Copper and Nickel Complexes of the New Phosphadithiamacrocycle 1-Phenyl-1-phospha-4,7-dithiacyclononane

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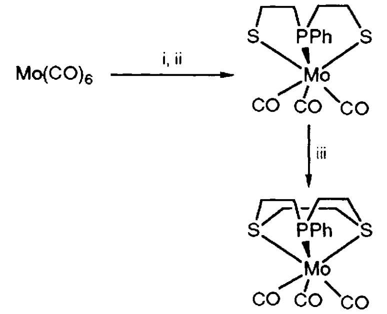
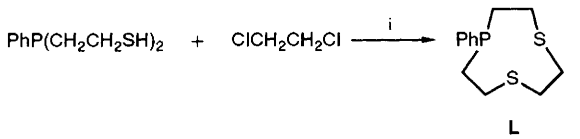
The novel cyclic ligand 1-phenyl-1-phospha-4-7-dithiacyclononane forms highly stable transition metal and d^{10} metal complexes; the X-ray structure of the tetrahedral copper(I) complex shows the ligand to be capable of both facial tridentate coordination and monodentate coordination, and the nickel(II) complex is easily and reversibly converted electrochemically to nickel(I) and nickel(III) complexes.

The trithiamacrocyclic ligand 1,4,7-trithiacyclononane (9S3) complexes metals with high thermodynamic and kinetic stability compared with other macrocyclic and non-cyclic thioether chelators. There is a consensus that this is due to the limited flexibility of the nine-membered ring and to the minimal conformational change associated with facial tridentate coordination. In addition to (and perhaps, in part, because of) this extra complex stability, many of the complexes exhibit interesting electronic and electrochemical properties.[1–3] These observations lead to speculation as to whether combination of the nine-membered ring conformational properties with the donor properties of alternative soft donor atoms might offer complexes with even greater stability and novelty. Elsewhere the chemistry of the ligand series $9N_xS_{3-x}$ has been explored,[4–7] most vigorously in the case of $x = 3$. We have now begun to investigate substitution of the thioether donors of 9S3 with phosphine donors, with the expectation of taking advantage of the stronger coordinating ability of phosphines



Scheme 1 *Reagents and conditions*: i, MeCN, reflux, 3 h; ii, $PhP(CH_2CH_2SH)_2$ (bistetramethylammonium salt), MeCN, 20 h, room temp.; iii, $ClCH_2CH_2Cl$, MeCN, 30 min, room temp.



L

Scheme 2 *Reagents and conditions*: i, dimethylformamide Cs_2CO_3, high dilution, 70 °C, 22 h

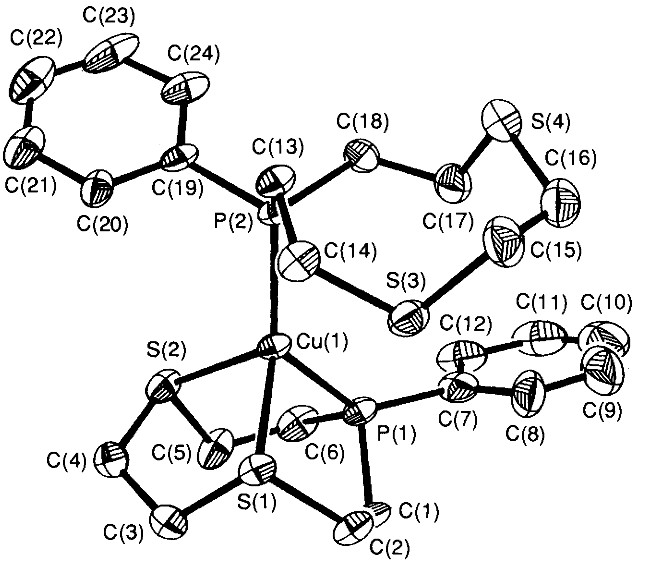


Fig. 1 Structure of CuL_2^+. Atoms represented as 50% probability ellipsoids. Hydrogen atoms omitted for clarity. Selected distances (Å) and angles (°): Cu(1)–P(1): 2.246(3); Cu(1)–S(1): 2.354(3); Cu(1)–S(2): 2.366(4); Cu(1)–P(2): 2.215(3); P(1)–Cu(1)–P(2): 130.5(1); P(1)–Cu(1)–S(1): 91.5(1); S(1)–Cu(1)–S(2): 91.2(1); Cu(1)–P(1)–C(7): 131.5(4).

compared with thioethers, and their ability to bind metals in a range of oxidation states. Tridentate eleven- and twelve-membered macrocycles incorporating phosphine and thioether donors have been reported previously.[8,9] In this communication we report the synthesis and preliminary coordination chemistry of the new ligand 1-phenyl-1-phospha-4,7-dithiacyclononane **L**, the first example of a ligand in which a phosphine donor is constrained within a nine-membered ring.

First attempts to synthesize the ligand **L** from $PhP(CH_2CH_2SH)_2$[10] by the molybdenum template reaction (Scheme 1) analogous to that described for 9S3[11] led to efficient ring closure to generate the complex $[Mo(CO)_3L]$.† However, all attempts to dislodge **L** from this complex [*e.g.* by reaction with $PhP(CH_2CH_2S)_2{}^{2-}$ or ethanedithiolate] were unsuccessful, yielding only unconverted $[Mo(CO)_3L]$. This confirms the expected increase in stability over the 9S3 analogue. A high-dilution approach, previously used successfully for synthesis of 9S3,[12] was then employed (Scheme 2), and proved remarkably successful giving **L** as a colourless, mobile oil in 44% yield (unoptimised). All spectroscopic properties were consistent with the proposed structure.

