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Four Soft Donors and a Hard Centre: Rhodium Complexes of a Novel Tetrakis(NHC)-Encapsulated Crown Ether Ligand

Sumi Shrestha,[a] Carolina Gimbert-Suriñach,*[a] Mohan Bhadbhade,[b] and Stephen B. Colbran*[a]

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2,3,13,14-Tetrakis(bromomethyl)dibenzo-18-crown-6 (**1**) has been demonstrated to be a versatile synthetic intermediate for constructing multinucleating ligands with a hard-donor, crown ether centre. By using this intermediate, novel salts of tetrakis(imidazoliomethyl)dibenzo-18-crown-6, $[H_4L^1]X_4$ (**2**: $X^- = Br^-$; **4**: $X^- = PF_6^-$), and tetrakis(benzimidazoliomethyl)-dibenzo-18-crown-6, $[H_4L^2]X_4$ (**3**: $X^- = Br^-$; **5**: $X^- = PF_6^-$), were prepared. These salts are precursors to novel tetrakis(N-heterocyclic carbene) complexes spanned by a crown ether bridge capable of binding various hard metal ions. The tetrakis(imidazoliomethyl) salt **4** was used to prepare the bimetallic rhodium complexes $[\{(cod)Rh\}_2(\mu\text{-}L^1)][PF_6]_2$ (**6**) and $[\{(CO)_2Rh\}_2(\mu\text{-}L^1)][PF_6]_2$ (**7**). These complexes selectively bind alkali metal ions.

Introduction

Dimeric metal complexes continue to fascinate because synergic cooperativity may mean "two metals do it better than one". This cooperative effect has been observed in many catalytic reactions in which bimetallic complexes show greater activities than the sum of the corresponding monomeric metal species.[1] Simple ditopic ligands formed by appending an inert bridge to two metal binding domains are commonly used to form metal dimers (e.g., Figure 1).

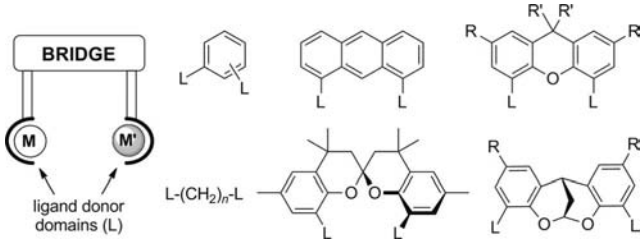

Figure 1. Cartoon depiction of generic symmetric (LM = LM′) and asymmetric (LM ≠ LM′) binucleating ligands for the formation of homo- and heterometallic dimers, respectively. A selection of bridging groups from the literature are shown and may range from simple aliphatic or aromatic linkages[1,2] through to more sophisticated bridges such as the xanthenyl[3] or chiral bis(chroman) and dibenzodioxocin[4] backbones shown. L = ligand donor domain; M, M′ = metal ions/centres.

[a] School of Chemistry, University of New South Wales, Sydney, NSW 2052, Australia
Fax: +61-2-9385 6141
E-mail: s.colbran@unsw.edu.au
c.gimbert@unsw.edu.au
[b] Mark Wainwright Analytical Centre, University of New South Wales, Sydney, NSW 2052, Australia

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The bridging ligands may be symmetric, thereby providing homodimeric metal complexes, or asymmetric, for example, with soft and hard donor domains to selectively bind soft organo-transition-metal centres and hard s/p-block or early high-oxidation-state d/f-block metal ions, respectively, to give the so-called "hard–soft" dimers.[1–8]

A particularly common and simple strategy for forming asymmetric "hard–soft" metal dimers is to directly co-join hard crown ether and soft ligand donor domains. Amongst the soft donors used are phosphanes and phosphites,[5] sp^2 nitrogen donors such as imines and pyridines,[6] and thiolates.[7] The resulting soft organo-transition-metal centres bind and activate organic substrates to a myriad of useful reactions. The crown ether ligand domains, on the other hand, selectively bind hard metal ions. Thus, the role of the crown ether may be as simple as solubilizing an s-block metal salt that is a reagent in the reaction or it may act as a binding site for hard Lewis acidic metal ions that polarize and further activate a reactant.

In this work we have used a crown ether to bridge two bis(N-heterocyclic carbene) [bis(NHC)] donor domains. NHC ligands are strong σ donors and form robust organo-transition-metal complexes with superior durability to heating in air and moisture.[9,10] The crown ether bridge adds functionality:[5–8] it introduces the potential to span two organometallic NHC centres by a hard, Lewis acidic bridge formed by complexation of the crown ether moiety with a hard metal ion. The results in this paper add to a growing body of work on multi-metal complexes spanned by NHC-based ditopic ligands with functional bridges.[10] However, we are unaware of other reports of organometallic centres spanned by crown ethers. The only carbene-functionalized crown ether ligands have been developed by Espinet and co-workers who showed that gold(I) complexes of an isocy-

anide-substituted crown ether X–Au–C≡N–R [R = 5-(1,2-benzo-15-crown-5)] were susceptible to nucleophilic attack by methanol or primary amines (Y–H), affording the corresponding gold(I) exocyclic carbene complexes X–Au–C(NHR)Y.[8]

