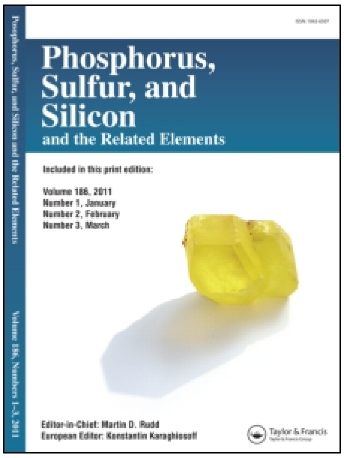

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Synthesis and Characterization of Aminophosphines, Bis(amino)phosphine Derivatives, and Their Molybdenum(0) Complexes

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Synthesis and Characterization of Aminophosphines, Bis(amino)phosphine Derivatives, and Their Molybdenum(0) Complexes

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*Functionalized bis(amino)phosphines of the type $PhP(NHR)_2$ (**1a–c**) and aminophosphines of the type Ph_2PNHR (**2a–c**) have been synthesized by treating $PhPCl_2$ or Ph_2PCl with corresponding primary amines of H_2N-R where R = -CH_2SO_3H, -$C_6H_4SO_3H$, and benzo-15-crown-5. The molybdenum(0) complex of the aminophosphine (**3**) has been obtained by reacting* cis-*[$Mo(CO)_4$(bipy)] with aminophosphine (**2c**). The synthesized aminophosphines, bis(amino)phosphines, and the molybdenum(0) complex have been characterized by IR, ^1H NMR, ^{31}P NMR, and MS spectroscopic techniques and by elemental analysis.*

Keywords Aminophosphine; bis(amino)phosphines; crown ethers; molybdenum(0) complexes

INTRODUCTION

Phosphine ligands have many important applications in organometallic chemistry and catalysis.[1,2] It is not surprising that there continues to be considerable interest in synthesis of new phosphines that have specific and well-characterized steric, electronic, and solubility properties.[3] Aminophosphines of the type $R_2PNR^1R^2$ have been relatively neglected as ligands, despite a number of potentially attractive features. The mild conditions required for formation of P–N bond allow facile incorporation of additional functionalities, and problems caused

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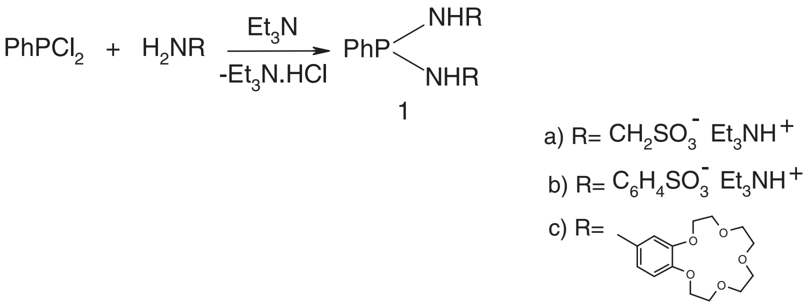
by the sensitivity of this bond to hydrolysis are often eliminated upon coordination.[4] The chemistry of aminophosphines containing direct P–N bonds is one of the most challenging areas in main group chemistry.[5] The coordination and organometallic chemistry of phosphorus bearing ligands possessing one (or more) P–N bond(s) have received some attention especially of late.[4,6–11] Interest in phosphines with P–N bonds arises from the different electronic properties transferred by the nitrogen center to the phosphorus center(s).[12] P–N bond formation as a method for ligand construction has become increasingly popular in recent years.[13] Potentially this ligand family is extremely attractive, since preparative routes enable access to various structural modifications via simple P–N bond formation.[9] Since both steric and electronic effects exerted by a functional group on the amine play a significant role on the outcome of the reaction,[12] aminophosphines possessing P–N bonds have attracted considerable interest in recent years because of their versatile coordination chemistry. Although they posses two potential donor atoms, their coordination compounds involve almost exclusively the metal–phosphorus bond.[14] Many aminophosphine ligands and their complexes have been investigated in a number of catalytic processes.[5,9,15–17] Some aminophosphines and derivatives have also found application as anticancer drugs, herbicides, and antimicrobial agents, as well as neuroactive agents.[5]

