sulfur distances in $CpW(\eta^1\text{-}S_2CNMe_2)(CO)_3$ (3.905 (1) Å) and **2** are considerably longer than those observed previously (3.097[25b] to 3.633 Å[25a]). The shorter distances appear to reflect some bonding interaction in the late-transition-metal "η^1-dithiocarbamate" complexes. Steric interactions involving S4 and the N21- and N31-containing pyrazolyl rings clearly dictate the Mo–S4 distance in **2**.

Concluding Remarks

The anaerobic reaction of $[\{HB(Me_2pz)_3\}Mo(CO)_3]^-$ and tetraalkylthiuram disulfides in refluxing acetonitrile results in the formation of η^1-dithiocarbamato–Mo(III) complexes, $\{HB(Me_2pz)_3\}Mo(\eta^2\text{-}S_2CNR_2)(\eta^1\text{-}S_2CNR_2)$. The complexes are postulated to form via the oxidation of Mo(II) intermediates, the monodentate ligation of the dithiocarbamate being dictated by the steric demands of the $HB(Me_2pz)_3^-$ ligand. Oxidative addition of tetraalkylthiuram disulfides to other molybdenum complexes containing bulky *fac*-tridentate ligands, e.g., $(Me_3[9]aneN_3)Mo(CO)_3$,[26] may provide a general route to six-coordinate $\eta^1\text{-}S_2CNR_2^-$ complexes.

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Registry No. **1**, 102512-75-4; **2**, 102512-76-5; $Et_4N[\{HB(Me_2pz)_3\}Mo(CO)_3]$, 22357-70-6; tetramethylthiuram disulfide, 137-26-8; tetraethylthiuram disulfide, 97-77-8.

Supplementary Material Available: Tables of bond distances and angles, anisotropic thermal parameters, and calculated hydrogen atom positions (6 pages); a table of observed and calculated structure factors (34 pages). Ordering information is given on any current masthead page.

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Biological Analogues. A Structural Model for the Binding Site of Blue Copper Proteins

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A quadridentate chelate containing the ligands of the binding site of blue copper proteins has been synthesized. The chelate contains two imidazole, one thioether, and one mercaptan ligand, which can adopt a tetrahedral geometry about a metal ion. The mercaptan sulfur atom is sterically hindered in order to slow the rate of disulfide formation when copper(II) is coordinated. The ligand, when coordinated to cobalt(II), produces a spectacular blue complex, which, from physical data, is undoubtedly a tetrahedral species. Further, the electronic absorption spectrum of this complex is an excellent reproduction of the spectra observed for the cobalt(II)-substituted proteins plastocyanin and azurin. Although deep blue-green solutions are formed when the ligand is allowed to form a copper(II) complex, the copper is rapidly reduced in solutions even at low temperatures. A stable copper(II) complex could be isolated as a solid. Copper(II), however, does not form a tetrahedral monomer to any detectable extent; instead, tetragonal coordination oligomers appear to be the major species. The copper(I) complex also deposits as oligomers.

The design and synthesis of low molecular weight facsimiles of the copper binding site of blue proteins represents a challenge of considerable complexity. It is now known that the metal binding site of the plant protein plastocyanin consists of a copper atom coordinated to one mercaptide, one thioether, and two imidazole ligands in a highly distorted tetrahedral array with an exceptionally long copper–thioether bond.[1] A similar structure obtains for the related protein azurin,[2,3] but this does not appear to be the case for another spectroscopically similar blue protein, stellacyanin, which is devoid of methionine.[4] A number of attempts have been made to replicate some of the structural and electronic[5] features of these proteins,[6-11] but none has involved the use of a single ligand or a combination of ligands that incorporates all of the features of the blue binding site. These studies, however, have served to illustrate the difficulties of designing a stable system with all of the necessary characteristics.

This paper describes a partially successful attempt at incorporating all of the donor ligands about a tetrahedral metal center by means of a quadridentate chelate.