Results and Discussion

Synthesis of (Benz)imidazolium Crown Ether Salts 2–5

Our synthetic strategy for introducing NHC ligands into a crown ether bridge is based on the facile bromomethylation of the commercially available dibenzo-18-crown-6 (Scheme 1). After modification and optimization of a literature procedure,[11] we were able to reproducibly obtain 2,3,13,14-tetrakis(bromomethyl)dibenzo-18-crown-6 (**1**) in over 90% yield (Scheme 1). Compound **1** is a versatile intermediate: a broad range of new multifunctional ligands with a hard crown ether centre spanning two sets of two donor groups can be prepared by simple nucleophilic addition reactions. For example, the reactions of **1** with *N*-methylimidazole or *N*-methylbenzimidazole afforded the tetrakis-*N*-(benz)imidazolium crown ether salts $[H_4L^1]Br_4$ (**2**) and $[H_4L^2]Br_4$ (**3**), respectively. Anion exchange using $[NH_4][PF_6]$ in methanol gave the more easily-handled hexafluorophosphate salts $[H_4L^1][PF_6]_4$ (**4**) and $[H_4L^2][PF_6]_4$ (**5**) in good yields (Scheme 1).

The ^1H NMR spectra of **4** and **5** in CH_3CN show characteristic peaks of the (benz)imidazolium salts; of note, the singlet for the acidic (benz)imidazolium 2-H is at δ = 8.19 ppm for **4** and at δ = 8.87 ppm for **5**, and the methylene singlet is at δ = 5.22 ppm for **4** and at δ = 5.57 ppm for **5**, downfield shifts relative to the methylene signal for **1** at δ = 4.69 ppm.

A crystal of $(\mathbf{4})_2 \cdot 3CH_3CN$ suitable for a single-crystal X-ray diffraction study was obtained by slow evaporation of a concentrated acetonitrile/diethyl ether solution. Two different views of the crystal structure of the cation are presented in Figure 2. The macrocyclic ring adopts a "W" conformation leading, overall, to the "umbrella" shape that typifies dibenzo-18-crown-6 derivatives.[12] The angle between the cisoid flanking phenyl rings is 123.1°. The four (*N*-methylimidazoliomethylene) groups adopt three different orientations relative to the crown ether ring. The

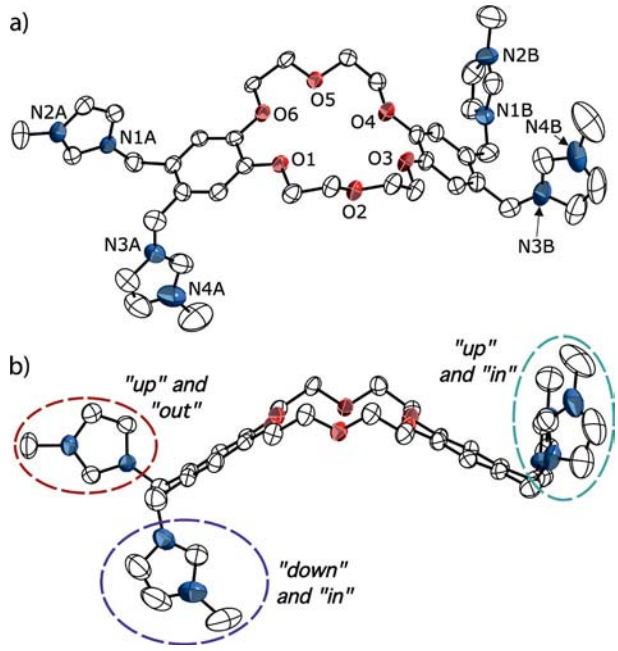
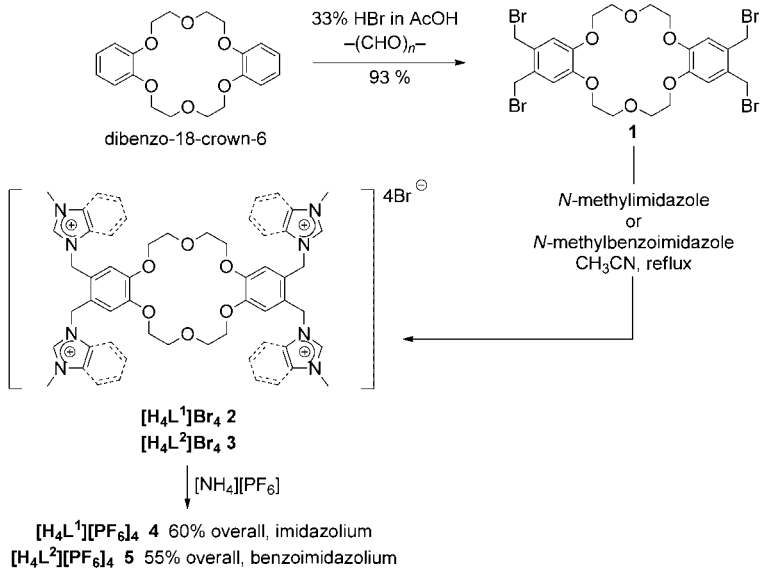


Figure 2. Views of the X-ray crystal structure of cation $[H_4L^1]^{4+}$ in $(\mathbf{4})_2 \cdot 3CH_3CN$ showing a) the heteroatom labeling scheme and b) the crown conformation of the central ether ring and, relative to this, the orientations of the imidazolium substituents (both views show 50% thermal ellipsoids at 155 K and the hydrogen atoms have been omitted for clarity).

