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Anion recognition and sensing by neutral and charged transition metal co-ordinated ferrocene phosphine amide receptors

Justine E. Kingston,[a] Lynette Ashford,[a] Paul D. Beer *[a] and Michael G. B. Drew[b]

[a] *Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford, UK OX1 3QR*
[b] *Department of Chemistry, University of Reading, Whiteknights, Reading, UK RG6 2AD*

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A new bis(phosphine) amide linked ferrocene ligand [Fe{η-$C_5H_4CONH(CH_2)_3PPh_2$}$_2$] and molybdenum, chromium, rhodium and ruthenium transition metal chelated receptors of it have been prepared. Proton NMR anion-binding investigations revealed that in general the combination of the Lewis acid transition metal centre and the ferrocene amide moiety enhances the strength of anion binding. Electrochemical studies showed all receptors can electrochemically sense halide, dihydrogenphosphate and hydrogensulfate anions *via* significant cathodic perturbations of the respective ferrocene and transition metal oxidation wave.

Negatively charged species are known to play numerous fundamental roles in biological and chemical processes and consequently intense current interest is being shown in the design and syntheses of positively charged or neutral electron-deficient anion receptors.[1] In addition, the importance of being able to detect and extract certain environmental anionic pollutants has only recently been recognised.[2] As part of a research programme aimed at developing anion sensor technology we have shown that positively charged and neutral transition-metal organometallic and co-ordination receptor systems in combination with amide (CONH) hydrogen-bond donor groups can complex and sense *via* electrochemical and optical responses a variety of anions in organic and aqueous media.[3] In particular a range of neutral ferrocenoyl amide receptors[4] have been shown electrochemically to recognise halide, dihydrogenphosphate, nitrate[4,5] and hydrogensulfate anions *via* cathodic perturbations of their respective ferrocene oxidation wave. The combination of additional Lewis acid transition metal centres with the redox-responsive ferrocenoyl amide moiety may lead to new acyclic and macrocyclic heteropolymetallic receptors that exhibit greater anion thermodynamical stability and new selectivity trends (Fig. 1). By co-ordinating a variety of Lewis acidic transition metal centres to a new ferrocene phosphine amide ligand we report here the syntheses, structures, anion co-ordination and electrochemical recognition properties of a new class of bimetallic redox-active macrocyclic anion receptor.

Experimental

Instrumentation

Nuclear magnetic resonance spectra were obtained on a Bruker AM300 instrument using the solvent deuterium signal as internal reference, fast atom bombardment (FAB) mass spectra at the EPSRC mass spectrometry service, University College, Swansea. Electrochemical measurements were carried out using an E. G. and G. Princeton Applied Research 362 scanning potentiostat. Elemental analyses were performed at the Inorganic Chemistry Laboratory, University of Oxford.

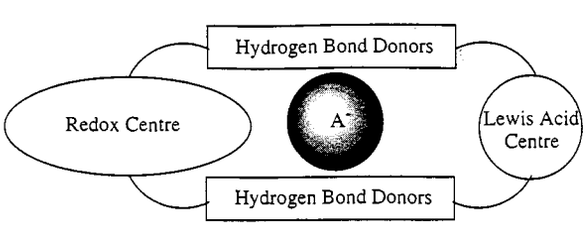


Fig. 1 Anion receptor design, combining a redox-active moiety with an additional Lewis acidic centre.

Solvent and reagent pretreatment

Where necessary, solvents were purified prior to use and stored under nitrogen. Acetonitrile was predried over class 4A molecular sieves (4–8 mesh) and then distilled from calcium hydride. Unless stated to the contrary, commercial grade chemicals were used without further purification. 1,1′-Bis(chlorocarbonyl)-ferrocene **1**[6] and 3-aminopropyldiphenylphosphine[7] were prepared according to literature procedures.

Syntheses

1,1′-Bis(3-diphenylphosphinopropylaminocarbonyl)ferrocene 2. A solution of 1,1′-bis(chlorocarbonyl)ferrocene **1** (0.83 g, 266 mmol) in toluene (50 ml) was added dropwise under a nitrogen atmosphere to a solution of 3-aminopropyldiphenylphosphine (1.33 g, 5.32 mmol) and triethylamine (0.54 g, 5.32 mmol) in toluene (50 ml). Once addition was complete, the reaction was stirred for 2 h at room temperature during which time a fine precipitate formed.

The solvent was removed *in vacuo* to give an orange oil which was redissolved in dichloromethane (100 ml) and washed with water (3 × 50 ml). The organic layer was dried over anhydrous magnesium sulfate and evaporated to dryness *in vacuo*. This residue was purified by column chromatography on alumina, using 99:1 dichloromethane–methanol as the eluent. After recrystallising from dichloromethane the product was obtained as orange microcrystals. Yield: 0.97 g, 47%. ^{1}H NMR (CD_2Cl_2): δ 1.75 (m, 4 H, CCH_2C), 2.15 (m, 4 H, PCH_2), 3.48 [dt (obs. q), J = 6.6, 4 H, NCH_2], 4.32 [dd (obs. t), J = 1.9, 4 H, Cp H], 4.43 [dd (obs. t), J = 1.9, 4 H, Cp H], 6.85 (t, J = 5.8 Hz, 2 H, NH) and 7.31–7.47 (m, 20 H, aryl-H), ^{13}C NMR (CD_2Cl_2): δ 25.5 [d, J(P–C) = 12.2, CCH_2C], 26.3 [d, J(P–C) = 13.8, PCH_2], 40.7 [d, J(P–C) = 13.8, NCH_2], 70.7 (Cp C–H), 70.8 (Cp C–H), 78.8 (Cp C–C), 128.5 [d, J(P–C) = 6.2, aryl C–H], 128.6 (aryl C–H), 132.7 [d, J(P–C) = 18.5, aryl C–H], 138.4 [d, J(P–C) = 12.3 Hz, aryl C–C] and 170.3 (C=O). ^{31}P NMR (CD_2Cl_2): δ −19.4 (Found: C, 69.39; H, 5.78; N, 3.77. $C_{42}H_{42}FeN_2O_2P_2$ requires C, 69.62; H, 5.84; N, 3.87%). IR: $\tilde{\nu}_{max}$/cm^{-1}