1. Strategy

It has proved especially difficult to form stable copper(II)–mercaptide complexes because of the extremely rapid reduction of the metal and the irreversible formation of the corresponding disulfide (eq 1). There are a number of possible mechanisms

$$2Cu(II) + 2RS^- \rightarrow 2Cu(I) + RSSR \quad (1)$$

for this metal reduction, but we assume a radical coupling scheme after a one-electron reductive elimination of the copper(II)–mercaptide bond (eq 2 and 3). The reductive elimination (eq

$$Cu(II)\text{–}SR \rightleftharpoons Cu(I) + RS^\bullet \quad (2)$$

$$2RS^\bullet \rightarrow RSSR \quad (3)$$

2) is a reversible reaction, but the overall system is driven to completion by the formation of disulfide (eq 3). Clearly, the

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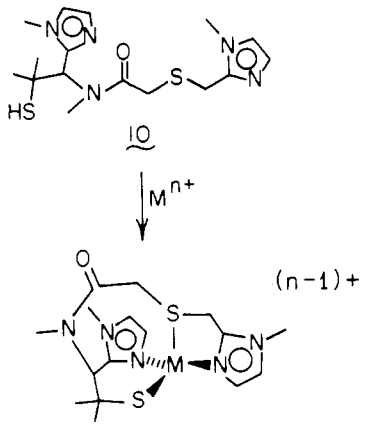

Figure 1. The quadridentate model ligand, plazH (**10**), and its possible binding mode to a metal ion, $[M(plaz)]^{n+}$.

position of the equilibrium in eq 2 will lie more to the left as the redox potential of the mercaptide becomes more negative and as the potential of the mercaptide ligand becomes more positive. But any reasonable facsimile of the blue protein binding site requires a high positive potential and the use of the readily oxidizable alkyl mercaptide ligands. Hence approaches that seek to manipulate relative redox potentials avoid one of the central challenges in the synthesis of blue copper models.

Given the inadmissibility of changing the relative redox potentials, one is left with two other possible approaches. The first would employ a ligand that drastically slows, or essentially prevents, the exchange of the copper from the complex. The well-known lability of copper(II) complexes makes the design and synthesis of such a ligand that incorporates the biological donor groups a formidable task. The other approach, which we adopt here, is to try to slow the rate of coupling of the $RS^{\bullet}$ radical by the use of steric hindrance.

The target molecule (plazH) is shown in Figure 1. It was designed with the following considerations in mind. First, it has all of the biological donor groups. Second, the mercaptan sulfur atom is sterically protected to some extent by being bound to a tertiary carbon atom. Third, the weakly coordinating thioether group is placed at an inner coordination position to ensure coordination by the presence of strongly coordinating ligands at the terminal positions of the quadridentate chelate. Fourth, the amide nitrogen atom has been methylated in order to prevent it from coordinating. Fifth, the quadridentate ligand can adopt a tetrahedral arrangement about the metal.

2. Ligand Synthesis

The target plazH (**10**) was obtained by the convergent synthesis outlined in Figure 2. The protected thioloacetate **1**, prepared from thioloacetic acid and DHP, was hydrolyzed with sodium ethoxide to give the somewhat unstable THP mercaptide anion which, in situ, was allowed to react with chloroacetonitrile to give **2** in good yield. This procedure delivers the sulfur atom in a protected form. We have also used the CH_3OCH_2-protecting group in a similar way[8] but found that this group does not survive the subsequent lithium imidazolate reaction. The *gem*-dimethylation of **2** proceeds reliably and in high yield only if DMF is added to the DME solvent. Compound **3** was reacted with lithium *N*-methylimidazolate and the imine anion produced was quenched with methyl iodide, in situ, to give a good yield of the hydrolytically stable imine **4**. Reduction of **4** proved troublesome, neither LAH nor $NaBH_4$ under normal conditions gave the desired amine. A clean reduction, however, was effected by $NaBH_4$ under weakly acidic conditions[12] to give **5** in high yield yield as a mixture of diastereomers. The synthesis of **8** was uneventful and followed conventional lines.

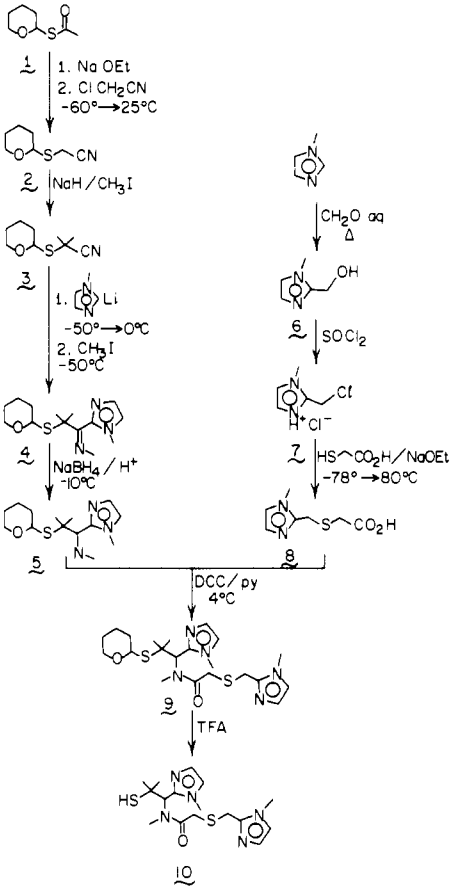

Figure 2. Outline of the synthesis of the ligand **10**.

