Ion Pair Cooperative Binding of Potassium Salts by New Rhenium(I) Bipyridine Crown Ether Receptors

Lindsay H. Uppadine,[†] James E. Redman,[†] Simon W. Dent,[†] Michael G. B. Drew,[‡] and Paul D. Beer*,[†]

Inorganic Chemistry Laboratory, Department of Chemistry, University of Oxford, South Parks Road, Oxford, U.K. OX1 3QR, and Department of Chemistry, University of Reading, Reading, U.K. RG6 6AD

Received December 27, 2000

The new rhenium(I) bipyridine crown ether receptors **1**−**4** have been prepared and their ion pair recognition properties examined. The crystal structure of $[\mathbf{1}\cdot KCl]_2\cdot 2H_2O$ demonstrates that potassium is coordinated by benzo-18-crown-6 and chloride is hydrogen bonded to the amide groups. Receptor **3** extracts solid KCl and KOAc into chloroform via ion pair complexation. NMR and emission titration studies with receptors **1**−**4** and KCl/KOAc show that cobound potassium enhances anion binding strength by electrostatic and conformational effects. Significant cooperative interactions are observed between the anion and cation sites for host **4** in CH_3CN. This molecule coordinates potassium to form a 1:1 intramolecular sandwich complex, which preorganizes the host for acetate binding.

Introduction

The syntheses of abiotic receptors for anion[1] or cation[2] coordination are well-established fields of research. In contrast, the simultaneous recognition of anion−cation pairs is a relatively new area in supramolecular chemistry.[3] This is surprising, given the range of practical applications for ion pair recognition. For example, ion pair receptors can be used to mimic important biological functions[4] and coordinate biologically significant species such as zwitterionic amino acids[5] and peptides.[6] Ion pair recognition can also increase the lipophilicity of ionic guests and therefore enhance ion pair solubility in nonpolar media. This phenomenon has been exploited by neutral receptors in both extraction and membrane transport systems.[7]

Ion pair receptors to date have been based on hydrogen bonding, positively charged or Lewis acidic groups to coordinate the anion, and calixarene or crown moieties to bind the cation.[3−8] These host molecules often exhibit cooperative and allosteric effects, whereby the association of one ion alters the binding affinity of the counterion.[8] The cooperativity can be positive or negative, depending on whether the binding affinity is enhanced or reduced, respectively. Cooperative behavior can result from several factors, such as through-bond or through-space electrostatic interactions between bound ions, or conformational changes induced by binding.

We have previously shown how transition metal amide bipyridine receptors coordinate anionic guests by electrostatic and hydrogen-bonding interactions.[9] We present here the synthesis of new ion pair receptors **1**−**4**, based on a rhenium(I) amide bipyridine crown ether architecture (Chart 1). The anion binding site is formed by the bipyridyl amide and 3,3′-protons, while the cation site is composed of either a benzo-18-crown-6

* To whom correspondence should be addressed. E-mail: paul.beer@chem.ox.ac.uk.

[†]University of Oxford.

[‡]University of Reading.

(1) (a) Schmidtchen, F. P.; Berger, M. *Chem. Rev.* **1997**, *97*, 1609. (b) Beer, P. D.; Smith, D. K. *Prog. Inorg. Chem.* **1997**, *46*, 1. (c) Katz, H. E. In *Inclusion Compounds*; Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Eds.; Oxford University Press: New York, 1991; Vol. 4, Chapter 9. (d) Antonisse, M. M. G.; Reinhoudt, D. N. *Chem. Commun.* **1998**, 443. (e) Pierre, J.-L.; Baret, P. *Bull. Soc. Chim. Fr.* II-367, **1983**, 367.

(2) (a) Lindoy, L. F. *The Chemistry of Macrocyclic Ligand Complexes*; Cambridge University Press: Cambridge, 1989. (b) Weber, E.; Vögtle, F. *Top. Curr. Chem.* **1981**, *98*, 1. (c) Pedersen, C. J. *J. Am. Chem. Soc.* **1967**, *89*, 7017. (d) Pedersen, C. J.; Frensdorff, H. K. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 16. (e) Lamb, J. D.; Izatt, R. M.; Christensen, J. J.; Eatough, D. J. In *Co-ordination Chemistry of Macrocyclic Ligands*; Melson, G. A., Ed.; Plenum: New York, 1979; Chapter 3.

(3) For recent examples, see: (a) Redman, J. E.; Beer, P. D.; Dent, S. W.; Drew, M. G. B. *Chem. Commun.* **1998**, 231. (b) Nishizawa, S.; Shigemori, K.; Teramae, N. *Chem. Lett.* **1999**, 1185. (c) Beer, P. D.; Cooper, J. B. *Chem. Commun.* **1998**, 129. (d) Cooper, J. B.; Drew, M. G. B.; Beer, P. D. *J. Chem. Soc., Dalton Trans.* **2000**, 2721. (e) Shukla, R.; Kida, T.; Smith, B. D. *Org. Lett.* **2000**, *2*, 3099.

(4) Kinnear, K. I.; Mousley, D. P.; Arafa, E.; Lockhart, J. C. *J. Chem. Soc., Dalton Trans.* **1994**, 3637.

(5) (a) Tsukube, H.; Wada, M.; Shinoda, S.; Tamiaki, H. *Chem. Commun.* **1999**, 1007. (b) Rosa, D.; Young, V. G.; Coucouvanis, D. *Inorg. Chem.* **1998**, *37*, 5042.

(6) (a) Hossain, M. A.; Schneider, H.-J. *J. Am. Chem. Soc.* **1998**, *120*, 11208. (b) Sirish, M.; Schneider, H.-J. *Chem. Commun.* **1999**, 907.

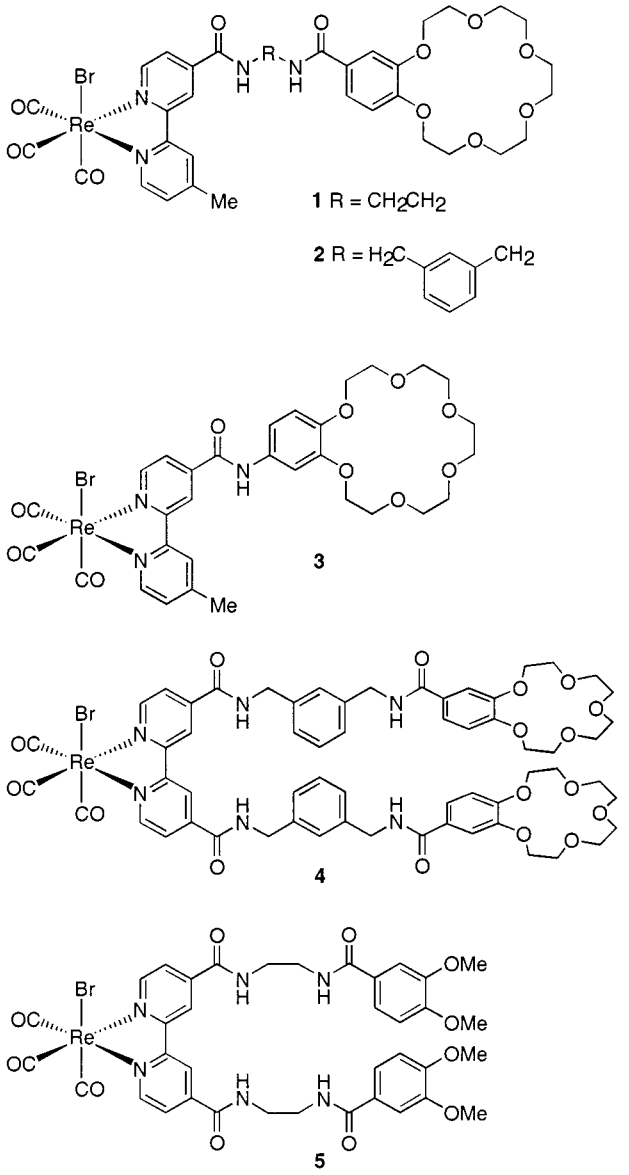
(7) (a) Pelizzi, N.; Casnati, A.; Friggeri, A.; Ungaro, R. *J. Chem. Soc., Perkin Trans. 2* **1998**, 1307. (b) Reetz, M. T.; Niemeyer, C. M.; Harms, K. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1472. (c) Reetz, M. T.; Johnson, B. M.; Harms, K. *Tetrahedron Lett.* **1994**, *35*, 2525. (d) Flack, S. S.; Chaumette, J.-L.; Kilburn, J. D.; Langley, G. J.; Webster, M. *J. Chem. Soc., Chem. Commun.* **1993**, 399. (e) Rudkevich, D. M.; Brzozka, Z.; Palys, M.; Visser, H. C.; Verboom, W.; Reinhoudt, D. N. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 467. (f) Rudkevich, D. M.; Mercer-Chalmers, J. D.; Verboom, W.; Ungaro, R.; de Jong, F.; Reinhoudt, D. N. *J. Am. Chem. Soc.* **1995**, *117*, 6124. (g) Beer, P. D.; Hopkins, P. K.; McKinney, J. D. *Chem. Commun.* **1999**, 1253.

(8) For examples of allosteric behavior in ion pair recognition, see: (a) Scheerder, J.; van Duynhoven, J. P. M.; Engbersen, J. F. J.; Reinhoudt, D. N. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1090. (b) Beer, P. D.; Stokes, S. E. *Polyhedron* **1995**, *14*, 2631.

(9) (a) Beer, P. D. *Chem. Commun.* **1996**, 689. (b) Beer, P. D.; Dent, S. W.; Hobbs, G. S.; Wear, T. J. *Chem. Commun.* **1997**, 99. (c) Beer, P. D.; Drew, M. G. B.; Hesek, D.; Shade, M.; Szemes, F. *Chem. Commun.* **1996**, 2161. (d) Beer, P. D.; Timoshenko, V.; Maestri, M.; Passaniti, P.; Balzani, V. *Chem. Commun.* **1999**, 1755.

10.1021/ic001450v CCC: $20.00
Published on Web 05/10/2001

Chart 1



group (**1**−**3**) or two benzo-15-crown-5 moieties (**4**). Receptor **5** is a model compound and contains a binding site for the anionic guest, but no crown ether to coordinate the cation.

The diameter of K^+ (2.66 Å) provides a good match for the cavity size of 18-crown-6 (2.6−3.2 Å),[2b] and so this cation is predicted to form 1:1 complexes with receptors **1**−**3**. In contrast, the potassium cation is significantly larger than the cavity dimensions of 15-crown-5 (1.7−2.2 Å).[2b] Bis(crown ethers) are well-known to form intramolecular sandwich complexes with cations larger than the diameter of each ring,[10] and a 1:1 sandwich complex is therefore anticipated for host **4** and potassium. This would yield a pseudomacrocycle, with a binding site preorganized for anionic guests.

The ion pair recognition properties of receptors **1**−**4** have been analyzed by a variety of techniques, including NMR and emission spectroscopy, X-ray crystallography, and solid−liquid extraction experiments. The results reveal that these receptors complex potassium cations and simultaneously bind chloride or acetate anions via positive cooperative effects.[11]

Experimental Section

Instrumentation. NMR spectra were recorded on Varian or Bruker 300 MHz, Bruker 400 MHz, and Varian 500 MHz spectrometers. Mass spectrometry was carried out at the SERC Mass Spectrometry Service, Swansea. Elemental analysis was performed at the Inorganic Chemistry Laboratory, University of Oxford. Emission and absorption spectra were recorded in dry solvents using a Perkin-Elmer LS 50 B fluorescence spectrometer and a Perkin-Elmer Lambda 6 UV−vis spectrometer, respectively.