In recent years the synthesis and coordination chemistry of phosphorus(III) ligands containing P–N linkages, generally derived by the condensation of chlorophosphines with primary amines in the presence of a tertiary amine base, has received widespread attention.[10] In the present article, we report the synthesis and metal complex formation of new aminophosphine ligands. Ligands **1a–c** and **2a–c** can be prepared from the corresponding commercially available amines and dichlorophenylphosphine or chlorodiphenylphosphine according to the literature.[9,18,19] The synthesized aminophosphines, bis(amino)phosphines, and the molybdenum(0) complex have been characterized by IR, ^1H NMR, ^{31}P NMR, and MS spectroscopic techniques and by elemental analysis.

RESULTS AND DISCUSSION

Synthesis and Spectroscopic Properties of Bis(amino)phosphines

Earlier works had shown that primary amines react with alkyl- or aryldichlorophosphines ($RPCl_2$) in the presence of an HCl scavenger, either excess primary amines or added tertiary amine, to form bis(amino)phosphines.[19] Bis(amino)phosphines (**1a–c**) were prepared from dichlorophenylphosphine and primary amines (aminomethanesulfonic acid, sulfanilic acid, and 4-aminobenzo-15-crown-5) in the presence of triethylamine as is shown in Scheme 1.



SCHEME 1 Synthesis of bis(amino)phosphine ligands.

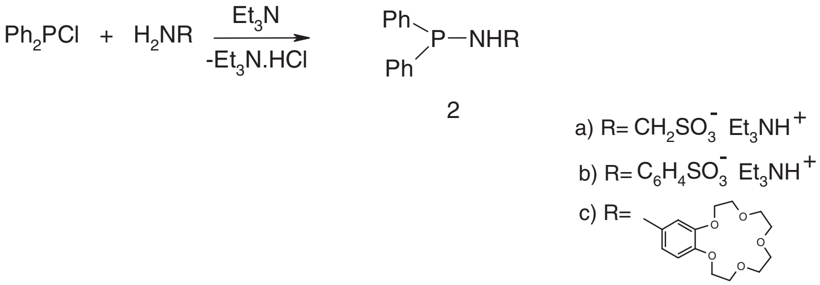
Compounds (**1a–c**) were characterized by ^{31}P-{^{1}H}, ^{1}H-NMR, and IR spectroscopic techniques and by elemental analysis. The ^{31}P-{^{1}H} NMR spectra of the bis(amino)phosphines show singlets at 21.3 ppm (for **1a**), 18.2 ppm (for **1b**), and 18.7 ppm (for **1c**). No $^{2}J_{PH}$ coupling is observed in the ^{31}P NMR spectra. The chemical shifts in the ^{31}P-{^{1}H} NMR spectra are in accordance with the electronic properties of the substituents on nitrogen and phosphorus. A similar chemical shift is observed for bis(amino)phosphines (**1a–c**), suggesting that the difference in δ(P) is primarily due to the presence of an alkyl group rather than a hydrogen atom on the bis(amino)phosphine nitrogen atom.[4] The electronic effect of the quaternary ammonium functionality on the ^{31}P chemical shift is negligible. This is not unexpected, since electronic effects generally contribute only slightly to the chemical shifts in similar compounds, and the quarternized nitrogen is well removed from the phosphorus atom.[20] In the ^{31}P NMR spectra, no peak is observed for unreacted $PPhCl_2$ compound around 160.2 ppm.[21]

In the ^{1}H NMR spectra, the NH signals are observed as singlet at 2.6 ppm for **1a**, as broad at 5.3 ppm for **1b**, and as singlet at 2.2 ppm for **1c**. ^{1}H NMR spectra shows that **1a** and **1b** ligands are in SO_3Et_3NH form. The signal at 12 ppm is assigned to the NH proton of $Et_3\underline{NH}^+$.[22] Methylenic (-CH_2-) protons of the triethylamine counterion of **1a** and **1b** are observed 3.6 and 3.1 ppm, respectively, where methyl (CH_3-) protons are at 1.4 ppm.[23] The ^{1}H NMR of **1a** shows a doublet for the $PNH\underline{CH_2}$ protons at δ 1.9 (J_{PH} = 29 Hz), which is consistent with reported studies.[9] In the ^{1}H NMR spectra of **1c**, while the resonances due to aromatic protons appear in the range δ 6.6–7.8, NH signals were observed as singlet at 2.2 ppm. In addition, the resonances due to O-CH_2 protons of **1c** appear in the region δ 3.0–4.1. The ^{1}H NMR spectra are consistent with the structure proposed.

