Synthetic receptors for dicarboxylates and diammoniums: templated assembly of functionalized catechols around molybdenum and complexation studies

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The spontaneous templated formation of receptors by assembling organic fragments around a transition metal core has been extended to catechols bearing thioureas and crown ethers. Symmetrical molybdenum complexes were obtained and characterized, and their suitability for the complexation of dicarboxylates and alkyl diammoniums have been determined. The relative flexibility of the fully assembled receptors is responsible for a low binding selectivity. The association constants of the bis crown ether receptor with diammonium are consistently high, most probably because the dianionic receptors develop additional electrostatic interactions with the diammoniums to produce neutral supramolecular complexes.

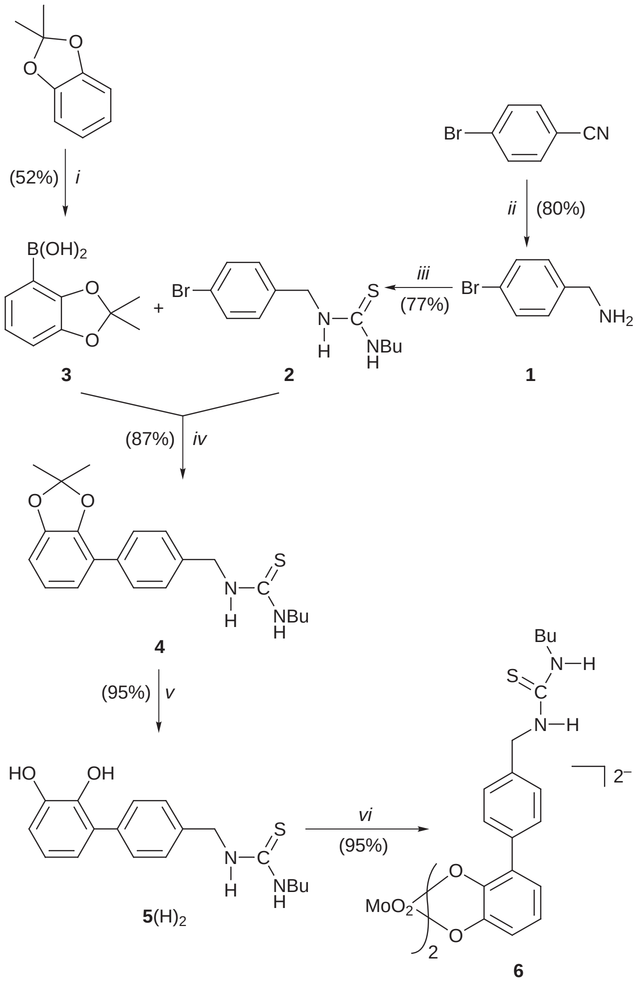
The formation of receptors based on the orienting of 'half receptors' around a transition metal template allows for specific and selective orientation of binding groups. Previous work on aminopyridine substituted phenanthrolines,[1,2] and terpyridines,[3,4] organized around, respectively, copper(I) and, ruthenium(II), has demonstrated the validity of this directed assembly concept. The ability of aminopyridine substituted catecholates organized around a *cis*-dioxomolybdenum(VI) template to complex carboxylic acids has been recently reported[5,6] and these results prompted us to extend this template approach to the synthesis of receptors for carboxylates and ammoniums. Results obtained using a *cis*-MoO$_2$ core and thiourea or crown ether substituted catecholates are presented in this paper.

Results and discussion

Synthesis and characterization of a dicarboxylate receptor

The synthesis of the half-receptor **5** is depicted in Scheme 1, starting from *p*-bromobenzonitrile and the acetonide of catechol.[7] The amine **1** was prepared from *p*-bromobenzonitrile by reduction with LiAlH$_4$[8] in Et$_2$O and condensed with butyl isothiocyanate in ethanol[9] to afford **2** in good yield (77%) after chromatography (SiO$_2$, CH$_2$Cl$_2$). Low temperature lithiation of the acetonide, followed by quenching with trimethyl borate and acidic work up, afforded the boronic acid **3** (52%) after chromatography over silica gel. This product was coupled to the phenyl spacer bearing the thiourea **2** by the Suzuki reaction[10] in excellent yield (87%), using Pd(PPh$_3$)$_4$ in alkaline homogeneous solution (MeOH : 2 M Na$_2$CO$_3$ aq. : THF, 1 : 1 : 5). Finally, deprotection of the catecholate chelating site[7] was performed by treatment with an aqueous solution of CH$_3$COOH, affording the half-receptor **5** in 95% yield. Synthesis of the fully assembled receptor **6** was realized by reacting *cis*-bis(acetylacetonato)dioxomolybdenum(VI) in stoichiometric amounts with the half-receptor **5** in dilute conditions and in the presence of a base, (NBu$_4$)OH. As expected, the nature of the base allows the solubility of the assembled dianionic receptors in organic solvents to be controlled.

