Synthesis, luminescence and ion-binding properties of palladium(II) complexes with 1,2-bis[di(benzo-15-crown-5)phosphino]ethane (dbcpe)

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A series of palladium(II) complexes with 1,2-bis[di(benzo-15-crown-5)phosphino]ethane ligand (dbcpe), [Pd(dbcpe)X2] (X = Cl 1, Br 2 and I 3), have been successfully synthesised and characterised. The X-ray crystal structure of dbcpe has also been determined. The cation-binding properties of the complexes have been studied and the stability constants with alkali metal cations determined. The crown-free analogue of dbcpe, 1,2-bis[3,4-dimethoxyphenyl]phosphino]ethane (ddmppe), and the related complexes have also been prepared and comparison studies have been made.

Introduction

Phosphines continue to be of considerable interest as ligands that are used in conjunction with transition metals for a wide variety of applications. In particular, diphosphine ligands have attracted much attention as a result of their tunable bite angles that may find specific functions in catalytic applications. In recent years, complexes containing monophosphine-crown ligands have been extensively investigated due to their specific and characteristic electronic and steric properties, enhanced solubility as well as their versatile potential application. Despite numerous studies on palladium(II) phosphine systems, most of the studies are directed towards their applications in organic transformation reactions and catalysis, with the utilization of such systems for applications in molecular recognition and chemosensing being very rare; in particular, those related to the crown ether-containing palladium(II) systems and their ion-binding properties. The study of crown ethers and other related inclusion compounds in molecular recognition as well as the design of molecular sensors and probes have been of growing interest in the field of host–guest chemistry, and several review articles devoted to the chemistry of crown ethers and their analytical, chemical, and biological applications have been published. As an extension to our previous report on the novel trans-cis isomerization process of a series of palladium(II) complexes containing the monophosphine-crown ligands induced upon the binding of alkali metal ions, and to further explore the design of new potential catalysts and molecular-based probes and switches, attempts have been made to investigate the palladium(II) crown ether-containing diphosphine systems based on the well-known 1,2-bis(diphenylphosphino)ethane (dppe) and benzo-15-crown-5 (b15c5) skeletons. Herein are reported the synthesis and characterisation of a crown ether-containing dppe, 1,2-bis[di(benzo-15-crown-5)phosphino]ethane (dbcpe), and its crown-free analogue, 1,2-bis[3,4-dimethoxyphenyl]phosphino]ethane (ddmppe). The X-ray crystal structure of dbcpe has also been determined. These ligands have been successfully coordinated to the palladium(II) centres to give a series of dihalopalladium(II) complexes, [Pd(dbcpe)X2] (X = Cl 1, Br 2 and I 3) and [Pd(ddmppe)Cl] 4. Their photophysical and ion-binding properties have also been investigated.

Results and discussion

Synthesis

Dbcpe was synthesised by the reaction of the crown ether-containing aryllithium, generated in situ from 4'-bromobenzo-15-crown-5 and BuLi at low temperature, with 1,2-bis(dichlorophosphino)ethane in THF. The Li–Br exchange reaction was particularly facile and readily took place at temperature as low as −90 °C, and subsequent reaction with 1,2-bis(dichlorophosphino)ethane gave the crown ether modified diphosphines. Since the lithiated crown ethers are thermally unstable, it is necessary to keep the temperature below −90 °C during the addition of BuLi and Cl,PCH2CH2PCl2. Dichloro- and dibromopalladium(II) complexes, [Pd(dbcpe)Cl] 1 and [Pd(dbcpe)Br] 2, could be readily prepared by the reaction of [PdX2(PhCN)2] with dbcpe in benzene at 80 °C. The diiodo counterpart, [Pd(dbcpe)I] 3, was synthesised by the direct reaction of the dbcpe ligand with PdI2 in benzonitrile, via the in situ formation of [PdI2(PhCN)2].

Structure

The crystal structure of dbcpe with the atomic numbering is depicted in Fig. 1. The dbcpe molecule adopts a structure similar to
that of dppe.\(^{17}\) Selected bond distances and angles are summarised in Table 1. Most of the bond distances and angles are unremarkable and are almost identical within experimental error to those of dppe.\(^{17}\) As shown in Fig. 1, a crystallographic centre of symmetry is present at the C(1)−C(1′) bond. The two benzo-15-crown moieties attached to the same phosphorus atom are pointing in opposite directions due to their steric bulkiness, while the two benzo-15-crown moieties, which are on the same side and attached to adjacent phosphorus atoms, are facing each other to form an almost parallel sandwich structure. The “P−C−C−P” backbone lies on a common plane and adopts an anti-conformation.

