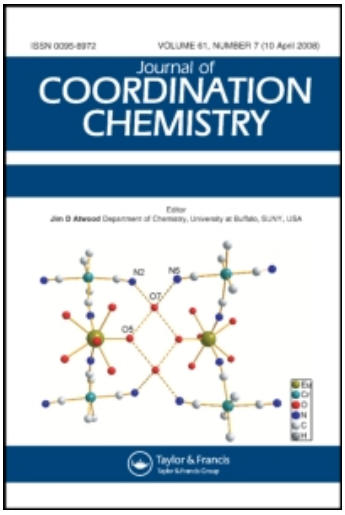

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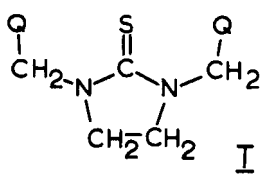
N,N'-di(p-tolylthiomethyl)ethylene thiourea, (L), the thiourea sulphur atom of which is a potential bridging centre, gave the cropper(I) derivatives, LCu_2Cl_2 and $LCu_2Cl_2 \cdot CH_3CN$. However, with silver(I) and palladium(II) L disintegrated, leaving the thiolate fragment coordinated to the metal. Synthetic approaches to a range of 1,5-bis(substituted thio)-pentane-3-thiol ligands incorporating a variety of donors at the termini of the thioether side arms were investigated but the only sequence which was developed to the stage where metal complexes could satisfactorily be generated involved the side arms ortho-$S.C_6H_4 \cdot NH_2$. The S-protected derivatives, 1,5-bis-(2'-aminophenylthio)-3-triphenylmethylthiopentane and 1,5-bis-(2'-aminophenylthio)-3-benzylthiopentane afforded accessible and convenient sources of the binucleating ligand 1,5-bis-(2'-aminophenylthio)pentane-3-thiol. With palladium(II) the S-trityl derivative was smoothly S-deprotected at temperatures below 100° C but the S-benzyl derivative required temperatures as high as that of boiling DMF. The binucleating ligands discussed here appear, at this stage, less versatile with regard to ready synthesis and structural modification and of generally less potential usefulness than analogous systems, described elsewhere,[2] involving a bridging thiophenoxide component.

INTRODUCTION

As part of a long-term project concerned with the synthesis of binuclear systems containing two soft metal centres in close proximity, which it is hoped may show unusual reactivity at a bridging site, we have extended our earlier studies concerning phenoxide-based ligands[1] to include potential binucleating systems containing a bridging component with a sulphur donor. Concurrently with studies, discussed elsewhere,[2] on binucleating ligands with imine-type side arms and with a bridging thiophenoxide component, we have explored some synthetic approaches to systems containing either a bridging thiourea component as in I or a bridging aliphatic thiolate component with a saturated backbone as in II. Our initial objective was to develop general synthetic methods for the introduction of a range of either single donors at the termini (e.g. $-Q = -SR, -PR_2$, etc.) or polydentate groups at these positions (e.g. $-Q = -SNH_2, -SPR_2$, etc.) The present report is concerned with synthetic approaches to systems of the types I and II including some of their complexes and an assessment of their suitability for our long-term objectives.



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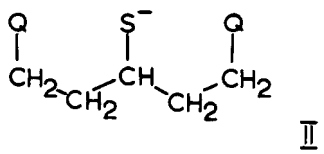


II

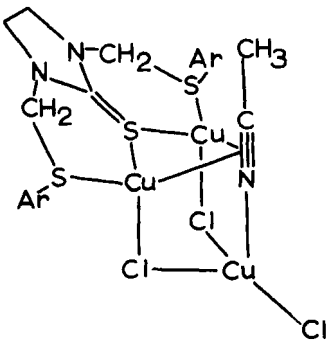
RESULTS AND DISCUSSION

Thiourea-based Systems

A simple thioether terminus (–Q in I = $-S.C_6H_4 \cdot pCH_3$) was chosen to test the

proposed synthetic approach to systems of the type I. N,N'-di(p-tolylthiomethyl)ethylene thiourea (I with $-Q = -S.C_6H_4.pCH_3$; hereafter referred to as L) was readily prepared by the reaction of ethylenethiourea with paraformaldehyde and p-thiocresol in the presence of an acid catalyst.

Complexes with an accessible bridging site between pairs of d^{10} metal centres offer the possibility of unusual reactivity at the site and, since the cuprous ion forms a variety of complexes with both thioreas and thioethers, a study of the cuprous complexes of L was undertaken. A solid of composition LCu_2Cl_2 slowly crystallised out when solutions of L and cuprous chloride in acetonitrile were allowed to stand at room temperature. However, if diethyl ether was added to the initial solution a material of composition $LCu_3Cl_3 \cdot CH_3CN$ separated. Attempts to recrystallise $LCu_3Cl_3 \cdot CH_3CN$ from either acetonitrile or N,N-dimethylformamide yielded LCu_2Cl_2, which was also obtained from attempts to generate $LCu_3Cl_3 \cdot C_6H_5CN$ by recrystallisation of $LCu_3Cl_3 \cdot CH_3CN$ from benzonitrile and from attempts to generate $LCu_3Cl_3 \cdot CH_2 = CH.CN$ by reaction of L with cuprous chloride in acrylonitrile. Comparison of the ir spectra of LCu_2Cl_2 and $LCu_3Cl_3 \cdot CH_3CN$ suggested that additional bands of medium intensity shown by the latter at 1600 cm^{-1} and 1285 cm^{-1} could be associated with the acetonitrile. No other bands ascribable to the nitrile were observed in the range 1600–2400 cm^{-1}. Upon being heated under vacuum at 100° C, $LCu_3Cl_3 \cdot CH_3CN$ lost acetonitrile and the bands in the ir spectrum at 1600 and 1285 cm^{-1} were very much reduced in intensity, although not completely removed. On this basis we tentatively assign the band at 1600 cm^{-1} to the CN st. mode and that at 1285 cm^{-1} to the CH bending mode of the acetonitrile. So drastic a lowering of the CN st. frequency is consistent with a nitrile group σ-bonded to one cuprous ion and π-bonded to two others, possibly as in III, whereby all three cuprous centres achieve the commonly preferred pseudo-tetrahedral environment.