In the IR spectra (KBr) of the ligands, the ν(NH) band is observed at 3166 cm^{-1} (**1a**), 3234 cm^{-1} (**1b**), and 3347 cm^{-1} (**1c**).[24,25] The ν(PN) vibration is tentatively assigned to a very strong absorption at 856 cm^{-1} for **1a–b** and 835 cm^{-1} for **1c** respectively.[18] The ν(PPh) bands are observed in 1442 cm^{-1}. The IR spectrum of **1a–b** shows νSO_3 bands at 1186 and 1045 cm^{-1}for **1a** and 1178 and 1043 for **1b**. The IR spectrum of **1c** shows $\nu_{C-Oalifatic}$ and $\nu_{C-Oaromatic}$ bands, respectively, at 1143 and 1253 cm^{-1}.

Synthesis and Spectroscopic Properties of Aminophosphines

Aminophosphines (**2a–c**) were prepared from chlorodiphenylphosphine and primary amines (aminomethanesulfonic acid, sulfanilic acid, and 4-amino-benzo-15-crown-5) in the presence of triethylamine as was shown in Scheme 2.



SCHEME 2 Synthesis of aminophosphine ligands.

Compounds (**2a–c**) were characterized by ^{31}P-{^{1}H}, ^{1}H-NMR, and IR spectroscopic techniques and by elemental analysis. In phosphorus chemistry, ^{31}P NMR spectroscopy has been widely used to monitor reactions, which allows the rapid identification of product based on characteristic signals in the spectrum. In general, diphenylphosphinoamines exhibit a singlet resonance typically around 64–70 ppm (67.7 ppm in $PhN(PPh_2)_2$ and 65.6 ppm in $C_6H_4(o\text{-}OCH_3)N(PPh_2)_2$]. Arylaminodiphenylphosphines also give rise to singlet resonances between 25 and 35 ppm (29.4 ppm in PhNH-PPh_2, 26.4 ppm in PyNH-PPh_2, 27.2 ppm in $C_6H_4(o\text{-}OCH_3)NH\text{-}PPh_2$).[12] A similar chemical shift is observed for aminophosphines, suggesting that the difference in δ(P) is primarily due to the presence of an alkyl group rather than a hydrogen atom on the aminophosphine nitrogen atom.[4] The ^{31}P-{^{1}H}

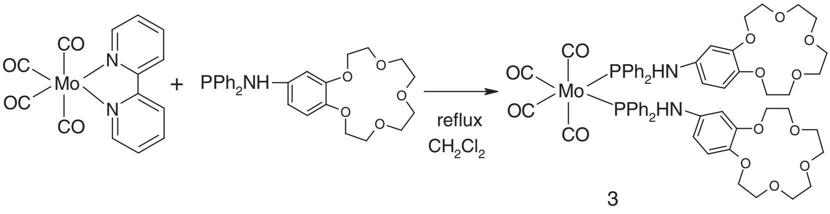
NMR spectra of the aminophosphines show singlets at 22.7 ppm (for **2a**), 22.5 ppm (for **2b**), and 22.6 ppm (for **2c**). No $^2J_{PH}$ coupling is observed in the ^{31}P NMR spectra. The ^{31}P NMR spectra are consistent with the structure proposed. The chemical shifts in the ^{31}P-^1H NMR spectra are in accordance with the electronic properties of the substituents on nitrogen and phosphorus. The electronic effect of the quaternary ammonium functionality on the ^{31}P chemical shift is negligible.[20] The absence of a signal at 81.5 ppm indicates that no unreacted PPh_2Cl remained.[21]

In the ^1H NMR spectra, the NH signals are observed as broad resonances at 5.4 ppm for **2a** and as a singlet at 1.7 ppm for **2b**. ^1H NMR spectra shows that **2a** and **2b** ligands are in the $-SO_3Et_3NH$ form. In the ^1H NMR of **2a–b**, there are signals at δ 10.8 and 10.9 for $Et_3\underline{NH}^+$.[22,26] Peaks at 2.9 ppm (quartet) and 1.0 ppm (quartet) for **2a** and 3.1 ppm (multiple), 1.4 ppm (triplet) for **2b** are due to the methylenic ($-CH_2-$) and methyl (CH_3-) proton of the triethylamine counterion.[23] In addition, in the ^1H NMR of **2a**, a $PNH\underline{CH}_2$ signal is observed at 2.9 ppm.