Reagent and Solvent Pretreatment. Commercially available materials were used without further purification unless otherwise stated. Acetonitrile and dichloromethane were distilled from calcium hydride and calcium chloride, respectively, and tetrahydrofuran was dried over sodium. Thionyl chloride was distilled from triphenyl phosphite and used immediately in subsequent reactions. 4′-Carboxy-benzo-15-crown-5,[12] 4′-carboxy-benzo-18-crown-6,[13] 1-*tert*-butoxycarbonyl-1,2-diaminoethane,[14] 4,4′-dicarboxy-2,2′-bipyridine,[15] and 4-carboxy-4′-methyl-2,2′-bipyridine[16] were synthesized according to literature procedures.

Protocol for the NMR and Optical Titrations. NMR. Aliquots of TBAOAc, TBACl, or KSCN (250 μmol in 0.5 mL of deuterated solvent) were added to a solution of the host (5 μmol in 0.5 mL) for the ^{1}H NMR anion or cation titrations. The concentrations of host and guest were doubled for the ^{13}C NMR titration. For the ion pair recognition studies, aliquots of TBAOAc or TBACl (250 μmol in 0.5 mL) were added to a mixture of the host (5 μmol in 0.4 mL) and KSCN (0.1 mL of a 250 μmol solution in 5 mL). In all cases, the chemical shift of a specific nucleus on the host was monitored for each addition from 0 to 5 equiv of guest. The resulting titrations were analyzed by the EQNMR program.[17]

Absorption/Emission. Spectra were obtained for a solution of the receptor (2×10^{-5} M) in 3 mL of dry solvent. For the optical titrations, a solution of the guest (6×10^{-3} M) in dry solvent was added to the host solution and the absorption/emission spectrum was recorded for titration points between 0 and 10 equiv of guest. The data was analyzed by the Specfit program.[18]

4′-(Chlorocarbonyl)-benzo-18-crown-6, 4′-(Chlorocarbonyl)-benzo-15-crown-5, and 4,4′-Bis(chlorocarbonyl)-2,2′-bipyridine. Typical Preparation. 4′-Carboxy-benzo-18-crown-6, 4′-carboxy-benzo-15-crown-5, or 4,4′-dicarboxy-2,2′-bipyridine was refluxed in thionyl chloride (ca. 30 mL) for 18 h under nitrogen. The excess thionyl chloride was then removed by distillation, and the yellow residues were dried under vacuum (4 h). The acid chlorides were assumed to form in quantitative yield and were used immediately in subsequent reactions.

4-(Chlorocarbonyl)-4′-methyl-2,2′-bipyridine. Typical Preparation. A suspension of 4-carboxy-4′-methyl-2,2′-bipyridine in dry CH_2Cl_2 (20 mL) and thionyl chloride (3 mL) was refluxed for 3 h under nitrogen. The excess liquid was then removed by distillation under high vacuum and the yellow solid dried under vacuum for 1 h. The acid chloride was assumed to form in quantitative yield and was used immediately in subsequent reactions.

1-*tert*-Butoxycarbonyl-1,3-bis(aminomethyl)benzene. Di-*tert*-butyl-dicarbonate (2.45 g, 0.0112 mol) in dioxane (30 mL) was added dropwise to a stirred solution of *m*-xylylenediamine (6.12 g, 0.0449

(10) (a) Beer, P. D.; Drew, M. G. B.; Knubley, R. J.; Ogden, M. I. *J. Chem. Soc., Dalton Trans.* **1995**, 3117. (b) Kikukawa, K.; He, G.-X.; Abe, A.; Goto, T.; Arata, R.; Ikeda, T.; Wada, F.; Matsuda, T. *J. Chem. Soc., Perkin Trans. 2* **1987**, 135. (c) Beer, P. D.; Tite, E. L.; Ibbotson, A. *J. Chem. Soc., Dalton Trans.* **1990**, 2691. (d) Inoue, Y.; Hakushi, T.; Liu, Y.; Tong, L.-H.; Hu, J.; Zhao, G.-D.; Huang, S.; Tian, B.-Z. *J. Phys. Chem.* **1988**, *92*, 2371. (e) Shinkai, S.; Nakaji, T.; Ogawa, T.; Shigematsu, K.; Manabe, O. *J. Am. Chem. Soc.* **1981**, *103*, 111.

(11) Part of this work has been published as a preliminary communication (ref 3a).

(12) Bourgoin, M.; Wong, K. H.; Hui, J. Y.; Smid, J. *J. Am. Chem. Soc.* **1975**, *97*, 3462.

(13) Ungaro, R.; El Haj, B.; Smid, J. *J. Am. Chem. Soc.* **1976**, *98*, 5198.

(14) Krapcho, A. P.; Kuell, C. S. *Synth. Commun.* **1990**, *20*, 2559.

(15) Garelli, N.; Vierling, P. *J. Org. Chem.* **1992**, *57*, 3046.

(16) Peek, B. M.; Ross, G. T.; Edwards, S. W.; Meyer, G. J.; Meyer, T. J.; Erickson, B. W. *Int. J. Pept. Protein Res.* **1991**, *38*, 114.

(17) Hynes, M. J. *J. Chem. Soc., Dalton Trans.* **1993**, 311.

(18) Binstead, R. A.; Zuberbühler, A. D. *Specfit Global Analysis*, Version 2.90X.

mol) in dioxane (30 mL). The mixture was stirred at room temperature for 19 h. The solvent was then removed and the white solid suspended in water (75 mL) and filtered to remove the insoluble bis-substituted product. The filtrate was extracted with CH_2Cl_2 (3 × 50 mL), and the combined organic layers were washed with water (6 × 50 mL) to remove the excess diamine. The organic fraction was dried over $MgSO_4$ before the solvent was evaporated to give a colorless oil, which was stored under vacuum (1.98 g, 75% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.27 (1H, t, J = 7.5 Hz, ArCH4), 7.20 (1H, s, ArCH1), 7.18 (1H, d, J = 7.5 Hz, ArCH3), 7.14 (1H, d, J = 7.5 Hz, ArCH5), 5.04 (1H, s, br, CONH), 4.26 (2H, d, J = 6 Hz, CH_2NHCO), 3.80 (2H, s, CH_2NH$_2$), 1.44 (2H, s, NH$_2$), 1.40 (9H, s, OCMe$_3$). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 155.77 (CONH), 143.56, 139.09, 128.70, 126.06, 125.96, 125.80, 79.42 (O*C*(CH$_3$)$_3$), 46.35 (CH$_2$NH), 44.62 (CH$_2$-NH), 28.41 (OC(*C*H$_3$)$_3$).

1-*tert*-Butoxycarbonyl-2-(4′-carbonyl-benzo-18-crown-6)-1,2-diaminoethane (6). 4′-(Chlorocarbonyl)-benzo-18-crown-6 (5.06 g, 0.0135 mol) was dissolved in dry CH_2Cl_2 (40 mL) and added dropwise to a stirred solution of 1-*tert*-butoxycarbonyl-1,2-diaminoethane (2.49 g, 0.0155 mol) and triethylamine (2.73 g, 0.0270 mol) in dry CH_2Cl_2 (30 mL) under nitrogen. The mixture was stirred at room temperature for 24 h and then filtered to remove a white precipitate. The residue was washed with CH_2Cl_2 (10 mL), H_2O (2 × 10 mL), and Et_2O (2 × 10 mL) to give the product as a white solid (1.25 g, 19% yield).

The yellow filtrate was evaporated and redissolved in $CHCl_3$ (100 mL), washed with HCl(aq) (2 M, 2 × 75 mL) and H_2O (2 × 75 mL), and then dried over $MgSO_4$. The solvent was removed under vacuum to give a second batch of the product (4.19 g, 62% yield). Combined yield: 5.44 g, 81%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.43 (1H, d, J = 2 Hz, ArCH3), 7.34 (1H, d, J = 8 Hz, ArCH5), 7.14 (1H, m, br, ArCONH), 6.84 (1H, d, J = 8.5 Hz, ArCH6), 5.01 (1H, m, br, NHCOO), 4.18 (4H, m, OCH$_2$), 3.90 (4H, m, OCH$_2$), 3.74 (4H, m, OCH$_2$), 3.69 (4H, m, OCH$_2$), 3.66 (4H, s, OCH$_2$), 3.50 (2H, m, NHC*H*$_2$), 3.36 (2H, m, NHC*H*$_2$), 1.38 (9H, s, OCMe$_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.33 (ArCONH), 157.48 (NHCOO), 151.51, 148.44, 126.91, 120.17, 112.58, 112.26, 79.71 (O*C*(CH$_3$)$_3$), 70.82, 70.79, 70.69, 70.64, 70.58, 70.51, 69.39, 69.34, 68.88, 68.79, 41.94 (CH$_2$NH), 40.06 (CH$_2$NH), 28.31 (OC(*C*H$_3$)$_3$). Anal. Calcd for $C_{24}H_{38}N_2O_9$: C, 57.8; H, 7.7; N, 5.6. Found: C, 57.6; H, 7.8; N, 5.5. MS-FAB: *m*/*z* 521 (M + Na)$^+$, 499 (M + H)$^+$.

1-*tert*-Butoxycarbonyl-3-(4′-carbonyl-benzo-18-crown-6)-1,3-bis(aminomethyl)benzene (7). A solution of 4′-(chlorocarbonyl)-benzo-18-crown-6 (1.81 g, 4.83 mmol) in dry CH_2Cl_2 (40 mL) was added dropwise to a stirred solution of 1-*tert*-butoxycarbonyl-1,3-bis(aminomethyl)benzene (1.31 g, 5.54 mmol) and triethylamine (0.977 g, 9.65 mmol) in dry CH_2Cl_2 (20 mL) under nitrogen. The solution was stirred at room temperature for 18 h and then washed with saturated $NaHCO_3$(aq) (2 × 100 mL) and water (2 × 50 mL). The organic layer was dried over $MgSO_4$ before the solvent was evaporated to give the product as a white solid (2.41 g, 87% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.43 (1H, d, J = 1.5 Hz, ArCH3crown), 7.20−7.32 (5H, m, ArCH1, ArCH3, ArCH4, ArCH5, ArCH5crown), 6.82 (1H, d, J = 8.5 Hz, ArCH6crown), 6.49 (1H, s, br, NHCOcrown), 4.89 (1H, s, br, NHCOO), 4.58 (2H, d, J = 6 Hz, CH_2NHCOcrown), 4.28 (2H, d, J = 6 Hz, CH_2NHCOO), 4.16 (4H, m, OCH$_2$), 3.90 (4H, m, OCH$_2$), 3.73 (4H, m, OCH$_2$), 3.68 (4H, m, OCH$_2$), 3.65 (4H, s, OCH$_2$), 1.40 (9H, s, OCMe$_3$). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 166.74 (NHCOcrown), 151.42 (NHCOO), 148.38, 139.40, 138.73, 128.91, 126.94, 126.76, 126.39, 119.84, 112.60, 112.04, 79.52 (O*C*(CH$_3$)$_3$), 70.70 (OCH$_2$), 70.59 (OCH$_2$), 70.54 (OCH$_2$), 69.31 (OCH$_2$), 69.24 (OCH$_2$), 68.77 (OCH$_2$), 68.65 (OCH$_2$), 44.45 (CH$_2$NH), 43.92 (CH$_2$NH), 28.40 (OC(*C*H$_3$)$_3$). Anal. Calcd for $C_{30}H_{42}N_2O_9 \cdot H_2O$: C, 60.8; H, 7.5; N, 4.7. Found: C, 61.1; H, 7.2; N, 4.9. MS-FAB: *m*/*z* 597 (M + Na)$^+$, 574 (M + H)$^+$.