3315 (N–H), 1622 (C=O) and 1542 (C–H aryl). FAB MS: *m/z* 725, $[M + H]^+$; 747, $[M + Na]^+$. mp 145–147 °C.

[1,1′-Bis(3-diphenylphosphinopropylaminocarbonyl)ferrocene]tetracarbonylmolybdenum 3. A solution of compound **2** (240 mg, 0.33 mmol) in dichloromethane (50 ml) and a solution of $[Mo(CO)_4(nbd)]$ (100 mg, 0.33 mmol) in dichloromethane (50 ml) were added simultaneously and dropwise to dichloromethane (100 ml) whilst stirring at room temperature in a nitrogen atmosphere. After addition was complete the reaction mixture was stirred at room temperature for 12 h before the solvent was removed *in vacuo*. The pure product was obtained as a yellow solid following recrystallisation from chloroform. Yield: 160 mg, 53%. ^{1}H NMR (CD_2Cl_2): δ 1.67–1.73 (m, 4 H, CCH_2C), 1.97–2.05 (m, 4 H, PCH_2), 3.31 [dt (obs. q), J = 6.2, 4 H, NCH_2], 4.39 [dd (obs. t), J = 1.9, 4 H, Cp H], 4.48 [dd (obs. t), J = 1.9 Hz, 4 H, Cp H], 6.56 (br s, 2 H, NH) and 7.36–7.51 (m, 20 H, aryl H). ^{31}P NMR (CD_2Cl_2): δ 21.6 (Found: C, 57.46; H, 4.41; N, 3.37. $C_{46}H_{42}FeMoN_2O_6P_2\cdot H_2O$ requires C, 58.10; H, 4.63; N, 2.94%). IR: $\tilde{\nu}_{max}$/cm^{-1} 3440 (H_2O), 3270 (N–H), 2017 (Mo–C=O), 1895 (br Mo–C=O), 1634 ($C{=}O_{amide}$) and 1532 (C–H, aryl). FAB MS: *m/z* 933, M^+; 876/8, $[M - (CO)_2]^+$; 850, $[M - (CO)_3]^+$; and 820/2, $[M - (CO)_4]^+$. mp 76–78 °C.

[1,1′-Bis(3-diphenylphosphinopropylaminocarbonyl)ferrocene]tetracarbonylchromium 4. A solution of compound **2** (280 mg, 0.39 mmol) in dichloromethane (10 ml) and benzene (40 ml) and a solution of $[Cr(CO)_4(nbd)]$ (100 mg, 0.39 mmol) in benzene (50 ml) were added simultaneously and dropwise to refluxing benzene (50 ml) under a nitrogen atmosphere. The resultant mixture was stirred at reflux for 12 h before the benzene was removed *in vacuo*. The residue was recrystallised from methanol–acetonitrile (50:50) to yield the pure products as yellow crystals. Yield: 160 mg, 46%. ^{1}H NMR (CD_2Cl_2): δ 1.67–1.72 (m, 4 H, CCH_2C), 2.05–2.10 (m, 4 H, PCH_2), 3.29 [dt (obs. q), J = 6.0, 4 H, NCH_2], 4.40 [dd (obs. t), J = 1.7, 4 H, Cp H], 4.48 [dd (obs. t), J = 1.7 Hz, 4 H, Cp H], 6.65 (br s, 2 H, NH) and 7.3–7.5 (m, 20 H, aryl H). ^{31}P NMR (CD_2Cl_2): δ 40.2 (Found: C, 62.17; H, 4.76; N, 3.15. $C_{46}H_{42}CrFeN_2O_6P_2$ requires C, 62.27; H, 5.02; N, 3.00%). IR: $\tilde{\nu}_{max}$/cm^{-1} 2005 (Cr–C=O), 1880 (br Cr–C=O), 1640 ($C{=}O_{amide}$) and 1532 (C–H, aryl). FAB MS: *m/z* 889, $[M + H]^+$; 776, $[M - (CO)_4]^+$. mp 186–189 °C.

