretch vibration.

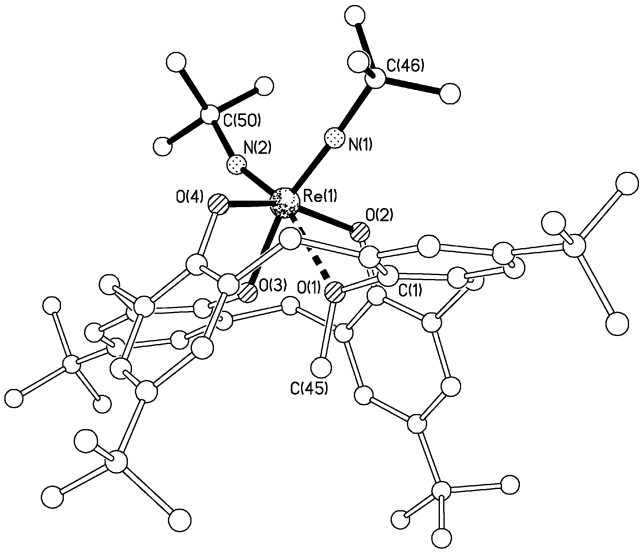


Figure 10. Molecular structure of **13**. H atoms omitted for clarity.

Table 10. Molecular dimensions in **13** [Å/°].

Re(1)–O(1)	2.4010(10)
Re(1)–O(2)	1.9847(10)
Re(1)–O(3)	1.9871(9)
Re(1)–O(4)	1.9780(10)
Re(1)–N(1)	1.7489(12)
Re(1)–N(2)	1.7288(12)
O(1)–Re(1)–O(3)	68.03(3)
O(2)–Re(1)–O(4)	156.98(5)
O(3)–Re(1)–O(4)	84.44(4)
N(2)–Re(1)–O(4)	99.85(5)
N(1)–Re(1)–N(2)	105.93(6)

Conclusions

In conclusion, a number of unusual products with novel structural features have been isolated from reactions between high valent oxo or organoimido rhenium precursors and the calix[4]arene ligands $Cax(OH)_4$ and $Cax(OH)_3$(OMe). These complexes represent rare examples of rhenium bound directly to a calixarene frame. The complex nature of many of these reactions and their products coupled with issues of air and moisture sensitivity preclude the use of many of these new complexes as potential imaging and/or therapy agents. However, we are now focussing our attention on complex $[Re(NtBu)_2Cax(O)_3(OMe)]$ (**13**), as a potential entry into a new class of imaging and therapy agent due both to its facile synthesis and comparatively simple structure. Our calixarene scaffolds are not in themselves toxic as demonstrated using cell culture,[29] and we are now poised to take advantage of imido exchange protocol to construct systems with useful biological (and solubility) properties.

Experimental Section

General: All manipulations were carried out under nitrogen using standard Schlenk and cannula techniques or in a conventional nitrogen-filled glove-box. Solvents were refluxed in the presence of an appropriate drying agent, and distilled and degassed prior to use. Elemental analyses were performed by the microanalytical services of the School of Chemical Sciences and Pharmacy at The University of East Anglia or Medac Ltd. ^{1}H NMR spectra were recorded with a Varian VXR 400 S spectrometer at 400 or a Gemini at 300 MHz at 298 K unless otherwise stated; chemical shifts are referenced to the residual protio impurity of the deuterated solvent. IR spectra (nujol mulls, KBr/CsI windows), Perkin–Elmer 577 and 457 grating spectrophotometers. The precursors $[ReOCl_3(PPh_3)_2]$, $[Re(NtBu)_2Cl_3]$ and $[Re(NtBu)_3(OSiMe_3)]$ were made by the methods of Wilkinson, Nugent and Schrock.[30] The ligands $Cax(OH)_4$ and $Cax(OH)_3(OMe)$ were prepared by the previously published procedures.[9,27] All other chemicals were obtained commercially and used as received unless stated otherwise. Rhenium powder was purchased from China Rhenium Ltd.

Complex Syntheses

Preparation of $[Re(O)(PPh_3)Cax(O)_4Na(NCMe)_2]\cdot 4MeCN$ (1): A mixture of NaO*t*Bu (0.23 g, 2.39 mmol) and $Cax(OH)_4$ (0.33 g, 0.51 mmol) was stirred in toluene (20 mL) for 30 min. $[ReOCl_3(PPh_3)_2]$ (0.42 g, 0.50 mmol) in toluene (20 mL) was added to the resultant white suspension and stirring was continued for a further 12 h. Following filtration, volatiles were removed in vacuo and the residue was taken up in acetonitrile (40 mL). Concentration (to ca. 10 mL) and prolonged standing (1–2 d) at ambient temperature afforded green crystals of **1** (0.10 g, 16.5% yield). $C_{64}H_{70}NO_5PNaRe$ (1173.39, sample dried in vacuo, i.e. –5MeCN): calcd. C 65.51, H 6.01, N 1.19; found C 65.47, H 6.02, N 0.61. MS (E.S. negative): *m*/*z* = 1108 [M$^+$ – Na]. IR: $\tilde{\nu}$ = 2267 (w), 2248 (w), 1313 (m), 1283 (m), 1260 (s), 1206 (s), 1169 (w), 1156 (w), 1095 (s, br.), 1019 (s, br.), 957 (m), 926 (m), 913 (w), 875 (w), 854 (m), 835 (m), 820 (s), 807 (s), 771 (w), 758 (w), 741 (m), 723 (m), 706 (w), 694 (m), 666 (w) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ = 7.72 (m, 6 H, aryl *H*), 7.22 (m, 9 H, aryl *H*), 7.04 (d, $^3J_{HH}$ = 2.6 Hz, 2 H, aryl *H*), 7.01 (s, 2 H, aryl *H*), 6.77 (s, 2 H, aryl *H*), 6.63 (d, $^3J_{HH}$ = 2.7 Hz, 2 H, aryl *H*), 4.64 (d, $^2J_{HH}$ = 14.2 Hz, 2 H, *endo*-C*H*$_2$), 3.62 (d, $^2J_{HH}$ = 12.8 Hz, 2 H, *endo*-C*H*$_2$), 3.27 (d, $^2J_{HH}$ = 14.2 Hz, 2 H, *exo*-C*H*$_2$), 2.52 (d, $^2J_{HH}$ = 12.8 Hz, 2 H, *exo*-C*H*$_2$), 1.25 [s, 9 H, C(C*H*$_3$)$_3$], 1.24 [s, 9 H, C(C*H*$_3$)$_3$], 1.02 [s, 18 H, C(C*H*$_3$)$_3$] ppm. ^{31}P NMR (CD_2Cl_2): δ = –27.6 ppm.