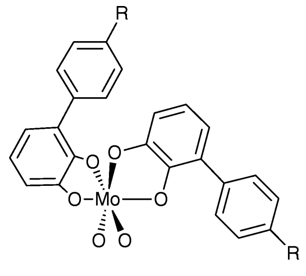
As already reported in a previous paper describing dicarboxylic receptors,[5,6] which also organize functionalized catecholates around a *cis*-MoO$_2$ core, only one pair of enantiomers out of the three possible pairs was obtained. FTIR characterization[11] clearly shows that the *cis* geometry for the MoO$_2$ core has been retained, as two bands corresponding to the ν(Mo=O) symmetrical and asymmetrical



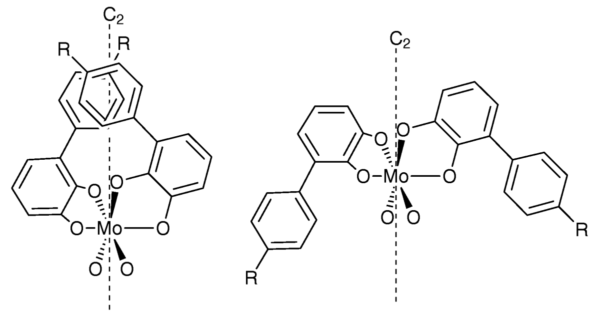
Scheme 1 Synthesis of receptor **6**: (*i*) Bu^{n}Li, 0 °C, THF, B(OMe)$_3$: THF, H$^+$ aq.; (*ii*) LiAlH$_4$: THF; (*iii*) BuNCS : EtOH; (*iv*) Na$_2$CO$_3$: MeOH : H$_2$O : Pd(PPh$_3$)$_4$: THF; (*v*) H$_2$O : CH$_3$COOH 1 : 4; (*vi*) MoO$_2$(acac)$_2$: NBu$_4$OH : EtOH

vibrations are observed. In addition, mass spectrometry measurements confirmed both the correct molecular mass and the presence of the two ammonium counter cations. Previously reported *cis*-MoO_2[11–13] complexes with substituted catecholates have shown crystal structures similar to the **B** type represented in Fig. 1, before ^1H NMR was used to demonstrate that only the **B** forms of our receptors are present in solution. The reasons for ruling out the two other possible structures have been extensively discussed in a previous paper.[6] Variable temperature ^1H NMR experiments resulted in the resolution of the resonance corresponding to the phenyl spacers and the butyl groups and none of the other signals were affected. Thus, it is assumed that no exchange occurs between the **B** form and the other possible enantiomers. Similarly to what has been observed with dicarboxylic acids, the complexation of dicarboxylates with receptor **6** is likely to occur as depicted in Fig. 2.

UV/VIS titrations were performed to assay the receptor affinities for dicarboxylates ranging from C_4 to C_7. As it has been reported,[1–6] significant changes in the electronic absorption spectrum of receptors assembled around transition metal centers renders UV/VIS titrations more accurate than NMR for the determination of binding constants in the case of strong complexation.



A: no symmetry elements



B and C: C2 axis

R: H-bonding Recognition Site

Fig. 1 Three possible enantiomeric forms (**A**, **B** and **C**) of molybdenum complexes (mirror images not represented)

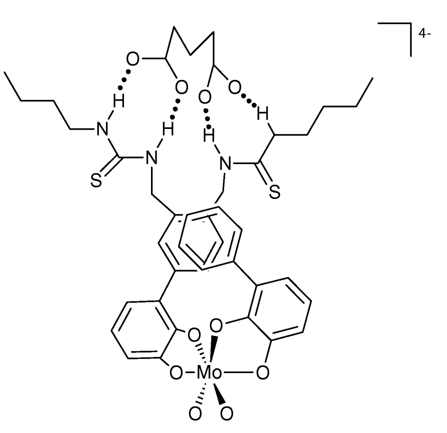


Fig. 2 Probable binding mode receptor **6** with glutarate

Dicarboxylates complexation studies

Titration studies of carboxylate ions are usually performed in solvents like MeOH or DMSO. These solvents are polar and favor the dissociation of the ion pairs in solution. Titration tests in these solvents with receptor **6** and dicarboxylates lead only to decomposition of receptor **6**; no complexation was observed. Most probably, this decomposition occurs in presence of water traces that instigate the hydrolysis of Mo—O bonds. The study of carboxylates complexation was performed in acetonitrile. Acetonitrile (dielectric constant of 37.5) leads to enough solvation to separate the ion pairs, but is less nucleophilic than MeOH or DMSO.