III

Both LCu_2Cl_2 and $LCu_3Cl_3 \cdot CH_3CN$ showed very low solubilities in the common solvents and no useful n.m.r. data could be obtained. The best solvent for LCu_2Cl_2 was nitromethane and that for $LCu_3Cl_3CH_3CN$ was nitrobenzene, the saturated solutions in both cases at room temperature being $10^{-2} - 10^{-3}$M. Electrical conductances of such solutions were consistent with nonelectrolyte solute species.

Attempts to incorporate π-bridging acetylenes between the two cuprous centres were unseccessful. Reactions of L and cuprous chloride with disubstituted acetylenes yielded only LCu_2Cl_2 and with monosubstituted acetylenes yielded LCu_2Cl_2 and the cuprous acetylide.

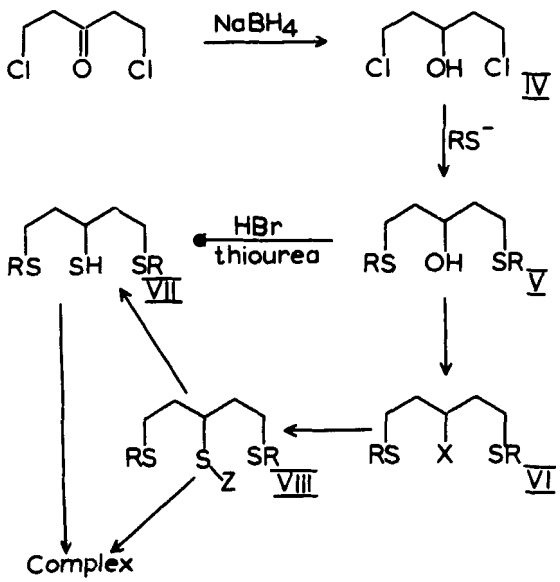
Attempts to form binuclear complexes of L with silver(I) and palladium(II) were discouraging. In both cases L disintegrated under the influence of the metal ion leaving the thiolate ($CH_3.C_6H_4.S^-$) fragment coordinated to the metal centre.

Although further studies of the coordination behaviour of L and related ligands would doubtless afford interesting structures the weakness of the basic system at the formaldehyde-derived methylene group leads us to regard it as unsuitable for our long-term objectives, despite the attraction of the easy synthesis.

Systems Containing an Aliphatic Thiolate Bridging Component

In Scheme 1 is outlined the general synthetic approach, starting from the known 1,5-dichloro-3-pentanone,[3] to systems of the type II, where Q is a thioether function. It appears that the better of the two routes shown in Scheme 1 from intermediates V to complexes is via VI and VIII in which X is some functional group susceptible to nucleophilic substitution, such as Cl, Br or O-tosyl, and in which Z is some S-protecting group which can be removed during the complex forming step.

Attempts to develop a synthesis of VII with $-R = -CH_2CH_2P(C_6H_5)_2$, which is a desirable potential binucleating ligand, foundered at stage V, which was never obtained in a completely pure state.[4] Numerous attempts to obtain what promised to be solid, purifiable derivatives and simultaneously to protect the two PS functions by chelation (e.g. in



SCHEME 1

$[(CO)_4Mo^{\circ}(P-S)(CH_2)_2]_2CHOH$) as a preliminary to further reaction at the alcohol centre gave impure gummy materials in all cases except for a mercury(II) derivative, viz. $[\{(C_6H_5)_2PCH_2CH\}_2CHOH]\,Hg_3Cl_6$.

Synthetic approaches were explored to the simpler phosphine ligand IX (–E = –SH, –A = $-P(C_6H_5)_2$) which promised to be an interesting binucleating agent in its own right, in the hope that the experience

IX

gained with this system might then be applied in approaches to the more desirable ligand VII (–R = $-CH_2CH_2P(C_6H_5)_2$). The synthetic intermediate IX (–E = –OH, –A = $-P(C_6H_5)_2$) could be isolated in pure crystalline form, as could the P-protected derivatives IX (–E = –OH, –A = either $-P(C_6H_5)_2O$ or $-P(C_6H_5)_2S$ or $-P(C_6H_5)_2(CH_2C_6H_5)^+Br^-$). Only in the case of the benzyl phosphonium derivative were we able to replace the central alcohol group cleanly, pure IX (–E = –Br, –A = $-P(C_6H_5)_2CH_2C_6H_5^+\,Br^-$) being obtained by reaction with hydrogen bromide. However, attempts to convert the central bromo group to thiol either by substitution with hydrosulphide or by substitution with thiourea followed by hydrolysis of thiouronium salt gave uselessly low yields.

The pyridyl derivative V (–R = $-CH_2-\alpha.C_5H_4N$) was a viscous oil which we were unable to purify by distillation. However, it was itself an effective binucleating ligand, yielding a crystalline cupric complex of formulation $[L'Cu_2(OCH_3)]\,CuCl_4$ (where L′ represents the mono-anion VI in which –X = $-O^-$ and –R = $-CH_2-\alpha.C_5H_4N$) and this complex afforded a convenient means of purification; removal of copper by treatment with H_2S readily gave pure V (–R = $-CH_2-\alpha.C_5H_4N$). Intractable gummy materials were obtained from attempts to convert V (–R = $-CH_2-\alpha.C_5H_4N$) to the corresponding VI (–X = either –Br or –O–tosyl). On one occasion analytically pure VI (–X = –Cl, –R = $-CH_2-\alpha.C_5H_4N$) was obtained from reaction with thionyl chloride but this was a very dirty reacton, which, in our hands, was not reproducible.