[1,1′-Bis(3-diphenylphosphinopropylaminocarbonyl)ferrocene]carbonylchlororhodium 5. A solution of compound **2** (90 mg, 0.12 mmol) in dichloromethane (10 ml) and a solution of dirhodium dichloride tetracarbonyl (30 mg, 0.06 mmol) in dichloromethane (10 ml) were added dropwise and simultaneously to dichloromethane (80 ml) whilst stirring at room temperature under a nitrogen atmosphere. After addition was complete, the reaction mixture was stirred at room temperature for 12 h before the solvent was removed *in vacuo*. The residue was recrystallised from dichloromethane and hexane to yield the pure product. Yield: 50 mg, 45%. ^{1}H NMR (CD_2Cl_2): δ 1.97–2.02 (m, 4 H, CCH_2C), 2.63–2.67 (m, 4 H, PCH_2), 3.48–3.52 (m, 4 H, NCH_2), 4.35 [dd, (obs. t), J = 1.6, 4 H, Cp H], 4.67 [dd, (obs. t), J = 1.6 Hz, 4 H, Cp H], 6.97 (br s, 2 H, NH), 7.40–7.50 (m, 12 H, aryl H) and 7.65–7.72 (m, 8 H, aryl H). ^{31}P NMR [$(CD_2Cl)_2$]: δ 21.1 [J(P–Rh) = 122 Hz] (Found: C, 56.78; H, 4.71; N, 2.97. $C_{43}H_{42}ClFeN_2O_3P_2Rh\cdot H_2O$ requires C, 56.82; H, 4.85; N, 3.08%). IR: $\tilde{\nu}_{max}$/cm^{-1} 3500 (H_2O), 3335 (N–H), 1970 (Rh–C=O), 1635 ($C{=}O_{amide}$) and 1539 (C–H, aryl). FAB MS *m/z*: 891 M^+, 913 $(M+Na)^+$, 855 $(M - Cl)^+$.

[μ-1,1′Bis(3-diphenylphosphinopropylaminocarbonyl)ferrocene]-bis[bis(2,2′-bipyridyl)chlororuthenium] 6. *cis*-Bis(bipyridyl)ruthenium dichloride, *cis*-$[Ru(bpy)_2Cl_2]\cdot 2H_2O$ (72 mg, 0.14 mmol), and compound **2** (75 mg, 0.10 mmol) were dissolved in a mixture of ethanol (10 ml) and water (10 ml). The reaction mixture was deaerated with nitrogen for 15 min and then heated at reflux for 5 h under a nitrogen atmosphere. The ethanol was removed *in vacuo* and water (10 ml) added. The solution was filtered to remove unchanged ligand and a saturated aqueous solution of ammonium hexafluorophosphate was added to the filtrate. A red precipitate formed which was collected by filtration, washed with water and diethyl ether and dried. This product was recrystallised from acetone and diethyl ether. Yield: 85 mg, 64%. ^{1}H NMR (CD_2Cl_2): δ 1.23–1.29 (m, 4 H, CCH_2C), 2.40–2.45 (m, 4 H, PCH_2), 3.03–3.09 (m, 4 H, NCH_2), 4.34 [dd (obs. t), J = 2.0, 4 H, Cp H], 4.38 [dd (obs. t), J = 2.0, 2 H, Cp H], 4.44 [dd (obs. t), J = 2.0, 2 H, Cp H], 6.74–6.88 (m, 6 H, aryl H), 7.04 (t, J = 7.1, 4 H, aryl H), 7.15–7.29 (m, 12 H, aryl H), 7.38–7.56 (m, 10 H, aryl H, NH), 7.67–7.74 (m, 6 H, aryl H), 7.86–8.03 (m, 8 H, aryl H), 8.25 (dd, J = 8.3, 4 H, aryl H), 8.91 (d, J = 5.0 Hz, 2 H, aryl H) and 9.65 (t, 2 H, aryl H). ^{31}P NMR (CD_2Cl_2): δ 33.5 (Found: C, 49.34; H, 3.92; N, 6.85. $C_{82}H_{74}Cl_2F_{12}FeN_{10}O_6P_4Ru_2\cdot 4H_2O$ requires C, 49.60; H, 4.13; N, 7.06%). IR: $\tilde{\nu}_{max}$/cm^{-1} 3650 (H_2O), 3430 (N–H), 1636 ($C{=}O_{amide}$) and 1533 (C–H aryl). FAB MS: *m/z* 1912, M^+; 1765/7, $[M - (PF_6)]^+$; and 1622/4, $[M - (PF_6)_2]^+$.

3-Diphenylphosphinopropylaminocarbonylmethane. Acetyl chloride (0.48 g, 6.0 mmol) was dissolved in toluene (30 ml) and added dropwise to a solution of compound **2** (1.5 g, 6.0 mmol) and triethylamine (0.6 g, 6.0 mmol) in toluene (30 ml) whilst stirring under nitrogen. After addition was complete, the reaction mixture was stirred for 4 h before the solvent was removed *in vacuo*. The residue was dissolved in dichloromethane (50 ml) and washed with water (3 × 30 ml). The organic layer was dried over anhydrous magnesium sulfate and the solvent removed *in vacuo* to yield the product as a white solid. Yield : 1.21 g, 71%. ^{1}H NMR ($CDCl_3$): δ 1.59–1.66 (m, 2 H, CCH_2C), 1.94 (s, 3 H, CH_3), 2.00–2.08 (m, 2 H, PCH_2), 3.32 [dt (obs. q), J = 6.9 Hz, 2 H, NCH_2], 5.56 (br s, 1 H, N–H) and 7.32–7.48 (m, 10 H, aryl, H). ^{13}C NMR ($CDCl_3$): δ 23.3 (CH_3), 25.4 [d, J(P–C) = 10.9, CCH_2C], 26.1 [d, J(P–C) = 16.1, PCH_2], 40.5 [d, J(P–C) = 12.4, NCH_2], 128.5 (aryl C–H) 128.6 [d, J(P–C) = 12.4, aryl C–H], 130.7 (aryl C–H), 132.7 [d, J(P–C) = 18.3 Hz, aryl C–H], 138.4 (aryl C–C) and 170.0 (C=O). ^{31}P NMR (CD_2Cl_2): δ −19.2 (Found: C, 71.16; H, 7,41; N, 4.79. $C_{17}H_{20}NOP$ requires C, 71.50; H, 7.06; N, 4.91%). IR: $\tilde{\nu}_{max}$/cm^{-1} 1636 (C=O) and 1555 (C–H, aryl). mp 73–76 °C.