For each titration, the 1 : 1 stoichiometry of the complex was confirmed by two methods, the binding isotherm and the A diagram.[14] An example of titration curves and A diagrams is given in Fig. 3. Based on this 1 : 1 mode, titration curves were analyzed using the Letagrop (version 2.4.93) program. Binding constants are collected in Table 1. No complexation selectivity of the dicarboxylate ions is noticeable. This could be explained by the presence of the methylene group between the phenyl spacer and the thiourea subunit. The free rotation around this methylene group enables the receptor to adapt to the length of the dicarboxylate carbon chain, as in an induced-fit process. Adjustments of the distance between the two thiourea units during the dicarboxylate complexation do not lead to conjugation changes, and, as a consequence, no electronic density changes within the $MoO_2(catecholate)_2{}^{2-}$ based receptors. Thus, the methylene link is responsible for the weaker chromogenicity observed during titrations for the dicarboxylate receptor. Because of this flexible spacer, the distortion of the receptor required for adjustment to the guest is also less energetic and will easily explain the lack of selectivity observed in this case. The overall (2−) charge of the receptor is also important, as both the receptor and the substrate are dianions. Thus, the formation of a complex occurs by formation of four H bonds and involves a repulsive interaction between two species of same charge. These electrostatic interactions disfavor the formation of the complex.

^1H NMR titrations in acetonitrile clearly show and confirm the formation of the receptor-substrate complex. The evolution of the proton NMR spectrum during titration is represented in Fig. 4. Owing to the nature and the structure of

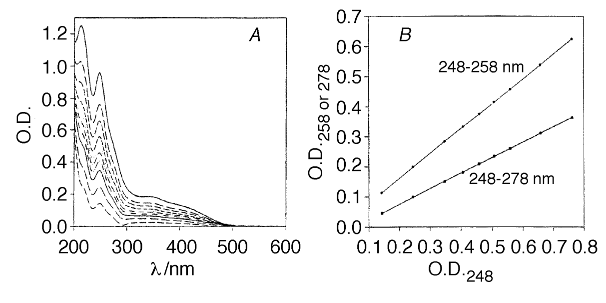


Fig. 3 (*A*) UV/VIS titration of **6** with glutarate (C_5); (*B*) Absorbance diagram: variation of O.D. at 258 and 278 nm *versus* the variation of O.D. at 248 during titration; straight lines are representative of 1:1 stoichiometry

Table 1 Binding constant values for the recognition of alkyldicarboxylates ranging from succinate (C_4) to pimelate (C_7) by receptor **6** in acetonitrile

Carboxylate	C_4	C_5	C_6	C_7
log *K*	6.2 ± 0.6	5.7 ± 0.6	6.9 ± 0.7	6.1 ± 0.6

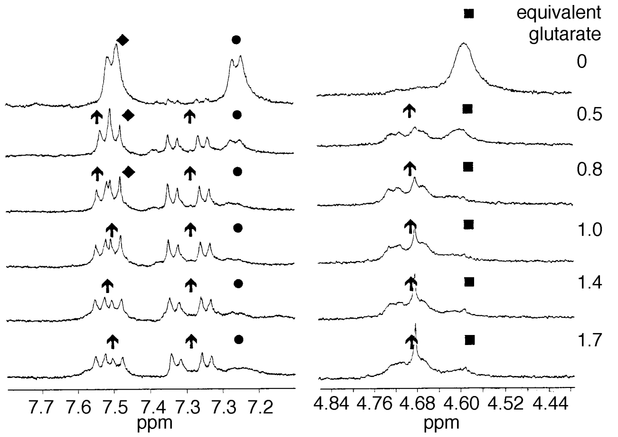


Fig. 4 Evolution of the ^1H NMR spectrum during titration of glutarate with **6** in acetonitrile: ↑ complex formed; ◆, ■ and ● free receptor, [**6**] = 8.0 × 10^{-3} M

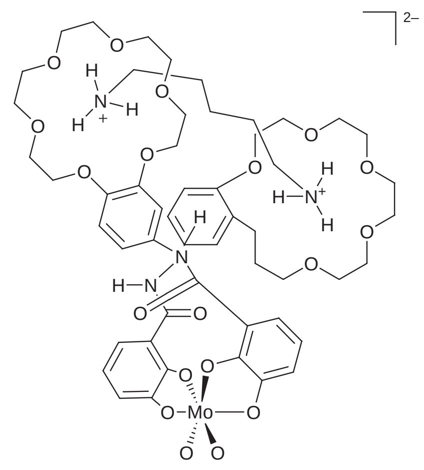


Fig. 5 Proposed binding mode of receptor **9** with pentane diammonium.

both the receptor and the substrate, only parts of the proton NMR spectrum can be precisely assigned and considered as significant. This evolution indicates that upon addition of glutarate one stable complex forms immediately and is in slow exchange with its dissociated form. When more than one equivalent of glutarate is added, all of the free receptor is consumed and no further changes are observed. Thus, dicarboxylate complexation with receptor **6** occurs in acetonitrile without selectivity and with only weak color changes.