1-*tert*-Butoxycarbonyl-3-(4′-carbonyl-benzo-15-crown-5)-1,3-bis(aminomethyl)benzene (8). A solution of 4′-(chlorocarbonyl)-benzo-15-crown-5 (1.27 g, 3.85 mmol) in dry CH_2Cl_2 (40 mL) was added dropwise to a solution of 1-*tert*-butoxycarbonyl-1,3-bis(aminomethyl)-benzene (1.05 g, 4.43 mmol) and triethylamine (0.780 g, 7.71 mmol) in dry CH_2Cl_2 (20 mL) under nitrogen. The yellow solution was stirred at room temperature for 18 h and then washed with saturated $NaHCO_3$(aq) (2 × 100 mL) and water (2 × 50 mL). The organic layer was dried over $MgSO_4$, and the solvent was evaporated to leave a pale yellow solid, which was redissolved in the minimum amount of $CHCl_3$. Dropwise addition of hexane to the stirred solution resulted in the formation of a white precipitate. This was collected by filtration to afford the product as a white solid (1.70 g, 83% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.42 (1H, d, J = 2 Hz, ArCH3crown), 7.30 (1H, dd, J = 8.5 Hz, J' = 2 Hz, ArCH5crown), 7.23−7.28 (3H, m, ArCH1, ArCH3, ArCH4), 7.18 (1H, d, J = 8 Hz, ArCH5), 6.79 (1H, d, J = 8 Hz, ArCH6crown), 6.70 (1H, s, br, NHCOcrown), 4.94 (1H, s, br, NHCOO), 4.56 (2H, d, J = 5.5 Hz, CH_2NHcrown), 4.26 (2H, d, J = 6 Hz, CH_2NHCOO), 4.11 (4H, m, OCH$_2$), 3.86 (4H, m, OCH$_2$), 3.72 (8H, m, OCH$_2$), 1.39 (9H, s, OCMe$_3$). ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.79 (NHCOcrown), 151.70 (NHCOO), 148.66, 139.49, 138.86, 128.98, 127.24, 126.86, 126.46, 120.11, 113.10, 112.38, 70.91 (OCH$_2$), 70.88 (OCH$_2$), 70.21 (OCH$_2$), 70.15 (OCH$_2$), 69.22 (OCH$_2$), 69.16 (OCH$_2$), 68.84 (OCH$_2$), 68.59 (OCH$_2$), 44.48 (CH$_2$NH), 43.93 (CH$_2$-NH), 28.37 (OC(*C*H$_3$)$_3$). Anal. Calcd for $C_{28}H_{38}N_2O_8 \cdot 0.5H_2O$: C, 62.3; H, 7.3; N, 5.2. Found: C, 62.5; H, 7.3; N, 5.3. MS-FAB: *m*/*z* clusters at 1081−1084 (2M + Na)$^+$, 1061 (2M)$^+$, 569 (M + K)$^+$, 553 (M + Na)$^+$, 530 (M)$^+$.

1-(4-Carbonyl-4′-methyl-2,2′-bipyridyl)-2-(4′-carbonyl-benzo-18-crown-6)-1,2-diaminoethane (9). Trifluoroacetic acid (5 mL) was added to a solution of crown ether **6** (0.859 g, 1.72 mmol) in dry CH_2Cl_2 (15 mL), and the solution was stirred at room temperature for 1 h. The excess liquid was then evaporated to yield a yellow oil, which solidified under high vacuum. The solid was dried under vacuum for 45 min and then redissolved in dry CH_2Cl_2 (30 mL). Triethylamine (2.91 g, 0.0288 mol) was added to the solution and the mixture stirred for 30 min under nitrogen before dropwise addition of 4-(chlorocarbonyl)-4′-methyl-2,2′-bipyridine (0.335 g, 1.44 mmol) dissolved in dry CH_2Cl_2 (40 mL). The red/brown solution was stirred at room temperature for 16 h and then washed with saturated $NaHCO_3$(aq) (2 × 100 mL) and water (2 × 100 mL). The organic layer was dried over $MgSO_4$ before the solvent was evaporated to give a yellow solid. This was suspended in MeCN (20 mL), filtered, and washed with MeCN (5 mL) to afford the product as a white solid (0.214 g, 25% yield). ^{1}H NMR (500 MHz, DMSO-d_6): δ 9.11 (1H, m, br, bpyNH), 8.84 (1H, d, J = 5.5 Hz, bpyH6), 8.81 (1H, s, bpyH3), 8.60 (1H, d, J = 5 Hz, bpyH6′), 8.53 (1H, m, br, NHcrown), 8.29 (1H, s, bpyH3′), 7.83 (1H, dd, J = 5.3 Hz, J' = 1.8 Hz, bpyH5), 7.48 (1H, dd, J = 8.3 Hz, J' = 1.8 Hz, ArCH5), 7.46 (1H, d, J = 2 Hz, ArCH3), 7.35 (1H, d, J = 5 Hz, bpyH5′), 7.02 (1H, d, J = 8 Hz, ArCH6), 4.11 (4H, m, OCH$_2$), 3.74 (4H, m, OCH$_2$), 3.59 (4H, m, OCH$_2$), 3.54 (4H, m, OCH$_2$), 3.51 (4H, s, OCH$_2$), 3.46 (4H, m, CH_2NH), 2.42 (3H, s, bpyMe). ^{13}C NMR (125 MHz, DMSO-d_6): δ 166.21 (CONH), 165.15 (CONH), 156.28, 154.76, 150.78, 149.95, 149.29, 148.30, 147.67, 142.92, 127.02, 125.45, 121.68, 121.52, 120.74, 118.34, 112.08, 70.08 (OCH$_2$), 70.05 (OCH$_2$), 70.02 (OCH$_2$), 69.96 (OCH$_2$), 69.92 (OCH$_2$), 68.79 (OCH$_2$), 68.76 (OCH$_2$), 68.32 (OCH$_2$), 20.87 (bpyMe). Anal. Calcd for $C_{31}H_{38}N_4O_8 \cdot 2H_2O$: C, 59.0; H, 6.7; N, 8.9. Found: C, 59.1; H, 6.5; N, 8.8. MS-FAB: *m*/*z* 617 (M + Na)$^+$, 595 (M + H)$^+$.

1-(4-Carbonyl-4′-methyl-2,2′-bipyridyl)-3-(4′-carbonyl-benzo-18-crown-6)-1,3-bis(aminomethyl)benzene (10). Trifluoroacetic acid (5 mL) was added to a solution of crown ether **7** (0.712 g, 1.24 mmol) in dry CH_2Cl_2 (10 mL) and the solution stirred at room temperature for 1.5 h. The excess liquid was then evaporated to yield a yellow oil, which was dried under vacuum for 2 h and then redissolved in dry CH_2Cl_2 (40 mL). Triethylamine (2.51 g, 0.0248 mol) was added to the solution and the mixture stirred for 30 min under nitrogen before dropwise addition of 4-(chlorocarbonyl)-4′-methyl-2,2′-bipyridine (0.346 g, 1.49 mmol) dissolved in dry CH_2Cl_2 (40 mL). The pink solution was stirred at room temperature for 21 h and then washed with saturated $NaHCO_3$(aq) (2 × 100 mL) and water (2 × 100 mL). The organic layer was dried over $MgSO_4$ before the solvent was evaporated to give a pale orange solid. This was recrystallized from ethanol to afford the product as a white solid (0.288 g, 35% yield). ^{1}H NMR (500 MHz, DMSO-d_6): δ 9.55 (1H, t, J = 6 Hz, bpyNH), 8.93 (1H, t, J = 6 Hz, NHcrown), 8.83 (2H, m, bpyH6, bpyH3), 8.59 (1H, d, J = 5 Hz, bpyH6′), 8.30 (1H, s, bpyH3′), 7.84 (1H, dd, J = 5.5 Hz, J' = 1.5 Hz, bpyH5), 7.48 (2H, m, ArCH3crown, ArCH5crown), 7.33 (3H, m, bpyH5′, ArCH1, ArCH4), 7.24 (2H, m, ArCH3, ArCH5), 6.96 (1H, d,

J = 8.5 Hz, ArCH6crown), 4.51 (2H, d, J = 6 Hz, CH_2NHbpy), 4.46 (2H, d, J = 6 Hz, CH_2NHcrown), 4.09 (4H, m, OCH_2), 3.74 (4H, m, OCH_2), 3.59 (4H, m, OCH_2), 3.54 (4H, m, OCH_2), 3.52 (4H, s, OCH_2), 2.42 (3H, s, bpyMe). ^{13}C NMR (75.5 MHz, DMSO-d_6): δ 165.77 (CONH), 164.78 (CONH), 156.25, 154.65, 150.72, 150.02, 149.25, 148.30, 147.62, 142.67, 140.22, 139.39, 128.45, 126.68, 126.19, 126.01, 125.95, 125.48, 121.69, 121.53, 120.69, 118.23, 111.94, 111.79, 70.08 (OCH_2), 70.06 (OCH_2), 69.98 (OCH_2), 69.91 (OCH_2), 68.77 (OCH_2), 68.76 (OCH_2), 68.24 (OCH_2), 42.97 (CH_2NH), 42.72 (CH_2NH), 20.94 (bpyMe). Anal. Calcd for $C_{37}H_{42}N_4O_8 \cdot 1.5H_2O$: C, 63.7; H, 6.5; N, 8.0. Found: C, 63.8; H, 6.1; N, 7.7. MS-FAB: m/z 693 (M + Na)$^+$, 671 (M + H)$^+$.

4-(4′-Aminobenzo-18-crown-6)carbonyl-4′-methyl-2,2′-bipyridine. 4-(Chlorocarbonyl)-4′-methyl-2,2′-bipyridine (0.389 g, 1.67 mmol) was dissolved in dry CH_2Cl_2 (40 mL) and added dropwise to a solution of 4′-aminobenzo-18-crown-6 (0.456 g, 1.39 mmol) and triethylamine (0.564 g, 5.57 mmol) in dry CH_2Cl_2 (20 mL) under nitrogen. The mixture was then stirred at room temperature for 16 h. The brown solution was filtered, washed with saturated $NaHCO_3$(aq) (2 × 100 mL) and water (2 × 50 mL), and then dried over $MgSO_4$. The organic layer was evaporated to yield a brown solid, which was suspended in MeCN (30 mL) and stirred for 10 min before filtration. This gave the product as a gray solid, which was dried under vacuum (0.377 g, 52% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.83 (1H, d, J = 5 Hz, bpyH6), 8.71 (1H, s, bpyH3), 8.54 (1H, d, J = 5 Hz, bpyH6′), 8.29 (1H, s, bpyH3′), 8.20 (1H, s, br, bpyNH), 7.84 (1H, dd, J = 5 Hz, J' = 1.5 Hz, bpyH5), 7.45 (1H, d, J = 2.5 Hz, ArCH3), 7.19 (1H, d, J = 4 Hz, bpyH5′), 7.10 (1H, dd, J = 8.5 Hz, J' = 2.5 Hz, ArCH5), 6.87 (1H, d, J = 8.5 Hz, ArCH6), 4.20 (2H, m, OCH_2), 4.16 (2H, m, OCH_2), 3.93 (4H, m, OCH_2), 3.77 (4H, m, OCH_2), 3.72 (4H, m, OCH_2), 3.69 (4H, s, OCH_2), 2.46 (3H, s, bpyMe). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 163.55 (CONH), 156.82, 154.74, 150.08, 148.99, 148.81, 148.39, 146.01, 142.97, 131.35, 125.20, 122.09, 121.73, 117.17, 114.43, 113.03, 107.27, 70.82 (OCH_2), 70.70 (OCH_2), 70.63 (OCH_2), 69.62 (OCH_2), 69.45 (OCH_2), 68.91 (OCH_2), 21.53 (bpyMe). Anal. Calcd for $C_{28}H_{33}N_3O_7 \cdot H_2O$: C, 62.1; H, 6.5; N, 7.8. Found: C, 62.5; H, 6.2; N, 7.6. MS-FAB: m/z 546 (M + Na)$^+$, 524 (M + H)$^+$.