Tetracarbonylbis(3-diphenylphosphinopropylaminocarbonylmethane)molybdenum 7. A solution of $[Mo(CO)_4(nbd)]$ (110 mg, 0.36 mmol) in dichloromethane (30 ml) was added dropwise to a solution of the above compound (200 mg, 0.70 mmol) in dichloromethane (30 ml) whilst stirring under a nitrogen atmosphere. The reaction was stirred for 12 h and filtered. The solvent was removed from the filtrate and the residue recrystallised from dichloromethane and hexane to yield the pure product as beige microcrystals. Yield: 100 mg, 37%. ^{1}H NMR ($CDCl_3$): δ 1.28–1.38 (m, 4 H, CCH_2C), 1.92 (s, 6 H, CH_3), 1.97–2.02 (m, 4 H, PCH_2), 3.13 [dt (obs. q), J = 6.7, 4 H, NCH_2], 5.67 (t, J = 5.4 Hz, 2 H, NH) and 7.26–7.35 (m, 20 H, aryl H). ^{13}C NMR ($CDCl_3$): δ 23.2 (CH_3), 24.7 (CCH_2C), 30.1 [d, J(P–C) = 10.8, PCH_2], 40.1 (NCH_2), 128.4 (aryl C–H), 129.5 (aryl C–H), 132.3 (aryl C–H), 136.7 [d, J(P–C) = 15.6 Hz, aryl C–C], 170.2 (C=O) and 210.0 (Mo–C=O). ^{31}P NMR ($CDCl_3$): δ 22.7 (Found: C, 58.91; H, 5.29; N, 3.51. $C_{38}H_{40}MoN_2O_6P_2$ requires C, 58.56; H, 5.14; N, 3.60%). IR: $\tilde{\nu}_{max}$/cm^{-1} 2016 (Mo–C=O), 1903 (Mo–C=O), 1874 (Mo–C=O), 1646 ($C{=}O_{amide}$) and 1554 (C–H, aryl). FAB MS: *m/z* 779, M^+; 780, $[M + H]^+$; 802, $[M + Na]^+$; 723 $[M - (CO)_2]^+$; and 667, $[M - (CO)_4]^+$. mp 162–164 °C.

Crystallography

Crystal data for compounds **3** and **4** are given in Table 1, together with refinement details. Data for the two crystals were

collected with Mo-Kα radiation using the MARresearch Image Plate System. The crystals were positioned at 70 mm from the image plate. 95 Frames were measured at 2° intervals with a counting time of 2 min. Data analysis was carried out with the XDS program.[8] The structure of **4** was solved using direct methods with the SHELXS 86 program[9] and the structure of **3** was isomorphous. In both structures the non-hydrogen atoms were refined with anisotropic thermal parameters apart from those in solvent molecules which were refined isotropically and with reduced occupancies. The hydrogen atoms were included in geometric positions. Both structures were then refined on F^2 using SHELXL.[10] All calculations were carried out on a Silicon Graphics R4000 Workstation at the University of Reading.

CCDC reference number 186/1256.

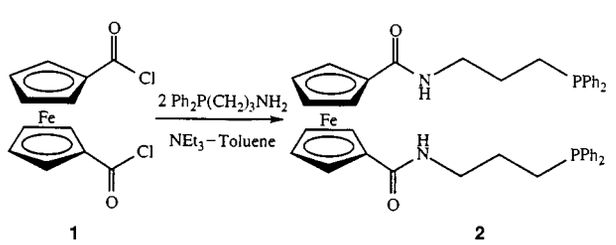
^{1}H NMR titrations

A solution of the receptor (500 μl) was prepared at a concentration typically of the order of 0.01 mol dm^{-3} in deuteriated dichloromethane. The initial ^{1}H NMR spectrum was recorded and aliquots of anion were added by gas-tight syringe from a solution made such that 1 mole equivalent was added in 20 μl. After each addition and mixing, the spectrum was recorded again and changes in the chemical shift of certain protons were noted. The result of the experiment was a plot of displacement in chemical shift as a function of the amount of added anion, which was subjected to analysis by curve-fitting since the shape is indicative of the stability constant for the complex. The computer program EQNMR[11] was used which requires the concentration of each component and the observed chemical shift (or its displacement) for each data point. Typically these titration experiments were repeated three times with at least fifteen data points in each experiment.

Results and discussion

Synthesis of ferrocene phosphine ligand

The new ferrocene appended phosphine amide ligand **2** was prepared *via* the condensation of 1,1′-bis(chlorocarbonyl)-ferrocene **1**[6] with 2 equivalents of 3-aminopropyldiphenyl-phosphine[7] in toluene in the presence of triethylamine (Scheme 1). The pure product was obtained after column chromatography and recrystallisation from dichloromethane as orange microcrystals in 47% yield.