Synthesis of a diammonium receptor

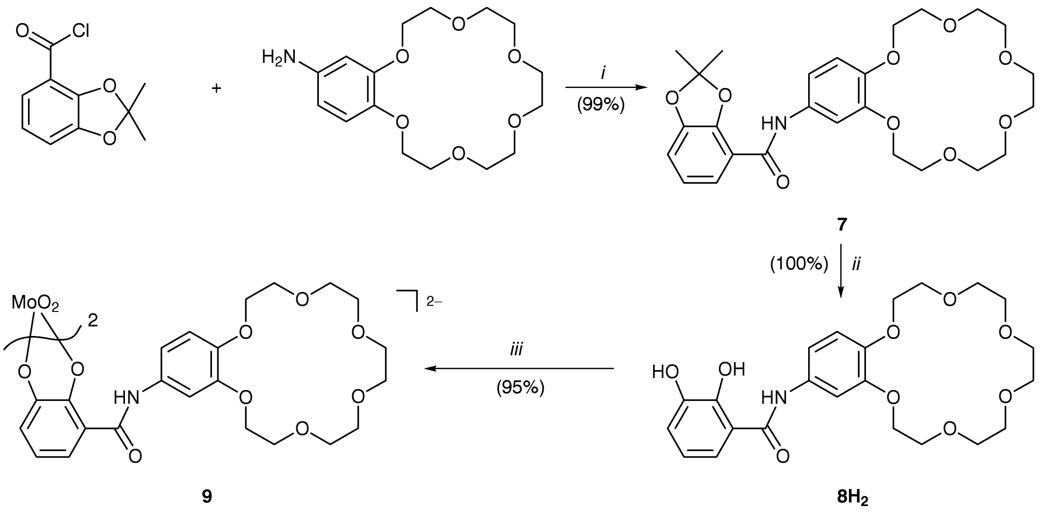
The synthesis of the fully assembled receptor **9** is outlined in Scheme 2. The intermediate 2,3-acetonide of 2,3-dihydroxybenzoyl chloride was prepared by a known procedure.[7] After condensation in THF with 4-aminobenzo-18C-6 in the presence of NEt_3, the protected catechol **7** was isolated in 99% yield. Deprotection of the catecholate chelating site was again realized with an aqueous solution of CH_3COOH, to afford the half-receptor **8** in quantitative yield. Synthesis of the fully assembled receptor **9** was performed as described for receptor **6**.

Again, FTIR characterization, mass spectrometry measurements and ^1H NMR titrations support the formation of only one pair of symmetrical enantiomers (type **B**). The proposed structure of the diammonium receptor and its interaction mode with diammoniums is represented in Fig. 5.

Complexation studies of diammonium salts

Crown ether subunits are known to be good receptors for alkaline and alkaline earth cations but also for ammoniums.[15] Thus, receptor **9** should exhibit binding affinities for alkyl diammonium salts. The binding properties of the bis crown ether receptor **9** in the presence of alkyl diammonium picrates ranging in length from C_4 to C_8 have been evaluated by liquid–liquid extraction and the results are compiled in Table 2.

All diammonium salts studied here are insoluble in CH_2Cl_2 without receptor **9**; thus, dissolution occurs only by complexation. The liquid–liquid extraction method was earlier described by Kyba *et al.*[16] and UV/VIS titrations were performed to show that the bis crown ether receptor **9** extracts 37 to 75% of diammonium salts into CH_2Cl_2 from an aqueous solution. The association constants based on these extraction values, assuming the formation of a 1 : 1 complex were calculated, and their log values are reported in Table 2. Only a slight preference for C_5 diammonium salt is noticeable. This low selectivity can be explained through the ability of the substrate to adapt to the receptor. Large variations of the diammonium length may occur as soon as the *gauche* conformation of the alkyl chain is not observed (other than C_5). The energetic requirements are apparently not large enough to allow selective binding of one diammonium *versus* another. The same study was repeated by ^1H NMR. This method confirms the formation of only one complex with a one-to-one stoichiometry and also that the dialkyl chain chemical shifts



Scheme 2 Synthesis of receptor **9**: (*i*) NEt_3 : THF; (*ii*) H_2O : CH_3COOH 1 : 4; (*iii*) EtOH : NBu_4OH : $MoO_2(acac)_2$.