4,4′-Bis[1-carbonyl-3-(4′-carbonyl-benzo-15-crown-5)-1,3-bis-(aminomethyl)benzene]-2,2′-bipyridine (11). Trifluoroacetic acid (5 mL) was added to a solution of crown ether **8** (1.68 g, 3.17 mmol) in dry CH_2Cl_2 (20 mL) and the mixture stirred at room temperature for 1.5 h. The excess liquid was then evaporated to yield an orange oil, which was dried under vacuum for 3 h and then redissolved in dry CH_2Cl_2 (40 mL). Triethylamine (3.20 g, 0.0317mol) was added to the solution and the mixture was stirred for 15 min under nitrogen before dropwise addition of 4,4′-bis(chlorocarbonyl)-2,2′-bipyridine (0.223 g, 0.792 mmol) dissolved in dry CH_2Cl_2 (30 mL). The mixture was stirred at room temperature for 2.5 days to yield a white precipitate. This was collected by filtration and washed with CH_2Cl_2 (100 mL), aqueous ammonia solution (1 M, 100 mL), and then water until the washings ran at neutral pH. The solid was suspended in diethyl ether (75 mL), stirred for 1h and then removed by filtration. This gave the product as a white solid, which was dried under vacuum (0.625 g, 74% yield). ^{1}H NMR (500 MHz, DMSO-d_6): δ 9.59 (2H, t, J = 6 Hz, bpyNH), 8.93 (2H, t, J = 6 Hz NHcrown), 8.87 (4H, m, bpyH6,6′, bpyH3,3′), 7.90 (2H, dd, J = 5 Hz, J' = 1.5 Hz, bpyH5,5′), 7.49 (4H, m, ArCH5crown, ArCH3crown), 7.33 (4H, m, ArCH1, ArCH4), 7.25 (4H, m, ArCH3, ArCH5), 6.94 (2H, d, J = 8 Hz, ArCH6crown), 4.52 (4H, d, J = 5 Hz, CH_2NHbpy), 4.47 (4H, d, J = 6 Hz, CH_2NHcrown), 4.04 (8H, m, OCH_2), 3.75 (8H, m, OCH_2), 3.60 (16H, s, OCH_2). ^{13}C NMR (125 MHz, DMSO-d_6): δ 165.81 (CONH), 164.71 (CONH), 155.70, 151.21, 150.18, 148.03, 142.85, 140.23, 139.37, 128.45, 126.94, 126.23, 126.04, 125.96, 122.10, 120.95, 118.41, 112.74, 112.50, 70.65 (OCH_2), 69.89 (OCH_2), 69.80 (OCH_2), 68.91 (OCH_2), 68.81 (OCH_2), 68.70 (OCH_2), 68.43 (OCH_2), 42.96 (CH_2NH), 42.69 (CH_2NH). Anal. Calcd for $C_{58}H_{64}N_6O_{14} \cdot H_2O$: C, 64.1; H, 6.1; N, 7.7. Found: C, 64.0; H, 5.9; N, 7.9. MS-FAB: m/z 1092 (M + Na)$^+$, 1070 (M + H)$^+$.

1-*tert*-Butoxycarbonyl-2-(4′-carbonyl-1′,2′-dimethoxyphenyl)-1,2-diaminoethane (12). Veratric acid (2.55 g, 0.0140 mol) was refluxed in thionyl chloride (50 mL) for 18 h under nitrogen. The excess thionyl chloride was then removed by distillation to give a purple solid after drying under vacuum. This was dissolved in dry CH_2Cl_2 (40 mL) and added dropwise to a solution of 1-*tert*-butoxycarbonyl-1,2-diaminoethane (2.58 g, 0.0161 mol) and triethylamine (2.83 g, 0.0280 mol) in dry CH_2Cl_2 (30 mL) under nitrogen. The mixture was stirred at room temperature for 3 days, and the white precipitate was then removed by filtration and washed with CH_2Cl_2 (10 mL) and H_2O (2 × 50 mL). This gave the product as a white solid (1.83 g, 40% yield). The washings and filtrate were combined to give a precipitate, which was collected by filtration and redissolved in the minimum amount of CH_2Cl_2. Dropwise addition of hexane yielded a white precipitate, which was removed by filtration and washed with hexane (2 × 20 mL) and H_2O (2 × 50 mL). This gave a second batch of the product (1.64 g, 36% yield). Combined yield: 3.47 g, 76%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.48 (1H, m, br, ArCONH), 7.41 (1H, d, J = 2 Hz, ArCH3), 7.36 (1H, d, J = 8 Hz, ArCH5), 6.78 (1H, d, J = 8.5 Hz, ArCH6), 5.33 (1H, t, J = 5.5 Hz, NHCOO), 3.83 (3H, s, OMe), 3.83 (3H, s, OMe), 3.46 (2H, m, CH_2NH), 3.32 (2H, m, CH_2NH), 1.33 (9H, s, $OCMe_3$). ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.53 (ArCONH), 158.50 (NHCOO), 152.44, 149.53, 127.24, 120.37, 110.64, 110.53, 79.66 (O*C*(CH_3)$_3$), 55.53 (OMe), 41.41 (CH_2NH), 39.51 (CH_2NH), 27.58 (OC(*C*H$_3$)$_3$). Anal. Calcd for $C_{16}H_{24}N_2O_5$: C, 59.2; H, 7.5; N, 8.6. Found: C, 59.0; H, 7.2; N, 8.4.

4,4′-Bis(1-carbonyl-2-(4′-carbonyl-1′,2′-dimethoxyphenyl)-1,2-diaminoethyl)-2,2′-bipyridine (13). A solution of trifluoroacetic acid (5 mL) in dry CH_2Cl_2 (5 mL) was added to a solution of compound **12** (1.00 g, 3.08 mmol) in dry CH_2Cl_2 (5 mL) and the mixture stirred at room temperature for 30 min. The excess liquid was then evaporated to yield a brown oil, which was dried under vacuum for 3 h. The oil was redissolved in dry THF (30 mL) and triethylamine (6.24 g, 0.062 mol) added. A solution of 4,4′-bis(chlorocarbonyl)-2,2′-bipyridine (0.225 g, 0.80 mmol) in dry THF (30 mL) was added dropwise over 20 min under nitrogen, and the mixture was then stirred at room temperature overnight. The precipitate was collected by filtration, washed with THF (100 mL), aqueous ammonia solution (1 M, 100 mL) and water (100 mL), and then dried to afford the product as a pale brown solid (0.38 g, 74% yield). ^{1}H NMR (300 MHz, DMSO-d_6): δ 9.10 (2H, s, br, bpyNH), 8.86 (2H, d, J = 4.8 Hz, bpyH6,6′), 8.81 (2H, s, bpyH3,3′), 8.52 (2H, s, br, ArCONH), 7.86 (2H, d, J = 5 Hz, bpyH5,5′), 7.47 (2H, d, J = 8.6 Hz, ArCH5), 7.44 (2H, s, ArCH3), 7.01 (2H, d, J = 8.3 Hz, ArCH6), 3.79 (6H, s, OMe), 3.78 (6H, s, OMe). Anal. Calcd for $C_{34}H_{36}N_6O_8 \cdot H_2O$: C, 60.5; H, 5.7; N, 12.5. Found: C, 60.7; H, 5.6; N, 12.2. MS-ES: m/z 715 (M + OAc)$^-$, 691 (M + Cl)$^-$, 657 (M + H)$^+$.

Receptor 1. Ligand **9** (0.143 g, 0.240 mmol) and rhenium(I) pentacarbonyl bromide (0.103 g, 0.254 mmol) were refluxed in dry THF (100 mL) for 17 h under nitrogen. The orange solution was then cooled to room temperature and filtered, and the filtrate was evaporated to give an orange solid, which was dried under vacuum. The solid was dissolved in dry MeCN (3 mL) and allowed to stand at room temperature overnight. This gave a yellow precipitate, which was collected by filtration and dried under vacuum (0.132 g, 58% yield). ^{1}H NMR (500 MHz, DMSO-d_6): δ 9.28 (1H, m, br, bpyNH), 9.20 (1H, d, J = 5.5 Hz, bpyH6), 9.01 (1H, s, bpyH3), 8.92 (1H, d, J = 6 Hz, bpyH6′), 8.68 (1H, s, bpyH3′), 8.58 (1H, m, br, NHcrown), 8.06 (1H, dd, J = 6 Hz, J' = 1.5 Hz, bpyH5), 7.65 (1H, d, J = 5 Hz, bpyH5′), 7.49 (1H, dd, J = 8.5 Hz, J' = 2 Hz, ArCH5), 7.45 (1H, s, ArCH3), 7.03 (1H, d, J = 8 Hz, ArCH6), 4.09 (4H, m, OCH_2), 3.73 (4H, m, OCH_2), 3.58 (4H, m, OCH_2), 3.48−3.54 (12H, m, OCH_2, CH_2-NH), 2.57 (3H, s, bpyMe). ^{13}C NMR (75.5 MHz, DMSO-d_6): δ 197.30 (ReCO cis to Br), 197.06 (ReCO cis to Br), 189.33 (ReCO trans to Br), 166.09 (CONH), 163.32 (CONH), 156.04, 154.40, 153.87, 152.57, 152.48, 150.61, 147.47, 144.68, 128.85, 126.72, 125.29, 121.73, 120.64, 111.91, 111.76, 70.04 (OCH_2), 70.01 (OCH_2), 69.94 (OCH_2), 69.88 (OCH_2), 68.73 (OCH_2), 68.70 (OCH_2), 68.23 (OCH_2), 68.20 (OCH_2), 21.22 (bpyMe). Anal. Calcd for $ReC_{34}H_{38}N_4O_{11}Br \cdot H_2O$: C, 42.4; H, 4.2; N, 5.8. Found: C, 42.5; H, 4.4; N, 5.8. MS-FAB: m/z 967 (M + Na)$^+$.

Receptor 2. Ligand **10** (0.224 g, 0.334 mmol) and rhenium(I) pentacarbonyl bromide (0.144 g, 0.354 mmol) were refluxed in dry THF (100 mL) for 19 h under nitrogen. The solvent was evaporated to give an orange solid, which was purified by column chromatography

on silica gel 60 using a CH_2Cl_2/MeOH (9:1 v/v) eluent. The fractions with $R_f = 0.35$ were collected and the solvent was removed to afford the product as a yellow solid (0.242 g, 71% yield). ^{1}H NMR (500 MHz, DMSO-d_6): δ 9.72 (1H, t, $J = 6$ Hz, bpyNH), 9.20 (1H, d, $J = 5.5$ Hz, bpyH6), 9.07 (1H, s, bpyH3), 8.96 (1H, t, $J = 6$ Hz, NHcrown), 8.92 (1H, d, $J = 5.5$ Hz, bpyH6′), 8.72 (1H, s, bpyH3′), 8.08 (1H, d, $J = 5.5$ Hz, bpyH5), 7.65 (1H, d, $J = 6$ Hz, bpyH5′), 7.50 (2H, m, ArCH3crown, ArCH5crown), 7.34 (2H, m, ArCH1, ArCH4), 7.29 (1H, d, $J = 7$ Hz, ArCH3), 7.25 (1H, d, $J = 7.5$ Hz, ArCH5), 7.00 (1H, d, $J = 9$ Hz, ArCH6crown), 4.58 (2H, d, $J = 5.5$ Hz, CH_2NHbpy), 4.47 (2H, d, $J = 6$ Hz, CH_2NHcrown), 4.11 (4H, m, OCH_2), 3.77 (4H, m, OCH_2), 3.60 (4H, m, OCH_2), 3.55 (4H, m, OCH_2), 3.52 (4H, s, OCH_2), 2.56 (3H, s, bpyMe). ^{13}C NMR (125 MHz, DMSO-d_6): δ 197.49 (ReCO cis to Br), 197.27 (ReCO cis to Br), 189.49 (ReCO trans to Br), 165.80 (CONH), 163.21 (CONH), 156.31, 154.50, 153.97, 152.63, 152.58, 150.52, 147.46, 144.49, 140.32, 138.83, 128.94, 128.54, 126.74, 126.37, 126.20, 126.02, 125.53, 125.44, 121.74, 120.70, 111.71, 111.46, 69.76 (OCH_2), 68.65 (OCH_2), 68.60 (OCH_2), 67.88 (OCH_2), 67.83 (OCH_2), 43.14 (CH_2NH), 42.70 (CH_2NH), 21.07 (bpyMe). Anal. Calcd for $ReC_{40}H_{42}N_4O_{11}Br\cdot 2H_2O$: C, 45.5; H, 4.4; N, 5.3. Found: C, 45.5; H, 4.1; N, 4.9. MS-FAB: m/z 1043 $(M + Na)^+$.