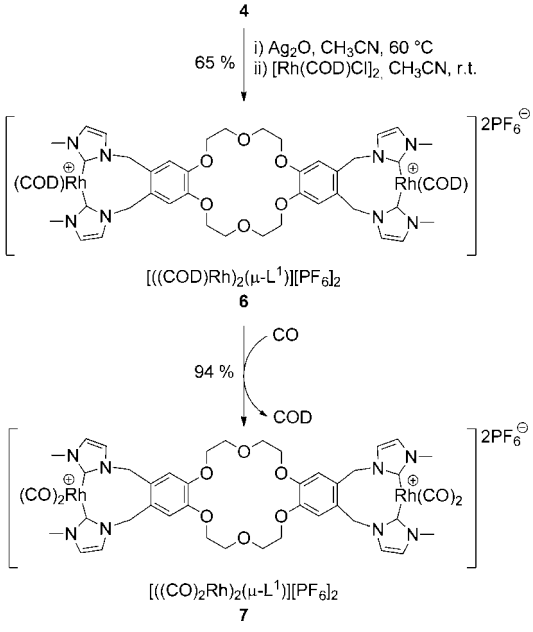


Scheme 1. Synthesis of tetrakis(imidazolium) salts $[H_4L^1][PF_6]_4$ (**4**) and $[H_4L^2][PF_6]_4$ (**5**).

imidazolium moieties defined by N1B–N2B, N3B–N4B and N1A–N2A all point "up" (relative to the arc of the umbrella), but the C-2 of the first two point inwards whereas the latter points away from the crown ether. Finally, the imidazolium group defined by N3A–N4A points "down" and "in".

Synthesis of Rhodium Dimers 6 and 7

The tetrakis(imidazolium) salt **4** was used to obtain the first crown ether tethered NHC complexes. By using a standard synthetic protocol, **4** was treated with silver oxide and then, without isolation of the intermediate silver–NHC species, with $[RhCl(cod)]_2$ to afford the bis{$(NHC)_2$-rhodium(I)} dimer $[\{(cod)Rh\}_2(\mu\text{-}L^1)][PF_6]_2$ (**6**; Scheme 2). Interestingly, the possible tetrakis{(NHC)rhodium} derivative $[\{Cl(cod)Rh\}_4(\mu\text{-}L^1)]$ was not an observed product. Our results concur with those of Crabtree and co-workers who showed bis(imidazolium) salts with longer $(CH_2)_{3\text{ or }4}$ linkers form [bis(NHC)Rh(cod)]$^+$ chelate monomers, whereas bis(imidazolium) salts with shorter $(CH_2)_{1\text{ or }2}$ bridges form dimers with two [(NHC)Rh(cod)X] (X = halide) centres.[2b]



Scheme 2. Synthesis of rhodium dimers $[\{(cod)Rh\}_2(\mu\text{-}L^1)][PF_6]_2$ (**6**) and $[\{(CO)_2Rh\}_2(\mu\text{-}L^1)][PF_6]_2$ (**7**).

Dimer **6** was characterized by NMR spectroscopy and HRMS. The absence of the imidazolium 2-H resonance and upfield shift of the 4,5-H peaks to δ = 6.93 and 7.29 ppm in the ^{1}H NMR spectrum recorded in CH_3CN is indicative of NHC formation and coordination to rhodium. Doublets at δ = 4.96 and 6.53 ppm are observed for the diastereotopic (AA′) methylene protons. A characteristic carbene carbon doublet at δ = 181.7 ppm ($^1J_{C\text{-}Rh}$ = 53 Hz) in the $^{13}C\{^1H\}$ NMR spectrum in CH_3CN confirms NHC formation. The (+)-ESI HRMS spectrum of **6** shows a unique signal for $[\{(cod)Rh\}_2(\mu\text{-}L^1)]^{2+}$ at *m*/*z* = 579.1821 (calcd. 579.1837) with the expected isotopic pattern.