Preparation of $[Re(O)(PPh_3)Cax(O)_4K(NCMe)_2]\cdot 4MeCN$ (2): As for **1**, but using KO*t*Bu (0.27 g, 2.41 mmol), $Cax(OH)_4$ (0.33 g, 0.51 mmol) and $[ReOCl_3(PPh_3)_2]$ (0.42 g, 0.50 mmol) affording **2** as banana-yellow crystals (0.24 g, 35%). $C_{66}H_{73}KN_2O_5PRe$ (1230.55, sample dried in vacuo for 12 h): calcd. C 64.44, H 6.01, N 2.30; found C 64.99, H 5.91, N 1.59. MS (E.S. negative): *m*/*z* = 1109

[M^+ – K], 847 [M^+ – K – PPh_3]. IR: $\tilde{\nu}$ = 2360 (m), 2342 (m), 1314 (m), 1283 (w), 1261 (s), 1207 (m), 1152 (w), 1097 (s, br.), 1020 (s, br.), 925 (m), 801 (s), 722 (m), 694 (m), 668 (m) cm^{-1}. ^1H NMR (CD_2Cl_2): δ = 7.72 (m, 6 H, aryl *H*), 7.22 (m, 9 H, aryl *H*), 7.04 (d, $^3J_{HH}$ = 2.8 Hz, 2 H, aryl *H*), 7.02 (s, 2 H, aryl *H*), 6.75 (s, 2 H, aryl *H*), 6.61 (d, $^3J_{HH}$ = 2.8 Hz, 2 H, aryl *H*), 4.60 (d, $^2J_{HH}$ = 14.4 Hz, 2 H, *endo*-CH_2), 3.62 (d, $^2J_{HH}$ = 13.0 Hz, 2 H, *endo*-CH_2), 3.23 (d, $^2J_{HH}$ = 14.4 Hz, 2 H, *exo*-CH_2), 2.50 (d, $^2J_{HH}$ = 13.0 Hz, 2 H, *exo*-CH_2), 1.26 [s, 9 H, C(CH_3)$_3$], 1.24 [s, 9 H, C(CH_3)$_3$], 1.02 [s, 18 H, C(CH_3)$_3$] ppm. ^{31}P NMR (CD_2Cl_2): δ = –27.8 ppm.

Preparation of [Re(O)$_2$Cax(O)$_4$Na(NCMe)$_2$]·2.8MeCN (3): Acetonitrile (40 mL) was added to compound **1** (1.00 g, 0.82 mmol) and the system was refluxed for 48 h. Following filtration, the volume was reduced in vacuo to ca. 20 mL and on prolonged standing at 0 °C red/brown crystals formed. The reaction was conducted in an NMR tube and the conversion of **1** to **3** was near quantitative (> 95%). $C_{53.6}H_{66.4}N_{4.8}NaO_6Re$ (1083.92): calcd. C 59.39, H 6.17, N 6.20; found C 58.94, H 6.03, N 6.41. MS (E.S. positive mode): *m*/*z* = 911 [M^+ – MeCN – O]. IR: $\tilde{\nu}$ = 2351 (w), 1626 (w), 1604 (w), 1312 (w), 1260 (s), 1202 (m), 1093 (s, br.), 1020 (s, br.), 935 (w), 906 (w), 876 (w), 845 (m), 802 (s), 756 (w), 722 (w), 701 (w) cm^{-1}. ^1H NMR (CD_2Cl_2): δ = 7.11 (s, 4 H, aryl *H*), 7.08 (d, 4 H, aryl *H*), 4.42 (d, $^2J_{HH}$ = 14.4 Hz, 4 H, *endo*-CH_2), 3.42 (d, $^2J_{HH}$ = 14.4 Hz, 4 H, *exo*-CH_2), 1.28 [s, 18 H, C(CH_3)$_3$], 1.10 [s, 18 H, C(CH_3)$_3$] ppm.