Receptor 3. 4-(4′-Aminobenzo-18-crown-6)carbonyl-4′-methyl-2,2′-bipyridine (0.243 g, 0.465 mmol) and rhenium(I) pentacarbonyl bromide (0.200 g, 0.492 mmol) were refluxed in dry THF (100 mL) for 15 h under nitrogen. The orange solution was allowed to cool and was then filtered. The solvent was evaporated to give an orange solid, which was dissolved in dry MeCN (50 mL) with warming and filtered. The filtrate was condensed to ca. 10 mL to encourage formation of a yellow precipitate. The precipitate was collected by filtration after standing for 1.5 h, and the yellow solid was then dried under vacuum (0.240 g, 59% yield). ^{1}H NMR (500 MHz, DMSO-d_6): δ 10.75 (1H, s, bpyNH), 9.22 (1H, d, $J = 6$ Hz, bpyH6), 9.11 (1H, s, bpyH3), 8.93 (1H, d, $J = 6$ Hz, bpyH6′), 8.83 (1H, s, bpyH3′), 8.11 (1H, dd, $J = 5.3$ Hz, $J' = 1.8$ Hz, bpyH5), 7.66 (1H, d, $J = 5.5$ Hz, bpyH5′), 7.47 (1H, d, $J = 2$ Hz, ArCH3), 7.36 (1H, dd, $J = 8.5$ Hz, $J' = 2.5$ Hz, ArCH5), 7.02 (1H, d, $J = 9$ Hz, ArCH6), 4.08 (4H, m, OCH_2), 3.75−3.80 (4H, m, OCH_2), 3.61 (4H, m, OCH_2), 3.56 (4H, m, OCH_2), 3.53 (4H, s, OCH_2), 2.58 (3H, s, bpyMe). ^{13}C NMR (75.5 MHz, DMSO-d_6): δ 197.40 (ReCO cis to Br), 197.20 (ReCO cis to Br), 189.45 (ReCO trans to Br), 162.11 (CONH), 156.13, 154.46, 153.83, 152.62, 152.54, 147.96, 145.58, 145.29, 131.81, 128.92, 125.60, 122.20, 119.43, 113.19, 112.89, 106.58, 70.05 (OCH_2), 69.97 (OCH_2), 68.92 (OCH_2), 68.82 (OCH_2), 68.38 (OCH_2), 68.26 (OCH_2), 21.16 (bpyMe). Anal. Calcd for $ReC_{31}H_{33}N_3O_{10}Br$: C, 42.6; H, 3.8; N, 4.8. Found: C, 42.5; H, 4.2; N, 4.7. MS-FAB: m/z 896 $(M + Na)^+$, 794 $(M - Br)^+$.

Receptor 4. Ligand **11** (0.272 g, 0.254 mmol) and rhenium(I) pentacarbonyl bromide (0.109 g, 0.269 mmol) were refluxed in dry THF (100 mL) for 15 h under nitrogen. The mixture was filtered and the filtrate evaporated to give an orange solid, which was purified by column chromatography on silica gel 60 using a CH_2Cl_2/MeOH (9:1 v/v) eluent. The fractions with $R_f = 0.3$ were collected and the solvent removed to afford an orange solid. This was suspended in diethyl ether (40 mL), filtered, and washed with diethyl ether (2 × 10 mL). The resulting orange solid was dried under vacuum (0.135 g, 37% yield). ^{1}H NMR (500 MHz, DMSO-d_6): δ 9.79 (2H, t, $J = 5.5$ Hz, bpyNH), 9.25 (2H, d, $J = 5.5$ Hz, bpyH6,6′), 9.14 (2H, s, bpyH3,3′), 8.93 (2H, t, $J = 6$ Hz, NHcrown), 8.13 (2H, d, $J = 4.5$ Hz, bpyH5,5′), 7.49 (4H, m, ArCH3crown, ArCH5crown), 7.33 (4H, m, ArCH1, ArCH4), 7.26 (4H, m, ArCH3, ArCH5), 6.98 (2H, d, $J = 8$ Hz, ArCH6crown), 4.57 (4H, d, $J = 5.5$ Hz, CH_2NHbpy), 4.46 (4H, d, $J = 5.5$ Hz, CH_2NHcrown), 4.06 (8H, m, OCH_2), 3.76 (8H, m, OCH_2), 3.60 (16H, s, OCH_2). ^{13}C NMR (125 MHz, DMSO-d_6): δ 197.13 (ReCO), 165.81 (CONH), 163.06 (CONH), 155.82, 154.09, 151.22, 148.03, 144.51, 140.32, 138.75, 128.57, 126.90, 126.42, 126.20, 126.04, 125.74, 122.34, 120.97, 112.75, 112.59, 70.62 (OCH_2), 69.86 (OCH_2), 69.77 (OCH_2), 68.91 (OCH_2), 68.78 (OCH_2), 68.72 (OCH_2), 68.44 (OCH_2), 43.21 ($NHCH_2$), 42.70 ($NHCH_2$). Anal. Calcd for $ReC_{61}H_{64}N_6O_{17}Br\cdot 4H_2O$: C, 49.1; H, 4.9; N, 5.6. Found: C, 48.9; H, 4.9; N, 5.6. MS-FAB: m/z 1553 $(M + Cs)^+$, 1458 $(M + K)^+$, 1442 $(M + Na)^+$, 1420 $(M + H)^+$, 1340 $(M - Br)^+$.

Receptor 5. Ligand **13** (0.200 g, 0.305 mmol) was dissolved in dry THF (50 mL) and heated to 50 °C under nitrogen. Rhenium(I) pentacarbonyl bromide (0.131 g, 0.323 mmol) was then added and the mixture refluxed for 12 h. The orange solution was evaporated and the residue chromatographed on neutral alumina using an acetonitrile eluent. The orange fraction was collected and the solvent removed under vacuum. The solid was dissolved in acetonitrile (5 mL) and allowed to stand for 2 h. The resulting precipitate was collected by filtration and dried under vacuum to give the product as an orange solid (0.27 g, 88% yield). ^{1}H NMR (300 MHz, DMSO-d_6): δ 9.37 (2H, t, br, bpyNH), 9.21 (2H, d, $J = 5.7$ Hz, bpyH6,6′), 9.12 (2H, s, bpyH3,3′), 8.57 (2H, t, br, ArCONH), 8.09 (2H, d, $J = 5.8$ Hz, bpyH5,5′), 7.49 (2H, d, $J = 8.5$ Hz, ArCH5), 7.44 (2H, s, ArCH3), 7.01 (2H, d, $J = 8.4$ Hz, ArCH6), 3.79 (6H, s, OMe), 3.77 (6H, s, OMe), 3.51 (8H, s, br, CH_2CH_2). ^{13}C NMR (75.5 MHz, DMSO-d_6): δ 196.95 (ReCO cis to Br), 189.00 (ReCO trans to Br), 166.12 (CONH), 163.17 (CONH), 155.60, 151.27, 144.71, 126.61, 125.52, 122.06, 120.48, 110.96, 110.86, 55.61 (OMe). Anal. Calcd for $ReC_{37}H_{36}N_6O_{11}Br\cdot H_2O$: C, 43.4; H, 3.7; N, 8.2. Found: C, 43.5; H, 3.9; N, 8.3. MS-FAB: m/z 1029 $(M + Na)^+$, 1007 $(M)^+$, 927 $(M - Br)^+$.

Crystal Structure Determination. Crystal data were collected with Mo Kα radiation using the MARresearch Image Plate System at room temperature. $C_{37}H_{41}Cl_2KN_4O_{12}Re$, $M = 1029.94$, $a = 11.445(12)$ Å, $b = 14.668(17)$ Å, $c = 16.328(17)$ Å, $\alpha = 115.27(1)°$, $\beta = 90.02(1)°$, $\gamma = 112.34(1)°$, $V = 2294$ Å^3, $D_c = 1.463$ M gm^{-3}, $\mu = 2.973$ mm $^{-1}$, $F(000) = 1030$. The crystal was positioned at 70 mm from the image plate, respectively; 100 frames were measured at 2° intervals with a counting time of 10 min to give 7585 independent reflections. Data analysis was carried out with the XDS program.[19] The structure was solved using direct methods with the Shelx86 program.[20] The non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were included in geometric positions and given thermal parameters equivalent to 1.2 times those of the atom to which they were attached. An empirical absorption correction was applied using DIFABS.[21] The structure was refined on F^2 using Shelxl[22] to R1 0.0917, wR2 0.1876 for 2187 relections with $I > 2\sigma(I)$ and R1 0.2733, wR2 0.2549 for all data.

Results and Discussion

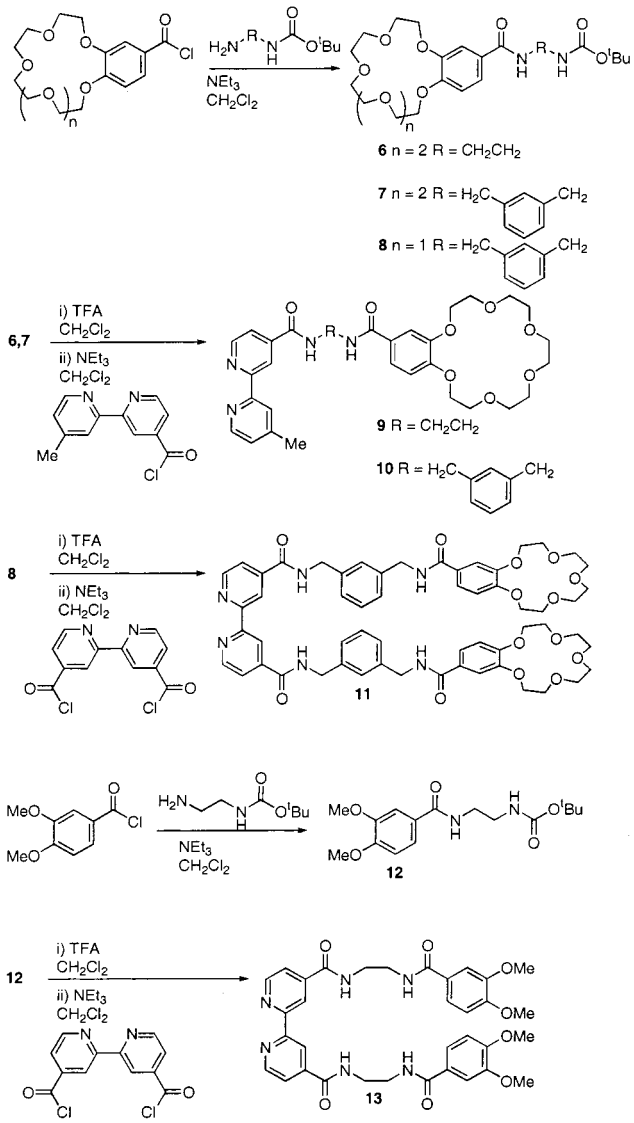
Synthesis of Ion Pair Receptors. The benzo-18-crown-6 compounds **6** and **7** were prepared by condensing monoprotected 1,2-diaminoethane[14] or *m*-xylylenediamine respectively with 4′-(chlorocarbonyl)-benzo-18-crown-6[13] in the presence of triethylamine (Scheme 1). The crown ethers **6** and **7** were then deprotected with TFA and condensed with 4-(chlorocarbonyl)-4′-methyl-2,2′-bipyridine[16] to afford the 4-amide-4′-methyl-2,2′-bipyridine ligands **9** and **10**. Compounds **9** and **10** were reacted with $Re(CO)_5Br$ in THF to produce the target receptors **1** and **2** in yields of 58% and 71%, respectively.