We found that the simplest and most efficient method of coupling **5** with **8** was by allowing **5** to react slowly with an excess of both DCC and the acid **8** at 4 °C in pyridine solutions.[13] This product, **9**, was cleanly deprotected with trifluoroacetic acid to give the required ligand **10** as a relatively air-stable oil. The ligand **10** was purified by isolation of its off-white zinc salt, $[Zn(plaz)]ClO_4$. It was set free of the metal by sequestration with the disodium salt of EDTA.

3. Copper(I) Complexes

The reaction of ligand **10** with $[Cu(CH_3CN)_4]ClO_4$ and a base, Et_3N, NaOAc, $NaOH/H_2O$, or $NaOCH_3/CH_3OH$, in acetonitrile solutions under an inert atmosphere produced a light green solution. Addition of ethanol followed by the removal of the acetonitrile yielded a fluffy light green solid, which rapidly became more green upon exposure to air. The anaerobically formed solid is soluble in acetronitrile, dimethyl sulfoxide, and dimethylformamide but is insoluble in alcohols and in chlorinated solvents. Changing the reaction solvent to acetone, to dimethylformamide, or to higher molecular weight nitriles did not improve the consistency of the product, which tended to deposit as a gelatinous precipitate and dried to a faintly green powder. The green color could not be removed by the use of a variety of reducing agents, and no solvent or solvent mixture was found for which an analytically satisfactory crystalline solid could be obtained. Copper(I) does not destroy the ligand because we have recovered the intact ligand after removal of the copper with cyanide ions. We suspect that the solid products are polymeric copper(I) species that are less soluble than the monomer.

4. Copper(II) Complexes

The copper(II) complexes of the ligand were prepared in either methanol or ethanol solutions below −40 °C under an inert atmosphere from copper(II) acetate and the ligand. At these low

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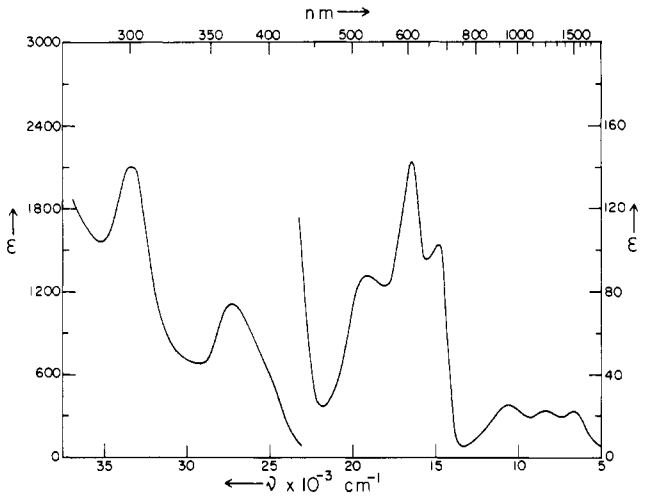

Figure 3. Electronic absorption spectrum of $[Co(plaz)]ClO_4$ in acetonitrile solution.

temperatures, deep green-blue solutions were produced, but as the solutions were allowed to warm to 25 °C, the color rapidly faded, indicating the reduction of the copper. At low temperatures, addition of large counterions (BPh_4^-, PF_6^-, ClO_4^-, BF_4^-) to the intensely colored solutions deposited pale green-blue powders. In the solid state, the complex is stable indefinitely. Analytical data for these solid complexes indicated compositions of one copper(II) per ligand molecule. The tetraphenylborate salt was insoluble in alcohols, but was soluble in methylene chloride and acetone at 25 °C, giving, upon dissolution, colorless solutions. This salt can be dissolved in dimethylformamide or acetonitrile at −35 °C to give green-blue solutions.