Electronic absorption and emission properties

All the complexes show low-energy absorption bands at ca. 310–400 nm and higher energy bands at ca. 240–290 nm in acetonitrile. The high energy absorption bands are assigned as intraligand (IL) transitions of complexes 1–3 based on their similarities to that of the free ligand dbcpe (250 and 286 nm in MeCN). The photophysical data for complexes 1–3 are summarised in Table 2. In view of the fact that the energy of the low-energy absorption band in acetonitrile at 298 K follows the order Cl (344 nm) > Br (354 nm) > I (396 nm), which is in line with the assignment of the HOMO having predominant halo ligand character. With reference to previous spectroscopic work on a series of cis- and trans-[M(PR\(_3\))\(_2\)(X)(Y)] (M = Pd, Pt),\(^{18–20}\) [Ni(PMe\(_3\))\(_2\)X\(_2\)],\(^{21}\) [Pd\(_2\)(P\(_3\)P\(_2\))X\(_2\)]\(^2\) and the close analogy of palladium(t) compounds with the platinum analogues and the nickel(t) congeners, the low energy absorption band at ca. 350–400 nm is tentatively assigned as a ligand-to-metal charge transfer [LMCT, \(p\rightarrow r\)] emission is attributed to be originated from the low-energy ligand field d–d states.\(^{23}\) This has further been supported by the fact that there were only minor shifts in the emission maxima upon varying the halo ligands, where a much more significant shift would have been expected for an assignment of a LMCT \([p\rightarrow r] \rightarrow 4d(Pd)]\) transition.

The luminescence properties of the crown ether-containing dihalopalladium(t) diphosphine complexes have also been investigated. Complexes 1–3 were found to exhibit orange–red luminescence upon photo-excitation both in the solid state and in butyronitrile glass at 77 K, in contrast to their non-emissive behaviour at room temperature. Like many other square-planar mononuclear palladium(t) and platinum(t) complexes that do not contain low-lying ligand-centred acceptor orbitals, such an emission is attributed to be originated from the low-energy ligand field d–d states.\(^{23}\) This has further been supported by the fact that there were only minor shifts in the emission maxima upon varying the halo ligands, where a much more significant shift would have been expected for an assignment of a LMCT \([p\rightarrow r] \rightarrow 4d(Pd)]\) origin.

Cation-binding studies

The addition of alkali metal ions to a solution of 1 in MeCN resulted in changes in the UV/Vis spectrum with well-defined isosbestic points (Fig. 2). Similar spectral changes were not observed in a control experiment using the crown-free analogue, [Pd(ddmppe)Cl],\(^4\), indicating that these changes could be ascribed...
to the binding of the cations to the polyether cavity. The inserts in Fig. 2 show the titration curves of 1 with NaClO4 and KClO4 together with their theoretical fits to the equation for the formation of 1 : 1 adduct. Stoichiometry studies indicate that 1 forms 1 : 1 complexes with both Na+ and K+ ions under the conditions studied. For complexes 2 and 3, the binding of both the Na+ and K+ ions also gave a perfect fit to the equation in acetonitrile based on a model of 1 : 1 stoichiometry with different logK values (Table 3), which indicated that the spectral changes of complexes 1–3 in acetonitrile solution (0.1 mol dm−3 Bu4NPF6) upon addition of Na+ and K+ ions were mainly due to the complexation of Na+ or K+ ion to the complexes in a 1 : 1 ratio. The binding constants of complexes 1–3 for various ions in acetonitrile are of the order: K+ ≥ Na+. In view of the anomalous trend in the binding of Na+ and K+ to benzo-15-crown-5, a proposed mechanism involving the binding of K+ ion by the two benzo-15-crown-5 moieties in a tweezer-type of binding mode is suggested.

The ion-binding studies have further been confirmed by positive ESI-MS. 1 : 1 adducts of the ion-bound species were observed as the predominant species in acetonitrile solutions of complexes 1–3 with the respective NaClO4 and KClO4. In addition, it is noteworthy to mention that the ion-bound species with high complexation stoichiometries could also be observed in the respective ESI mass spectra at higher metal ion concentrations but of much lower intensities. Similar to the absorption studies, control experiments with the crown-free analogue did not show the presence of such ion-bound species upon the addition of metal ions, providing further supporting evidence for the binding of cations to the crown ether moieties. The preferential 1 : 1 binding may be a result of the electrostatic effects that hinder further complexation of the metal ions.