Table 2 Binding constants for the recognition of alkyl diammoniums ranging from butyl diammonium (C_4) to octyl diammonium (C_8) by receptor **9**[a]

Ammonium	K_e	log K	r/%
C_4	3.94×10^{11}	4.0 ± 0.4	60
C_5	2.22×10^{12}	5.2 ± 0.5	75
C_6	3.20×10^{11}	3.9 ± 0.4	56
C_7	1.69×10^{11}	3.7 ± 0.4	49
C_8	3.19×10^{10}	3.5 ± 0.4	37

[a] K_e is a constant defined by Cram relating the formation of the ammonium-receptor complex in the organic phase with the concentration of free ammonium picrate in the aqueous phase and the concentration of free receptor in the organic phase. r is the ratio beteen the concentration of ammonium picrate complexed by **9** and the total concentration of receptor (both in the organic phase). For details see ref. 16.

are not affected by the complexation. These results are in agreement with the proposed binding mode for the complexation of diammonium with receptor **9** depicted in Fig. 5. It should be noticed that the obtained association constants compare quite efficiently with those reported in the literature, most probably because of the formal charge of the receptor. When the dianionic receptor interacts with the dicationic guest, complexation generates a neutral diammonium complex. Beside the fact that this will be favored in CH_2Cl_2, it will also benefit from the electrostatic interactions between the two oppositely charged species. This aspect of the templated formation of receptors is very attractive and global charge control may open new areas of research in molecular recognition.

Conclusion

The concept of preorganizing multiple H bonds around a *cis*-MoO_2 core has been extended to obtain receptors for the complexation of dicarboxylates and diammoniums. These receptors, **6** and **9**, were obtained under mild conditions with very good yields. The receptors are able to complex substrates with nevertheless low selectivity. The nature of the spacer between the recognition site and the reporting metal template may have two main consequences. If not conjugated with both parts, it will prevent the propagation of electronic effects between the recognition site and the chromophore (metal complex), and, if flexible, this spacer will also allow the receptor to adapt to the size of the substrate. Thus, it will define the chromogenicity of the receptor and also its selectivity. Beside the complexation studies of more rigid substrates, we are currently extending this approach to metal complexes that will recruit three or more binding regions to complete the recognition. The use of binding groups like guanidiniums, which will allow for a global charge control on the receptor, is also being investigated.

Experimental

General

All commercial reagents were used without purification except for $MoO_2(acac)_2$, which was purified by extraction of commercial material (5–10 g) placed in a 60 mL glass filtering funnel (medium porosity) with three 30 mL aliquots of boiling acetyl acetone. To the resulting yellow filtrate was added petroleum spirit to yield a yellow precipitate, which was collected by filtration and washed with several portions of petroleum spirit. Spectroscopic characterization of the purified material was in excellent agreement with literature data.[11] When anhydrous conditions were required, all glassware was flame-dried under an inert gas flow, experiments were run under argon and all solvents were dried as follows. Toluene, ether and tetrahydrofuran were distilled from sodium–benzophenone and methylene chloride, MeOH, EtOH and CH_3CN were distilled from CaH_2. NMR spectra were recorded on a Bruker AM 300 spectrometer and data were processed with Bruker-WINNMR™ for Windows. Chemical shifts were determined taking the solvent as an internal reference: $CHCl_3$ (7.26 ppm), $CHDCl_2$ (5.32 ppm), CHD_2OD (3.30 ppm), CHD_2CN (1.94 ppm), acetone-d_5 (2.04 ppm), DMSO-d_5 (2.49 ppm). UV/VIS experiments were run on a Hewlett–Packard HP8452A diode array spectrophotometer using a 2 nm resolution in quartz cells with an optical path length of 1 cm. Unless otherwise stated, FTIR spectra were recorded on a Bruker IFS 28 apparatus with KBr pellets as samples. Melting points were determined on a Kofler Heating Plate type WME and are uncorrected. Elemental analyses were performed by the Service de Microanalyse of the Institut de Chimie de Strasbourg. Mass spectra were obtained on a FAB:ZAB-HF mass spectrometer. Thin layer chromatography (TLC) was performed using Macherey-Nagel Polygram Sil G/UV_{254} (0.25 mm) and Polygram Alox N/UV_{254} analytical polyethylene coated plates. E. Merck silica gel 60 (70–230 mesh), aluminium oxide 90 (70–230 mesh, act. II-III), octadecyl functionalized silica gel (Aldrich) and sephadex G-25 (Aldrich) were used for column chromatography.