Preparation of [Re(O)$_2$Cax(O)$_4$K(NCMe)$_2$]·3MeCN (4): Prepared as for **3**, but using **2**. Again by NMR the conversion of **2** to **4** was near quantitative. $C_{54}H_{67}KN_5O_6Re$ (1107.43): calcd. C 58.56, H 6.10, N 6.33; found C 57.44, H 6.04, N 6.41. MS (E.S. negative mode): *m*/*z* = 863 [M^+ – K]. IR: $\tilde{\nu}$ = 2258 (w), 2243 (w), 1619 (w), 1592 (w), 1574 (w), 1412 (m), 1362 (s), 1313 (s), 1297 (m), 1284 (m), 1254 (s), 1203 (s), 1117 (m), 1104 (m), 1026 (m), 997 (w), 931 (m), 911 (s), 874 (m), 848 (w), 832 (s), 804 (s), 759 (s), 723 (m), 696 (m), 676 (w), 666 (w), 647 (m) cm^{-1}. ^1H NMR (CD_2Cl_2): δ = 7.10 (s, 4 H, aryl *H*), 7.06 (d, $^3J_{HH}$ = 2.4 Hz, 4 H, aryl *H*), 4.40 (d, $^2J_{HH}$ = 14.4 Hz, 4 H, *endo*-CH_2), 3.39 (d, $^2J_{HH}$ = 14.4 Hz, 4 H, *exo*-CH_2), 1.29 [s, 18 H, C(CH_3)$_3$], 1.10 [s, 18 H, C(CH_3)$_3$] ppm.

Preparation of [ReCax(O)$_4$Na(NCMe)$_2$(μ-O)]$_2$·4MeCN (5) and [ReCax(O)$_4$K(NCMe)$_2$(μ-O)]$_2$·4MeCN (6): [$ReOCl_3(PPh_3)_2$] (0.42 g, 0.50 mmol) and excess MO*t*Bu (2.00 mmol) were combined in dichloromethane at –78 °C. The suspension was warmed to ambient temperature and stirring was continued for 4 h. Following removal of volatiles in vacuo, $Cax(OH)_4$ (0.32 g, 0.49 mmol) in toluene (30 mL) was added. The system was refluxed for 12 h, volatiles were removed in vacuo and the residue was extracted into warm MeCN (40 mL). Prolonged standing (1–2 d) at ambient temperature afforded yellow/brown prisms of either **3** (for M = Na) or **4** (for M = K), together with brown/red prisms of the respective dimer (**5**, M = Na; **6**, M = K). The similar solubility of **3** with **5** and of **4** with **6**, precluded fractional crystallisation and it was necessary to physically/manually separate the species. Yield **5** (ca. 0.15 g, 22%), **6** (ca. 0.12 g, 17%, based on rhenium). $C_{104}H_{128}N_8Na_2O_{10}Re_2$ (2068.52): calcd. C 60.38, H 6.24, N 5.42; found C 60.61, H 6.31, N 5.73. MS (Maldi): *m*/*z* = 1913 [M^+ – 2O – 3MeCN], 1754 [M^+ – Re – 2Na – 2MeCN], 1738 [M^+ – Re – O – 2Na – 2MeCN], 1722 [M^+ – Re – 2O – 2Na – 2MeCN]. IR: $\tilde{\nu}$ = 2295 (w), 2268 (w), 2249 (w), 1608 (w), 1586 (w), 1306 (m), 1282 (m), 1261 (s), 1205 (s), 1153 (m), 1095 (s, br.), 1020 (s, br.), 909 (m), 870 (m), 819 (s), 804 (s), 757 (w), 742 (m), 723 (w), 695 (m), 541 (s) cm^{-1}. ^1H NMR (C_6D_6, 400 MHz, sample dried in vacuo prior to): δ = 7.15–6.80 (several br. m, 16 H, aryl *H*), 4.43 (br. m, 8 H, *endo*-CH_2), 3.00 (br. m, 8 H, *exo*-CH_2), 1.84 (s, 9 H, 3 *Me*CN), 0.93 [br. s, 36 H, C(CH_3)$_3$], 0.06 (s, 16 H, 4 *Me*CN) ppm. $C_{104}H_{128}K_2N_8O_{10}Re_2$ (2100.74): calcd. C 59.46, H 6.14, N 5.34; found C 59.52, H 6.11, N 5.33. MS (Maldi): *m*/*z* = 1841 [M^+ – O – K – 5MeCN], 1759 [M^+ – O – K – 7MeCN]. IR: $\tilde{\nu}$ = 2280 (w), 2252 (w), 1592 (w), 1312 (m), 1278 (w), 1260 (s), 1203 (m), 1095 (s, br.), 1020 (s, br.), 932 (w), 912 (m), 873 (w), 803 (s), 759 (w), 722 (w), 695 (w) cm^{-1}. ^1H NMR (C_6D_6, 400 MHz, sample dried in vacuo prior to addition of C_6D_6): δ = 7.21–6.73 (several br. m, 16 H, aryl *H*), 4.10 (br. m, 8 H, *endo*-CH_2), 3.02 (br. m, 8 H, *exo*-CH_2), 1.81 (s, 9 H, 3 *Me*CN), 0.87–0.82 [2 br. s, 36 H C(CH_3)$_3$], 0.00 (s, 9 H, 3 *Me*CN) ppm.

Preparation of {ReCax(O)$_4$K(NCMe)$_2$[μ-OK(NCMe)$_2$]}$_2$Cax(O)$_2$(OH)$_2$·7MeCN (7): [$ReOCl_3(PPh_3)_2$] (0.42 g, 0.50 mmol), excess MO*t*Bu (2.00 mmol) and $Cax(OH)_4$ (0.32 g, 0.49 mmol) were refluxed in toluene (10 mL) for 12 h. On cooling, volatile components were removed in vacuo, and the residue was extracted into warm MeCN (10 mL). Prolonged standing at ambient temperature afforded small red prisms. Yield < 5%.