Treatment of **6** with carbon monoxide gave the corresponding carbonyl derivative, $[\{(CO)_2Rh\}_2(\mu\text{-}L^1)][PF_6]_2$ (**7**) in 94% yield (Scheme 2). The ^{1}H NMR spectrum of **7** in CH_3CN is similar to that of **6**, but the signals for the cyclooctadiene ligand have disappeared and the peaks for the non-equivalent methylene protons slightly shifted to δ = 4.97 and 6.00 ppm. In the $^{13}C\{^1H\}$ NMR spectrum, doublets at δ = 171.8 ($^1J_{C\text{-}Rh}$ = 45 Hz) and 187.8 ppm ($^1J_{C\text{-}Rh}$ = 57 Hz) correspond to the carbene and carbonyl ligands, respectively. The FTIR spectrum of **7** in acetonitrile shows two CO bands at 2084 and 2026 cm^{-1}, indicative of the successful incorporation of the carbonyl ligand into the coordination sphere of the rhodium. The (+)-ESI HRMS spectrum shows a prominent set of peaks at *m*/*z* = 1199.1251, which correspond to $[\{(CO)_2Rh\}_2(\mu\text{-}L^1) + PF_6]^+$ (calcd. 1199.1240).

Binding of Rhodium Dimers 6 and 7 by Metal Ions

The ability of dimer **6** to bind simple metal ions was assessed by (+)-ESI HRMS and ^{1}H NMR spectroscopy. The mass spectra of solutions containing **6** and $K[PF_6]$, NaBr, CsCl, $CaCl_2$ and $ScCl_3$ were recorded. In the spectra, characteristic peaks for metal ion adducts of **6** are observed for the alkali metal ions (Table 1), but not for Ca^{2+} and Sc^{3+}. All peaks in the ^{1}H NMR spectrum of **6** in CD_3CN shifted upon addition of excess (15–20 equiv.) $K[PF_6]$, NaBr or CsCl, whereas no peak shifts were observed upon addition of $CaCl_2$ or $ScCl_3$. The largest $\Delta\delta$ values are observed with potassium and sodium ions for the ethylene resonances of the crown ether moiety: the maximum ethylene proton $\Delta\delta$ values are 0.09 and 0.08 ppm in the case of complex **6** with $K[PF_6]$ (see Figure S1 in the Supporting Information). Overall, the maximum $\Delta\delta$ for **6** vary as follows: $Na^+ \approx K^+ > Cs^+ >> Ca^{2+} \approx Sc^{3+} \approx 0$. Thus, the $\Delta\delta$ values suggest only the alkali metal cations bind to **6**. This is surprising as both Ca^{2+} and Sc^{3+} form stable complexes with dibenzo-

Table 1. (+)-ESI HRMS peaks (*m*/*z* values) observed for solutions containing rhodium dimer **6** and $K[PF_6]$, NaBr, CsCl, $CaCl_2$ or $ScCl_3$.

Cation	Observed species	Observed	Calculated
–	$[\{(cod)Rh\}_2(\mu\text{-}L^1)]^{2+}$	579.1821	579.1837
Na^+	$[\{(cod)Rh\}_2(\mu\text{-}L^1)]^{2+}$	579.1837	579.1837
	$[\{(cod)Rh\}_2(\mu\text{-}L^1)Na]^{3+}$	393.7852	393.7855
	$[\{(cod)Rh\}_2(\mu\text{-}L^1)Na + PF_6]^{2+}$	663.1599	663.1606
	$[\{(cod)Rh\}_2(\mu\text{-}L^1)Na + 2PF_6]^+$	1471.2860	1471.2861
K^+	$[\{(cod)Rh\}_2(\mu\text{-}L^1)]^{2+}$	579.1836	579.1837
	$[\{(cod)Rh\}_2(\mu\text{-}L^1)K + PF_6]^{2+}$	671.1473	671.1476
	$[\{(cod)Rh\}_2(\mu\text{-}L^1)K + 2PF_6]^+$	1487.2602	1487.2600
Cs^+	$[\{(cod)Rh\}_2(\mu\text{-}L^1)]^{2+}$	579.1839	579.1837
	$[\{(cod)Rh\}_2(\mu\text{-}L^1)Cs + 2PF_6]^+$	1581.2031	1581.2017
Ca^{2+}	$[\{(cod)Rh\}_2(\mu\text{-}L^1)]^{2+}$	579.1831	579.1837
Sc^{3+}	$[\{(cod)Rh\}_2(\mu\text{-}L^1)]^{2+}$	579.1845	579.1837

18-crown-6.[13] A possible reason for this is that through-space electrostatic interactions between the entering cation and the tethered cationic Rh centres diminish the effective binding strength of the central crown ether ligand domain. Such electrostatic interactions would increase with the charge of the entering metal ion thus neatly accounting for our observations. Studies of binding constants to confirm these ideas are underway. It is noteworthy that the carbonyl bands in the FTIR spectra of an acetonitrile solution of dimer **7** remained unshifted when excess $K[PF_6]$ (15 equiv.) was added, which suggests that the Rh^I centres are electronically isolated from what happens at the crown ether site. The ^1H NMR spectrum of the same mixture (**7** + $K[PF_6]$ in acetonitrile) shows similar $\Delta\delta$ shifts to those observed for complex **6** (see Figure S2 in the Supporting Information).

