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Synthesis and structural characterization of 2,6-bis(1,2,4-diazaphospholyl-1-yl)pyridine zinc and 2,6-bis(1,2,4-diazaphospholyl-1-yl)pyrazine copper complexes

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ABSTRACT

Several novel derivatives of mono- and bis(1,2,4-diazaphosphol-1-yl)pyridine (or pyrazine) as well as the first 2,6-bis(1,2,4-diazaphosphol-1-yl)pyridine (bdppy) and 2,6-bis(1,2,4-diazaphosphol-1-yl)pyrazine (bdppz) metal complexes $[Zn(bdppy)_2]^{2+}\cdot 2ClO_4^-$ and $[(bdppz)Cu(NCMe)]^{2+}\cdot 2ClO_4^-$ were prepared and structurally characterized. The complex $[Zn(bdppy)_2]^{2+}\cdot 2ClO_4^-$ has a higher local concentration of low-valent phosphorus ($\sigma^2\lambda^3$) on the periphery of the molecule. All the compounds were characterized using ^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$ NMR and IR spectroscopy, and X-ray crystallography. The properties of the compound $[(bdppz)Cu(NCMe)]^{2+}\cdot 2ClO_4^-$ were studied using EPR spectroscopy and magnetic susceptibility measurements.

1. Introduction

Heterocycles containing a low-coordinated phosphorus center [1] have found widespread applications, ranging from ligands in metal complexes [2], devices in material science [3] to fundamental importance in theoretical and experimental research [4–7]. 1*H*-1,2,4-Diazaphospholes H[3,5-R_2dp], exhibiting electrochemical and coordinating properties endowed by the low-coordinated P($\sigma^2\lambda^3$) atom, represent a class of unique aromatic five-membered heterocyclic system [8,6] and may be viewed as hybrid molecules of the corresponding phospholes [9] and pyrazoles [10] (P-doping pyrazoles) [5], or as a 1*H*-1,2,4-trizole analogue in which the 4-nitrogen atom is replaced by a phosphorus atom ($\sigma^2\lambda^3$) [7]. Recent work has shown that deprotonated 1*H*-1,2,4-diazaphospholes ([3,5-R_2dp]$^-$) are highly versatile ligands for metals across the periodic table [11,12]. Due to their unique electronic requirements, the resulting complexes of 1,2,4-diazaphospholides have presented novel molecular structure characteristics with varied coordination of the types $\eta^1(N)$, $\eta^1(N1):\eta^1(N2)$ and $\eta^2(N1,N2)$ via the nitrogen atom(s), and of the η^5 type via the π-electron system [12]. Further studies have evidenced that several 1,2,4-diazaphospholide complexes are excellent catalysts for organic transformations [12d] and/or have an unusual redox activity toward a persistent dianionic radical species [12b].

It has been know that incorporation of different heterocycles into a ligand framework, with differing basicities and π-orbital energies, has a substantial effect on the electron richness, kinetic liability and luminescent properties of the resultant metal complexes. For example, derivatives of 2,6-bis(pyrazol-1-yl)pyridine (bppy) and 2,6-bis(pyrazol-1-ly)pyrazine (bppyz) [13a–c], versatile terpyridine analogues, arising from an incorporation of pyrazoles into pyridine and pyrazine, respectively, have been used as ligands and presented both advantages and disadvantages in this regard compared to the much more widely investigated terpyridines. In this content, a few transition metal bppy and bppyz complexes with high-spin molecular structures and a Jahn–Teller distortion, such as $[Fe(II)bppy_2]^{2+}$ and $[Cu(II)bppy_2]^{2+}$, have been investigated [13].

Impetus was provided by the recent results [12,14] that 1*H*-1,2,4-diazaphospholes may be incorporated with pyridine and pyrazine to give the derivatives 2,6-bis(1,2,4-diazaphosphol-1-yl) pyridine (bdppy) and 2,6-bis(1,2,4-diazaphosphol-1-yl)pyrazine (bdppz) that may be used as ligands for metal ions. Due to the extraordinary electronic structure and redox-active behavior of the 1,2,4-diazaphopholide moiety [12,14], the resultant bdppy (or bdppz) complexes may provide a unique molecular

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environment with a low-valent phosphorus ($\sigma^2\lambda^3$) on the molecule [1–5,12c]. Such complexes are expected to be fundamentally interesting as potential coordinated catalysis [12d] or with distinct magnetic and luminescent properties due to the doping low-valent phosphorus atom ($\sigma^2\lambda^3$) in the molecules [4]. Herein, we describe the synthetic approach to several new 6-mono- and 2,6-bis(1,2,4-diazaphosphol-1-yl)pyridines(pyrazines) ligands (**1**–**6**) as well as the first bdppy and bdppz metal complexes $[Zn(bdppy)_2]^{2+}\cdot 2ClO_4^-$ (**7**·2ClO_4^-) and [(bdppz)Cu(NCMe)]·2ClO_4 (**8**·2ClO_4^-).