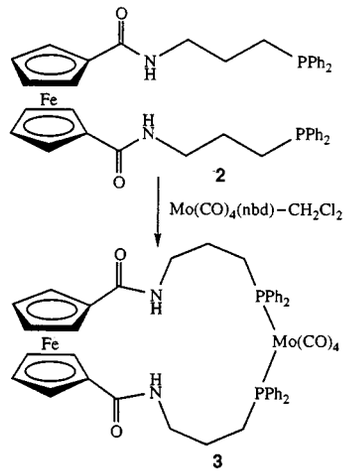


Scheme 1

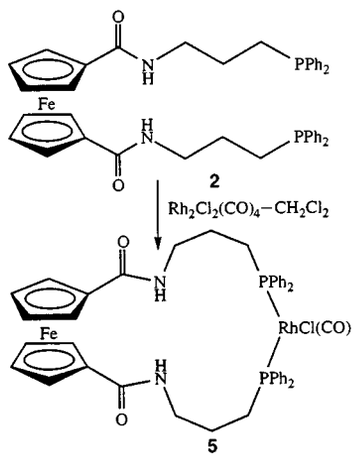
Synthesis of transition metal co-ordinated macrocycles of compound 2

Adapting the synthetic methodology used in the preparation of molybdenum carbonyl phosphine chelated metallocrown ether macrocycles,[12] the high-dilution reaction of 1 equivalent of $[Mo(CO)_4(nbd)]$ with 1 equivalent of compound **2** in dichloromethane produced, after recrystallisation from dichloromethane, the macrocyclic receptor **3** in 53% yield (Scheme 2). An analogous synthetic procedure with $[Cr(CO)_4(nbd)]$ afforded a crude product which was recrystallised from a 1:1 mixture of methanol–acetonitrile to give **4** in 46% yield.

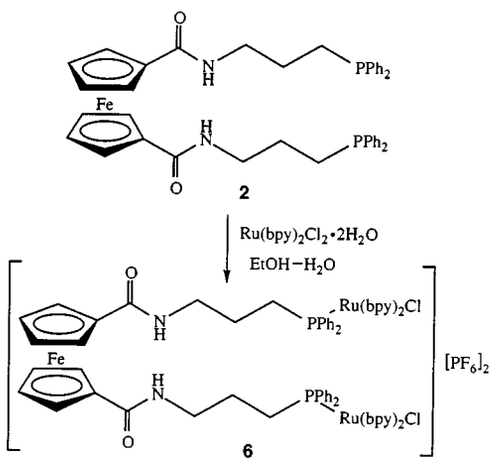
The rhodium(I) containing receptor **5** was prepared by the high-dilution reaction of $[Rh_2Cl_2(CO)_4]$ with 0.5 equivalent of **2** in dichloromethane in 45% yield (Scheme 3). The reaction of



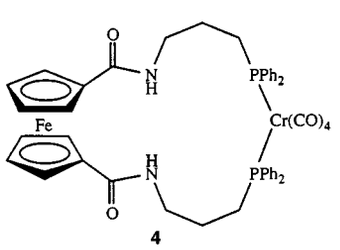
Scheme 2



Scheme 3



Scheme 4



$[Ru(bpy)_2Cl_2]\cdot 2H_2O$ and **2** in refluxing aqueous ethanol gave on addition of an excess of NH_4PF_6 a red product which was characterised as being the bis(ruthenium) compound **6** (Scheme 4).

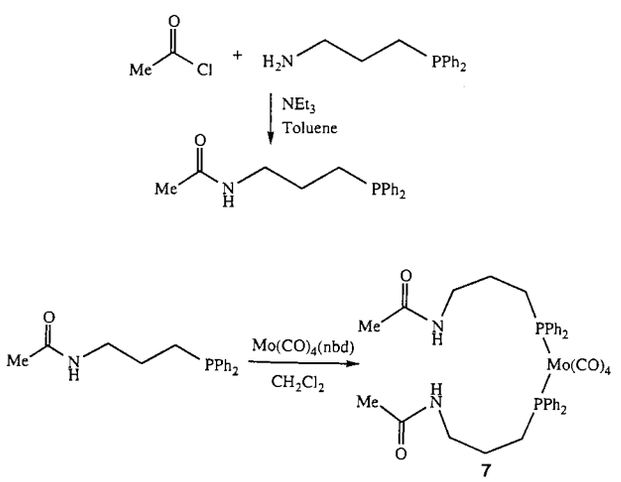
No trace of the expected chelated product was found and attempts to prepare this complex using high-dilution experimentation proved unsuccessful.

All four transition metal–ferrocene receptors were characterised by ^{1}H and ^{31}P NMR, IR spectroscopy, elemental analysis and FAB mass spectrometry (see Experimental section). The ^{31}P NMR data reveal a single resonance for all the complexes which suggests a single isomer has been produced in each case. This indicates the rhodium(I) compound **5** is square planar with the two phosphine ligands arranged in a *trans* conformation; the corresponding *cis* isomer would have given rise to two resonances.

Synthesis of model phosphine ligand and its molybdenum complex

In an effort to elucidate the individual effects the ferrocene redox active moiety and co-ordinated transition metal Lewis acid centre have on the anion binding properties of these receptor systems a model phosphine ligand and its molybdenum complex were prepared.

Condensation of 3-aminopropyldiphenylphosphine with acetyl chloride in toluene in the presence of triethylamine gave the amide in 71% yield. Reaction of 2 equivalents of it with 1 of $[Mo(CO)_4(nbd)]$ in dichloromethane afforded after recrystallisation from dichloromethane–hexane **7** as beige microcrystals in 37% yield (Scheme 5).