To demonstrate conclusively that compound **6** binds to alkali metal ions, crystals were grown by slow evaporation of an acetonitrile/acetone solution of the dimer and excess $K[PF_6]$. X-ray crystallography proved that $[\{(cod)Rh\}_2(\mu\text{-}L^1)K(\eta^3\text{-}PF_6)][PF_6]_2$ (**8**) was formed. The crystal structure of trimetallic **8** is shown in Figure 3. Centrosymmetric pairs of the $[\{(cod)Rh\}_2(\mu\text{-}L^1)K(\eta^3\text{-}PF_6)]^{2+}$ cation (Figure 3a) co-crystallize with two further PF_6^- counterions and lattice acetone and acetonitrile molecules. Selected bond lengths and angles are presented in Table 2. The bridging tetrakis(NHC)-crown ether ligand in **8** adopts the "umbrella" shape observed for the parent ligand **4** (Figure 2). The angle between the planes of the phenyl rings is 121.1°, which indicates that the crown ether "umbrella" closes up (puckers) slightly upon binding the metal ion.[12,13] The potassium ion is bound by the six oxygen donors of the crown ether moiety and by three fluorine atoms of a $[PF_6]^-$ ion. The mean K–O and K–F distances, 2.790(5) and 2.804(8) Å, respectively, are in the range for similar reported compounds.[12b] Weak inter-ion K···H–C interactions [mean distance K···C(cod): 3.395(8) Å] are also observed (indicated by the purple dashed lines in Figure 3a). The tendency of alkaline metal ions coordinated by dibenzo-18-crown-6 ether to form "hexagonal-bipyramidal-like" coordination spheres could be responsible for this interaction and thus the highly centrosymmetric pairing shown in Figure 3a.[12] The rhodium centres in **8** adopt a square-planar conformation typical of bis(NHC)Rh(cod) complexes[2b] with bite angles for the chelated bis(carbene) donors of 92.4(3)° for C9B–Rh1–C4B and 93.2(3)° for C9D–Rh2–C4D. The Rh–C(carbene) bond lengths are unexceptional and lie in the range of 2.022(9)–2.031(7) Å.[2b]

Table 2. Selected bond lengths and inter-bond angles for $[\{(cod)Rh\}_2(\mu\text{-}L^1)K(\eta^3\text{-}PF_6)][PF_6]_2$ (**8**).

Bond lengths [Å]			
Rh–C (carbene)		K1–O (crown ether)	
Rh1–C4B	2.031(7)	K1–O1A	2.758(5)
Rh1–C9B	2.024(6)	K1–O2A	2.786(7)
Rh2–C4D	2.030(8)	K1–O3A	2.829(6)
Rh2–C9D	2.022(9)	K1–O4A	2.820(6)
Rh–C (cod)		K1–O5A	2.789(7)
Rh1–C1C	2.199(7)	K1–O6A	2.763(6)
Rh1–C2C	2.181(7)	K1–F (PF_6)	
Rh1–C5C	2.174(7)	K1–F3A	2.913(9)
Rh1–C6C	2.203(8)	K1–F4A	2.772(14)
Rh2–C1E	2.198(10)	K1–F5A	2.729(12)
Rh2–C2E	2.202(11)	K1···C (cod)	
Rh2–C5E	2.212(11)	K1···C3C	3.412(11)
Rh2–C6E	2.196(10)	K1···C4C	3.378(11)
Bond angles [°]			
Rh1 centre		K1 centre	
C4B–Rh1–C9B	92.4(3)	O1A–K1–O2A	60.62(17)
C2C–Rh1–C5C	81.9(3)	O1A–K1–O6A	55.87(16)
C1C–Rh1–C6C	81.3(3)	O2A–K1–O3A	59.88(18)
C4B–Rh1–C1C	91.5(3)	O3A–K1–O4A	54.59(18)
C4B–Rh1–C2C	89.6(3)	O4A–K1–O5A	60.36(18)
C9B–Rh1–C5C	89.8(3)	O5A–K1–O6A	60.08(17)
C9B–Rh1–C6C	90.9(3)	O2A–K1–O5A	160.1(2)
Rh2 centre		F3A–K1–O2A	99.3(3)
C4D–Rh2–C9D	93.2(3)	F4A–K1–O2A	76.9(3)
C5E–Rh2–C2E	81.2(5)	F5A–K1–O2A	121.4(4)
C6E–Rh2–C1E	81.3(4)	F3A–K1–O5A	97.6(3)
C4D–Rh2–C1E	89.6(4)	F4A–K1–O5A	122.8(4)
C4D–Rh2–C2E	91.0(4)	F5A–K1–O5A	78.3(3)
C9D–Rh2–C5E	90.7(4)		
C9D–Rh2–C6E	89.3(4)		