Syntheses

4-Bromobenzylamine, 1. To a suspension of $LiAlH_4$ (0.209 g, 5.5 mmol) in 5.5 mL of dry Et_2O was added dropwise a solution of 4-bromobenzonitrile (1.00 g, 5.5 mmol) in 15 mL of Et_2O. After 15 min at room temperature, the reaction mixture was cooled to 0 °C and carefully hydrolyzed by the addition of 15 mL of 15% aqueous NaOH. The organic phase was separated and the aqueous phase was extracted with ether (2 × 50 mL). To the aqueous layer were added 50 mL of concentrated ammonia and 50 mL Et_2O; the resulting mixture was stirred for 20 min before collecting the aqueous layer. This treatment was repeated twice. All organic phases were combined and extracted with 5 N hydrochloric acid (100 mL). The aqueous extract was made alkaline with aqueous 5 N sodium hydroxide and extracted with Et_2O (3 × 100 mL). The Et_2O extract was dried over $MgSO_4$. After filtration, the solvent was removed and the product was used without further purification. Yield 0.82 g (4.4 mmol, 80%). $R_f = 0.8$ in CH_2Cl_2 on SiO_2; mp: 104 °C; ^1H NMR in $CDCl_3$: 7.44 (d, $J = 8.3$ Hz, 2H), 7.18 (d, $J = 8.3$ Hz, 2H), 3.82 (s, 2H).

1-Butyl-3-(4-bromobenzyl)thiourea, 2. The bromo amine **1**, (0.5 g, 2.6 mmol) and butyl isothiocyanate (0.77 g, 6.7 mmol) were added to 50 mL of ethanol. The reaction mixture was stirred at room temperature for 72 h. After evaporation of the solvent, the residue was passed through a silica gel column eluted with CH_2Cl_2. Yield: 0.6 g (1.99 mmol, 77%). $R_f = 0.2$ in CH_2Cl_2 on SiO_2; mp: 102 °C; ^1H NMR in $CDCl_3$: 7.47 (d, $J = 8.4$ Hz, 2H), 7.21 (d, $J = 8.4$ Hz, 2H), 6.05 (s, 1H), 5.89 (s, 1H), 4.67 (s, 2H), 3.35 (m, 2H), 1.53 (m, 2H), 1.32 (m, 2H), 0.91 (t, 3H); anal. calcd for $C_{12}H_{17}BrN_2S$ (%) C (47.68), H (5.63), N (9.27); found: C (47.72), H (5.45), N (9.19).

2,2-Dimethylbenzo(1,3)dioxol-4-boronic acid, 3. The acetonide of the catechol was lithiated as described in the literature.[7] A solution of 18 mL *n*-butyl lithium (1.6 M in hexane) was added under argon to a solution of 4.0 g (25 mmol) protected catechol and 3.4 g (29 mmol) of tetramethylethylenediamine in 80 mL of hexane at 0 °C. After 6 h at 0 °C, the solution was transferred *via* cannula into 80 mL of THF containing 6.0 mL (53 mmol) of $B(OMe)_3$ at −78 °C. The resulting solution was stirred for an additional hour at room temperature and the solvent was removed. Extraction with a 0.5 M solution of NH_4Cl and Et_2O yielded the crude product, which was purified over a silica gel column (CH_2Cl_2) to yield 2.5 g (13 mmol, 52%). $R_f = 0.3$ in CH_2Cl_2 on SiO_2; mp: 89 °C; ^1H NMR in $CDCl_3$: 7.18 (t, $J = 4.4$ Hz, 1H), 6.82 (m, 2H) 1.70 (s 6H). Owing to the presence of acidic protons and an acid-sensitive protecting group (acetonide) in the same molecule, elemental analyses always resulted in a low carbon percentage because of partial deprotection upon standing. Boronic acid **3** is not used as the limiting reagent in the following reaction.