In the IR spectra (KBr) of the ligands, the ν(NH) band is observed at 3197 cm^{-1} (**2a**), 3230 cm $^{-1}$ (**2b**), and 3393 cm^{-1} (**2c**).[24,25] The ν(PN) vibration is tentatively assigned to a very strong absorption at 850 cm^{-1} for **2a**, 900 cm^{-1} for **2b**, and 835 cm^{-1} for **2c**.[24] The ν(PPh) bands are observed in 1442 cm^{-1} for **2a**, **2c** and 1438 cm^{-1} for **2b**. The IR spectrum of **2a–b** shows νSO_3 bands at 1187 and 1039 cm^{-1} for **2a** and 1182 and 1030 for **2b**. The IR spectrum of ligand **2c** shows $\nu_{C-Oaliphatic}$ and $\nu_{C-Oaromatic}$ bands, respectively, at 1132 and 1234 cm^{-1}.

Synthesis and Characterization of *cis*-[Mo(CO)$_4$(Ph$_2$PNH-benzo-15-crown-5)$_2$]

The aminophosphine ligand **2c** reacts readily with *cis*-[Mo(CO)$_4$(bipy)] to give *cis*- [Mo(CO)$_4$(PPh$_2$NH-benzo-15-crown-5)$_2$] (**3**) in high yield as shown in Scheme 3.



SCHEME 3 Synthesis of *cis*-[Mo(CO)$_4$(Ph$_2$PNH-benzo-15-crown-5)$_2$].

Molybdenum(0) complex (**3**) was characterized by microanalytical data, infrared, mass, and NMR spectroscopic data. In the ^{1}H NMR spectra of complex **3**, while the resonances due to aromatic protons appear in the range δ 6.4–8.3, NH signals were observed as singlet at 4.9 ppm. In addition, the resonances due to O-CH_2 protons of the complex appear in the region δ 3.3–4.3.[27,28] The ^{31}P-^{1}H NMR spectra of the complex shows singlet at 70.74 ppm, which is in accord with the data reported for $Mo(CO)_4P$ analogous complexes.[18,24] Ligands bearing both amine and tertiary phosphine donors can behave as monodentate ligand (via P or N) or bidentate ligand (via P and N).[29] The P–N bond in aminophosphines is essentially a single bond, so the lone pairs on nitrogen and phosphorus are available for donor bonding towards metal atoms. The phosphorus chemical shift for complexes indicates P–Mo interaction due to the low coordination shift value of complexes ($\Delta\delta$). In the ^{31}P-$\{^{1}H\}$ NMR spectra, the complex exhibits singlet, which shows the expected low-field shift relative to the uncoordinated ligand ($\Delta\delta =$ 48.1 ppm). The phosphorus chemical shifts at δ 70.74 ppm for the complex indicates P–Mo interaction. IR spectrum of this complex has bands at 3405, 1443, and 835 cm^{-1} due to NH, PPh, and PN vibrations, respectively. The IR spectrum of the complex shows $\nu_{C-Oaliphatic}$ and $\nu_{C-Oaromatic}$ bands, respectively, at 1137 and 1255 cm^{-1}. NH bands also do not show a significant shift with respect to that of the free ligand, suggesting that ligation of **2c** is through the phosphorus atom. Several of the absorption bands of phenylphosphines in infrared are very sensitive to coordination; significant shifts are observed. The strong C–H phenyl out-of-plane vibration at 750 cm^{-1} of the phenylphosphine group in the IR spectra of the ligand shifts significantly upwards in the molybdenum complex.[30] The shift of this complex is 8 cm^{-1}. The shift of the strong C-H phenyl out-of-plane vibration of phenylphosphine group of ligand **2c** in the molybdenum complex indicates that ligation of ligand **2c** is through phosphorus. The infrared spectra of the complex exhibits four intense ν(CO) absorptions, typically in the region 1771–2009, consistent with a cis tetracarbonylmolybdenum fragment.[9,24,31–34] The generation of $Mo(CO)_4L$ complexes may be used to as a rapid "spot test" for the donor properties of new ligands. This attribute has been recognized for many years, and an extensive literature exists for these complexes, allowing ready comparison with a variety of other phosphorus (III) ligands. The value ν_{CO} has been used to evaluate the ligand electronic properties, and it has been found that for π-acceptor ligands, ν_{CO} is at higher wave number than for σ-donor ligands. A shift to lower frequency indicates a stronger donation of electron density from ligand to metal to carbonyl ligand and thereby indicates a stronger σ-donor ability for the P–N ligands.[1] We also have also re-prepared Mo(CO)$_4$(Ph$_2$PNHPh)$_2$ and recorded its IR spectra to calibrate our values. It was found that in the molybdenum complex **3**, the CO stretching frequency (2009 cm^{-1}) is significantly lower than in the Mo(CO)$_4$(Ph$_2$PNHPh)$_2$ complex (2024 cm^{-1}). The distinct CO strectching frequences can be explained due to having a very electron-rich ligand. The new very electron-rich ligand prepared here should, given its ease of preparation, be a useful tool in organometallic chemistry and catalysis.