When the complex was dissolved in acetonitrile at −60 °C in a low-temperature UV cell, a broad electronic spectrum was observed between 350 and 800 nm. Even at these low temperatures a considerable amount of reduction occurred, and hence we were unable to obtain accurate extinction coefficients. In outline, the spectrum consisted of a broad band centered at 650 nm and a stronger shoulder at around 420 nm, which was contiguous with a stronger band to higher energies. Such a spectrum is characteristic of tetragonal copper(II)[8] and is not consistent with a tetrahedral species. For technical reasons we were unable to prepare either KBr disks or MgO mulls to record transmission or reflectance spectra, respectively, of the solid complexes. The tetragonal nature of the dissolved complex was confirmed by ESR. Thus glassy samples of the complex prepared in dimethylformamide at −60 °C showed typical tetragonal copper(II) spectra[14] as did samples of the solid.

It is clear from the above results that the ligand does not form stable tetrahedral copper(II) complexes although they do demonstrate that the copper(II)–thiolate bond is stable in the solid state.

5. Cobalt(II) Complexes

Reaction of cobalt(II) acetate with the ligand in methanol solution under argon led to the generation of an intense royal blue solution. These solutions are stable under an inert atmosphere but rapidly turn brown when exposed to oxygen. Addition of ClO_4^- or BPh_4^- ions to the blue methanol solutions led to the deposition of blue powders. The solid complexes are conveniently stable in air.

A Feltham–Hayter conductivity vs. concentration plot ($\Lambda_0 - \Lambda_e$ vs. $c^{1/2}$)[15] of the $[Co(plaz)]ClO_4$ complex in acetonitrile gave a straight line, which was superimposible on the straight line obtained for the same plot for the $(n\text{-}Bu)_4N^+ClO_4^-$ salt in acetonitrile solution. These results confirm that $[Co(plaz)]ClO_4$ is a monomeric 1:1 electrolyte in acetonitrile solution where it was found that $\Lambda_0 = 119\ cm^2\ \Omega^{-1}\ mol^{-1}$ $\Lambda_0 - \Lambda_e/c^{1/2} = 375$.

The magnetic susceptibility of $[Co(plaz)]ClO_4$ in acetonitrile solution was measured by the Evans[16] method at 30 °C. A value $\mu_{eff} = 4.35\ \mu_B$ ($S = {}^3/_2$) was obtained. This value for the magnetic moment is characteristic of a tetrahedral cobalt(II) center.[17]

The essentially tetrahedral geometry of the $[Co(plaz)]^+$ ion is confirmed by the electronic absorption spectra in solution and as the solid. The relevant solution spectrum is shown in Figure 3. A reflectance spectrum of the solid complex dispersed in MgO displayed three overlaping bands centered around 600 nm, suggesting a similar structure in the solid.

The two manifolds of transitions centered at 8600 cm^{-1} and at 17 000 cm^{-1} are ascribed to the d–d transitions $^4A_2 \rightarrow {}^4T_1(F)$ and $^4A_2 \rightarrow {}^4T_1(P)$, respectively. The large splittings observed in each of these transitions probably reflect the considerable geometrical and donor atom distortions away from the T_d field. The intensities of these two bands are consistent with the d–d assignment. To higher energies there appear two moderately intense transitions at 27 250 and 33 250 cm^{-1}, which can be ascribed to sulfur-to-metal charge-transfer transitions. Tetrahedral complexes of the type $[Co(SR)_4]^{2-}$, where R is an alkyl group, show a charge-transfer band at around 28 000 cm^{-1}, which has been ascribed to the $S(\sigma) \rightarrow Co(II)$ transition.[18,19] Accordingly we assign the lower energy band at 27 250 cm^{-1} of our complex to the *thiolate* $S(\sigma) \rightarrow Co(II)$ charge-transfer excitation. The higher energy transition at 33 250 cm^{-1} is assigned to the *thioether* $S(\sigma) \rightarrow Co(II)$ transition. In neither case are the corresponding (weaker intensity) $S(\pi) \rightarrow Co(II)$ charge-transfer transitions clearly resolved in the spectrum.

Table I. Comparison of Energy Positions of the Transitions Associated with the Co(II) Proteins[a] and the Model System $[Co(plaz)]^+$

compd	transitions,[b] cm^{-1}			
	$^4T_1(F)$[c]	$^4T_1(P)$[c]	$RS(\sigma) \rightarrow Co(II)$	$R_2S(\sigma) \rightarrow Co(II)$
plastocyanin	8250	17 000	26 000	30 000
azurin	8375	17 400	26 700	30 300
stellacyanin	8450	17 400	27 400	*d*
$[Co(plaz)]^+$	8625	17 000	27 250	33 250
$[CoCl_4]^{2-}$	5260[e]	14 700[e]		

[a] Values taken from ref 20. [b] The energy reflects the center of gravity of the transitions. [c] Ground state $^4A_2(F)$. [d] Stellacyanin has no methionine. [e] Taken from: Cotton, F. A.; Goodgame, D. M. L.; Goodgame, M. *J. Am. Chem. Soc.* **1961**, *83*, 4690.