Another system which yielded a pure alcohol intermediate, V, but which we were unable to take satisfactorily beyond that stage involved the side arm –R = $CH_2CH_2NH_2$.

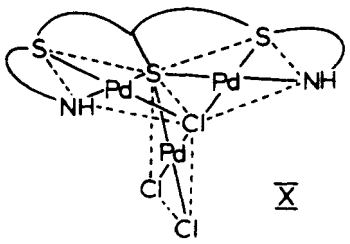
The only satisfactory synthesis of the type represented in Scheme 1 which has so far been developed involves the side arms –R = ortho – $C_6H_4NH_2$. The synthesis in this case was facilitated by the accessibility of solid amine hydrobromide intermediates. Many attempts to convert V (–R = –o. $C_6H_4.NH_3^+Br^-$) directly to the thiol VII by the thiourea –HBr reaction[5] were unsuccessful. Attempts to convert VI (–X = –Br, –R = –o. $C_6H_4.NH_3^+Br^-$) to VII by reaction with hydrosulphide or by reaction with thiourea followed by hydrolysis of the thiouronium salt gave dirty mixtures of products from which the thiol could be retrieved in unsatisfactory yield. We were unable to isolate any pure palladium(II) complexes of the thiolate directly from the thiouronium derivative by attempted metal-promoted hydrolysis. However, the S-protected derivatives VIII (–Z = either $-CH_2C_6H_5$ or $-C(C_6H_5)_3$, –R = –o. $C_6H_4.NH_2$) could be obtained in a satisfactory and reproducible manner and they afforded convenient sources of the ligand, being S-deprotected in the presence of appropriate metal centres.

The S-trityl derivative was S-deprotected in the presence of palladium(II) at temperatures less than 100° C; thus, reaction with palladium(II) chloride, lithium acetate and pyrazole in dimethylsulphoxide at approximately 90° C yielded a pink crystalline material of composition consistent with the formulation $L''Pd_2(C_3H_3N_2)$ where $(L'')^{3-}$ represents

the N-deprotonated trianionic binucleating ligand II in which $-Q = -S.C_6H_4.NH^-$.

Reaction of the S-trityl derivative with $PdCl_4^{2-}$ in boiling methanol gave a yellow solid which consistently has composition in agreement with the formulation $(L''H_2)Pd_{2.5}Cl_4$. Reaction of this complex with pyrazole in methanol gave a product of composition consistent with formulation $(L''H_2)Pd_2(C_3H_3N_2)Cl_2$ which was in turn converted to the above $L''Pd_2(C_3H_3N_2)$ by the action of lithium acetate.

The S-benzyl derivative suffered S-deprotection in the presence of palladium(II) chloride much less readily than the S-trityl derivative, temperatures as high as that of boiling N,N-dimethylformamide being required, under which circumstances an orange crystalline product of composition $L''Pd_3Cl_3.2DMF$ was obtained. Structure X indicates a likely way in which the additional $PdCl_2$ unit might be included.



X

All of the above palladium complexes were effectively insoluble in common solvents, which precluded the recording of n.m.r. spectra, etc.

With regard to the long-term objectives of exploring the reactivity at a bridging site within complexes containing a range of pairs of soft metal centres, the approaches to the thiolate systems described here are less than ideal. The only synthetic procedure we developed to the final binucleating ligand stage gave one of the least desirable systems for our general purposes, ligands with terminal phosphine or pyridine donors being much more attractive. Moreover, the disappointingly low solubilities shown by the palladium complexes cast serious doubt on the usefulness of this ligand for further studies. However, the successful overall synthesis with this particular side arm does indicate that analogous procedures with other more desirable side arms could very probably, with further work, be developed to a satisfactory stage. Our recurrent purification problem, arising from the intractable gummy nature of many of the synthetic intermediates above, no doubt stems from their floppy long chain molecular structures. Perhaps preparative scale h.p.l.c., which was not available to us during this work, may afford a simple solution to these purification problems. At this stage, however, the binucleating systems containing a bridging thiophenoxide[2] promise both easier general synthesis and wider scope for facile structural variation, such as the introduction of solubilising peripheral groups, than the aliphatic thiolates described here.

EXPERIMENTAL

N,N'-di(p-tolylthiomethyl)ethylene thiourea, L

p-Thiocresol (53g), ethylenethiourea (21.7g) and paraformaldehyde (13.0g) in toluene (300 ml) were heated under reflux for 10 hours in the presence of p-toluenesulphonic acid (0.5g). Most of the solvent was removed under reduced pressure and methanol was added to the residue yielding a yellowish precipitate. Recrystallisation from methanol gave colourless plates (45g). Anal. Calcd. for $C_{19}H_{22}N_2S_3$: C, 60.9; H, 5.9; N, 7.5; S, 25.7. Found: C, 60.9; H, 6.0; N, 7.4; S, 26.0. ^{1}H n.m.r. spectrum ($CDCl_3$ –TMS) δ 2.30 (singlet, 6 tolyl methyl protons), 3.50 (singlet, 4 protons of ethylene unit), 5.05 (singlet, 4 methylene protons), 7.20 (8 aromatic protons of tolyl group, AB quartet).