1-Butyl-3-(4-(2,2-dimethylbenzo(1,3)dioxol)benzyl)thiourea, 4. To a solution of the bromide **2** (1.0 g, 3.1 mmol) and $Pd(PPh_3)_4$ (0.12 g, 0.1 mmol) in 20 mL of degassed THF were added 3.5 mL of degassed aqueous Na_2CO_3 (2 M) and the boronic acid **3** (0.73 g, 3.7 mmol) dissolved in 4 mL of degassed EtOH. After refluxing overnight and evaporation of the solvents, the crude compound was dissolved in 150 mL of CH_2Cl_2 and washed three times with 2 M aqueous Na_2CO_3 and water. After removal the solvents, the crude mixture was purified by chromatography (SiO_2, CH_2Cl_2). Yield 1.05 g (2.7 mmol, 87%). $R_f = 0.3$ in CH_2Cl_2 on SiO_2; mp: 51 °C; ^1H NMR in $CDCl_3$: 7.68 (d, $J = 8.4$ Hz, 2H), 7.37 (d, $J = 8.4$ Hz, 2H), 6.97 (dd, $J = 7.7$ Hz, $J = 1.4$ Hz, 1H), 6.85 (t, $J = J = 7.7$ Hz, 1H), 6.71 (dd, $J = 7.7$ Hz, $J = 1.4$ Hz, 1H), 6.19 (s, 1H), 5.95 (s, 1H), 4.89 (s, 2H), 3.38 (m, 2H), 1.70 (s, 6H), 1.52 (m, 2H), 1.31 (m, 2H), 0.89 (t, $J = 7.3$ Hz, 3H). Analysis: Despite many efforts, all the analyses obtained for compound **4** gave carbon percentages lower than expected, which is in agreement with a slow spontaneous deprotection of the acetonide upon standing. However, compound **4** was generally used without further purification to give **5** as follows.

1-Butyl-3-(4-(2,3-dihydroxyphenyl)benzyl)thiourea, 5H$_2$. Protected catecholthiourea **4** (0.5 g, 1.3 mmol) was dissolved in 1 L of a 1 : 4 mixture of $H_2O : CH_3COOH$. After refluxing overnight, the solvents were removed and the crude product was purified by chromatography (SiO_2, CH_2Cl_2 : MeOH 90 : 10) to yield 0.42 g (1.2 mmol, 95%). $R_f = 0.4$ in CH_2Cl_2 : MeOH, 80 : 20 on SiO_2; mp: 95 °C; ^1H NMR in $CDCl_3$: 7.44 (d, $J = 8.1$ Hz, 2H), 7.32 (d, $J = 8.1$ Hz, 2H), 6.80 (m, 3H), 4.67 (m, 2H), 3.36 (m, 2H), 1.54 (m, 2H), 1.31 (m, 2H), 0.9 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR in MeOH-d_4: 147.80, 129.62, 119.01, 117.04, 115.71, 102.00, 86.018, 21.30, 9.97, 3.18; anal. calcd for $C_{18}H_{22}N_2O_2S \cdot 0.5H_2O$ (%): C (63.69), H (6.82), N (8.25); found: C (63.56), H (6.39), N (8.37). UV/VIS λ_{max}/nm (ε/M^{-1} cm^{-1}) in MeOH: 248 (21,200), 292 (4,300); FTIR ν/cm^{-1}: 1555 (νC=S).

2,2-Dimethylbenzo-(1,3)-dioxol-4-amido-*N*-4-benzo[18]-crown[6], 7. A solution of 0.5 g (1.28 mmol) of 4-aminobenzo-18-crown-6 sesquihydrate hydrochloride,[5] 0.65 g triethylamine (6.4 mmol) and 0.6 g (2.8 mmol) of the acetonide of 2,3-dihydroxybenzoyl chloride in 300 mL of THF were stirred overnight at room temperature. After evaporation of the solvent, the residue was dissolved in 200 mL of CH_2Cl_2 and washed three times with 200 mL water to yield 0.65 g of a brown oil (1.28 mmol, 100%), which was used without further purification. ^1H NMR in $CDCl_3$: 8.62 (s, 1H), 7.55 (dd, $J = 7.4$ Hz, $J = 2.0$ Hz, 1H), 7.51 (d, $J = 2.0$ Hz, 1H), 6.90 (m, 4H), 4.3–3.6 (3 m, 20H), 1.77 (s, 6H).

(2,3-Dihydroxo)-*N*-(4-benzo[18]crown[6])benzamide, 8H$_2$. To a solution of protected catechol **7** (0.5 g, 0.99 mmol) in 60 mL water were added 240 mL of a 1 : 4 mixture of H_2O : acetic acid. After refluxing overnight, the solvents were removed and the crude product was purified by chromatography (SiO_2, CH_2Cl_2 : MeOH 90 : 10) to yield 0.46 g of a brown solid (0.99 mmol, 100%). $R_f = 0.4$ in CH_2Cl_2 : MeOH, 80 : 20 on SiO_2; mp: 91 °C; ^1H NMR in MeOH-d_4: 7.45 (m, 2H), 7.15 (d, $J = 7.9$ Hz, 1H), 6.96 (m, 2H), 6.75 (dd, $J = 7.9$ Hz, $J = 8.0$ Hz, 1H), 4.3–3.6 (3 m, 20H); ^{13}C NMR in MeOH-d_4: 148.55, 119.73, 117.89, 115.20, 112.32, 107.54, 97.32, 71.05, 70.89, 70.82, 70.08, 70.02, 68.17; anal. calcd for $C_{23}H_{29}NO_9 \cdot H_2O$ (%): C (57.37), H (6.48), N (2.90); found: C (57.46), H (6.31), N (2.73); UV/VIS λ_{max}/nm (ε/M^{-1} cm^{-1}) in MeOH: 290 (11,300); FTIR ν/cm^{-1}: 1637 (ν C=O), 1517 (δ N—H), 1227 and 1255 (ν C—O—C).