Scheme 5

X-Ray structural investigations of compounds 3 and 4

Crystals of compound **3** suitable for structural determination were grown from a 1 : 1 acetronitrile–ethanol solvent mixture, and those of **4** from a dichloromethane–methanol–hexane solvent mixture. The two structures, **3** containing molybdenum and **4** containing chromium respectively, are isomorphous, though with some differences in the solvent. The Mo and Cr atoms are octahedral being bonded to four carbonyls and two mutually *cis* phosphorus atoms. The two phosphorus atoms form a chelate ring containing 10 atoms and additionally a ferrocene moiety. The structure of **4** is shown in Fig. 2 together with the common numbering scheme.

The dimensions of the metal co-ordination spheres are as expected with those in the Mo longer by *ca.* 0.14 Å than those for Cr reflecting the difference in the metal radii. The two amide groups in the molecule have a different orientation in that O(15) is directed out and N(14) directed in while O(25) is directed in and N(24) is directed out. This arrangement facilitates the formation of a hydrogen bond between N(24) and O(15) in a neighbouring molecule [2.96(2) in **4**, 2.95(2) Å **3**]. The ferrocene moieties have the expected dimensions with the eclipsed conformation as is apparent from Fig. 2. The remaining dimensions in the molecule are also as expected.

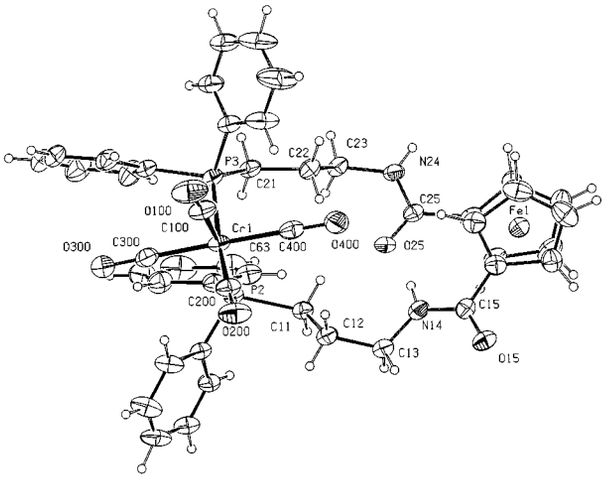


Fig. 2 Structure of compound **4** with the atomic numbering scheme. The structure of **3** is isomorphous. The ellipsoids are shown at 30% occupancy. Cr(1) to carbonyl 1.853(8), 1.856(8), 1.887(8), 1.899(8), Cr(1)–P(2) 2.422(2), Cr(1)–P(3) 2.448(2) Å. Dimensions in the isomorphous molybdenum compound are Mo(1) to carbonyl 2.013(8), 1.995(8), 2.042(7), 2.046(7) and Mo(1)–P(2) 2.546(2), 2.568(2) Å.

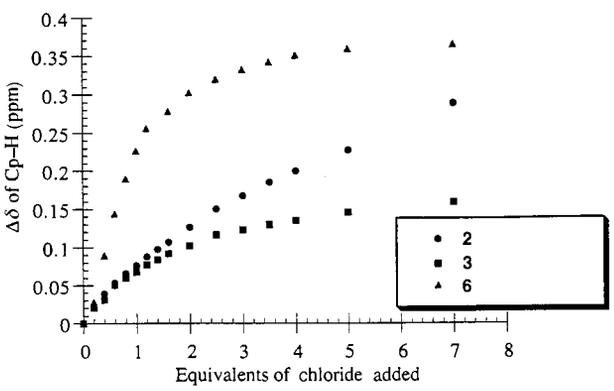


Fig. 3 Proton NMR titration curves of compounds **2**, **3** and **6** with Cl^- in CD_2Cl_2.

Anion co-ordination studies

Proton NMR titrations. Proton NMR titration experiments were carried out in deuteriated dichloromethane with compound **2**, the transition metal co-ordinated receptors and various tetrabutylammonium anion salts. Typically significant downfield shifts of the amide and cyclopentadienyl protons were observed following the addition of anions. The EQNMR [11] analysis of the resulting titration curves (Fig. 3) gave stability constant values for 1 : 1 solution anion complexes shown in Table 2. A comparison of the stability constant data for chloride anion binding reveals several noteworthy features. As was hoped compared with **2**, the presence of the phosphine co-ordinated transition metal increases the strength of anion binding. The largest increase in magnitude of binding occurs with the charged ruthenium(II) receptor **6** which highlights the importance of attractive electrostatic forces in the anion complexation process. The chloride anion stability constant values for the neutral molybdenum **3** and chromium **4** receptors are an order of magnitude larger than that of the parent ferrocene phosphine ligand **2** which suggests a macrocyclic effect may be responsible. However, the similarity between stability constant values determined for the two molybdenum receptors **3** and **7** implies the interaction between the anion and the chelated Lewis acid metal may be the dominant favourable binding effect.