LCu_2Cl_2

A solution of L (0.69g) in acetonitrile (10 ml) was added under dinitrogen to a solution of CuCl (0.35g) in acetonitrile (10 ml). After standing under dinitrogen for approximately 20 min. the initially clear solution began to deposit colourless LCu_2Cl_2. After 1 hour the solid was collected, washed with petroleum ether and dried in a stream of air at room temperature. Yield, 0.38g. Anal. Calcd. for LCu_2Cl_2: C, 39.8; H, 3.7; Cl, 12.4; N, 4.9; S, 16.8; Cu, 22.2. Found: C, 39.7; H, 3.9; Cl, 12.4; N, 5.0; S, 16.3; Cu, 22.5.

A procedure similar to the above using acrylonitrile in place of acetonitrile (in the hope of producing an acrylonitrile-containing complex) led to the separation of crystalline LCu_2Cl_2 within seconds of mixing. Anal. Found: C, 39.3; H, 3.7; Cl, 12.7; N, 5.0; S, 16.4; Cu, 22.3. Crystalline samples of LCu_2Cl_2 were also obtained by recrystallisation of $LCu_3Cl_3.CH_3CN$ (below) under dinitrogen from either N,N-dimethylformamide or benzonitrile.

$LCu_3Cl_3 . CH_3CN$

A solution of L (0.41g) in acetonitrile (5 ml) was added under dinitrogen to a solution of CuCl (0.32g) in acetonitrile (5 ml). Within a minute or so diethyl ether (20 ml) was added under dinitrogen to the

resulting clear solution. The solid which separated was collected, washed with diethyl ether and dried in a stream of air at room temperature. Yield, 0.62g. Anal. Calcd. for $LCu_3Cl_3.CH_3CN$: C, 35.4; H, 3.5; Cl, 14.9; N, 5.9; S, 13.5; Cu, 26.7. Found: C, 35.3; H, 3.5; Cl, 15.6; N, 5.9; S, 13.2; Cu, 26.4.

Reaction of L with silver(I)

Silver nitrate (0.47g) dissolved in methanol (10 ml) was added to a solution of L (0.52g) in methanol (15 ml). A light ochre solid precipitated and after 2 hours this was collected, washed with chloroform and dried in a stream of air at room temperature. Yield, 0.44g. Anal. Calcd. for C_7H_7SAg : C, 36.4; H, 3.1; S, 13.9; Ag, 46.7. Found: C, 36.6; H, 3.1; S, 13.8; Ag, 45.1.

1,5-dichloro-3-pentanol

An ice-cold solution of sodium borohydride (6.0g) in water (25 ml) was added dropwise during approx. 20 min. to a stirred solution of 1,5-dichloro-3-pentanone[3] (49g) in methanol (300 ml) maintained at −10° C. The reaction mixture was then maintained at 0° C for 2 hours. Ice-water (600 ml) was added and the mixture was extracted with chloroform (300 ml and 3 x 100 ml). The extract was filtered and the solvent was removed under reduced pressure at 30–35° C yielding a brown oily residue which was dissolved in diethyl ether (200 ml) and dried over molecular sieves (4A). The ether was removed under vacuum and the residue was distilled at 0.1 mm.
1,5-dichloro-3-pentanol distilled as a colourless liquid at 64–70° C/0.1 mm. Yield, 42g. On being stored at room temperature in a stoppered vessel in the dark, the initially colourless liquid first turned pink and then within a few days dark brown, but even after several months' storage it showed i.r. and n.m.r. spectra identical to those of the analytically pure material. Anal. Calcd. for $C_5H_{10}Cl_2O$: C, 38.3; H, 6.4; Cl, 45.1. Found: C, 38.6; H, 6.5; Cl, 45.0.
^1H n.m.r. ($CDCl_3$ – TMS) δ 4.01 (quintet, one proton on C(3)), 3.64 (triplet, 4 protons on C(1) and C(5)), 3.07 (singlet, one OH proton), 1.89 (approx. quartet, 4 protons on C(2) and C(4)).

1,5-bis-(diphenylphosphino)-3-pentanol and derivatives

Clean sodium (1.89g) was dissolved under argon in freshly distilled anhydrous liquid ammonia (approx. 200 ml) cooled in ethanol-dry ice. Anhydrous triphenylphosphine (10.5g) was added and the resulting mixture, cooled in ethanol-dry ice, was stirred vigorously under argon for 2½–3 hours. Anhydrous ammonium bromide (3.93g) was added to the dark brown mixture producing an immediate change to an orange-yellow solution with suspended white solid. 1,5-dichloro-3-pentanol (2.10g) was added to the stirred mixture and after 30 min. the cooling bath was removed. The mixture was left under a slow argon stream overnight during which time the ammonia evaporated leaving a yellowish gummy residue. Water (50 ml) and diethyl ether (70 ml) were added under argon. After being shaken, the two layers were separated and the ethereal layer was washed with further water (50 ml) under argon. The ethereal layer was filtered and the ether was removed under vacuum yielding a yellowish-brown oil (8.2g). Isopropanol (20 ml) was added to the residue under argon. Petroleum ether (60–80°, 50 ml) was then added under argon to the solution so-formed and the solution was set aside sealed under argon at 0° C for 2 days. The resulting colourless crystals were collected under argon and washed with a little isopropanolpetrol. The solid was dried under vacuum at room temperature under which circumstances it retained a molecule of isopropanol of solvation. Yield, 4.4g. Anal. Calcd. for $C_{29}H_{30}OP_2 \cdot C_3H_7OH$: C, 74.4; H, 7.4; P, 12.0. Found: C, 75.0; H, 7.4; P, 12.4. The crystalline isopropanol-solvate upon being heated at 100° C under vacuum melted with frothing to yield the isopropanol-free diphosphine as a colourless viscous liquid. Anal. Calcd. for $C_{29}H_{30}OP_2$: C, 76.3; H, 6.6; P, 13.6. Found: C, 76.4; H, 6.7; P, 13.4.