Receptor **3** was synthesized from 4-(4′-aminobenzo-18-crown-6)carbonyl-4′-methyl-2,2′-bipyridine and $Re(CO)_5Br$ in 59% yield. The bipyridine ligand was obtained by condensing 4-(chlorocarbonyl)-4′-methyl-2,2′-bipyridine[16] with 4′-aminobenzo-18-crown-6 in the presence of triethylamine.

The benzo-15-crown-5 ether **8** was prepared from monoprotected *m*-xylylenediamine and 4′-(chlorocarbonyl)-benzo-15-crown-5[12] in high yield. Compound **8** was then deprotected with TFA and condensed with 4,4′-bis(chlorocarbonyl)-2,2′-bipyridine[15] to produce the 4,4′-diamide-2,2′-bipyridine **11**. Coordination of ligand **11** to rhenium(I) in THF afforded the bis(crown ether) receptor **4** in 37% yield.

(19) Kabsch, W. *J. Appl. Crystallogr.* **1988**, *21*, 916.
(20) Sheldrick, G. M. Shelx86. *Acta Crystallogr.* **1990**, *A46*, 467.
(21) Walker, N.; Stuart, D. DIFABS program. *Acta Crystallogr.* **1983**, *A39*, 158.
(22) Sheldrick, G. M. *Shelxl, program for crystal structure refinement*; University of Göttingen: Göttingen, 1993.

Scheme 1



Condensation of 4-(chlorocarbonyl)-1,2-dimethoxybenzene with monoprotected 1,2-diaminoethane[14] gave compound **12**, which was deprotected in acid and then condensed with 4,4′-bis(chlorocarbonyl)-2,2′-bipyridine[15] to produce ligand **13**. The model receptor **5** was synthesized in 88% yield by coordinating ligand **13** to rhenium(I) in THF.

Solid State Structure of the Ion Pair KCl Complex of 1. Receptor **1** was slowly cocrystallized with KCl from a methanol/THF mixture. The structure of [**1**·KCl]$_2$ is a centrosymmetric dimer, as illustrated in Figure 1.[23] The individual monomer is shown in Figure 2. In the Re(CO)$_3$(bpy)Cl moieties the environment of the metal atom is octahedral with dimensions in the expected range, Re−C distances being 1.95(1)−1.98(1) Å, Re−N 2.23(1) and 2.19(1) Å, and Re−Cl 2.520(6) Å. Each bpy is linked via an amide group to a benzo-18-crown-6 in which is encapsulated a potassium ion. As shown in Figure 2, the chloride anion is located within the cavity formed by the diamide and the crown and forms several hydrogen bonds with close contacts of 3.20 and 3.26 Å to the two amide nitrogen atoms N(63) and N(66) and 3.48, 3.49, 3.64, and 3.64 Å to the carbon atoms C(15), C(95), C(76), and C(18), respectively. These six hydrogen bond donor atoms form an approximate plane (maximum deviation 0.22 Å), with the chloride anion 0.50 Å from the plane. The chloride anion has high thermal motion perpendicular to the plane with principal mean square atomic displacements 0.37, 0.06, and 0.06 Å^2 and could be considered to be disordered over two sites although this could not be established through the refinement. The benzo crown has a planar conformation with the six oxygen atoms coplanar to within 0.07 Å with the potassium 0.30 Å from this plane. The hexagonal bipyramidal potassium coordination is completed by two axial bonds to a water molecule and to an amide oxygen atom from another substituted Re(CO)$_3$(bpy) moiety thus forming the centrosymmetric dimer shown in Figure 1. The six equatorial K−O distances range from 2.66(2) to 2.84(2) Å. The K−water distance is 2.71(2) Å, while the K−O(62) to the amide oxygen is the shortest bond at 2.59(2) Å.

It is interesting to consider whether the dimer formation is necessary for the chloride complexation or indeed the chloride complexation is necessary for the dimer formation. Clearly the conformation of the monomer is likely to be highly flexible in solution, but it can be seen that the conformation observed in the crystal with the six potential hydrogen bond donors forming a cavity is favored by the dimer formation, and therefore it seems likely that the formation of the dimer and the encapsulation of the chloride are concerted.

Binding Studies by NMR Spectroscopy. Potassium binding was investigated by adding aliquots of potassium thiocyanate to 1:1 CD$_3$CN/DMSO-d_6 NMR solutions of hosts **1**−**4**. For the benzo-18-crown-6 receptors **1**−**3**, potassium coordination was signified by downfield shifts of the crown OCH$_2$ signals in the ^{1}H NMR spectrum. The change in shift of the OCH$_2$(5,6) singlet was recorded during each titration, and the resulting binding curves were analyzed by the program EQNMR.[17] All three receptors bound potassium to form 1:1 complexes, with stability constants of 850 ± 85 and 1070 ± 85 M^{-1} for hosts **1** and **3**, respectively. The complex between receptor **2** and potassium was too strong for the binding constant to be determined with accuracy; K was estimated to be >1000 M^{-1}.

Potassium coordination by the bis(benzo-15-crown-5) host **4** could not be monitored by ^{1}H NMR spectroscopy, due to insufficient perturbation of the crown ether proton signals during the titration. ^{13}C NMR spectroscopy was therefore used to analyze the host−guest interaction, since this technique is more sensitive to changes in crown ether conformation on binding than ^{1}H NMR.[24] The ^{13}C NMR spectrum of host **4** consists of seven OCH$_2$ resonances, which all move upfield on addition of potassium (Figure 3). The binding isotherms slope gently and can be fitted to either 1:1 or 1:2 host:guest stoichiometries. However, it is likely that a 1:1 intramolecular sandwich complex is present in solution, since bis(benzo-15-crown-5) ethers are well-known to form sandwich complexes with potassium cations.[10]

Anion recognition was studied by ^{1}H NMR spectroscopic titrations in 1:1 CD$_3$CN/DMSO-d_6. Addition of tetrabutylammonium chloride or acetate to receptors **1**−**4** resulted in significant downfield perturbations of the bpyNH, bpyH3, and bpyH3′ signals, indicating that these protons form hydrogen bonds with the anionic guests. The program EQNMR[17] was used to calculate anion binding constants from the ^{1}H NMR titration data, and the results are presented in Table 1.

(23) A substitution of Br for Cl has occurred at the Re(I) center. During the NMR titrations, no evidence of this reaction was seen over the course of the experiment (ca. 2 h).

(24) Wilson, M. J.; Pethrick, R. A.; Pugh, D.; Saiful Islam, M. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 2097.

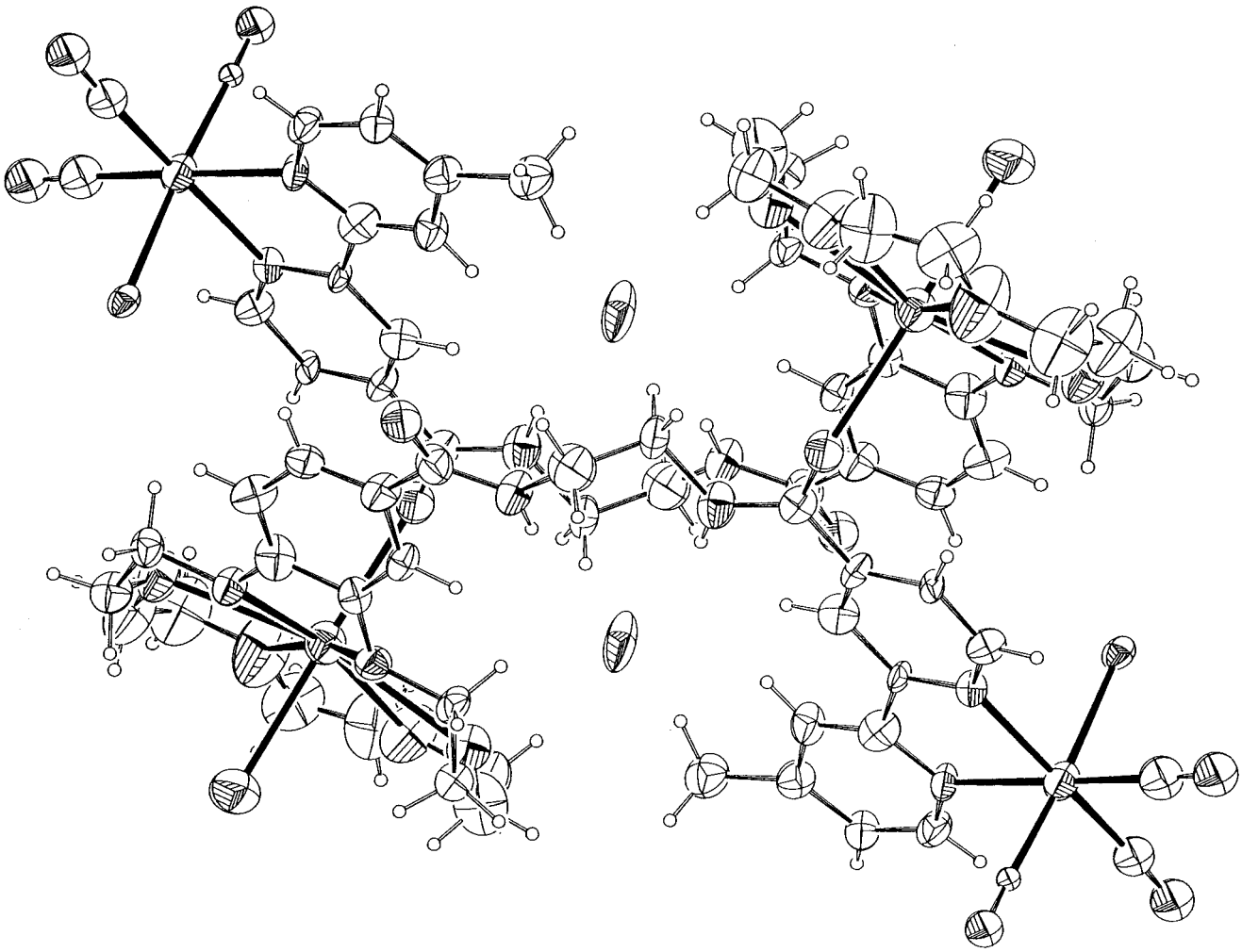


Figure 1. The structure of $[\mathbf{1}\cdot KCl]_2$ with ellipsoids shown at 30% probability.

The first point to note from Table 1 is that each receptor displays selectivity for acetate over chloride. For example, hosts **1** and **3** bind acetate ca. six times more strongly than the chloride anion. This result is to be anticipated from the relative basicities of the anions; acetate is significantly more basic than chloride and will therefore have an increased propensity to form hydrogen bonds with the receptor. It may also reflect the different size and shape of the two anions and their geometric compatibility with the host.

The second point is that the 4,4′-diamidebipyridine group in receptor **4** binds anions more strongly than the 4-amide-4′-methylbipyridine site in hosts **1**−**3**. This is because receptor **4** possesses four protons (two bpyNH and two bpyH3) which can form strong, cooperative hydrogen bonds with the anion, whereas hosts **1**−**3** each contain only one bipyridyl NH proton.