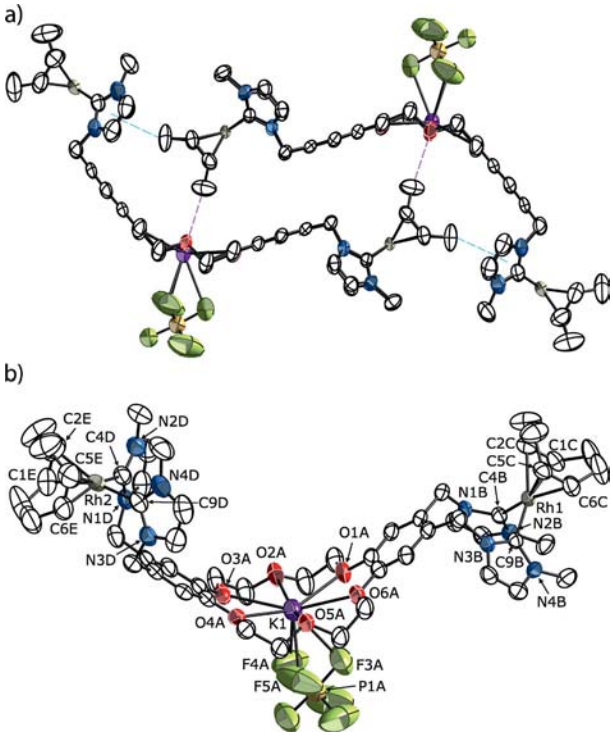


Figure 3. Views of the crystal structure of $[\{(cod)Rh\}_2(\mu\text{-}L^1)K(\eta^3\text{-}PF_6)][PF_6]_2$ (**8**) illustrating a) the packing of pairs of the $[\{(cod)Rh\}_2(\mu\text{-}L^1)K(\eta^3\text{-}PF_6)]^{2+}$ cations and b) the labelling scheme for a single cation of complex **8** (both views show 50% thermal ellipsoids at 150 K and hydrogen atoms have been omitted for clarity).

Conclusions

A straightforward and versatile synthetic methodology to access new crown ether derivatives functionalized with four (or, potentially, more) ligand donor groups is described. The route has been employed to make the new tet-

rakis(imidazoliomethyl)- and tetrakis(benzimidazoliomethyl)-substituted dibenzo-crown ether salts **2**, **4** and **3**, **5**, respectively. These salts are useful precursors to crown ether bridged N-heterocyclic carbene complexes, as demonstrated by the isolation of rhodium(I) dimers **6** and **7**. Each of these compounds contains two bis(NHC)Rh^{I} reactive centres, which are known to catalyse important classes of organic reaction such as hydrogenation, hydroformylation or hydroamination.[9] At the same time, compounds **6** and **7** bind alkali metal ions and, therefore, solubilize and make available inorganic salts that are commonly insoluble in organic solvents. We predict, therefore, a rich chemistry for the new NHC-encapsulated crowns and their metal complexes.

Experimental Section

General Procedures: $[RhCl(cod)]_2$ was synthesized as described previously.[14] All other reagents are commercially available and were used as received. Solvents were taken from an Innovative Technology Pure Solvent Dispenser prior to use. NMR spectra were recorded with a Bruker DPX 300 or Avance III 400 spectrometer. (+)-ESI HRMS were acquired by using a Orbitrap Velos XL spectrometer.

Synthesis of $[H_4L^1][PF_6]_4$ (4)

(a) Bromomethylation of Dibenzo-18-crown-6: In our hands, the literature methods[11] were poorly reproducible. The following adaptation gave consistently good yields of 2,3,13,14-tetrakis(bromomethyl)dibenzo-18-crown-6 (**1**). Under nitrogen, dibenzo-18-crown-6 (200 mg, 0.55 mmol), paraformaldehyde (150 mg, 5 mmol) and 33% hydrobromic acid in acetic acid (1.6 mL) were stirred for a few minutes until all the solids had dissolved. The mixture was then left to stand without stirring for 2 d while a white precipitate formed. The solid was collected by filtration, washed consecutively with water, ethanol and diethyl ether, and then dried to give compound **1** (374 mg, 0.51 mmol, 93%) as a white powder; m.p. 210 °C (dec.) (lit.:[11b] 212–215 °C). ^{1}H NMR (300 MHz, CD_3CN): δ = 6.98 (s, 4 H, Ar), 4.69 (s, 8 H, CH_2Br), 4.11 (m, 8 H, OCH_2), 4.09 (m, 8 H, OCH_2) ppm.

(b) Reaction of 1 with *N*-Methylimidazole: A stirred solution of compound **1** (4.9 g, 6.69 mmol) in acetonitrile (110 mL) was heated at reflux in a three-necked flask fitted with a pressure-equalizing dropping funnel under nitrogen. A solution of *N*-methylimidazole (0.2 mL, 30 mmol) in acetonitrile (20 mL) was added dropwise to this solution and the resulting mixture was heated at reflux overnight. The solvent was evaporated to give a white solid identified as compound $[H_4L^1]Br_4$ (**2**; 6.53 g, 6.10 mmol, 91%). ^{1}H NMR (300 MHz, CD_3CN): δ = 9.03 (s, 4 H, N-CH=N), 7.43 (t, J = 1.6 Hz, 4 H, imidazole), 7.28 (t, J = 1.6 Hz, 4 H, imidazole), 7.10 (s, 4 H, Ar), 5.48 (s, 8 H, CH_2), 4.17–4.19 (m, 8 H, OCH_2), 3.87–3.89 (m, 8 H, OCH_2), 3.79 (s, 12 H, CH_3) ppm.