6. Comparison of Protein and Model Spectra

The cobalt(II) derivatives of plastocyanin, azurin, and stellacyanin have been studied,[20] and we compare the electronic spectra of these protein derivatives with the spectrum shown by our model system (Table I). As will be seen, the correspondence of the respective absorption energies of the Co(II) proteins and those of our model system is remarkable. Moreover, the extinction coefficients for the corresponding transitions of the Co(II) proteins and those of the model system are very similar.

7. Discussion

The present attempt at generating a structural model of the binding site of blue proteins has been successful to a degree. The $[Co(plaz)]^+$ complex reproduces the electronic properties of the Co(II) proteins remarkably well and suggests that the cobalt(II) ion does indeed occupy the copper(II) binding site in the reconstituted proteins.[20] Despite considerable effort, we were unable

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to obtain suitable crystals of various [Co(plaz)]X salts for X-ray analysis in order to specify the binding site precisely.

Although the present ligand is an excellent analogue for cobalt(II) proteins, it fails in generating satisfactory analogues of copper(I) and copper(II) proteins. We are persuaded that the ligand has two principal flaws when copper is involved. First, the high lability of the copper(II) species and the lack of sufficient steric protection of the mercaptide sulfur atom lead to rapid reduction of the copper ion. Lability appears to be the key factor since the copper(II) complex is stable in the solid state. The second problem with ligand **10** is that it is much too flexible to force copper(II) to adopt a tetrahedral geometry and the flexibility allows for the formation of coordination polymers for both the copper(II) and copper(I) complexes.

Thus the present work suggests that a successful blue copper analogue will incorporate a ligand that has a very protected marcaptide sulfur atom and a rigid structure which enforces exclusively a tetrahedral geometry and prevents coordination polymerization and that forms a relatively nonlabile complex. Although the above prescription seems plausible, the search for low molecular weight structural analogues for the blue proteins remains a daunting form of natural product synthesis. Thus unlike the case of natural product synthesis where the structure of the target molecule is defined and its stability is known, the targets for blue copper protein models are not defined and the stability of the chosen target is revealed only in the last (complexation) step.

Experimental Section

Ligand Preparation. *S*-Tetrahydropyran-2-yl Thioacetate (1). This compound was made by a modification of the method of Martin.[21] 3,4-Dihydro-2*H*-pyran (46.8 g, 0.56 mol) in CH_2Cl_2 (100 mL) was added dropwise over 0.5 h to an ice-cold solution of thioacetic acid (38.0 g, 0.50 mol) and *p*-toluenesulfonic acid (0.1 g) in CH_2Cl_2 (150 mL). The solution was refluxed for 1.5 h, ice-cooled, washed with 5% aqueous $NaHCO_3$ and water, and then was dried over Na_2SO_4. The solvent was removed under vacuum, and the residue was distilled to give **1**, a colorless liquid (66.9 g, 83%; bp 88–92 °C (15 mm), lit.[21] bp 61 °C (0.4 mm)).