Preparation of {[Re(O)Cax(O)$_4$K(NCMe)$_2$]$_2$(μ-O)}·2MeCN (8): Compound **2** (0.62 g, 0.44 mmol) in toluene (10 mL) was refluxed for 48 h to afford a purple solution. On cooling, the resulting brown solid was removed by filtration, the mother liquor was concentrated to ca. 1 mL, and large dark brown crystals formed on prolonged standing at ambient temperature. Yield 0.23 g, 45%. $C_{96}H_{116}K_2N_4O_{11}Re_2$ (1952.54, sample dried in vacuo for 12 h): calcd. C 59.05, H 5.99, N 2.87; found C 59.11, H 5.93, N 2.04. MS (E.S. positive mode): 1164 [M^+ – O – K – 2MeCN – Cax(O)(OH)$_3$]. IR: $\tilde{\nu}$ = 1586 (w), 1309 (m), 1260 (m), 1171 (s), 1122 (w), 1089 (m), 1071 (m), 1028 (s), 975 (w), 913 (w), 870 (w), 850 (m), 802 (m), 742 (s), 695 (s), 665 (w) cm^{-1}. ^1H NMR (CD_2Cl_2): δ = 7.17–7.04 (m, 8 H, aryl *H*), 6.95–6.19 (m, 8 H, aryl *H*), 4.73 (d, $^2J_{HH}$ = 14.4 Hz, 4 H, *endo*-CH_2), 4.4 (d, $^2J_{HH}$ = 14.4 Hz, 4 H, *endo*-CH_2), 3.27 (d, $^2J_{HH}$ = 14.4 Hz, 4 H, *exo*-CH_2), 3.19 (d, $^2J_{HH}$ = 14.4 Hz, 4 H, *exo*-CH_2), 1.88 (s, 12 H, *Me*CN), 1.25 [s, 18 H, C(CH_3)$_3$], 1.17 [s, 18 H, C(CH_3)$_3$], 1.06 [s, 36 H, C(CH_3)$_3$] ppm.

Preparation of [Re(N*t*Bu)$_2$ClCax(O)$_2$(OH)$_2$]·MeCN (9): [Re(N*t*Bu)$_2$Cl$_3$] (0.67 g, 1.54 mmol) and $Cax(OH)_4$ (1.00 g, 1.54 mmol) in toluene (40 mL) were refluxed for 12 h. On cooling, the volatiles were removed in vacuo, and the residue was extracted into warm MeCN (30 mL). Prolonged standing at ambient temperature (2–3 d) afforded orange **9** (0.92 g, 57%). $C_{54}H_{75}ClN_3O_4Re$ (1051.82): calcd. C 61.66, H 7.19, N 4.00; found C 61.42, H 7.23, N 4.91. MS (E.S. positive mode): *m*/*z* = 1051 [M^+ – H]. IR: $\tilde{\nu}$ = 3385 (w, br.), 3166 (w, br.), 2361 (w), 2337 (w), 1304 (w), 1261 (s), 1199 (w), 1093 (s, br.), 1019 (s, br.), 871 (w), 800 (s), 722 (w), 667 (w) cm^{-1}. ^1H NMR (C_6D_6): δ = 9.53 (s, 1 H, O*H*), 8.60 (s, 1 H, O*H*), 7.04 (m, 3 H, aryl *H*), 6.86 (m, 3 H, aryl *H*), 6.80 (m, 1 H, aryl *H*), 6.61 (m, 1 H, aryl *H*), 4.85 (d, $^2J_{HH}$ = 13.4 Hz, 1 H, *endo*-CH_2), 4.81 (d, $^2J_{HH}$ = 12.1 Hz, 1 H, *endo*-CH_2), 4.62 (d, $^2J_{HH}$ = 13.2 Hz, 1 H, *endo*-CH_2), 4.13 (d, $^2J_{HH}$ = 15.9 Hz, 1 H, *endo*-CH_2), 3.62 (d, $^2J_{HH}$ = 15.9 Hz, 1 H, *exo*-CH_2), 3.35 (d, $^2J_{HH}$ = 13.4 Hz, 1 H, *exo*-CH_2), 3.27 (d, $^2J_{HH}$ = 12.1 Hz, 2 H, *exo*-CH_2), 1.62 [s, 9 H, C(CH_3)$_3$], 1.22 [s, 9 H, C(CH_3)$_3$], 1.17 [s, 9 H, C(CH_3)$_3$], 0.94 [s, 9 H, C(CH_3)$_3$], 0.84 [s, 9 H, C(CH_3)$_3$], 0.80 [s, 9 H, C(CH_3)$_3$] ppm.