Elemental analysis data is in agreement with calculated values. FAB$^+$ mass spectrometry of the molybdenum complex (**3**) confirms the proposed identity of the complex (**3**) by showing the expected parent-ion peak. Electronic spectra of ligand **2c** and their molybdenum complex (**3**) were recorded in CHCl$_3$ solution. In addition to the absorption bands of the ligand, an absorption maximum is observed in the 547 nm for the metal complex, which may be assigned to a charge transfer transition.

The reactions of *cis*-[Mo(CO)$_4$(bipy)] with aminophosphines (**1a–b** and **2a–b**) were investigated, but in their ^{31}P-{^{1}H} NMR spectra, the other molybdenum(0) complexes do not show any significant differences between the coordinated and free ligand.

EXPERIMENTAL

Reactions were routinely carried out using Schlenk–line techniques under pure dry dinitrogen. Solvents were dried and distilled prior to use. Mo(CO)$_4$(bipy) was prepared by reacting Mo(CO)$_6$ with 2,2′ bipyridine in toluene and used in the synthesis of further molybdenum complexes. All other chemicals were reagent grade, available commercially and used without further purification. Melting points were determined on a Electrothermal A 9100 and are uncorrected. ^{31}P-{^{1}H} and ^{1}H NMR spectra were taken on a Bruker Avance DPX-400 spectrometer. Infrared spectra were recorded on a Jasco FTIR 300E spectrometer in KBr. FAB-MS spectra were measured on a VG-Zapspec MS. Elemental analyses were performed in a CHNS-932 (LECO). UV-Vis spectra were recorded on a Shimadzu 160-A spectrophotometer.

Preparation of PhP(NHCH$_2$SO$_3$Et$_3$NH)$_2$ (1a)

Triethylamine (2.60 mL, 18.6 mmol) and PhPCl$_2$ (0.61 mL, 4.5 mmol) were sequentially added with stirring to a solution of NH$_2$CH$_2$SO$_3$H (1.00 g, 9.0 mmol) in THF (20 mL). The reaction mixture was stirred for 3 h and then filtered to remove NEt$_3$HCl. The resulting solution was evaporated under reduced pressure, and the product was extracted with diethyl ether at –78°C. The resulting solution was evaporated under reduced pressure to give a colorless powder. Yield 2.05 g (88%). Mp: 98 °C. ^{1}H NMR (CDCl$_3$, DMSO): 12.0 (b, NEt$_3$H$^+$2H), 6.7–8.6 (m, Ph, 5H), 1.9 (d, PNCH$_2$,4H, J$_{PH}$ =29), 2.6 (s, NH, 2H), 3.6 (m, NH($\underline{CH_2}$CH$_3$)$_3^+$, 12H), 1.4 (m, NH(CH$_2$$\underline{CH_3}$)$_3^+$, 18H). ^{31}P-{^{1}H} NMR (CDCl$_3$): 21.3 (s). IR (KBr, cm^{-1}): 856 (PN), 3166 (NH), 1442 (PPh), 3054 (CH$_{aromatic}$), 2975 (CH$_{alifatic}$), 1186 and 1045 (SO$_3$). Elemental Analysis: $C_{20}H_{43}PN_4O_6S_2$ (530.64 g) Found (Required): C, 45.53 (45.27); H, 8.18 (8.17); N, 10.44 (10.56) ; S, 11.82 (12.08).