2-((Tetrahydropyran-2-yl)thio)-2-methylpropionitrile (3). *S*-Tetrahydropyran-2-yl thioacetate (**1**) (41.0 g, 0.256 mol) was added dropwise over 0.25 h to an ice-cooled solution of NaOEt (made from sodium (5.9 g, 0.256 mol)) in EtOH (250 mL) under nitrogen. The solution was cooled to −60 °C, and chloroacetonitrile (17.0 mL, 0.268 mol) was added over 5 min. The temperature of the milky solution was raised to −30 °C over 0.5 h, and then the mixture was stirred for 1.5 h at ambient temperature. Saturated aqueous NH_4OAc (100 mL) was added, and most of the EtOH was removed under reduced pressure. The residue was thoroughly extracted with Et_2O, and the combined organic extracts were washed with water and brine and then were dried over Na_2SO_4. Removal of the Et_2O under reduced pressure left a viscous oil, which was carefully distilled through a vacuum-jacketed Vigreux column to give **2** as a light green oil (28.7 g, 71%; bp 76–80 °C (0.2 mm)). ^1H NMR ($CDCl_3$): δ 1.5–2.2 (6 H, m), 3.34 (2 H, AB quartet, J = 18 Hz), 3.40–4.30 (2 H, m), 5.06–5.30 (1 H, m). Sodium hydride (58.0 g of a 50% mineral oil dispersion, 1.21 mol) was washed twice with dry hexane and was then suspended in dry DME (600 mL) and dry DMF (100 mL) under nitrogen. A solution of **2** (90.0 g, 0.572 mol) and CH_3I (75.0 mL, 1.20 mol) in dry DME (600 mL) was added dropwise over 3.25 h to the vigorously stirred mixture maintained at 30 °C by external cooling. After 18 h at room temperature, the reaction was quenched by he careful addition of saturated aqueous NH_4Cl (250 mL). DME was removed under reduced pressure and water (1700 mL) was added. The resultant mixture was thoroughly extracted with Et_2O, and the combined organic extracts were washed with water, 2% aqueous $Na_2S_2O_3$, water, and brine and then were dried over $MgSO_4$. The ether was removed under reduced pressure and the residue was distilled through a vacuum-jacketed Vigreux column to give 2-((tetrahydropyran-2-yl)thio)-2-methylpropionitrile (**3**) (97.2 g, 92%; bp 58–64 °C (0.2 mm)). ^1H NMR ($CDCl_3$): δ 1.66 (3 H, s), 1.75 (3 H, s), 1.5–2.1 (6 H, m), 3.4–4.4 (2 H, m), 5.2–5.5 (1 H, m). Anal. Calcd for $C_9H_{15}NOS$: C, 58.4; H, 8.2; N, 7.6; S, 17.3. Found: C, 58.2; H, 8.2; N, 7.4; S, 17.4.

***N*-Methyl-(1-(1-methylimidazol-2-yl)-2-methyl-2-((tetrahydropyran-2-yl)thio)propyl)amine (5).** *n*-Butyllithium (1.6 M in hexane, 200 mL, 0.32 mol) was added dropwise over 0.5 h to an ice-cooled solution of dry 1-methylimidazole (30.0 mL, 0.38 mol) in dry THF (500 mL) under nitrogen. After the yellow solution had been stirred for 0.75 h at room temperature, it was cooled to −50 °C and a solution of **3** (45.6 g, 0.25 mol) in dry THF (120 mL) was added dropwise over 0.5 h. The temperature of the solution was raised to 0 °C over 0.5 h. After 0.5 h at 0 °C, the reaction was again cooled to −50 °C, and CH_3I (20.0 mL, 0.32 mol) in dry THF (100 mL) was added over 0.5 h. The cooling bath was removed, and after 1.25 h, water (100 mL) was added. The layers were separated, and the aqueous layer was thoroughly extracted with Et_2O. The solvents were removed from the combined organic layers under reduced pressure, the residue was treated with water (200 mL), and the mixture was extracted with Et_2O. The combined ethereal layers were washed with water and brine and then dried over $MgSO_4$. Removal of the Et_2O under reduced pressure yielded **4**, a light yellow-green oil (46.5 g, 67%). ^1H NMR ($CDCl_3$): δ 1.3–2.1 (12 H, m), 2.97 (3 H, s), 3.56 (3 H, br s), 3.2–4.4 (2 H, m), 4.6–5.1 (1 H, m), 6.88 (1 H, br s), 7.04 (1 H, br s). Without further purification, **4** (46.5 g, 0.165 mol) was dissolved in THF (200 mL) and 95% EtOH (200 mL). The solution was cooled to −10 °C and was neutralized with aqueous HCl (9 M). Then a solution of $NaBH_4$ (12.5 g, 0.33 mol) in water (40 mL, containing a few drops of aqueous NaOH (40%)) was added dropwise over 1.75 h to the vigorously stirred and cooled reaction. Simultaneously, aqueous HCl (9 M) was added to maintain a pH of 6–8. The reaction mixture was stirred a further 0.75 h at −10 °C, and more aqueous HCl (9 M) was added to keep the pH at 6–8. Most of the organic solvents were removed under reduced pressure, and the aqueous residue was made basic with aqueous NaOH (40%) and was then thoroughly extracted with benzene. The combined benzene layers were washed with brine and were dried over Na_2SO_4. Removal of the benzene under reduced pressure yielded **5** as a light green oil (38.9 g, 84%). ^1H NMR ($CDCl_3$): δ 1.1–2.1 (13 H, m), 2.21 (3 H, s), 3.70 (3 H, s), 3.2–4.3 (3 H, m), 4.4–5.1 (1 H, m), 6.77 (1 H, br s), 7.01 (1 H, br s).