Preparation of [Re(N*t*Bu)Cax(O)$_4$Cax(O)(OH)$_3$]·6MeCN (10): [Re(N*t*Bu)$_2$Cl$_3$] (0.67 g, 1.54 mmol) and $Cax(OH)_4$ (1.50 g, 2.31 mmol) in toluene (40 mL) were refluxed for 12 h. On cooling, the volatiles were removed in vacuo, and the residue was extracted into warm MeCN (30 mL). Prolonged standing at ambient temperature (2–3 d) afforded orange **9** (0.22 g, 37%) and dark red **10**; concentration and cooling of the mother liquor afforded further yields of **10** [total yield 0.81 g, 42%, based on $Cax(OH)_4$]. Analytically pure **9** can be obtained from this mixture by washing the

mixture with cold hexane (2 × 20 mL), which removes complex **10**. $C_{104}H_{134}N_7O_8Re$ (1796.38): calcd. C 69.53, H 7.52, N 5.46; found C 69.91, H 7.44, N 5.61. MS (E.S. positive mode): 1641 (M^+ – tBuNH$_2$ – 2MeCN), 993 [M^+ – tBuNH$_2$ – 2MeCN – Cax(OH)$_4$], 943 [M^+ – 5MeCN – Cax(OH)$_4$]. IR: $\tilde{\nu}$ = 3121 (w, br.), 2351 (w), 1606 (w), 1312 (w), 1260 (s), 1207 (s), 1093 (s, br.), 1019 (s, br.), 929 (s), 911 (m), 875 (w), 842 (w), 802 (s), 758 (w), 726 (w) cm^{-1}. ^{1}H NMR (C_6D_6): δ = 9.63 (s, 1 H, O*H*), 9.41 (s, 2 H, O*H*), 7.16–6.58 (6 m, 8 H, aryl *H*), 4.60 (m, 4 H, *endo*-CH_2), 4.23 (d, $^2J_{HH}$ = 12.4 Hz, 2 H, *endo*-CH_2), 4.12 (d, $^2J_{HH}$ = 12.3 Hz, 2 H, *endo*-CH_2), 3.38 (overlapping d, 2 H, *exo*-CH_2), 3.22 (m, 2 H, *exo*-CH_2), 3.03 (overlapping d, 2 H, *exo*-CH_2), 1.13 [s, 9 H, C(CH_3)$_3$], 1.02 [s, 9 H, C(CH_3)$_3$], 0.98 [s, 27 H, C(CH_3)$_3$], 0.82 [s, 9 H, C(CH_3)$_3$], 0.78 [s, 9 H, C(CH_3)$_3$], 0.63 [s, 9 H, C(CH_3)$_3$], 0.54 [s, 9 H, C(CH_3)$_3$] ppm.

Data for {[Re(N*t*Bu)Cax(O)$_4$]$_2$(μ-O)}·3MeCN (11): $C_{102}H_{131}N_5O_9Re_2$ (1943.52): calcd. C 63.03, H 6.79, N 3.60; found C 63.61, H 7.01, N 3.34. MS (MALDI mode): *m*/*z* = 1820 [M^+]. IR: $\tilde{\nu}$ = 2362 (w), 2337 (w), 1314 (w, br.), 1304 (w, br.), 1261 (s), 1238 (w, br.), 1203 (m), 1191 (m), 1169 (w), 1154 (w), 1095 (s, br.), 1021 (s, br.), 975 (w), 928 (w), 918 (w), 870 (w), 829 (m), 799 (s), 759 (w), 722 (m), 676 (w), 666 (w) cm^{-1}. ^{1}H NMR (C_6D_6): δ = 7.28–7.25 (m, 16 H, aryl *H*), 5.25 (d, $^2J_{HH}$ = 14.4 Hz, 4 H, *endo*-CH_2), 5.03 (d, $^2J_{HH}$ = 14.4 Hz, 4 H, *endo*-CH_2), 3.57 (d, $^2J_{HH}$ = 14.4 Hz, 4 H, *exo*-CH_2), 3.54 (d, $^2J_{HH}$ = 14.4 Hz, 4 H, *exo*-CH_2), 1.34 [s, 18 H, C(CH_3)$_3$], 1.32 [s, 18 H, C(CH_3)$_3$], 1.23 [s, 9 H, C(CH_3)$_3$], 1.18 [s, 36 H, C(CH_3)$_3$], 1.12 [s, 9 H, C(CH_3)$_3$], 0.58 (s, 3 H, *Me*CN), 0.30 (s, 3 H, *Me*CN), 0.28 (s, 3 H, *Me*CN) ppm.

Preparation of [Re(N*t*Bu)$_2$Cax(O)$_4$Li(NCMe)$_2$][Re(N*t*Bu)$_2$Cax(O)$_4$-Li(NCMe)]·2MeCN (12): Cax(OH)$_3$(OMe) (1.00 g, 1.51 mmol) in diethyl ether (40 mL) was treated with *n*BuLi (2.83 mL, 1.60 M, 4.53 mmol) at –78 °C. After stirring for 6 h, volatiles were removed in vacuo, and [Re(N*t*Bu)$_2$Cl$_3$] (0.66 g, 1.52 mmol) in toluene (30 mL) was added. The system was refluxed for 6 h, volatiles were removed in vacuo, and the residue taken-up in acetonitrile (30 mL). On cooling to –40 °C for 2 d, small yellow prisms formed. Yield 0.98 g, 60%. $C_{57}H_{77.5}LiN_{4.5}O_4Re$ (1082.88): calcd. C 63.22, H 7.21, N 5.82; found C 62.64, H 7.31, N 5.74. MS (FAB): *m*/*z* = 981 [M^+ – 2MeCN]. IR: $\tilde{\nu}$ = 1612 (w), 1304 (m), 1260 (s), 1208 (s), 1161 (m), 1153 (m), 1092 (s, br.), 1019 (s, br.), 973 (m), 871 (w), 800 (s), 723 (s), 665 (w) cm^{-1}. ^{1}H NMR (C_6D_6): δ = 7.06 (s, 2 H, aryl *H*), 6.96 (s, 2 H, aryl *H*), 6.87 (m, 4 H, aryl *H*), 4.62 (d, $^2J_{HH}$ = 14.2 Hz, 4 H, *endo*-CH_2), 4.56 (d, $^2J_{HH}$ = 14.2 Hz, 4 H, *endo*-CH_2), 3.38 (overlapping d, 8 H, *exo*-CH_2), 1.70 (s, 3 H, *Me*CN), 1.14 [s, 9 H, C(CH_3)$_3$], 1.02 [s, 9 H, C(CH_3)$_3$], 0.86 [s, 9 H, C(CH_3)$_3$], 0.78 [s, 9 H, C(CH_3)$_3$], 0.77 [s, 18 H, C(CH_3)$_3$] (pre-C_6D_6 sample dried in vacuo for 12 h) ppm.