Bis-phosphine oxide derivative, IX
(−E = −OH, −A = −P(C$_6$H$_5$)$_2$O)

A mixture of methanol (5 ml) and aqueous hydrogen peroxide (130 vol., 1.5 ml) was added to the above isopropanol-solvated diphosphine (0.48g) dissolved in methanol (10 ml). Some heat was evolved. The mixture was heated on steam and hot water was added until the mixture became cloudly. After being cooled to room temperature, the mixture deposited a small quantity of gummy precipitate which was removed by filtration. The filtrate after standing overnight at 0° C deposited colourless needles of the bis-phosphine oxide which were collected, washed with ice-cold aqueous methanol and dried under vacuum at room temperature. Anal. Calcd. for $C_{29}H_{30}O_3P_2 \cdot H_2O$: C, 66.8; H, 6.4; P, 12.2. Found: C, 68.5; H, 6.2; P, 12.1.

Bis-phosphine sulphide derivative, IX (–E = –OH, –A = –P(C$_6$H$_5$)$_2$S

Sulphur (0.135g) in benzene (5 ml) was added to the isopropanol-solvated diphosphine (0.99g) in benzene (1 ml). The solution was heated at the boiling point for 1 hour and then the benzene was removed under vacuum. Trituration of the syrupy residue with ethanol (7 ml) yielded a colourless partly crystalline solid with i.r. spectrum identical to that of analytically pure material. The solid was recrystallised from dichloromethane-petrol. Anal. Calcd. for $C_{29}H_{30}OP_2S_2$: C, 66.9; H, 5.8; P, 11.9; S, 12.3; Found: C, 66.4; H, 5.7; P, 11.6; S, 12.4.

Bis-benzylphosphonium bromide derivative, IX (–E = –OH, –A = –P(C$_6$H$_5$)$_2$CH$_2$C$_6$H$_5^+$Br$^-$)

Benzyl bromide (4 ml) was added to the above isopropanol-solvated diphosphine (1.0g) in methanol (5 ml). After being allowed to stand at room temperature overnight, the mixture was filtered and the filter paper and its contents were washed with hot methanol (5 ml), the washings being combined with the filtrate. Boiling ethyl acetate (70 ml) was added to the boiling filtrate. On cooling to room temperature the solution deposited colourless needles which were collected, washed with ethyl acetate-methanol (20:1) and dried under vacuum at room temperature. Yield, 1.77g. The solid was recrystallised from methanol-ethyl acetate. Anal. Calcd. for $C_{43}H_{44}Br_2OP_2.2H_2O$: C, 61.9; H, 5.8; Br, 19.2; P, 7.4. Found: C, 61.6; H, 6.0; Br, 19.2; P, 7.8.

1,5-bis-(benzyldiphenylphosphonium bromide)-3-bromopentane, IX (–E = –Br, – A = –P(C$_6$H$_5$)$_2$CH$_2$C$_6$H$_5^+$Br$^-$)

The above bis-phosphonium salt (2.0g) was heated with concentrated hydrogen bromide (48%, 35 ml) under reflux for 18 hours. On cooling to 0° C, the mixture deposited a yellow-brown gum which was dissolved in chloroform (50 ml) after the aqueous layer had been decanted. After the chloroform solution had been dried over magnesium sulphate, the solvent was removed under vacuum yielding a gummy residue which solidified. Recrystallisation from ethanol-ethyl acetate gave colourless crystals (1.71g). Anal. Calcd. for $C_{43}H_{43}Br_3P_2$: C, 59.9; H, 5.0; Br, 27.8; P, 7.2. Found: C, 60.0; H, 5.1; Br, 27.5; P, 7.2.

1,5-bis-(benzyldiphenylphosphonium bromide)-pentane-3-thiol, IX (–E = –SH,–A = –P(C$_6$H$_5$)$_2$CH$_2$C$_6$H$_5^+$Br$^-$)

The 3-bromo derivative (0.13g) and thiourea (0.13g) in ethanol (2 ml) were heated under reflux for 18 hours. The ethanol was removed under vacuum and the residue was dissolved in ethanolamine (1 ml) under argon. The solution was heated under argon on steam for 3 hours after which the ethanolamine was removed under vacuum leaving a yellow gummy residue. The gum was triturated with aqueous hydrogen bromide (1 ml conc. HBr + 5 ml H_2O) and the aqueous layer was decanted. The gum was dissolved in methanol (3 ml). Evaporation under vacuum of this solution gave a residue which solidified on cooling and which was recrystallised from methanol-ethyl acetate yielding colourless crystals. Yield, 0.042g. Anal. Calcd. for $C_{43}H_{44}Br_2P_2S$: C, 63.4; H, 5.5; Br, 19.6; P, 7.6; S, 3.9. Found: C, 61.6; H, 5.8; Br, 18.9; P, 7.4; S, 4.2.

1,5-bis-(2'-pyridylmethylthio)-3-pentanol

To a solution of 2-pyridine methane thiol[6] (6g) and 1,5-dichloro-3-pentanol (3.7g) in methanol (35 ml) was added potassium hydroxide (2.7g) in methanol (50 ml) and the resulting mixture was heated under reflux for 2 hours under dinitrogen. After the precipitated potassium chloride and been filtered off, the methanol was removed under vacuum to yield a light brown oily residue. The oil was shaken with water (100 ml) and diethyl ether (2 x 100 ml). The ether extract was washed with water (75 ml) and was then dried over magnesium sulphate. After filtration of the drying agent the solvent was removed under reduced pressure to yield a red-brown viscous residue (5.8g). Purification of the crude product was effected by passing hydrogen sulphide through a suspension of the copper(II) derivative (below) in methanol followed by filtration of the precipitated copper sulphide and evaporation of the filtrate. The residue was extracted into diethyl ether following neutralisation. After drying over calcium sulphate, evaporation of the ether extract gave the pure alcohol. Anal. Calcd. for $C_{17}H_{22}N_2OS_2$: C, 61.0; H, 6.6; N, 8.4; S, 19.2. Found: C, 61.3; H, 6.7; N, 8.2; S, 18.8. ^{1}H n.m.r. ($CDCl_3$-TMS) δ 1.67 (approx. quartet, 4 protons on C(2) and C(4)), 2.57 (triplet, 4 protons on C(1) and C(5)), 3.21 (singlet, 1 proton of OH), 3.75 (broad, 1 proton on C(3) superimposed on 4 protons of methylene groups adjacent to pyridine

rings), 7.10, 7.55, 8.35 (complex multiplets, 8 protons of pyridine rings).