Conclusion

A diphosphine ligand functionalized with four crown ether units has been successfully synthesized and structurally characterised.

Table 3 Binding constants of complexes 1–3 for Na+ and K+ metal cations in MeCN (0.1 mol dm−3 Bu4NPF6) at 298 K

<table>
<thead>
<tr>
<th>Complex</th>
<th>LogK Na+</th>
<th>LogK K+</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>3.78</td>
<td>4.10</td>
</tr>
<tr>
<td>2</td>
<td>3.70</td>
<td>3.94</td>
</tr>
<tr>
<td>3</td>
<td>3.42</td>
<td>3.90</td>
</tr>
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Incorporation of this tetracrown ether diphosphine into the PdX2 (X = Cl, Br, I) units results in a series of dihalopalladium(II) diphosphine complexes. The binding abilities of these complexes toward Na+ and K+ metal ions have also been studied by electronic absorption spectroscopy and ESI mass spectrometry, demonstrating the slight preferential binding of K+ ions over Na+ ions. Control experiments with the crown-free analogue did not give any spectral changes upon addition of alkali metal ions. It is envisaged that such a class of complexes could serve as model systems and be exploited for the design and development of new molecular-based ion probes and switches, as well as new catalysts.

Experimental

n-Butyllithium (2.5 M in hexane) was obtained from Aldrich Chemical Co. 1,2-Bis(dichlorophosphino)ethane, palladium(II) chloride, palladium(II) bromide and palladium(II) iodide were obtained from Strem Chemicals, Inc. 4′-Bromobenzo-15-crown-5 and [(PhCN)2PdCl2] were synthesized according to published procedures. [(PhCN)2PdBr2] was synthesized in a way similar to that reported for [(PhCN)2PdCl2]. Solvents were purified and distilled according to standard procedures before use. All other reagents were of analytical grade and were used as received.

Synthesis

All reactions have been carried out in anhydrous and anaerobic conditions using standard Schlenk technique in an inert atmosphere of nitrogen unless otherwise specified.

1,2-Bis(di(benzo-15-crown-5)phosphino)ethane, dbcpe

4′-Bromobenzo-15-crown-5 (3.0 g, 8.64 mmol) was dissolved in distilled THF (30 ml) and cooled in a methanol/liquid nitrogen slush-bath. n-Butyllithium (3.8 ml, 2.5 M, 9.5 mmol) in hexane was added via syringe over a period of 10 min to the cooled solution with stirring. After an additional 1 h at this temperature, freshly distilled 1,2-bis(dichlorophosphino)ethane (0.32 ml, 2 mmol) was added over a period of 20 min. The mixture was stirred for a further 16 h. Triethylamine (1 ml) and aqueous ammonium chloride (5 ml, 20%) were subsequently added. Evaporation of solvents under reduced pressure gave a yellow oil. This was then dissolved in dichloromethane (100 ml) and washed with distilled water (50 ml). The organic phase was collected and dried over anhydrous magnesium sulfate. The solvent was removed, and the yellow residue was subsequently purified by column chromatography on
alumina using dichloromethane as the eluent. Slow evaporation of the solvent yielded dbcep as a white solid. Yield: 0.42 g, 18%. 1H NMR (500 MHz, CDCl3, 298 K, relative to Me2Si): δ 1.96–1.97 (t, 4H, J = 3.8 Hz, –CH2CH2–), 3.74–3.75 (m, 32H, –OCH3), 3.85–3.91 (m, 16H, –OCH2–), 4.00–4.03 (m, 8H, –OCH2–), 4.12–4.13 (m, 8H, –OCH2–). δ 6.79–6.89 (m, 12H, –C6H3–). 31P NMR (202 MHz, CDCl3, 298 K, relative to 85% H3PO4): δ −11.51 (s). 13C NMR (125 MHz, CDCl3, 298 K, relative to Me2Si): δ 149.20, 126.26, 124.58, 117.79, 115.62, 113.59, 71.10, 70.43, 69.43, 69.36, 68.75. Positive FAB-MS: m/z 1158 [M]+. Elemental analyses, Found (%): C 60.10, H 6.96.