4-(1-Methylimidazol-2-yl)-3-thiabutanoic Acid (8). Mercaptoacetic acid (16.7 g, 0.181 mol) in EtOH (50 mL) was added dropwise over 0.5 h to a solution of NaOEt (made from sodium (12.5 g, 0.543 mol)) in EtOH (250 mL) under nitrogen. Then the solution was cooled to −78 °C and 2-(chloromethyl)-1-methylimidazole hydrochloride **7** (30.2 g, 0.181 mol) (made from 2-(hydroxymethyl)-1-methylimidazole **6** by the method of Jocelyn[22]) in EtOH (360 mL) was added rapidly. The cooling bath was removed, and the stirred mixture was allowed to come to ambient temperature and was then refluxed for 0.75. The mixture was cooled to 0 °C and was neutralized with aqueous HCl (1.8 M, 100.5 mL). After the solvents had been removed under reduced pressure, the solid white residue was triturated with hot MeOH (150 mL). Hot THF (300 mL) was then added, and the mixture was filtered. The precipitate was well washed with hot THF, and the combined filtrates were evaporated to dryness under vacuum, yielding a solid white residue, which was dissolved in hot MeOH (80 mL). Hot THF (180 mL) was then added, and the milky solution was filtered through paper, yielding a clear colorless solution, which on standing deposited 4-(1-methylimidazol-2-yl)-3-thiabutanoic acid **8** as white needles and plates (29.3 g, 86%, mp 142–4 °C). ^1H NMR (Me_2SO-d_6): δ 3.28 (2 H, s), 3.64 (3 H, s), 3.94 (2 H, s), 6.77 (1 H, d, J = 2 Hz), 7.10 (1 H, d, J = 2 Hz), 10.6 (1 H, s). Anal. Calcd for $C_7H_{10}N_2O_2S$: C, 45.1; H, 5.4; N, 15.0; S, 17.2. Found: C, 45.1; H, 5.5; N, 15.0; S, 17.3.

PlazH (10). Finely powdered **8** (28.55 g, 0.153 mol) was dissolved in hot dry pyridine (500 mL). The solution was rapidly cooled to room temperature, and **5** (14.5 g, 0.051 mol) in dry pyridine (100 mL) was quickly added. Then the slightly turbid mixture was cooled in ice, and DCC (20.1 g, 0.102 mol) was added in one portion to the vigorously stirred reaction. After 72 h at 4 °C the pyridine was removed under reduced pressure, the residue was triturated with benzene and filtered, and the light yellow precipitate was well washed with benzene. The filtrate was washed with water, dilute aqueous Na_2CO_3, and water and then was dried over Na_2SO_4. Removal of the benzene under reduced pressure yielded a viscous amber oil, which was chromatographed on Al_2O_3 (500 g, activity III) in benzene. Eluting with increasing concentrations of EtOAc yielded **9**, a light yellow oil (18.6 g, 80%). ^1H NMR ($CDCl_3$): δ 1.65 (6 H, br s), 1.0–2.0 (6 H, m), 3.10 (3 H, br s), 3.42 (2 H, s), 3.65 (6 H, br s), 3.2–4.3 (4 H, m), 4.6–5.1 (1 H, m), 6.18 (1 H, br s), 6.7–7.0 (4 H, m). Trifluoroacetic acid (35 mL) was added to **9** (7.2 g, 0.016 mol), and the solution, which rapidly turned red-brown, was stirred under nitrogen at room temperature for 24 h. Ice-cold water (600 mL) and benzene (150 mL) were added, and the mixture was vigorously stirred until all of the red-brown oil had dissolved. The layers were separated, and the aqueous layer was extracted with benzene. Then the aqueous layer was made basic by the addition of solid $NaHCO_3$ and was thoroughly extracted with benzene. The combined benzene extracts

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from the aqueous basic solution were washed with water and brine and were dried over Na_2SO_4. Removal of the benzene under reduced pressure yielded crude plazH (**10**), an amber oil (5.5 g).