Preparation of PhP(NHC$_6$H$_4$SO$_3$Et$_3$NH)$_2$ (1b)

A similar procedure to that described in 1a was used. Yield 1.90 g (50%). Mp: 118°C. ^{1}H NMR (CDCl$_3$): 12.0 (b, NEt$_3$H$^+$, 2H), 6.9–8.2 (m, Ph, 13H), 5.3 (bs, NH, 2H), 3.1 (q, NH($\underline{CH_2}$CH$_3$)$_3^+$,12 H), 1.4 (t, NH(CH$_2$$\underline{CH_3}$)$_3^+$, 18H). ^{31}P-{^{1}H} NMR (CDCl$_3$): 18.22 (s). IR (KBr, cm^{-1}): 856 (PN), 3234 (NH), 1442 (PPh), 3050 (CH$_{aromatic}$), 1178 and 1043 (SO$_3$). Elemental Analysis: $C_{30}H_{47}PN_4O_6S_2$ (654.77 g) Found (Required): C, 54.45 (55.03); H, 6.98 (7.23); N, 8.47 (8.56) ; S, 9.38 (9.79).

Preparation of PhP(NH-benzocrown-5)$_2$ (1c)

A similar procedure to that described in 1a was used. Yield 0.20 g (87%). Mp: 135°C. ^{1}H NMR (CDCl$_3$, ppm): 6.6–7.8 (m. Ph, 11H), 2.2 (s, NH, 2H), 3.0–4.1 (m, O-CH$_2$, 32 H). ^{31}P-^{1}H NMR (CDCl$_3$, ppm): 18.74 (s); IR (KBr, cm^{-1}): 835 (PN), 3347 (NH), 1442 (PPh), 3053 (CH$_{aromatic}$), 2937 (CH$_{alifatic}$), 1143 (COC$_{alifatic}$) and 1253 (COC$_{aromatic}$). Elemental Analysis: $C_{34}H_{45}PN_2O_{10}$ (672.63 g) Found (Required): C, 60.42 (60.71); H, 6.52 (6.74); N, 4.22 (4.16).

Preparation of PPh$_2$NHCH$_2$SO$_3$Et$_3$NH (2a)

Triethylamine (2.50 mL, 18.0 mmol) and Ph$_2$PCl (1.65 mL, 9.0 mmol) were sequentially added with stirring to a solution of NH$_2$CH$_2$SO$_3$H (1.00 g, 9.0 mmol) in THF (20 mL). The reaction mixture was stirred for 3 h and then filtered to remove NEt$_3$HCl. The resulting solution was evaporated under reduced pressure, and the product was extracted with diethyl ether at –78°C. The resulting solution was evaporated under reduced pressure to give a colorless powder. Yield 2.50 g (70%). Mp: 147°C. ^{1}H NMR (CDCl$_3$, ppm): 10.8 (b, NEt$_3$H$^+$, 1H), 6.9–8.0. (m, PPh, 10H), 5.4 (b, NH, 1H), 2.9 (q, NH($\underline{CH_2}$CH$_3$)$_3^+$, PNCH$_2$, 8H), 1.0 (q, NH(CH$_2$$\underline{CH_3}$)$_3^+$, 9H). ^{31}P-{^{1}H} NMR (CDCl$_3$, ppm): 22.7 (s). IR

(KBr, cm^{-1}): 850 (PN), 3197 (NH), 2680 (NCH_2), 1442 (PPh), 3054 ($CH_{aromatic}$), 2973 ($CH_{alifatic}$), 1187 and 1039 (SO_3). Elemental Analysis: $C_{19}H_{29}PN_2O_3S$ (396.45 g) Found (Required): C, 57.43 (57.56); H, 7.25 (7.37); N, 7.26 (7.07) ; S, 7.98 (8.09).