Preparation of [Re(N*t*Bu)$_2$Cax(O)$_3$(OMe)] (13): Cax(OH)$_3$(OMe) (1.00 g, 1.51 mmol) and [Re(N*t*Bu)$_3$(OSiMe$_3$)] (0.74 g, 1.51 mmol) were refluxed in toluene (30 mL) for 12 h. Following removal of volatiles in vacuo, the residue was extracted into warm MeCN (30 mL) affording **13** as small orange prisms on prolonged standing at 0 °C. Further crops of **13** could be obtained by concentration and cooling of the mother liquor. Yield 0.66 g, 44%. $C_{53}H_{73}N_2O_4Re$ (988.33): calcd. C 64.40, H 7.45, N 2.84; found C 64.61, H 7.33, N 2.73. MS (FAB): *m*/*z* = 988 [M^+]. IR: $\tilde{\nu}$ = 2362 (w), 2337 (w), 1303 (m), 1262 (m), 1248 (m), 1208 (s), 1169 (m), 1124 (m), 1097 (m), 1019 (m), 974 (m), 919 (s), 898 (s), 871 (m), 840 (s), 820 (m), 799 (m), 764 (w), 723 (s), 667 (w) cm^{-1}. ^{1}H NMR ([D$_8$]toluene, 500 MHz): δ = 7.42 (m, 1 H, aryl *H*), 7.39 (m, 1 H, aryl *H*), 7.26 (m, 1 H, aryl *H*), 7.23 (m, 1 H, aryl *H*), 7.20 (m, 1

Table 11. Crystal and structure refinement data for compounds **1**–**4**.

Compound	**1**	**2**	**3**	**4**
Formula	$C_{66}H_{73}N_2NaO_5PRe{\cdot}4(C_2H_3N)$	$C_{66}H_{73}KN_2O_5PRe{\cdot}4(C_2H_3N)$	$C_{48}H_{58}N_2NaO_6Re{\cdot}$ca.2.8$(C_2H_3N)$	$C_{48}H_{58}KN_2O_6Re{\cdot}3(C_2H_3N)$
Formula weight	1378.64	1394.75	1083.92	1107.43
Crystal system	triclinic	triclinic	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions				
a [Å]	13.2798(10)	13.4443(8)	11.5803(7)	12.9669(11)
b [Å]	13.9204(11)	13.9295(8)	12.9153(7)	13.9161(12)
c [Å]	19.1783(15)	19.1870(7)	19.0514(14)	15.5771(14)
α [°]	89.9448(13)	89.856(4)	74.921(6)	88.2258(14)
β [°]	81.8546(13)	81.883(4)	87.898(6)	88.9347(15)
γ [°]	79.6986(12)	79.344(5)	82.856(5)	66.2315(13)
V [Å^3]	3451.9(5)	3494.8(5)	2729.9(3)	2571.2(4)
Z	2	2	2	2
Temp. [K]	150(2)	140(2)	140(2)	150(2)
Radiation, λ [Å]	sealed tube, 0.71073	sealed tube, 0.71073	sealed-tube, 0.71073	synchrotron, 0.6861
$D_{calcd.}$ [g cm^{-3}]	1.326	1.325	1.319	1.430
Absorption coefficient [mm^{-1}]	1.843	1.874	2.283	2.497
Crystal size [mm]	0.34 × 0.30 × 0.13	0.35 × 0.17 × 0.06	0.48 × 0.32 × 0.17	0.12 × 0.10 × 0.02
$2\theta_{max}$ [°]	57.9	55.0	50.0	58.6
Reflections measured	29867	46198	28872	25144
Unique reflections	15757	15846	9487	13646
Reflections with $F^2 > 2\sigma(F^2)$	13274	11343	8709	11753
Transmission factors	0.57–0.80	0.58–0.90	0.40–0.68	0.75–0.95
R_{int}	0.0310	0.0753	0.0404	0.0297
Number of parameters	914	915	718	647
R[a] [$F^2 > 2\sigma(F^2)$]	0.0377	0.0414	0.0618	0.0365
R_w[b] (all data)	0.0956	0.0667	0.1586	0.0913
Largest difference peak and hole [e Å^{-3}]	2.773 and –1.904	1.673 and –1.392	4.478 and –1.741	2.294 and –3.311

[a] Conventional $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ for "observed" reflections having $F^2 > 2\sigma(F^2)$. [b] $R_w = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma_w(F_o^2)^2]^{1/2}$ for all data.