2. Experimental section

2.1. General considerations and spectroscopic measurements

All manipulations were carried out in an argon atmosphere under anaerobic conditions using standard Schlenk-line, vacuum-line and glovebox techniques. The solvents were thoroughly dried, deoxygenated and distilled under an argon atmosphere prior to use. DMSO-d_6 was degassed and dried over molecular sieves for 24 h before use. $CDCl_3$ was dried with CaH_2 and distilled before use. The ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded with a Bruker DRX-600 spectrometer. IR measurements were carried out on a Nicolet 360 Fourier transform IR spectrometer from Nujol mulls prepared in a drybox. The UV–Vis spectrum was recorded with a CARY 300 Scan spectrophotometer (Varian). Melting points were measured in sealed argon-filled capillaries without temperature correction with a XT4-100A apparatus (Electronic and Optical Instruments, Beijing, China). Magnetic susceptibility measurements of **8** as a polycrystalline sample were carried out on a Quantum Design SQUID MPMSXL-7 magnetometer. The EPR was carried out on a Bruker A300 apparatus (Germany).

2.2. Synthesis of compounds ***1***–***8***

2.2.1. Synthesis of 2,6-di(1,2,4-diazaphosphol-1-yl)pyridine (***1***)

To a mixture of 1*H*-1,2,4-diazaphosphole (1.20 g, 13.9 mol) [8] and potassium (0.51 g, 13.0 mmol), dry 2-methoxyethyl ether (60 mL) was added. The suspension was stirred at 70 °C until the metal disappeared. After the solution was cooled down, 2,6-dibromopyridine (1.42 g, 5.90 mmol) was added in one portion and the solution was further stirred at 110 °C for 3 days. During this time, the reaction process was monitored by TLC (R_f = 0.78, using a mixture of PE and EtOAC (5:1) as the eluent). After the solvent was removed under reduced pressure, water was added. The resulting suspension was filtered. The collected solid was dissolved in a mixed solvent of CH_2Cl_2 and methanol. The solvent CH_2Cl_2 was slowly removed on a rotary evaporator to give **1** as white crystals (1.09 g, 75%). M.p.: 146–148 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 9.92, 9.85 (d, $^1J_{P\text{-}H}$ = 40.8 Hz, 2 H for dp ring), 8.94, 8.86 (d, $^1J_{P\text{-}H}$ = 46.8 Hz, 2 H for dp ring), 8.13–8.12 (d, 2 H for py ring), 8.09–8.06 (q, 1 H for py ring). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ (ppm): 165.42, 164.99 (d, *C*H for dp ring), 154.47, 154.11 (d, *C*H for dp ring), 149.80 (s, *C* for py ring), 142.38 (s, *C*H for py ring), 112.36 (s, *C*H for py ring). ^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$) δ (ppm): (d, $^1J_{P\text{-}H}$ = 48.6 Hz, 100.08; d, $^1J_{P\text{-}H}$ = 48.6 Hz, 99.91). ^{1}H NMR (600 MHz, DMSO-d_6) δ (ppm): 10.39, 10.33 (d, $^1J_{P\text{-}H}$ = 40.2 Hz, 2 H for dp ring), 9.12, 9.04 (d, $^1J_{P\text{-}H}$ = 46.8 Hz, 2 H for dp ring), 8.32–8.29 (t, 1 H for py ring), 8.11–8.10 (d, 2 H for py ring). ^{31}P{^{1}H} NMR (243 MHz, DMSO-d_6) δ (ppm): (d, $^1J_{P\text{-}H}$ = 46.2 Hz, 99.785; d, $^1J_{P\text{-}H}$ = 48.6 Hz, 99.62). IR (KBr, Nujol mull, cm^{-1}): 3104(w), 2921(vw), 1594(s), 1448(vs), 1365(vs), 1203(m), 1145(m), 1033(m), 923(s), 796(s), 721(s), 663(m). *Anal.* Calc. for $C_9H_7N_5P_2$: C, 43.74; H, 2.85; N, 28.34. Found: C, 43.77; H, 2.81; N, 28.44%.