(c) Anion Exchange: The bromide salt **2** was dissolved in methanol and treated with a saturated solution of ammonium hexafluorophosphate in water. The resulting white precipitate was collected by filtration, washed with diethyl ether and dried under vacuum to afford compound **4** as a crystalline white solid (5.36 g, 4.00 mmol, 66%); m.p. 175–177 °C. ^{1}H NMR (300 MHz, CD_3CN): δ = 8.19 (s, 4 H, N-CH=N), 7.31 (t, J = 1.8 Hz, 4 H, imidazole), 7.23 (t, J = 1.8 Hz, 4 H, imidazole), 6.99 (s, 4 H, Ar), 5.22 (s, 8 H, CH_2), 4.13–4.15 (m, 8 H, -OCH_2-), 3.87–3.89 (m, 8 H, -OCH_2-), 3.75 (s, 12 H, CH_3) ppm. ^{13}C{^{1}H} NMR (100 MHz, CD_3CN): δ = 150.1 (N-CH=N), 136.8 (Ar), 124.9 (Ar), 124.7 (imidazole), 123.0 (imidazole), 115.6 (Ar), 69.6 (OCH_2), 68.8 (OCH_2), 50.6 (CH_2), 36.8 (CH_3) ppm.

$[H_4L^2][PF_6]_4$ (5): A stirred solution of compound **1** (0.1 g, 0.13 mmol) in acetonitrile (50 mL) was heated at reflux in a three-necked flask fitted with a pressure-equalizing dropping funnel under nitrogen. A solution of 1-methylbenzimidazole (80 mg, 0.61 mmol) in acetonitrile (5 mL) was added dropwise to the solution at reflux and the resulting mixture was heated at reflux overnight. The solvent was evaporated to give a white solid $[H_4L^2]Br_4$ (**3**), which was dissolved in the minimum amount of methanol and treated with a saturated solution of ammonium hexafluorophosphate in water. The resulting white precipitate of **5** was filtered, washed with diethyl ether and dried under vacuum (0.11 g, 0.072 mmol, 55%); m.p. 187 °C (dec.). ^{1}H NMR (300 MHz, CD_3CN): δ = 8.87 (s, 4 H, N-CH=N), 7.74–7.76 (m, 8 H, benzimidazole), 7.59–7.69 (m, 8 H, benzimidazole), 7.16 (s, 4 H, Ar), 5.57 (s, 8 H, CH_2), 4.17–4.18 (m, 8 H, OCH_2), 3.89–3.91 (m, 8 H, OCH_2), 3.86 (s, 12 H, CH_3) ppm. ^{13}C{^{1}H} NMR (100 MHz, CD_3CN): δ = 150.0 (N-CH=N), 142.1 (Ar), 133.0 (Ar), 131.9 (Ar), 128.1 (Ar), 128.0 (Ar), 124.6 (Ar), 116.2 (Ar), 114.2 (Ar), 114.1 (Ar), 69.9 (OCH_2), 68.5 (OCH_2), 48.7 (CH_2), 34.1 (CH_3) ppm.

$[\{(cod)Rh\}_2(\mu\text{-}L^1)][PF_6]_2$ (6): Silver oxide (175 mg, 0.75 mmol) was added to a solution of tetrakis(imidazolium) salt **4** (250 mg, 0.189 mmol) in acetonitrile (50 mL). The mixture was protected from light and heated at 60 °C for 6 h under nitrogen. The resulting black suspension was filtered through Celite™ under air and solid $[RhCl(cod)]_2$ (93 mg, 0.190 mmol) was added to the resulting filtrate. The mixture was stirred at room temperature overnight under a slow nitrogen flow. The crude reaction mixture was then filtered through Celite™, concentrated and crystallized with diethyl ether to afford the yellow microcrystalline **6** (177 mg, 0.122 mmol, 65%); m.p. 227 °C (dec.). ^{1}H NMR (300 MHz, CD_3CN): δ = 7.29 (t, J = 2.0 Hz, 4 H, imidazole), 7.20 (s, 4 H, Ar), 6.93 (t, J = 2.0 Hz, 4 H, imidazole), 6.53 (d, J = 7.2 Hz, 4 H, CH_2), 4.96 (d, J = 7.2 Hz, 4 H, CH_2), 4.44–4.47 (m, 8 H, cod), 4.19–4.20 (m, 8 H, OCH_2), 3.86–3.92 (m, 8 H, OCH_2), 3.91 (s, 12 H, CH_3), 2.48–2.52 (m, 8 H, cod), 2.21–2.24 (m, 8 H, cod) ppm. ^{13}C{^{1}H} NMR (100 MHz, CD_3CN): δ = 181.7 (d, J = 53 Hz, carbene), 148.7 (Ar), 129.3 (Ar), 124.2 (imidazole), 121.7 (imidazole), 115.2 (Ar), 90.9 (d, J = 7 Hz, allyl cod), 89.8 (d, J = 7 Hz, allyl cod), 69.6 (OCH_2), 68.6 (OCH_2), 51.8 (CH_2), 38.6 (CH_3), 31.1 (d, J = 13 Hz, CH_2 cod) ppm. HRMS (+, ESI): calcd. for $[C_{56}H_{72}N_8O_6Rh_2]^{2+}$ 579.1837; found 579.1821.