Regarding anion selectivity trends Table 2 shows with receptors **3**, **4** and **7** the strength of anion binding decreases in the order $Cl^- > Br^- > I^-$ which reflects the decrease in charge den-

Table 1 Crystal data and structure refinement for compounds **3** and **4**

	4	**3**
	$[CrL(CO)_4]\cdot 0.5EtOH\cdot MeOH$	$[MoL(CO)_4]\cdot 0.5MeCN\cdot 0.5EtOH$
Empirical formula	$C_{48.50}H_{49}CrFeN_2O_7P_2$	$C_{48}H_{46.5}FeMoN_{2.5}O_{6.5}P_2$
Formula weight	941.69	976.10
T/K	293 (2)	293 (2)
λ/Å	0.71073	0.71073
Crystal system, space group	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$
a/Å	14.093(11)	14.050(13)
b/Å	14.512(10)	14.344(13)
c/Å	26.82(2)	26.88(2)
β/°	103.720(10)	102.790(10)
V/Å^3	5328	5283
Z, D_c/Mg m^{-3}	2, 1.174	2, 1.227
μ/mm^{-1}	0.581	0.617
F(000)	1960	2008
Crystal size mm	0.25 × 0.25 × 0.30	0.25 × 0.25 × 0.25
θ range for data collection/°	2.49 to 28.60	1.90 to 23.99
Index ranges	$-16 \leqslant h \leqslant 0$, $-17 \leqslant k \leqslant 17$, $-31 \leqslant l \leqslant 32$	$-16 \leqslant h \leqslant 0$, $-16 \leqslant k \leqslant 16$, $-30 \leqslant l \leqslant 29$
Reflections collected/unique	16458/9256 [R(int) = 0.0582]	14791/7695 [R(int) = 0.0333]
Data/restraints/parameters	9256/0/558	7695/0/551
Final $R1$, $wR2$ [$I > 2\sigma(I)$]	0.0998, 0.2887	0.0653, 0.1697
(all data)	0.1370, 0.3224	0.0854, 0.1854
Extinction coefficient	0.024(3)	0.0061(6)
Largest difference peak and hole/e Å^{-3}	0.821 and −0.844	0.905, −0.547

Table 2 Anion stability constant data

	K^a/dm^3 mol^{-1}			
Receptor	Cl^-	Br^-	I^-	$H_2PO_4^-$
2	10	—	—	10
3	70	50	10	20
4	70	60	15	20
5	20	nb	nb	nb
6	240	320	250	ppt
7	70	40	20	50

[a] Determined in CD_2Cl_2, at 293 K, errors estimated to be ≤ 20%. nb = No binding; ppt = precipitate formed during titration, K could not therefore be calculated.

Table 3 Electrochemical data

Receptor	E_{pa}(Fc–Fc$^+$)[a]/mV	E_{pa}(Metal)[a]/mV
2	440	—
3	460	520
4	485	360
5	470	400
6	460	640
7	—	470

[a] E_{pa} = anodic peak potential. Obtained in 1:1 acetonitrile–dichloromethane solution containing 0.2 mol dm^{-3} NBu_4PF_6 as supporting electrolyte. Solutions were *ca.* 1 × 10^{-3} mol dm^{-3} in receptor and potentials were obtained with reference to a Ag–Ag$^+$ electrode at 293 K, scan rate = 100 mV s^{-1}.

sity of the anionic guest species. In contrast the ruthenium(II) receptor **6** displays a similar strength of binding for chloride and iodide whilst bromide forms the strongest complex. The binding of dihydrogenphosphate is generally weak for all receptors except **7**. In the case of **3** and **4** this may be a consequence of their macrocyclic cavities being too small to accommodate this relatively large anionic guest. Similarly the small macrocyclic cavity size of the rhodium(I) receptor **5** may account for this receptor's inability to complex the largest bromide, iodide and dihydrogenphosphate guest anions.

Electrochemical investigations

The electrochemical properties of the receptors were investigated by cyclic voltammetry in a 1:1 mixture of acetonitrile and dichloromethane with NBu_4BF_4 as supporting electrolyte (Table 3). The ferrocene phosphine ligand **2** displayed a single irreversible oxidation wave characteristic of an electrochemical step-chemical step (EC) mechanism. It is possible that the irreversible nature of this oxidation process arises from an interaction between the lone pairs of electrons of the phosphorus atoms and the positively charged ferrocenium unit. Interestingly in support of this the phosphine–transition metal co-ordinated receptors gave cyclic voltammograms of more reversible character (Fig. 4). Similar electrochemical findings have been reported with polyaza ferrocene ligands.[13] The cyclic voltammograms of **3**–**6** all contain two oxidation waves which can be assigned to the oxidation of the ferrocene moiety and

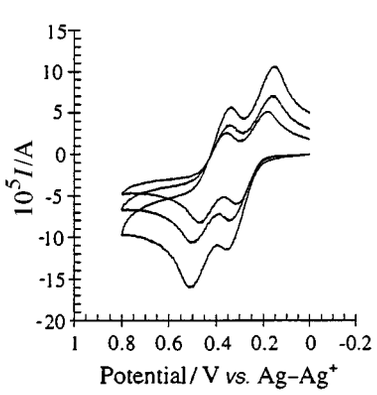


Fig. 4 Cyclic voltammograms of compound **4** in 1:1 acetonitrile–dichloromethane at scan rates 50, 100 and 200 mV s^{-1}.

the respective transition metal centre (Fig. 4) (Table 3). In the case of **3** thin layer coulometric experiments confirmed the two oxidation waves to be two one electron redox processes.