H, aryl *H*), 7.00 (m, 1 H, aryl *H*), 6.84 (m, 1 H, aryl *H*), 6.62 (m, 1 H, aryl *H*), 4.99 (d, $^2J_{HH}$ = 13.4 Hz, 1 H, *endo*-CH_2), 4.84 (d, $^2J_{HH}$ = 12.6 Hz, 1 H, *endo*-CH_2), 4.68 (d, $^2J_{HH}$ = 12.8 Hz, 1 H, *endo*-CH_2), 4.48 (d, $^2J_{HH}$ = 15.7 Hz, 1 H, *endo*-CH_2), 3.88 (d, $^2J_{HH}$ = 15.7 Hz, 1 H, *exo*-CH_2), 3.79 (s, 3 H, O*Me*), 3.56 (d, $^2J_{HH}$ = 13.4 Hz, 1 H, *exo*-CH_2), 3.51 (d, $^2J_{HH}$ = 12.6 Hz, 1 H, *exo*-CH_2), 3.43 (d, $^2J_{HH}$ = 12.8 Hz, 1 H, *exo*-CH_2), 1.94 [s, 9 H, C(CH_3)$_3$], 1.66 [s, 9 H, C(CH_3)$_3$], 1.60 [s, 9 H, C(CH_3)$_3$], 1.37 [s, 9 H, C(CH_3)$_3$], 1.17 [s, 9 H, C(CH_3)$_3$], 1.02 [s, 9 H, C(CH_3)$_3$] ppm.

Crystallography: Crystal data were collected with a Bruker SMART 1000 CCD diffractometer using narrow slice 0.3° ω-scans for **1**, **5**,

Table 12. Crystal and structure refinement data for compounds **5**–**9**.

Compound	**5**	**6**	**7**
Formula	$C_{96}H_{116}N_4Na_2O_{10}Re_2$·4($C_2H_3N$)	$C_{96}H_{116}K_2N_4O_{10}Re_2$·4($C_2H_3N$)	[$C_{104}H_{128}K_4N_8O_{10}Re_2$][$C_{44}H_{54}O_4$]·7($C_2H_3N$)
Formula weight	2068.52	2100.74	3115.21
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/c$
Unit cell dimensions			
a [Å]	14.0238(16)	13.9904(15)	15.9390(12)
b [Å]	16.4214(18)	16.6618(18)	40.119(3)
c [Å]	21.640(2)	21.321(2)	24.5302(18)
α [°]	90	90	90
β [°]	99.813(2)	99.274(2)	99.246(2)
γ [°]	90	90	90
V [Å^3]	4910.5(9)	4905.0(9)	15482(2)
Z	2	2	4
Temperature [K]	150(2)	150(2)	120(2)
Radiation, λ [Å]	sealed-tube, 0.71073	synchrotron, 0.6861	synchrotron, 0.6751
$D_{calcd.}$ [g cm^{-3}]	1.399	1.422	1.336
Absorption coefficient [mm^{-1}]	2.533	2.612	1.735
Crystal size [mm]	0.27 × 0.07 × 0.06	0.16 × 0.04 × 0.04	0.08 × 0.04 × 0.03
$2\theta_{max}$ [°]	50.0	58.8	50.0
Reflections measured	30319	30023	129809
Unique reflections	8647	13664	31733
Reflections with $F^2 > 2\sigma(F^2)$	5251	8455	20950
Transmission factors	0.55–0.86	0.68–0.90	0.87–0.95
R_{int}	0.1116	0.0678	0.0863
Number of parameters	609	634	1807
R[a] [$F^2 > 2\sigma(F^2)$]	0.0558	0.0472	0.0872
R_w[b] (all data)	0.1552	0.1005	0.2188
Largest difference peak and hole [e Å^{-3}]	1.911 and –1.432	0.863 and –1.280	3.414 and –2.203
Compound	**8**	**9**	
Formula	$C_{96}H_{116}K_2N_4O_{11}Re_2$·2($C_2H_3N$)	$C_{52}H_{72}ClN_2O_4Re$·C_2H_3N	
Formula weight	2034.64	1051.82	
Crystal system	monoclinic	monoclinic	
Space group	$P2_1/c$	$P2_1/n$	
Unit cell dimensions			
a [Å]	13.3207(5)	12.7011(14)	
b [Å]	23.1456(7)	30.741(4)	
c [Å]	16.7513(5)	13.6254(16)	
α [°]	90	90	
β [°]	110.702(2)	101.168(2)	
γ [°]	90	90	
V [Å^3]	4831.2(3)	5219.2(10)	
Z	2	4	
Temperature [K]	140(2)	150(2)	
Radiation, λ [Å]	sealed tube, 0.71073	synchrotron, 0.6892	
$D_{calcd.}$ [g cm^{-3}]	1.399	1.339	
Absorption coefficient [mm^{-1}]	2.649	2.424	
Crystal size [mm]	0.60 × 0.33 × 0.19	0.06 × 0.06 × 0.04	
$2\theta_{max}$ [°]	55.0	59.0	
Reflections measured	61294	52047	
Unique reflections	10965	14769	
Reflections with $F^2 > 2\sigma(F^2)$	9610	13169	
Transmission factors	0.30–0.63	0.87–0.91	
R_{int}	0.0281	0.0490	
Number of parameters	582	588	
R[a] [$F^2 > 2\sigma(F^2)$]	0.0247	0.0371	
R_w[b] (all data)	0.0541	0.0921	
Largest difference peak and hole [e Å^{-3}]	1.317 and –0.787	3.985 and –1.161	

[a] Conventional $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ for "observed" reflections having $F^2 > 2\sigma$ (F^2). [b] $R_w = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma_w(F_o^2)^2]^{1/2}$ for all data.