1,2-Bis[bis(3,4-dimethoxyphenyl)phosphino]ethane, ddmpe

The procedure was similar to that described for the preparation of dbcep except 4-bromoveratrole was used in place of 4-bromobenzo-15-crown-5. Yield: 48 mg, 73%. 1H NMR (500 MHz, CDCl3, 298 K, relative to Me2Si): δ 2.17–2.23 (t, 4H, J = 6.4 Hz, –CH2CH2–), 3.72–3.79 (m, 32H, –OCH2–), 3.85–3.88 (m, 8H, –OCH2–), 3.91–3.93 (m, 8H, –OCH2–), 4.08–4.10 (m, 8H, –OCH2–), 4.16–4.17 (m, 8H, –OCH2–), 6.88–6.89 (m, 4H, –C6H3–), 7.21–7.23 (m, 4H, –C6H3–), 7.38–7.40 (m, 4H, –C6H3–). 31P NMR (202 MHz, CDCl3, 298 K, relative to 85% H3PO4): δ 63.0 (s). 13C NMR (125 MHz, CDCl3, 298 K, relative to Me2Si): δ 151.90, 148.54, 126.62, 121.22, 119.59, 112.77, 71.00, 70.22, 69.11, 68.58, 28.93. Positive FAB-MS: m/z 1520 [M]+, 1393 [M–I]+. Elemental analyses, Found (%): C 44.94, H 5.26; Caled for C58H80Cl2O20P2Pd: %: C 44.98, H 5.23.

[Pd(dbcep)Cl2]. 1

To a hot benzene solution (5 ml) of bis(benzonitrile)palladium(II) chloride. Yield: 96 mg, 78%. 1H NMR (500 MHz, CDCl3, 298 K, relative to Me2Si): δ 2.31–2.39 (t, 4H, J = 5.8 Hz, –CH2CH2–), 3.73–3.75 (m, 32H, –OCH3), 3.82–3.85 (m, 8H, –OCH2–), 3.92–3.93 (m, 8H, –OCH2–), 4.10–4.11 (m, 8H, –OCH2–), 4.12–4.14 (m, 8H, –OCH2–), 6.79–6.89 (m, 4H, –C6H3–), 7.21–7.25 (m, 4H, –C6H3–), 7.54–7.58 (m, 4H, –C6H3–). 31P NMR (202 MHz, CDCl3, 298 K, relative to 85% H3PO4): δ 63.7 (s). 13C NMR (125 MHz, CDCl3, 298 K, relative to Me2Si): δ 152.33, 149.29, 126.08, 119.85, 119.37, 113.03, 71.10, 70.41, 69.20, 68.72, 28.29. Positive FAB-MS: m/z 816 [M]+, 780 [M–Cl]+. Elemental analyses, Found (%): C 51.19, H 5.96; Caled for C58H80Cl2O20P2Pd: %: C 50.95, H 5.92.

[1H, 31P] NMR (500 MHz, CDCl3, 298 K, relative to Me2Si): δ 152.27, 149.50, 125.76, 119.74, 116.96, 111.11, 56.44, 56.03, 28.16. Positive FAB-MS: m/z 816 [M]+, 780 [M–Cl]+. Elemental analyses, Found (%): C 48.21, H 4.89; Caled for C58H80Cl2O20P2Pd·2CH2Cl2: %: C 48.27, H 4.81.

Physical measurements and instrumentation

UV/Vis spectra were obtained on a Hewlett-Packard 8452A diode array spectrophotometer, and steady-state excitation and emission spectra on a Spex Fluorolog 111 spectrofluorometer equipped with a Hamamatsu R-928 photomultiplier tube. Low-temperature (77 K) spectra were recorded by using an optical Dewar sample holder. 1H, 31P [H] and 13C [H] NMR spectra were recorded on a Bruker DRX-500 FT-NMR spectrometer (500 MHz for 1H, 202 MHz for 31P and 125 MHz for 13C) in CDCl3 at 298 K. Chemical shifts (in ppm) of 1H and 13C [H] NMR spectra were recorded relative to tetramethylsilane (Me4Si), while that of 31P [H] spectra were recorded relative to 85% H3PO4 (external). Positive-ion FAB mass spectra were recorded on a Finnigan MAT95 mass spectrometer. Elemental analyses of the new complexes were performed on a Carlo Erba 1106
elemental analyzer at the Institute of Chemistry, Chinese Academy of Sciences.