[L'Cu$_2$(OCH$_3$)]CuCl$_4$

Crude 1,5-bis-(2'-pyridylmethylthio)-3-pentanol (2.45g) in methanol (20 ml) was added dropwise to a stirred solution of copper(II) chloride (2.89g) in methanol (10 ml) where upon a light green amorphous solid separated. Lithium acetate (1.46g) in methanol (20 ml) was added slowly whereupon the reaction mixture darkened, the light green solid began to redissolve and dark green crystals began to separate. Stirring at room temperature was continued for 15 min. and the mixture was then cooled to 0° C. The crystals were collected, washed with methanol and then with diethyl ether and dried under vacuum at room temperature. Yield, 4.10g. Anal. Calcd. for $C_{18}H_{24}Cl_4N_2O_2S_2Cu_3$: C, 31.1; H, 3.4; Cl, 20.4; N, 4.0; S, 9.2; Cu, 27.2. Found: C, 31.4; H, 3.3; Cl, 20.5; N, 4.2; S, 9.0; Cu, 26.9.

1,5-bis-(2'-aminoethylthio)-3-pentanol

A solution of aminoethanethiol hydrochloride (4.58g) in methanol (20 ml) was added to a solution of potassium hydroxide (4.45g) in methanol (50 ml). 1,5-dichloro-3-pentanol (3.15g) in methanol (5 ml) was added and the mixture was heated under reflux for 30 min. After the mixture had been cooled to 0° C the precipitated potassium chloride was filtered off and the solvent was removed from the filtrate under vacuum. Water (50 ml) was added to the residue and the mixture was made strongly alkaline by adding aqueous potassium hydroxide. Extraction with dichloromethane (5 x 50 ml) followed by drying over calcium sulphate and removal of solvent under vacuum yielded a pale yellow oily residue (4.25g) with i.r. and n.m.r. spectra identical to those of the analytically pure material. A small fraction was distilled for analysis, b.p., 210–230° C (bath)/0.3 mm. Anal. Calcd. for $C_9H_{22}N_2OS_2$: C, 45.3; H, 9.3; N, 11.8; S, 26.9. Found: C, 45.1; H, 9.3; N, 11.8; S, 26.9.

1,5-bis-(2'-aminophenylthio)-3-pentanol dihydrobromide

A solution of potassium hydroxide (3.45g) in methanol (50 ml) was added under dinitrogen to o-aminobenzenethiol (6.7 ml). A solution of 1,5-dichloro-3-pentanol (4.61g) in methanol (20 ml) was added and the resulting solution was heated under reflux. After ½ hour the precipitated potassium chloride was removed by filtration and methanol was removed from the filtrate by evaporation under reduced pressure. The residue was dissolved in diethyl ether (100 ml) and the resulting solution was washed with water (2 x 100 ml). Evaporation of the ether layer yielded a yellow-brown oil which was dissolved in acetonitrile (150 ml). Concentrated aqueous hydrogen bromide (48%, 20 ml) was added and the solution was shaken. After a few minutes, colourless solid started to separate. The mixture was left at 0° C overnight, after which the precipitate was collected, washed with acetonitrile and dried in vacuum at 80° C. Yield, 11.4g. Recrystallisation was unneceassary for material produced by the above procedure. Anal. Calcd. for $C_{17}H_{24}Br_2N_2OS_2$: C, 41.1; H, 4.9; N, 5.6; Br, 32.2. Found: C, 41.3; H, 4.9; N, 5.4; Br, 31.5.

1,5-bis-(2'-aminiphenylthio)-3-bromopentane dihydrobromide

1,5-bis-(2'-aminophenylthio-3-pentanol dihydrobromide (9.59g) and concentrated aqueous hydrogen bromide (48%, 55 ml) were heated with stirring at 120° C. All the solid dissolved within 5–10 min. The solution was then heated on steam for 18 hours during which time the colourless crystalline 3-bromocompound separated. After the mixture had been cooled to 0° C the crystals were collected, washed with acetonitrile and then diethyl ether and dried at 80° C under vacuum. Yield, 7.93g. Anal. Calcd. for $C_{17}H_{23}Br_3N_2S_2$: C, 36.5; H, 4.2; Br, 42.9; N, 5.0. Found: C, 36.7; H, 4.1; Br, 42.2; N, 4.7.