Ion pair complexation was analyzed by determination of the anion binding constants for receptors **1**−**4** in the presence of 1 equiv of potassium thiocyanate (Table 1). (Addition of tetrabutylammonium thiocyanate to host **1** did not perturb the bpyNH, bpyH3, or bpyH3′ resonances, which confirms that SCN^- is not complexed at the amide bipyridine site.) The general conclusion to draw from Table 1 is that all receptors (except hosts **2** and **4** with acetate) show an increase in anion binding strength as a result of electrostatic interaction with the crown ether bound potassium. This finding demonstrates that these hosts are ditopic receptors for ion pair recognition.

The percentage increase for anion binding in the presence of potassium is similar for hosts **1** and **3**, with chloride exhibiting the larger increase relative to acetate. It might be expected that the shorter spacer in host **1** would result in a larger cooperative effect between the bound cation and anion. However, the crystal structure of host **1** with KCl shows that the flexible ethylene linker allows the crown ether to approach the anion binding site (Figure 2). This site partly involves the amide group attached to the crown ether, which would bring the two coordinated ions even closer together.

Potassium coordination has a similar effect on anion binding for hosts **2** and **4**. Interestingly, the percentage increase for chloride binding in the presence of K^+ is much smaller for these two receptors (40−50%) compared to **1** and **3** (80−115%). This may be due to the long *m*-xylyl spacer in **2** and **4**, which reduces the through-space electrostatic interaction between the bound ions. Both these receptors also show a small decrease in acetate binding on addition of potassium cations. This indicates that KOAc ion pairing outside the cavity competes with ion binding to the receptor.

For host **4** and potassium, the contribution of a sandwich complex to the ion pair recognition behavior is unclear. The similarity between the ion pair results for receptors **2** and **4** suggests that this contribution may be small in the competitive 1:1 DMSO-d_6/CD_3CN solvent mixture, since **2** contains the same spacer unit as **4** but cannot form an intramolecular sandwich complex with potassium.

Solid−Liquid Extraction Experiments. One of the potential applications of neutral ion pair receptors is the extraction and/or transport of metal salts. The ability of receptor **3** to extract

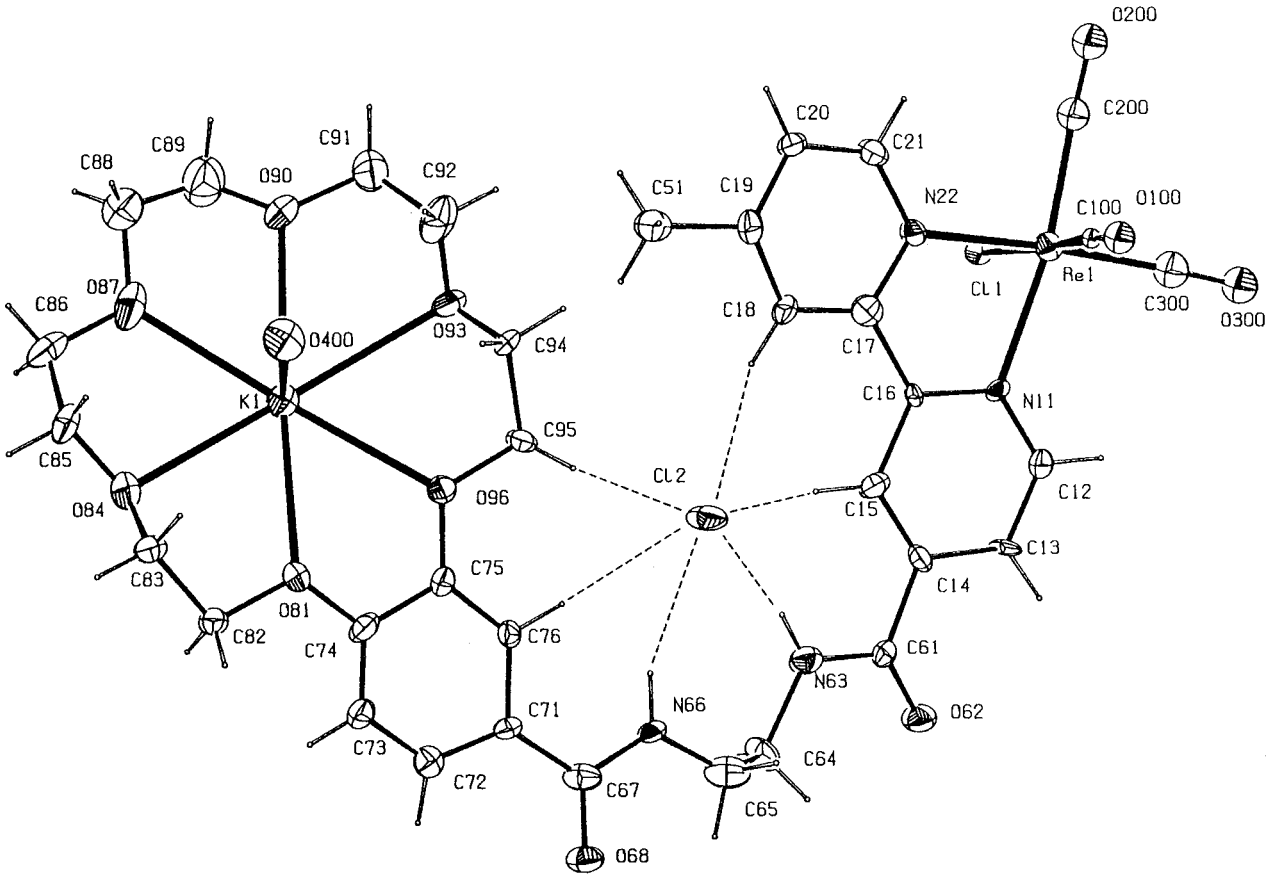


Figure 2. The structure of the [**1**·KCl] monomer with ellipsoids shown at 20% probability. Hydrogen bonds are shown as dotted lines.

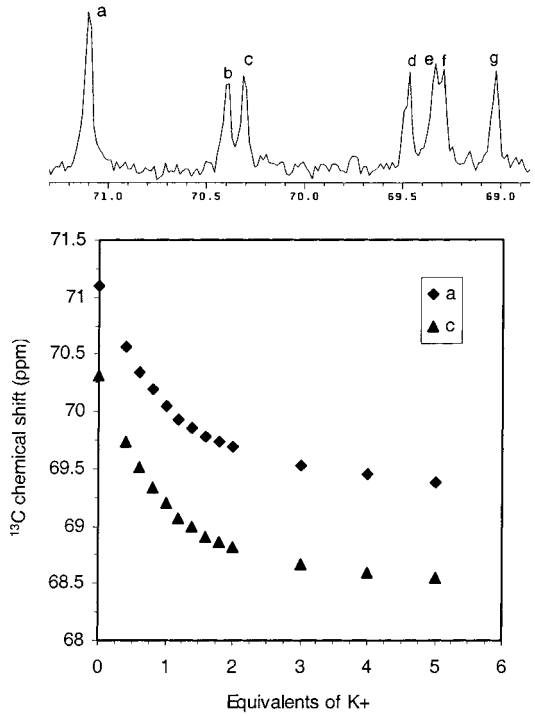


Figure 3. ^{13}C NMR spectrum of receptor **4** (125 MHz, 1:1 DMSO-d_6/CD_3CN) and associated ^{13}C NMR titration with KSCN.

solid KOAc and KCl into chloroform solution was therefore investigated. The ^{1}H NMR and FAB mass spectra of receptor **3** were recorded before and after shaking a $CDCl_3$ solution of the host with an excess of the solid potassium salt. The experiment was then repeated for the model compound **5**, which contains amide groups to coordinate anionic guests, but has no crown ether binding site for the cation. Unfortunately, receptors **1**, **2**, and **4** were not sufficiently soluble in $CDCl_3$ to perform solid−liquid extraction experiments.

Table 1. Stability Constants for Acetate and Chloride Binding in the Presence and Absence of 1 Equiv of KSCN in 1:1 CD_3CN/DMSO−d_6

	K (M^{-1})[a]			
receptor	AcO^-	AcO^- (K^+)	Cl^-	Cl^- (K^+)
1 (NH)	375	527	63	113
1 (H3)	371	560	62	117
2 (NH)	98	92	27	39
2 (H3)	101	94	27	40
3 (NH)	*b*	*b*	34	73
3 (H3)	209	314	35	74
4 (NH)	623	546	65	91
4 (H3)	661	540	73	107

[a] K determined from the change in chemical shift of the bpyNH and bpyH3 protons; errors ≤7%. [b] BpyNH becomes too broad on anion addition to determine K with accuracy.

The results of the extraction studies are summarized in Figure 4, which gives the change in ^{1}H NMR chemical shift of compounds **3** and **5** after shaking with KOAc or KCl. For the ion pair receptor **3**, the anion and cation binding sites show substantial alterations in chemical shift postextraction with KOAc or KCl. The largest downfield perturbations are observed with the bpyNH, bpyH3, and bpyH3′ protons, which are postulated to hydrogen bond with the anion. The crown ether OCH_2 region was too complicated to permit a simple analysis, but upfield shifts were recorded as well as a significant alteration in multiplet structure indicating a change in ring conformation on cation binding.[25] A singlet appeared at 1.98 ppm after shaking with solid KOAc, and this was assigned to the methyl group

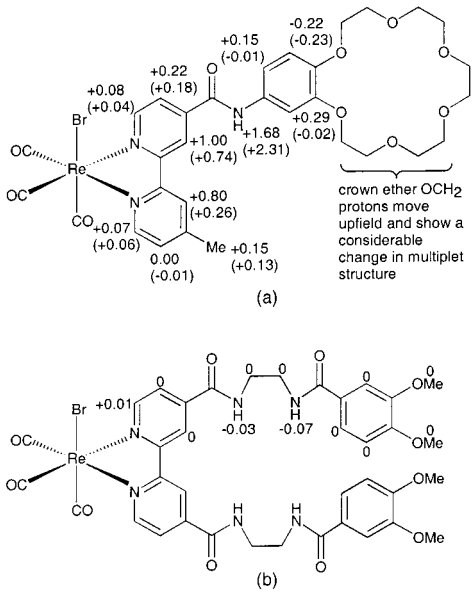


Figure 4. (a) Change in the ^{1}H NMR chemical shifts of receptor **3** (500 MHz, $CDCl_3$) after shaking with KOAc (values in parentheses) or KCl. (b) Change in the ^{1}H NMR chemical shifts of compound **5** (500 MHz, $CDCl_3$) after shaking with KCl. ("+" represents a downfield change in shift postextraction.)

on the acetate anion. Relative integration of the methyl singlets for host **3** and acetate demonstrated that extraction of KOAc was quantitative.

The positive FAB mass spectrum of receptor **3** postextraction with KOAc showed an intense cluster at 912 due to $(M + K)^+$ (which was very weak pre-extraction), in addition to peaks at 892 $(M + KOAc - Br)^+$ and 833 $(M + K - Br)^+$. FAB mass spectrometry on the postextraction sample with KCl revealed peaks at 912 $(M + K)^+$, 868 $(M + KCl - Br)^+$, and 833 $(M + K - Br)^+$, as well as the ion pair complex $(M + KCl + H)^+$ at 950. This supports the conclusion from ^{1}H NMR spectroscopy that host **3** solubilizes solid KOAc and KCl into chloroform.

To prove that extraction depends on the cooperative interaction between the cation and anion binding sites, the KCl extraction experiment was repeated with the model compound **5**. This host has previously been shown to complex chloride but not potassium in DMSO-d_6 solution.[3a] Figure 4 shows that there is negligible change in the proton resonances when the anion receptor **5** is shaken with KCl. The slight upfield shifts of the amide groups are believed to be due to a small increase in water content of the sample during the extraction experiment. This contrasts sharply with the large perturbations seen for the ion pair receptor **3**, which indicates that compound **5** does not extract KCl into chloroform.