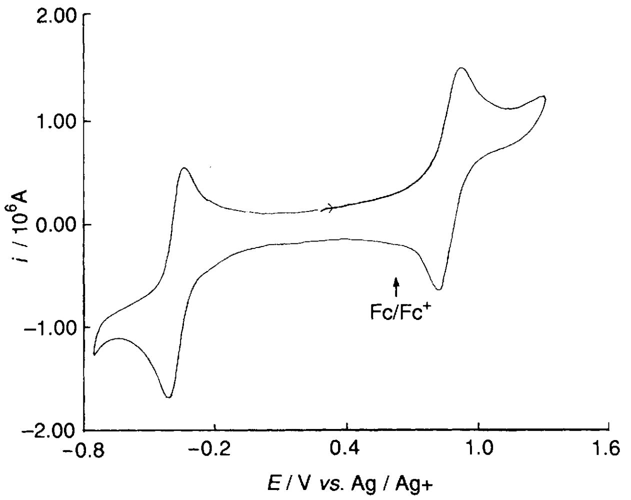


Fig. 2 Cyclic voltammogram of $NiL_2{}^{2+}$ (see text for conditions)

Complexes of **L** with Ni, Cu, Hg, Ag and Fe were prepared by the action of **L** on anhydrous perchlorate, hexafluorophosphate, or tetrafluoroborate salts of the metals in acetonitrile or nitromethane. Elemental microanalysis confirmed the stoichiometry of the complexes as $[ML_2]^{2+}$ (M = Ni, Hg, Fe or Cu) or $[ML_2]^+$ (M = Cu, Ag). Further evidence of enhanced stability compared with 9S3 complexes is provided by the inertness of $HgL_2{}^{2+}$ towards thiolate (thiocresolate, propanethiolate) in contrast to $Hg(9S3)_2{}^{2+}$, which reacts to form polymeric $Hg(SR)_2$.

The copper(I) complex was crystallized from acetonitrile as $[CuL_2](PF_6)\cdot MeCN$. The complex was shown by X-ray crystallography‡ (Fig. 1) to be tetrahedral, with one ligand facially tridentate and the other monodentate and coordinated though the phosphorus. **L** exhibits both endodentate and exodentate conformations in the complex. Thus, facial coordination is accessible but there is no overriding preference towards the endodentate conformation in this instance. The chelate bite angles are close to 90° suggesting that **L** would provide an excellent fit for octahedral complexes of metal ions with a similar ionic radius. The angle Cu(1)–P(1)–C(7) is extraordinarily large [131.5(4)°] presumably because of steric interaction with the non-chelating ligand.

Cyclic voltammetry studies (0.2 mol dm^{-3} tetrabutylammonium tetrafluoroborate/nitromethane, Pt electrode, Ag/Ag^+ reference electrode) were carried out in order to answer the

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† IR spectrum of $[Mo(CO)_3L]$: $\nu(CO)/cm^{-1}$ at 1940, 1850 and 1825 ($CHCl_3$ solution).

‡ *Crystal data*: $C_{26}H_{37}CuF_6NP_3S_4$, M_r = 762.3, triclinic, space group $P\bar{1}$, a = 9.631(3), b = 12.446(2), c = 14.404(5) Å, α = 101.12(2), β = 94.22(3), γ = 96.26(2)°, V = 1676.2(8) Å^3, Z = 2, D_c = 1.510 g cm^{-3}, Mo-Kα radiation (graphite monochromator), λ = 0.71073 Å, μ = 1.084 mm^{-1}, $F(000)$ = 784, 4127 observed reflections with $F > 6.0\sigma(F)$. 5947 Independent reflections were collected at 294 K in an ω scan. A semi-empirical absorption correction was applied. The structure was solved (Patterson synthesis) and refined (full-matrix least-squares analysis) using the Siemens SHELXTL PLUS (VMS) system. Refinement converged with R(unit weights) = 0.075. The highest residual electron density peak was associated with the $PF_6{}^-$ anion. All hydrogen atoms were placed at calculated positions. All atoms were refined anisotropically except the F atoms of the $PF_6{}^-$ anion and the atoms of the solvent molecule. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

question of whether or not substitution of a thioether donor by a phosphine donor renders the complex easier to oxidise (as a result of the greater σ-donor capacity of the phosphine), or easier to reduce (as a consequence of the greater π-acceptor capacity of the phosphine). Surprisingly, in the case of the nickel(II) complex (Fig. 2) both appear to be true. The Ni^{III} state is readily accessible *via* a reversible one-electron oxidation at $E_{1/2}$ = 0.27 V,§ ΔE_p = 79 mV [*cf.* $Ni(9S3)_2{}^{2+/3+}$, $E_{1/2}$ = 0.97 V, reversible[13]], while the Ni^I state is accessible *via* a one-electron reversible reduction at $E_{1/2}$ = −0.98 V, ΔE_p = 85 mV [*cf.* $Ni(9S3)_2{}^{+/2+}$, −1.1. V, irreversible§]. It is also surprising that the oxidation of $NiL_2{}^{2+}$ is easier than that of $Ni(9S2N)_2{}^{2+}$ (9S2N = aza-4,7-dithiacyclononane; $E_{1/2}$ = 0.887 V[5]) since the nitrogen ligand would be expected to favour the higher oxidation state more strongly. The structural and electronic factors responsible for this unexpected behaviour await further study.

The efficient synthesis of this new ligand, and the high stability and interesting properties of its complexes shown by this preliminary study may presage an interesting coordination chemistry of this and related phosphine ligands. The phosphine substituent offers an opportunity for elaboration of the structure, for example to produce ligands of higher denticity, or fine control of electronic properties of complexes.

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§ All redox potentials are measured and quoted relative to the ferrocene/ferrocinium couple (ΔE_p = 61 mV) as an internal standard.