2.2.2. Synthesis of 2,6-bis(3,5-diisopropyl-1,2,4-diazaphosphol-1-yl) pyridine (***2***)

Method A: To a mixture of 3,5-diisopropyl-1H-1,2,4-diazaphosphole (1.0 g, 5.88 mmol) [14] and potassium (0.226 g, 5.79 mmol), dry 2-methoxyethyl ether (60 mL) was added via a syringe. The suspension was stirred at 90 °C until the metal disappeared. After the solution was cooled down, 2,6-dibromopyridine was added (0.67 g, 2.81 mmol) in one portion and the resulting mixture was stirred at 160 °C for 4 days. During this time, the reaction process was monitored by TLC (R_f = 0.804, using a mixture of PE and EtOAC (5:1) as the eluent). After the solvent was removed under reduced pressure, the resulting residual was purified by chromatography on silica to give a white solid, which was further purified by recrystallization in petroleum ether and ethyl acetate (0.42 g, 35.8%). M.p.: 79–80 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.09–8.07 (t, 1 H on py ring), 7.73, 7.71 (d, $^1J_{H-H}$ = 12 Hz, 2 H on py ring), 3.80 (m, 2 H, *CH* for i-Pr), 3.23 (m, 2 H, *CH* for i-Pr), 1.40, 1.39 (d, $^1J_{H-H}$ = 6 Hz, 12 H, *CH*$_3$ for i-Pr), 1.29, 1.28 (d, $^1J_{H-H}$ = 6 Hz, 12 H, *CH*$_3$ for i-Pr). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ (ppm): 188.44, 188.07 (d, $^1J_{P-C}$ = 55.5 Hz, *C* on dp ring), 187.35, 186.95 (d, $^1J_{P-C}$ = 60 Hz, *C* on dp ring), 151.84 (s, *C* on py ring), 141.10 (s, *C*H on py ring), 119.48 (s, *C*H on py ring), 32.13, 32.30 (d, $^2J_{P-C}$ = 25.5 Hz, *C*H for i-Pr), 29.53, 29.43 (d, $^2J_{P-C}$ = 15 Hz, *C*H for i-Pr), 25.41, 25.33 (d, $^3J_{P-C}$ = 12 Hz, *C*H$_3$ for i-Pr), 24.53, 24.48 (d, $^3J_{P-C}$ = 7.5 Hz, *C*H$_3$ for i-Pr). ^{31}P{^{1}H} NMR(243 MHz, $CDCl_3$) δ (ppm): 85.51, 85.48, 85.45 (t, $^2J_{P-H}$ = 7.3 Hz). IR (KBr, cm^{-1}): 3070(w), 2964(s), 2919(m), 1589(s), 1450(vs), 1367(s), 1322(m), 1286(m), 1120(s), 1035(m), 813(m), 754(m), 732(m), 634(m). *Anal.* Calc. for $C_{21}H_{31}N_5P_2$: C, 60.71; H, 7.52; N, 16.86. Found: C, 60.48; H, 7.63; N, 16.73%.

Method B: To 1,3-bis(dimethylamino)-2-phosphaallyl-chloride [8] (2.121 g, 8.01 mmol) in chloroform (20 mL) 2,6-bis-hydrazinopyridine (0.374 g, 2.68 mmol) [15] was added at room temperature in chloroform (20 mL). After stirring for 10 h, the solution was refluxed for 3 days. The volatile components were removed under reduced pressure, and the resulting residue was extracted with ether (5 × 30 mL). The combined organic phase was washed with water (2 × 10 mL) to remove the remaining 2,6-bis-hydrazinopyridine and then dried over anhydrous magnesium sulfate. After the removal of ether on a rotary distillation apparatus, the resulting residue was recrystallized from *n*-hexane/ethyl acetate (1:1) (0.559 g, 50.2%).

2.2.3. Synthesis of 2,6-bis(3,5-diphenyl-1,2,4-diazaphosphol-1-yl-)pyridine (***3***)

Method A: To a mixture of 3,5-diphenyl-1*H*-1,2,4-diazaphosphole (1.39 g, 5.85 mmol) [8] and potassium (0.23 g, 5.76 mmol), anhydrous 2-methoxyethyl ether (60 mL) was added and then stirred at 100 °C until the metal disappeared. After the solution was cooled down, 2,6-dibromopyridine (0.66 g, 2.80 mmol) was added in one portion. The resulting mixture was stirred at 160 °C for 6 days and during this time, TLC was used to monitor the reaction process (R_f = 0.43, PE:EtOAC = (5:1) as the eluent). After the solvent was removed under reduced pressure, the residual was purified by chromatography on silica to provide a white solid (0.33 g, 21.2%). Crystals were obtained by diffusion of ether vapor into an EtOH solution of **3** as X-ray quality colorless prisms. M.p.: 186–188 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.962, 7.949 (d, $^3J_{P-H}$ = 7.8 Hz, 4 H, *CH* on Ph ring), 7.47–7.21 (m, 19 H, overlapped, *CH* on py and Ph rings). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ (ppm): 177.76, 177.38 (d, $^1J_{P-C}$ = 57 Hz, *C* on dp ring), 176.95, 176.63 (d, $^1J_{P-C}$ = 48 Hz, *C* on dp ring), 151.43 (s, *C* on py ring), 140.29 (s, *C*H on py ring), 129.09, 129.04 (d, $^2J_{P-C}$ = 7.5 Hz, *C*CH on Ph ring), 128.69, 128.60, 128.24 (m, *C*H on Ph ring), 126.61,126.55 (m, *C*H on Ph ring), 119.72 (s, *C*H on py ring). ^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$) δ (ppm): 98.90 (s). IR (KBr, cm^{-1}): 3058(m), 2964(m), 1590(s), 1494(w), 1454(vs), 1403(w), 1319(m), 1261(s), 1020(s), 914(vw), 863(vw),