The FAB mass spectrum of compound **5** after shaking with KCl showed peaks at 1007 (M^+) and 927 $(M - Br)^+$, but no peaks were found for $(M + K)^+$, $(M + K - Br)^+$, $(M + KCl - Br)^+$, or $(M + KCl + H)^+$ to suggest KCl binding. The presence of an anion binding site alone is therefore not sufficient to allow extraction of the KCl ion pair. In contrast, the extraction results for receptor **3** with KOAc and KCl are very promising. They demonstrate that the crown ether and amide bipyridine groups cooperate in ion pair binding.

UV−Vis and Emission Spectroscopy. The absorption and emission properties of $Re(CO)_3XL$ (X = halide, L = polypyridyl) molecules are well-documented[26] and could potentially be used to investigate ion pair recognition. The UV−vis spectroscopic parameters for hosts **1**−**4** in various CH_3CN/DMSO solvent mixtures are summarized in Table (SI)1 (Supporting Information). In all cases, the receptors show two high-energy bands assigned to LC transitions (248−256 and 287−297 nm) and one MLCT band to lower energy (383−403 nm).[26g] It is noteworthy that the MLCT transition for receptor **4** is bathochromically shifted ca. 20 nm relative to the other hosts. This is due to two electron-withdrawing amide groups on the bipyridine ligand in **4** (compared to one each for **1**−**3**), which lower the energy of the MLCT absorption. UV−vis anion titrations were performed by adding tetrabutylammonium acetate or chloride solutions in 1:1, 95:5, and 1:0 CH_3CN/DMSO solvent systems. However, the spectroscopic response to anion addition was too small and irregular to determine stability constants, and anion binding was therefore reinvestigated using emission spectroscopy.

The emission spectra of hosts **2** and **4** were recorded in CH_3CN by excitation into the MLCT absorption bands. Host **1** was not soluble in CH_3CN, so its emission spectrum was obtained in 95:5 CH_3CN/DMSO. Receptors **1**, **2**, and **4** show broad, featureless emission bands at 592, 594, and 600 nm, respectively (Table (SI)2, Supporting Information). Receptor **3** does not emit at room temperature in acetonitrile; it is not clear why the structure of this molecule prohibits luminescence.

The emission spectra of receptors **1** and **2** are very similar, as expected from the common features in molecular structure. In comparison, the luminescence of receptor **4** is bathochromically shifted and approximately half the intensity. The lower energy emission for host **4** is due to the presence of *two* electron-withdrawing amide groups on the bipyridine ligand, which reduce the energy of the MLCT emitting state. The decrease in intensity for this host is probably due to collisions between the two flexible substituents on the bipyridine ring, which promote nonradiative decay processes.

Emission anion titrations were carried out on receptors **1**, **2**, and **4** by sequential addition of tetrabutylammonium acetate or chloride. This generally resulted in intensity increases with concomitant hypsochromic shifts of up to 5 nm. The hypsochromic shift indicates that the MLCT state moves to higher energy in the presence of the anion. The MLCT state has the electron formally residing on the bipyridine ligand, and this configuration is less favorable when the negatively charged guest binds to the amide bipyridine group.[27] The emission enhancement is probably due to the bound anion rigidifying the receptor, which inhibits collisional deactivation.[27,28]

The Specfit program[18] was used to obtain stability constants from the emission titration data, and the calculated values are presented in Table 2. These binding constants are significantly larger than those determined from ^{1}H NMR spectroscopy (Table 1). This reflects the less competitive nature of the solvent used

(25) Live, D.; Chan, S. I. *J. Am. Chem. Soc.* **1976**, *98*, 3769.

(26) (a) Juris, A.; Campagna, S.; Bidd, I.; Jehn, J.-M.; Ziessel, R. *Inorg. Chem.* **1988**, *27*, 4007. (b) Giordano, P. J.; Wrighton, M. S. *J. Am. Chem. Soc.* **1979**, *101*, 2888. (c) Wrighton, M. S.; Morse, D. L. *J. Am. Chem. Soc.* **1974**, *96*, 998. (d) Kalyanasundaram, K. *J. Chem. Soc., Faraday Trans. 2* **1986**, *82*, 2401. (e) Worl, L. A.; Duesing, R.; Chen, P.; Ciana, L. D.; Meyer, T. J. *J. Chem. Soc., Dalton Trans.* **1991**, 849. (f) Kaim, W.; Kramer, H. E. A.; Vogler, C.; Rieher, J. *J. Organomet. Chem.* **1989**, *367*, 107. (g) Van Wallendael, S.; Shaver, R. J.; Rillema, D. P.; Yoblinski, B. J.; Stathis, M.; Guarr, T. F. *Inorg. Chem.* **1990**, *29*, 1761. (h) Kalyanasundaram, K. *Photochemistry of Polypyridine and Porphyrin Complexes*; Academic Press: New York, 1992.

(27) Beer, P. D.; Szemes, F.; Balzani, V.; Salà, C. M.; Drew, M. G. B.; Dent, S. W.; Maestri, M. *J. Am. Chem. Soc.* **1997**, *119*, 11864.

(28) Szemes, F.; Hesek, D.; Chen, Z.; Dent, S. W.; Drew, M. G. B.; Goulden, A. J.; Graydon, A. R.; Grieve, A.; Mortimer, R. J.; Wear, T.; Weightman, J. S.; Beer, P. D. *Inorg. Chem.* **1996**, *35*, 5868.

Table 2. Anion Binding Constants for Receptors **1**, **2**, and **4** in the Presence and Absence of 1 Equiv of KSCN[a]

receptor	log *K* (AcO^-)	log *K* (Cl^-)
1[b]	4.07	*d*
2[c]	4.00	*d*
4[c]	5.04	4.27
1[b] (K^+)	4.42	*d*
2[c] (K^+)	4.18	*d*
4[c] (K^+)	5.89	4.66

[a] $T = 298$ K; errors $\leq 1\%$. [b] 95:5 CH_3CN/DMSO. [c] CH_3CN. [d] Changes in emission intensity too small and irregular to calculate log *K*.

for the emission titrations (CH_3CN or 95:5 CH_3CN/DMSO) compared to the ^1H NMR binding studies (1:1 CD_3CN/DMSO-d_6). However, Table 2 does corroborate some of the same basic trends elucidated from the ^1H NMR anion titrations (Table 1). Thus, the anion selectivity trend again favors acetate over chloride, and acetate binds more strongly to receptor **4** compared to hosts **1** and **2**.

Ion pair recognition was analyzed by repeating the emission titrations in the presence of 1 equiv of KSCN. Except for the emission intensity of host **4**, the wavelength and intensity of the receptors' emission bands were unaffected on addition of potassium (Table (SI)2, Supporting Information). This suggests that the crown ethers are too far from the emitting $Re(CO)_3Br$(bpy) center to alter the observed spectra. The small intensity increase (16%) for **4** in the presence of potassium may indicate a rigidification of the host on formation of a K^+ sandwich complex. This would reduce collisions between the 4,4′-diamidebipyridine substituents and therefore decrease nonradiative decay.

Table 2 summarizes the anion stability constants for receptors **1**, **2**, and **4** in the presence and absence of K^+ cations. The results show that all receptors display an increase in anion binding strength on addition of potassium. Host **1** exhibits an enhancement of ca. 125% for acetate binding when potassium is bound at the crown ether. In contrast, only a moderate increase of 50% is seen for acetate complexation with receptor **2**. This confirms that the *m*-xylyl spacer is too long to allow appreciable electrostatic interaction between the bound ions. However, receptor **4** shows very different binding behavior from host **2**, even though both contain the same spacer unit. Table 2 reveals a 600% increase in the acetate binding constant when potassium is added to receptor **4**. As shown in Figure 5, the acetate binding curve for host [**4**·K^+] possesses a sharp plateau indicative of strong anion binding, whereas the curve for host **4** in the absence of K^+ has a gentler slope. A likely explanation for this phenomenon is that potassium forms a sandwich complex with host **4**, which creates a pseudomacrocyclic cavity preorganized for anion binding. This allosteric effect is not possible for the monobenzo-18-crown-6 analogue **2**, which explains the disparate behavior of hosts **2** and **4** toward KOAc in CH_3CN.

The above results contrast with the ^1H NMR binding studies, which revealed a negative cooperativity between K^+ and AcO^- for hosts **2** and **4** in 1:1 DMSO-d_6/CD_3CN. The different results for 1:1 DMSO-d_6/CD_3CN compared to CH_3CN probably reflect the decreased binding strength and reduced electrostatic interactions in the more competitive DMSO-d_6 solvent system. They also indicate that the intramolecular sandwich complex for host **4** is more significant in CH_3CN relative to 1:1 DMSO-d_6/CD_3CN.

Conclusions

A novel design of ion pair receptor has been developed, based on the combination of a rhenium(I) amide bipyridine with a crown ether. ^1H NMR studies in 1:1 DMSO-d_6/CD_3CN showed that the anionic guest was hydrogen bonded to the bpyH3 and bpyNH protons, while the potassium cation was complexed by ion−dipole interactions with the crown ether. Each receptor displayed selectivity for acetate over chloride, which reflected the different basicities of the anions. The presence of bound potassium had a positive cooperative effect on anion binding dependent on distance; the effect was significant for receptors **1** and **3**, but not for hosts **2** and **4** which possess long *m*-xylyl spacers between the anion and cation binding sites. This illustrates how the choice of spacer can be used to tune ion pair recognition. Solid−liquid extraction experiments demonstrated that receptor **3** could solubilize solid KOAc and KCl into chloroform.

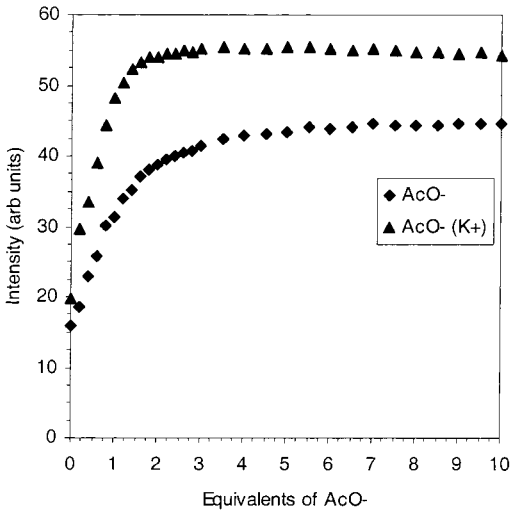


Figure 5. Binding curves for receptor **4** and TBAOAc in CH_3CN, in the presence and absence of 1 equiv of KSCN. (Shown for the emission response at 600 nm.)

Emission spectroscopic titrations revealed cooperative binding between acetate and potassium ions for receptors **1**, **2**, and **4**. In particular, the bis(benzo-15-crown-5) host **4** showed a marked increase in acetate binding constant in the presence of potassium. This suggests that host **4** forms a sandwich complex with K^+ in CH_3CN, which preorganizes the receptor for anion coordination.

In summary, rhenium(I) bipyridine crown ether receptors can selectively bind and sense anionic guests. The anion binding affinity can be enhanced by the presence of bound potassium, via electrostatic and conformational effects.

Acknowledgment. We thank the EPSRC and Kodak Limited for studentships (L.H.U. and S.W.D., respectively). We also thank the EPSRC for use of the mass spectrometry service at the University of Wales, Swansea, and the EPSRC and University of Reading for funds for the Image Plate System.

Supporting Information Available: An X-ray crystallographic file in CIF format for the structure determination of [**1**·KCl]$_2$·2H_2O. Absorption wavelengths/molar extinction coefficients for **1**−**4** (Table (SI)1). Emission wavelengths/intensities for **1**, **2**, and **4** in the presence and absence of KSCN (Table (SI)2). Increase in emission intensity for **1** on addition of TBAOAc (Figure (SI)1). This material is available free of charge via the Internet at http://pubs.acs.org.

IC001450V