Preparation of $PPh_2NHC_6H_4SO_3Et_3NH$ (2b)

A similar procedure to that described in **2a** was used. Yield 1.90 g (39%). Mp: 122°C. ^1H NMR (DMSO, ppm): 10.9 (b, NEt_3H^+, 1H), 6.6–8.0 (m, Ph, 14H), 1.7 (s, NH, 1H), 3.1 (m, $NH(\underline{CH_2}CH_3)_3^+$, 6H), 1.4 (t, $NH(CH_2\underline{CH_3})_3^+$, 9H). ^{31}P-{^1H} NMR ($CDCl_3$, ppm): 22.50 (s). IR (KBr, cm^{-1}): 900 (PN), 3230 (NH), 1438 (PPh), 3050 ($CH_{aromatic}$), 1182 and 1030 (SO_3). Elemental Analysis: $C_{24}H_{31}PN_2O_3S$ (458.51 g) Found (Required): C, 62.58 (62.86); H, 6.69 (6.81); N, 5.74 (6.12) ; S, 6.37 (6.99).

Preparation of Ph_2PNH-benzocrown-5 (2c)

A similar procedure to that described in **2a** was used. Yield 0.40 g (86%). ^{31}P-{^1H} NMR ($CDCl_3$, ppm): 22.60 (s); IR (KBr, cm^{-1}): 835 (PN), 3393 (NH), 1442 (PPh), 3067 ($CH_{aromatic}$), 2949 ($CH_{alifatic}$), 1132 ($COC_{alifatic}$) and 1234 ($COC_{aromatic}$). Elemental Analysis: $C_{26}H_{30}PNO_5$ (467.45 g) Found (Required): C, 66.65 (66.80); H, 6.16 (6.47); N, 3.35 (2.99).

Preparation of cis-[$Mo(CO)_4(Ph_2PNH\text{-benzocrown-5})_2$] (3)

Ligand (0.20 g, 0.43 mmol) and [$Mo(CO)_4$(bipy)] (0.08 g, 0.22 mmol) were refluxed in 20 mL CH_2Cl_2 for 5 h. The solution was concentrated in vacuo, and the purple product was precipitated with 30 mL diethylether. The purple residue was separated by filtration, washed with toluene (3 × 5 mL) and recrysallized from CH_2Cl_2-diethylether. Yield: 0.20 g (83%). Mp: 189–191 °C (decomp).^{1} H NMR ($CDCl_3$, ppm): 6.4–8.3 (m. Ph, 26H), 4.9 (s, NH, 2H), 3.3–4.3 (m, O-CH_2, 32 H). ^{31}P-{^1H} NMR ($CDCl_3$, ppm): 70.74. MS [m:z, %]: 955 [Mo (Ph_2PNH-benzocrown-5)(PhPNH-benzocrown-5)$^+$, 4), 763 [Mo(Ph_2PNH-benzocrown-5)($PhPNHC_6H_3$)$^+$, 4), 506 [$Mo(CO)_3(PPh_2NH)(PhPNH)^+$, 100], 490 [$Mo(CO)_3(PPh_2N)(PhP)^+$, 35], 467 ($Ph_2PNH$-benzocrown-5$^+$, 12), 313 [PNH-benzocrown-5$^+$, 7), 282 [NH-benzocrown-5$^+$, 7), 200 [PPh_2NH, 6] and fragmentation products thereof. IR (KBr, cm^{-1}): 835 (PN), 3405 (NH), 1443 (PPh), 3060 ($CH_{aromatic}$), 2933 ($CH_{alifatic}$), 1137 (COC_{al}), 1255 (COC_{ar}), 2009, 1913, 1820 and 1771 (CO). Elemental Analysis: $C_{56}H_{60}MoN_2O_{14}P_2$

(1142.98 g) Found (Required): C, 58.53 (58.84); H, 5.58 (5.31); N, 2.37 (2.45).

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