S-Thiouronium bromide derivative, VI (–X = –SC(NH$_2$)$_2^+$Br$^-$, –R = –S.C$_6$H$_4$.NH$_3^+$Br$^-$

1,5-bis-(2'-aminophenylthio)-3-bromopentane dihydrobromide (1.0g) and theiourea (1.93g) in water (4 ml) were heated on the steam bath for 16 hours. After the resulting solution had been cooled to room temperature, a solution of sodium hydroxide (0.3g) in water (20 ml) was added. The milky suspension so formed was extracted with diethyl ether (2 x 40 ml). Removal of the ether under vacuum gave a yellow gummy residue which was dissolved in acetonitrile (20 ml). Concetrated aqueous hydrogen bromide (48%, 3 ml) was added followed by diethyl ether (50 ml). The supernatant was decanted from the

somewhat gummy precipitate so formed. Further diethyl ether (100 ml) was added and the suspension was thoroughly titurated and then stirred vigorously for 2 hours which produced a colourless granular suspended solid. The solid was collected. washed with diethyl ether and dried at 80° C under vacuum. Yield, 0.85g. No satisfactory system for recrystallising this product was found. Anal. Calcd. for $C_{18}H_{27}Br_3N_4S_3.\frac{1}{2}(C_2H_5)_2O$: C, 35.3; H, 4.7; Br, 35.3; N, 8.2; S, 14.1. Found: C, 35.0; H. 4.6; Br, 34.6; N, 8.0; S, 14.4.

1,5-bis-(2'-aminophenylthio)-pentane-3-thiol dihydrobromide

1,5-bis-(2'-aminophenylthio)-3-bromopentane dihydrobromide (2.44g) and thiourea (5.32g) in water (8 ml) were heated on the steam bath for 16 hours whereby a clear yellow solution was obtained. The solution was made up to 25 ml with water and then sodium hydroxide (0.8g) in water (10 ml) was added. Extraction with diethyl ether (3 x 60 ml) followed by removal of the ether under vacuum yielded a yellow gummy residue (1.70g). Concentrated aqueous ammonia (6 ml) was added under dinitrogen to the residue in methanol (15 ml) and the mixture was heated under reflux in a dinitrogen atmosphere for 2 hours. After the reaction mixture had cooled, saturated aqueous $KHCO_3$ (20 ml) and water (20 ml) was added and the aqueous phase was extracted with diethyl ether (2 x 50 ml). The combined extracts were washed with water (4 x 20 ml) and then filtered to remove suspended water droplets. Evaporation gave a yellow gum to which acetonitrile (50 ml) and concentrated aqueous hydrogen bromide (48%, 10 ml) were added. A small quantity of gummy precipitate was removed by filtration and the filtrate, made up to 150 ml with further acetonitrile, upon standing yielded a colourless solid precipitate, which was collected, washed with diethyl ether and dried at 80° C under vacuum. Yield, 0.70g. The solid was recrystallised from dilute aqueous hydrobromic acid. Anal. Calcd. for $C_{17}H_{24}Br_2N_2S_3$: C, 39.9; H, 4.7; H, 5.5; S, 18.8. Found: C, 40.6; H, 4.8; N, 5.5; S, 18.0.

1,5-bis-(2'-aminophenylthio)-3-benzylthiopentane

A solution of potassium hydroxide (1.20g) in methanol (20 ml) was added under dinitrogen to 1,5-bis-(2'-aminophenylthio)-3-bromopentane dihydromide (2.27g) and benzyl thiol (2 ml). The mixture was heated under reflux in a dinitrogen atmosphere for 3 hours. Water (100 ml) and diethyl ether (75 ml) were added to the cooled reaction mixture. The two layers were separated and the aqueous phase was further extracted with ether (50 ml). The combined ether extracts were filtered and then evaporated under vacuum to a yellow-brown oily residue. Concentrated aqueous hydrobromic acid (48%, 5 ml) was added to the residue dissolved in diethyl ether (50 ml). The supernatant was decanted from the gummy precipitate so formed, which was then washed with further diethyl ether (100 ml). Excess aqueous potassium hydroxide and diethyl ether (50 ml) were then shaken with the gum. After separation from the ether layer, the aqueous phase was further extracted with diethyl ether (50 ml). The combined extracts were dried over calcium sulphate and evaporated to a brown oily residue (1.61g). Chromatography of the residue on neutral alumina (activity 1 deactivated with 5% water, 150g) gave 1.47g of the S-benzyl product as a pale yellow oil eluted with benzene. Anal. Calcd. for $C_{24}H_{28}N_2S_3$: C, 65.4; H, 6.4; N, 6.4; S, 21.8. Found: C, 65.3; H, 6.6; N, 6.2; S, 21.9. ^{1}H n.m.r. (CCl_4 – TMS) δ 1.50 (approx. quartet, 4 protons on C(2) and (C(4)), 2.57 (approx. triplet, 4 protons on C(1) and C(5) superimposed on 1 proton on C(3)), 3.32 (singlet, 2 benzylic protons), 3.97 (singlet, 4 NH_2 protons), 6.42, 7.00 (complex multiplets, 8 aromatic protons). A method less satisfactory than chromatography for the isolation and purification of the S-benzyl product was conversion to the dihydrobromide salt in acetonitrile-HBr followed by recrystallisation from methanol-isopropanol. Anal. Calcd. for $C_{24}H_{30}Br_2N_2S_3$: C, 47.8; H, 5.0; Br, 26.5; N, 4.7; S, 16.0. Found: C, 47.8; H, 5.1; Br, 25.6; N, 4.9; S, 15.3.