$[\{(CO)_2Rh\}_2(\mu\text{-}L^1)][PF_6]_2$ (7): Carbon monoxide was bubbled through a solution of compound **6** (24 mg, 0.016 mmol) in acetonitrile (20 mL) for 4 h. The solvent and cyclooctadiene byproduct were removed under dynamic vacuum to give a yellow powder identified as compound **7** (20 mg, 0.015 mmol, 94%). IR (CH_3CN): $\tilde{\nu}$ = 2084, 2026 cm^{-1}. ^{1}H NMR (300 MHz, CD_3CN): δ = 7.38 (t, J = 1.7 Hz, 4 H, imidazole), 7.23 (s, 4 H, Ar), 7.07 (t, J = 2.0 Hz, 4 H, imidazole), 6.00 (d, J = 7.2 Hz, 4 H, CH_2), 4.97 (d, J = 7.4 Hz, 4 H, CH_2), 4.21–4.22 (m, 8 H, OCH_2), 3.88–3.89 (m, 8 H, OCH_2), 3.80 (s, 12 H, CH_3) ppm. ^{13}C NMR (100 MHz, CD_3CN): δ = 187.8 (d, J = 57 Hz, carbonyl), 171.8 (d, J = 45 Hz, carbene), 149.2 (Ar), 128.4 (Ar), 125.5 (imidazole), 122.9 (imidazole), 115.6 (Ar), 69.7 (-OCH_2-), 68.8 (OCH_2), 52.3 (CH_2), 39.0 (CH_3) ppm. HRMS (+, ESI): calcd. for $[C_{44}H_{48}F_6N_8O_{10}PRh_2]^{2+}$ 1199.1240; found 1199.1251.

X-ray Crystallography: Data for **(4)$_2$**·3CH_3CN were recorded with a Bruker Kappa-Appex-II CCD diffractometer and data for $[\{(cod)Rh\}_2(\mu\text{-}L^1)K(\eta^3\text{-}PF_6)][PF_6]_2$·1.25$Me_2CO$·$CH_3CN$ (**8**·1.25Me_2CO·CH_3CN) were collected with beamline MX2 at the Australian Syn-

chotron, Melbourne. The crystals were mounted in inert oil on cryoloops and transferred to the cold gas stream for the diffraction measurements. Data for **4** were collected by using monochromated Mo-K_α radiation (λ = 0.71073 Å) in ω scans and data for **8** were measured with monochromated synchrotron radiation set to wavelength λ = 0.71085 Å. Absorption corrections based on multiple scans were applied only to data from **4** by using SADABS.[15] The structures were solved by direct methods and refined on F^2 against all reflections using the SHELXL-97 program.[16] All non-hydrogen atoms were refined anisotropically and hydrogen atoms were included by using a riding model. Further crystal and refinement data are given in Table 3.

Table 3. Crystal and refinement data for $(\mathbf{4})_2 \cdot 3CH_3CN$ and $\mathbf{8} \cdot 1.25Me_2CO \cdot CH_3CN$.

	$(\mathbf{4})_2 \cdot 3MeCN$	$\mathbf{8} \cdot 1.25Me_2CO \cdot CH_3CN$
Empirical formula	$C_{86}H_{113}F_{48}N_{19}O_{12}P_8$	$C_{61.75}H_{78.50}F_{18}KN_9O_{7.50}P_3Rh_2$
Crystal habit	colourless plates	thin yellow needles
Crystal size [mm]	0.43 × 0.13 × 0.06	0.10 × 0.02 × 0.02
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a [Å]	14.0321(8)	10.580(2)
b [Å]	14.9488(8)	15.860(3)
c [Å]	17.0833(8)	24.410(5)
α [°]	114.719(2)	105.84(3)
β [°]	96.821(2)	90.02 (3)
γ [°]	101.490(2)	109.20(3)
U [Å^3]	3106.6(3)	3702.8(13)
Z	1	2
D_{calcd} [Mg m^{-3}]	1.478	1.567
M	2764.71	1729.15
F(000)	1410	1776.0
T [°C]	155(2)	150
θ_{max} [°]	25.00	25.00
μ(Mo-K_α) [mm^{-1}]	0.244	0.66
Abs. T_{min}–T_{max}	0.9016–0.9855	–
Refl. measured	41537	45425
Unique reflections	10834	12250
Obsd. reflections [$I > 2\sigma(I)$]	6019	9816
R_{int}	0.0463	0.076
R [$F^2 > 2\sigma(F^2)$]	0.1705	0.080
wR (F^2)	0.3467	0.230
Reflections used	10834	12250
Parameters	929	942
Restraints	428	4
S	1.077	1.26
Max./min. $\Delta\rho$ [e·Å^{-3}]	1.05/–0.64	1.79/–1.58

CDCC-831317 (for **4**) and -831316 (for **8**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Additional NMR spectra for **6** and **7** before and after adding $K[PF_6]$.

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