The same procedure was followed for the syntheses of the complexes. The purification methods were selected depending on their respective solubility properties. A solution of the half receptor **5H$_2$** or **8H$_2$** (0.3 mmol) in 100 mL of EtOH containing $N(Bu^n)_4OH$ (0.65 mmol) was added dropwise, *via* cannula transfer, to 300 mL of an ethanolic solution of $MoO_2(acac)_2$ (0.051 g, 0.15 mmol). After two hours at room temperature, the solvents were removed under vacuum. The crude mixtures were treated as follows.

[*cis*-bis(5)MoO$_2$](NBu$_4$)$_2$, 6. The crude complex mixture was taken up in CH_2Cl_2 (200 mL), washed twice with water and the solvent removed. Filtration over sephadex (LH-20) in MeOH and evaporation of the solvent afforded the product as an orange solid (95%). mp: 89-91 °C; ^1H NMR in $CDCl_3$: 7.86 (d, 8.0 Hz, 4H), 7.11 (d, 8.0 Hz, 4H), 6.60 (m, 2H), 6.33 (m, 4H), 4.67 (m, 4H), 3.45 (m, 4H), 2.85 (m, 16H), 1.55 (m, 16H), 1.29 (m, 20H), 1.23 (m, 16H), 0.85 (m, 30H); UV/VIS λ_{max}/nm (ε/$M^{-1}cm^{-1}$) in CH_3CN: 248 (42,000), 340 (8,000), 400 (5,700) ; FTIR ν/cm^{-1}: 1559 (ν C=S), 889 and 858 (*cis* ν Mo=O); negative FAB-MS: *m*/*z* calc for $[M^{2-} + H - 2(NBu_4{}^+)]^- = C_{36}H_{41}O_6S_2N_4Mo^-$: 786.1, measured 786.3 (100%); anal. calcd for $C_{68}H_{112}N_6O_6S_2Mo \cdot 2H_2O$ (%): C (62.57), H (8.89), N (6.44); found: C (62.48), H (8.96), N (6.41).

[*cis*-bis(8)MoO$_2$](NBu$_4$)$_2$, 9. The crude mixture was taken up in CH_2Cl_2 (200 mL) and washed twice with water before the solvent were removed. Filtration over sephadex (LH-20) in MeOH and evaporation of the solvent afforded the product as an orange glue (95%). Trituration with hexane before drying under vacuum afforded easier to handle samples. ^1H NMR in $CDCl_3$: 7.19 (dd, $J = 8.1$ Hz, $J = 1.4$ Hz, 2H), 7.14 (s, 2H), 6.73 (d, $J = 7.3$ Hz, 2H), 6.59 (m, 6H), 6.37 (dd, $J = 8.1$ Hz, $J = 7.3$ Hz, 2H), 4.1–3.6 (m, 20H), 3.08 (m, 16H), 1.47 (m, 16H), 1.32 (m, 16H), 0.90 (m, 24H); UV/VIS λ_{max}/nm (ε/M^{-1} cm^{-1}) in CH_2Cl_2: 276 (31,900), 338 (7,500), 416 (2,400); FTIR ν in cm^{-1}: 908 and 880 (*cis* ν Mo=O); negative FAB MS: *m*/*z* calcd for $[M^{2-} + H^+ - (NBu_4)]^- = C_{62}H_{91}N_3O_{20}Mo^-$ and $[M^{2-} + H^+\text{-}2(NBu_4)]^- = C_{46}H_{55}N_2O_{20}Mo^-$: 1294.3 and 1051.7, measured: 1294.5 (25%) and 1052.2 (51%); anal. calcd for $C_{78}H_{126}N_4O_{20}Mo \cdot 2C_6H_{14}$ (%): C (63.26), H (9.08), found: C (63.25), H (9.40).

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Received in Montpellier, France, 26th August 1997; *revised m/s received* 16*th February* 1998; *Paper* 7/09267I