Reaction of 1,5-bis-(2'-aminophenylthio)-3-benzylthiopentane with palladium(II) chloride

A boiling solution of the S-benzyl derivative (0.14g) in acetonitrile (3 ml) was added to a solution of palladium(II) chloride (0.115g) in boiling acetonitrile (8 ml) whereupon a yellow precipitate formed immediately. The suspension was heated at the boiling point for 5 min. and the preipitate was then collected, washed with acetonitrile and dried in vacuum at 80° C. Whilst the solid was not completely pure the i.r. spectrum and the elemental composition left no doubt that the S-benzyl group remained attached. Anal. Calcd. for $C_{24}H_{28}Cl_4N_2S_3Pd_2$: C, 36.2; H, 3.5; Cl, 17.8; N, 3.5; S, 12.1. Found: C,

34.8; H, 3.5; Cl, 17.6; N, 3.5; S, 11.1. This solid was insoluble in most common solvents but dissolved in N,N-dimethylformamide upon heating. The palladium(II) derivative (0.20g) was heated with stirring in N,N-dimethylformamide (5 ml) and anisole (0.05 ml) in an oil bath maintained at 170° C. The solid dissolved completely after 15 min. After being heated for a total of 25 min., the hot mixture was filtered and boiling acetonitrile (15 ml) was added to the hot filtrate. Upon cooling the solution deposited an orange crystalline solid which was collected and recrystallised from N,N-dimethylformamide-acetonitrile. The crystalline product was dried at 80° C under vacuum under which conditions two moles of N,N-dimethylformamide of crystallisation were retained. Anal. Calcd. for $C_{23}H_{33}Cl_3N_4O_2S_3Pd_3$: C, 30.0; H, 3.6; Cl, 11.6; N, 6.1; S, 10.5. Found: C, 29.4; H, 3.2; Cl, 11.7; N, 6.6; S, 9.5. The same product was obtained from the direct reaction of the S-benzyl derivative and palladium(II) chloride in boiling DMF.

1,5-bis(2'-aminophenylthio)-3-triphenylmethylthiopentane

To a solution of triphenylmethylthiol[7] (5.4g) and potassium hydroxide (2.2g) in methanol (30 ml) was added under dinitrogen 1,5-bis-(2'-aminophenylthio)-3-bromopentane dihydrobromide (6.5g). The reaction mixture was heated under reflux in a dinitrogen atmosphere for 6 hours and was then allowed to cool. After potassium bromide had been filtered off solvent was removed from the filtrate under reduced pressure yielding a yellow-brown oily residue. Water (30 ml) and diethyl ether (50 ml) were added and the mixture was shaken and separated. The aqueous layer was extracted with further diethyl ether (50 ml). The combined ethereal extracts were washed with water (50 ml) and then dried over magnesium sulphate. Evaporation of the solvent under reduced pressure gave a clear brown oily residue which was triturated with petroleum ether (2 x 10 ml) to remove excess triphenylmethylthiol. The residue was purified by column chromatography first on cellulose, then on neutral alumina, the eluent being 1:1 petrol-di-isopropylether in both cases. The S-trityl derivative could be recrystallised from di-isopropylether. Yield, 1.8g. Anal. Calcd. for $C_{36}H_{36}N_2S_3$: C, 72.9; H, 6.1; N, 4.7; S, 16.2. Found: C, 72.6; H, 6.3; N, 4.9; S, 16.2. ^{1}H n.m.r. ($CDCl_3$ – TMS) δ 1.45 (approx. quartet, 4 protons on C(2) and C(4)), 2.43 (approx. triplet, 4 protons on C(1) and C(5) superimposed on 1 proton on C(3)), 4.05 (broad singlet, 4 amino protons), 6.35 – 7.35 (complex multiplets, 23 aromatic protons).

$(L''H_2)Pd_{2.5}Cl_4$

A solution of the S-trityl derivative (0.22g) in methanol (50 ml) was added to a hot filtered solution of palladium chloride (0.21g), lithium chloride (0.10g) and lithium acetate (0.044g) in methanol (100 ml). A yellow solid precipitated rapidly. The suspension was heated under reflux for 2 hours and then the yellow solid was filtered off, washed with hot methanol and then diethyl ether and was dried in air. Yield, 0.295g. Anal. Calcd. for $C_{34}H_{42}Cl_8N_4S_6Pd_5$: C, 27.0; H, 2.8; Cl, 18.7; N; 3.7; S, 12.7; Pd, 35.1. Found: C, 26.9; H, 2.9; Cl, 19.0; N, 3.8; S, 11.7; Pd, 34.9.

$[(L''H_2)Pd_2(C_3H_3N_2)]Cl_2$

A suspension of $(L''H_2)Pd_{2.5}Cl_4$ (0.20g) in methanol (50 ml) containing pyrazole (0.050g) was heated under reflux for 20 hours, throughout which solid remained suspended. After most of the solvent had been removed under vacuum the suspended pale yellow solid was collected, washed with methanol and then diethyl ether and dried in vacuum at 80° C. Yield, 0.17g. Anal. Calcd. for $C_{20}H_{24}Cl_2N_4S_3Pd_2$: C, 34.3; H, 3.3; Cl, 10.2; N, 8.0; Pd, 30.5. Found: C, 34.5; H, 3.7; Cl, 9.9; N, 7.6; Pd, 30.1.

$L''Pd_2(C_3H_3N_2)$

To a solution of palladium(II) chloride (0.120g) and pyrazole (0.052g) in dimethylsulphoxide (5 ml) at approximately 90° C was added the S-trityl derivative (0.195g). No observable colour change occurred until lithium acetate monohydrate (0.150g) dissolved in methanol (10 ml) was added, whereupon a pink crystalline solid separated. The solid was collected, washed with methanol, then diethyl ether and was dried at 100° C under vacuum. Yield,0.12g. Anal. Calcd. for $C_{20}H_{22}N_4S_3Pd_2$: C, 38.3; H, 3.5; N, 8.9; Pd, 33.9. Found: C, 38.5; H, 3.6; N, 9.3; Pd, 33.2. The same product was obtained by treating $[(L''H_2)Pd_2(C_3H_3N_2)]Cl_2$ with lithium acetate in methanol.

Physical Measurements

I.r. spectra were recorded on a Perkin-Elmer 457 spectrophotometer as KBr discs. N.m.r. spectra were

recorded on Varian HA-100 and Perkin-Elmer R12 spectrometers.

Analyses

Analyses were carried out by the Australian Microanalytical Service, Melbourne.

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