Table 13. Crystal and structure refinement data for compounds **10**–**13**.

Compound	**10**	**11**	**12**	**13**
Formula	$C_{92}H_{116}NO_8Re{\cdot}6(C_2H_3N)$	$C_{96}H_{122}N_2O_9Re_2{\cdot}3(C_2H_3N)$	$C_{55}H_{74.5}LiN_{3.5}O_4Re{\cdot}C_2H_3N$	$C_{53}H_{73}N_2O_4Re$
Formula weight	1796.38	1943.52	1082.88	988.33
Crystal system	triclinic	monoclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/n$	$P2_1/c$	$P2_1/n$
Unit cell dimensions				
a [Å]	13.2181(4)	16.2148(12)	14.0532(15)	14.2301(7)
b [Å]	17.361(5)	26.920(2)	31.237(3)	16.2040(8)
c [Å]	22.9013(7)	24.1439(18)	13.6346(15)	21.7209(11)
α [°]	74.6597(5)	90	90	90
β [°]	81.0820(5)	105.824(2)	118.192(2)	99.915(2)
γ [°]	73.1832(5)	90	90	90
V [Å^3]	4833.9(3)	10139.4(13)	5275.3(10)	4933.7(4)
Z	2	4	4	4
Temerature [K]	150(2)	150(2)	150(2)	120(2)
Radiation, λ [Å]	sealed tube, 0.71073	synchrotron, 0.8462	synchrotron, 0.6892	synchrotron, 0.6897
$D_{calcd.}$ [g cm^{-3}]	1.234	1.273	1.363	1.331
Absorption coefficient [mm^{-1}]	1.315	2.440	2.352	2.507
Crystal size [mm]	$0.51 \times 0.13 \times 0.07$	$0.14 \times 0.11 \times 0.06$	$0.09 \times 0.08 \times 0.04$	$0.16 \times 0.10 \times 0.05$
$2\theta_{max}$ [°]	55.0	58.0	59.1	62.2
Reflections measured	42335	60588	39726	51534
Unique reflections	21602	15921	14902	15193
Reflections with $F^2 > 2\sigma(F^2)$	17662	14137	13413	14529
Transmission factors	0.55–0.91	0.73–0.88	0.82–0.91	0.69–0.86
R_{int}	0.0332	0.0544	0.0553	0.0357
Number of parameters	1195	1209	643	586
R[a] [$F^2 > 2\sigma(F^2)$]	0.0359	0.0384	0.0338	0.0229
R_w[b] (all data)	0.0813	0.1041	0.0875	0.0589
Largest difference peak and hole [e Å^{-3}]	0.768 and –0.581	1.749 and –1.453	1.510 and –1.132	1.463 and –1.505

[a] Conventional $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ for "observed" reflections having $F^2 > 2\sigma(F^2)$. [b] $R_w = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma_w(F_o^2)^2]^{1/2}$ for all data.

and **10**. Data for **2**, **3**, and **8** were collected with an Oxford Diffraction Xcalibur3/CCD diffractometer. Data for **4**, **6**, **7**, **9**, **11**–**13**, were collected at Daresbury Laboratory SRS Station 9.8 (16.2 SMX for **11**) using silicon-111-monochromated X-radiation. Diffractometers used at Daresbury were Bruker SMART 1 K for **4**, **6**, **9**, and **12** and Apex 2 for **7**, **11** and **13**. Data were corrected for Lp effects and for absorption, based on repeated and symmetry equivalent reflections, and solved by direct methods (Patterson synthesis for **1** and **5**). Structures were refined by full-matrix least-squares on F^2. H atoms were included in a riding model except for some disordered MeCNs of crystallisation. Hydrogen atom U_{iso} values were constrained to be 120% of that of the carrier atom except for methyl- and hydroxy-H (150%). All structures except **8**, **9** and **12**, exhibited disorder in the calixarene *t*Bu groups. In **13**, one of the imido *t*Bu groups was modelled with disordered Me groups. This disorder was modelled with two sets of methyl carbon positions with restraints on geometry and anisotropic displacement parameters. MeCN molecules of crystallisation were also often disordered and where necessary were either modelled over two sets of positions or as partially occupied. The formula of **7** includes six, badly disordered, MeCN molecules that were modelled as regions of diffuse electron density by the Platon "Squeeze" procedure.[31] The diffraction data for **5** were non-merohedrally twinned via a twofold rotation about *b*. However, it was found that there was no benefit to using both twin components and only one was used in the final refinement. In **9** the largest residual peak lies ca. 2.3 Å from the Re atom and suggests positional disorder of the chloro and imido groups, but no decent model could be developed. Programmes used: Bruker SMART and APEX II and Oxford Diffraction Ltd. CrysAlis CCD, for data collection; Bruker SAINT and Oxford Diffraction Ltd. CrysAlis RED for data reduction; Bruker SHELXTL for structure solution and refinement, and local programs. Crystallographic data presented in Tables 11, 12 and 13.

CCDC-659450 (for **1**), -659451 (for **2**), -659452 (for **3**), -659453 (for **4**), -659454 (for **5**), -659455 (for **6**), -659456 (for **7**), -659457 (for **8**), -659458 (for **9**), -659459 (for **10**), -659460 (for **11**), -659461 (for **12**), -659462 (for **13**) contain the supplementary crystallographic data. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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