The electronic absorption spectral titration for binding constant determination was performed with a Hewlett-Packard 8452A diode array spectrophotometer at 25 °C, which was controlled by a Lauda RM6 compact low-temperature thermostat. Supporting electrolyte (0.1 mol dm$^{-3}$ Bu$_4$NBF$_4$) was added to maintain a constant ionic strength of the sample solution, which prevent any changes arising from a change in the ionic strength of the medium. Binding constants for 1:1 complexation were obtained by a nonlinear least-squares fit of the absorbance ($X$) vs. the concentration of the metal ion added ($c_M$) according to the equation:\textsuperscript{27}

$$X = X_0 + \frac{X_{\text{im}} - X_0}{2c_0} \left\{ c_0 + c_M + \frac{1}{K_M} \left[ \left( c_0 + c_M + \frac{1}{K_M} \right)^2 - 4c_0c_M \right] \right\}^{\frac{1}{2}}$$

where $X_0$ and $X$ are the absorbance of the complex at a selected wavelength in the absence and presence of the metal cation, respectively, $c_0$ is the total concentration of the complex, $c_M$ is the concentration of the metal cation, and $X_{\text{im}}$ is the limiting value of absorbance in the presence of excess metal ion. The close agreement of the experimental data to the theoretical fits is supportive of a 1:1 complexation stoichiometry.

**Crystal structure determination**

Single crystals of dcbpe were obtained by vapour diffusion of diethyl ether into a concentrated dichloromethane solution of the compound.

Crystal data for dcbpe. C$_6$H$_{16}$O$_3$P$_3$; $M = 1159.16$, monoclinic, space group $P2_1/c$, $a = 21.424(6)$ Å, $b = 22.577(1)$ Å, $c = 27.398(6)$ Å, $\beta = 104.48(3)^\circ$, $V = 2970.9(10)$ Å$^3$, $Z = 2$, $D_c = 1.296$ g cm$^{-3}$, $\mu$ (Mo-K$\alpha$) = 0.147 mm$^{-1}$, $F(000) = 1236$, $T = 301$ K. A crystal of dimensions 0.6 × 0.15 × 0.04 mm mounted in a glass capillary was used for data collection at 28 °C on a MAR diffractometer with a 300 mm image plate detector using graphite monochromatized Mo-K$\alpha$ radiation ($\lambda = 0.71073$ Å). Data collection was made with 2$^\circ$ oscillation step of $\theta$, 600 s exposure time and scanner distance at 120 mm. 100 images were collected. The images were interpreted and intensities integrated using program DENZO.\textsuperscript{28} The structure was solved by direct methods employing SIR-97 program\textsuperscript{29} on PC. Most atoms were located according to the direct methods and the successive least-squares Fourier cycles. The position of the other atoms was found by full-matrix least-squares refinements using program SHELXL-97\textsuperscript{30} on PC. Far-end atoms of the crown ether (relative to the P atom) are highly disordered and were treated with two sets of positions with equal occupancies. According to the SHELXL-97 program, all 2851 independent reflections ($R_{\text{int}} = 0.0420$, 1779 reflections larger than $4\sigma(F_i)$) from a total 9076 reflections were participated in the full-matrix least-squares refinement against $F^2$.

These reflections were in the range $-24 \leq h \leq 24$, $-4 \leq k \leq 5$, $-28 \leq l \leq 28$ with $2\theta_{\text{max}}$ equals to 47.70°. One crystallographic asymmetric unit consists of half of a formula unit. In the final stage least-squares refinement, disordered non-hydrogen atoms and O(3) were refined isotropically, and the other non-hydrogen atoms anisotropically. Partial H atoms were generated by program SHELXL-97. The position of H atoms were calculated based on riding mode with thermal parameters equal to 1.2 times that of the associated C atoms, and participated in the calculation of final R-indices.\textsuperscript{12} Convergence ([Mn(2)]max = 0.001, av. 0.001) for 344 variable parameters by full-matrix least-squares refinement on $F^2$ reaches to $R_I = 0.0751$ and $wR_F = 0.2090$ with a goodness-of-fit of 0.987, the parameters $a$ and $b$ for weighting scheme are 0.1648 and 0.0. The final difference Fourier map shows maximum rest peaks and holes of 0.368 and −0.320 e Å$^{-3}$ respectively.

CCDC reference number 253656.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b515024h

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