Table 3 shows the ferrocene oxidation potentials for the transition metal containing receptors are anodically shifted compared to that of the 'free' ligand **2**. This anodic shift can be ascribed to the presence of the closely bound Lewis acidic metal centre withdrawing electron density presumably *via* through space communication making the oxidation process less favourable. Surprisingly the largest magnitude of anodic per-

Table 4 Electrochemical anion recognition data

	$\Delta E_{pa}(Cl^-)^a$/mV		$\Delta E_{pa}(Br^-)^a$/mV		$\Delta E_{pa}(HSO_4^-)^a$/mV	
Receptor	Fc–Fc^+	Metal	Fc–Fc^+	Metal	Fc–Fc^+	Metal
2	65	—	30	—	70	—
3	90	95	30	30	35	50
4	85	30	30	55	35	30
5	65	80	—	—	60	30
6	70	25	35	—[b]	45	45
7	—	25	—	25	—	25

[a] Cathodic shift in oxidation potential produced by presence of 5 equivalents of anion added as its tetrabutylammonium salt. Solvent 1:1 acetonitrile–dichloromethane, 293 K. [b] Could not be investigated as oxidation potential is greater than oxidation potential of anion.

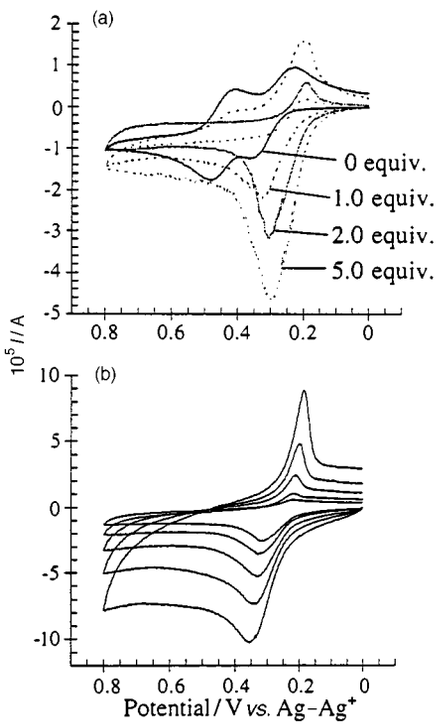


Fig. 5 Cyclic voltammograms of compound **4** in the presence of (a) increasing amounts of $H_2PO_4^-$ and (b) 5 equivalents of $H_2PO_4^-$ in 1:1 acetonitrile–dichloromethane. Scan rates in (b) are 50, 100, 200, 400 and 800 mV s^{-1}.

turbation occurs with the neutral chromium receptor **4** and not the positively charged ruthenium(II) receptor **6**.

The effect of anion binding on the electrochemical properties of compounds **2**–**6** and **7** was also investigated. Following the addition of chloride, bromide and hydrogensulfate anions, significant cathodic shifts were observed in the ferrocene and metal centre oxidation potentials (Table 4). The bound anion effectively stabilises the positively charged ferrocenium or oxidised transition metal facilitating the oxidation redox process. Interestingly Table 4 shows chloride causes larger cathodic perturbations than bromide, which reflects its higher charge : radius ratio. Chloride also causes larger perturbations than hydrogensulfate for the three macrocyclic receptors **3**–**5** which may be ascribed to a size selective effect; the chloride ion is of complementary size to the respective macrocyclic cavity whereas the larger tetrahedral hydrogensulfate anion is not.

The effects of dihydrogenphosphate anions on the electrochemical properties of compounds **2**–**4** and **6** were intriguing. For example the cyclic voltammograms obtained for the chromium receptor **4** in the presence of increasing amounts of $H_2PO_4^-$ are shown in Fig. 5. As the anion was added the chromium oxidation wave decayed and the ferrocene oxidation was significantly shifted to lower potential (Table 5). Similar observations were noted in the cyclic voltammograms of compounds **2**, **3** and **6** and Table 5 reports the relatively large

Table 5 Dihydrogenphosphate induced cathodic shifts of ferrocene–ferrocenium oxidation potential of receptors

Receptor	**2**	**3**	**4**	**6**
$\Delta E_{pa}{}^a$ /mV	135	135	185	180

[a] Cathodic shift in ferrocene–ferrocenium oxidation potential produced by presence of 5 equivalents of tetrabutylammonium dihydrogenphosphate in 1:1 acetonitrile–dichloromethane.

$H_2PO_4^-$ induced cathodic shifts of their respective ferrocene oxidation potentials.

The shape of the cyclic voltammogram following the addition of 5 equivalents of $H_2PO_4^-$ was characteristic of an EC mechanism. Fig. 5(b) shows with compound **4** that as the scan rate is increased the reduction peak becomes increasingly apparent. The sharp, symmetrical shape of the reverse peak is characteristic of electron transfer to a surface confined species suggesting the product of the chemical reaction is adsorbed onto the electrode surface.

Conclusion

The syntheses of a new bis(phosphine) amide linked ferrocene ligand and molybdenum, chromium, rhodium and ruthenium transition metal chelated receptors have been achieved. Single-crystal X-ray structural investigations of the molybdenum and chromium receptors reveal monomeric transition metal phosphine chelation with *cis*-co-ordination geometry at the metal centre. Proton NMR anion co-ordination investigations enabled stability constants to be determined for 1:1 stoichiometric receptor : anion complexes. A comparison of stability constant values suggests the combination of the transition Lewis acid metal centre and the ferrocene amide moiety enhances the strength of anion binding. It is noteworthy that the strength of anion binding was greatest with the positively charged ruthenium receptor **6** which indicates that attractive electrostatic forces are of significant importance to the anion recognition process. Electrochemical investigations show all receptors can electrochemically sense various anions *via* significant cathodic perturbations of the respective ferrocene and transition metal oxidation wave.

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