Purification of plazH (10). Crude plazH (**10**) (5.5 g) was dissolved in degassed EtOH (200 mL) under nitrogen, and solid $Zn(OAc)_2 \cdot 2H_2O$ (3.59 g, 0.016 mol) was added. The solution was heated to 60-70 °C and $LiClO_4 \cdot 3H_2O$ (5.23 g, 0.033 mol) in degassed EtOH (60 mL) was added dropwise over 0.5 h. The stirred mixture was slowly cooled to room temperature. After 1 h at room temperature, the mixture was filtered under nitrogen and the precipitate was washed with degassed EtOH and then with degassed hexane. Drying under high vacuum yielded $[Zn(plaz)]ClO_4$ (6.3 g, 74%) as an off-white solid. Anal. Calcd for $C_{16}H_{24}N_5S_2O_5ClZn$: C, 36.2; H, 4.6; N, 13.2; S, 12.1; Cl, 6.7. Found: C, 36.3; H, 4.8; N, 13.0; S, 12.2; Cl, 6.6.

$[Zn(plaz)]ClO_4$ (6.3 g, 0.012 mol) and Na_2EDTA (8.33 g, 0.012 mol) were suspended in degassed water (150 mL) under nitrogen. After the mixture was stirred for 0.5 h, the resulting clear light yellow solution was made basic with solid $NaHCO_3$ (2.99 g, 0.036 mol) and was thoroughly extracted under nitrogen with degassed EtOAc. The combined organic layers were dried over Na_2SO_4, and then the solvent was removed under reduced pressure, yielding **10** (4.2 g, 97%), a viscous yellow-green oil. ^1H NMR (CD_3CN): δ 1.50 (3 H, s), 1.60 (3 H, s), 2.95 (3 H, s), 3.47 (2 H, s), 3.54 (3 H, s), 3.67 (3 H, s), 3.82 (2 H, s), 5.96 (1 H, s), 6.8-6.9 (4 H, m).

Preparation of Metal Complexes. All metal complexes were made in degassed solvents under argon.

[Co(plaz)]ClO_4. A solution of plazH (**10**) (0.97 g, 2.6 mmol) in MeOH (20 mL) was added dropwise to $Co(OAc)_2 \cdot 4H_2O$ (0.66 g, 2.6 mmol) in MeOH (35 mL). $LiClO_4 \cdot 3H_2O$ (1.7 g, 10.4 mmol) in MeOH (20 mL) was added dropwise over 0.5 h to the resulting dark blue solution. The mixture as then heated to 70 °C, and the fluffy blue solid was dissolved by the addition of CH_3CN (30 mL). At this temperature the volume was reduced to 25-30 mL, and the reaction was slowly cooled to room temperature. The mixture was filtered, and the precipitate was washed with MeOH containing a little CH_3CN and was dried under reduced pressure, yielding $[Co(plaz)]ClO_4$, a light blue solid (0.90 g, 66%). Anal. Calcd for $C_{16}H_{24}N_5O_5S_2ClCo$: C, 36.6; H, 4.6; N, 13.3; S, 12.2; Cl, 6.8. Found: C, 36.9; H, 4.6; N, 13.2; S, 11.8; Cl, 6.7.

[Co(plaz)]BPh_4. The tetraphenyl borate salt was made in a similar manner by using $NaBPh_4$, but in this case no CH_3CN was added and the mixture was filtered directly from MeOH, yielding $[Co(plaz)]BPh_4$, a light blue powder (70%). Anal. Calcd for $C_{40}H_{44}N_5OS_2BCo$: C, 64.5; H, 6.0; N, 9.4; S, 8.6. Found: C, 64.3; H, 6.0; N, 9.6; S, 8.6.

"[Cu(plaz)]BPh_4". A solution of plazH (**10**) (0.90 g, 2.4 mmol) in MeOH (100 mL) was added dropwise to $Cu(OAc)_2 \cdot H_2O$ (0.48 g, 2.4 mmol) in MeOH (50 mL) at -50 °C. $NaBPh_4$ (0.92 g, 2.7 mmol) in MeOH (50 mL) was added dropwise over 1 h to the dark blue-green solution at -50 °C. The mixture was stirred a further 0.5 h at -50 °C and filtered cold, and the precipitate was washed with cold MeOH and dried under high vacuum, yielding "$[Cu(plaz)]BPh_4$", a light blue-green powder (1.2 g, 67%). Anal. Calcd for $C_{40}H_{44}N_5OS_2BCu$: C, 64.1; H, 5.9; N, 9.3; S, 8.6. Found: C, 64.0; H, 5.9; N, 9.3; S, 8.4.

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Registry No. **1**, 40446-60-4; **2**, 103817-34-1; **3**, 103817-35-2; **4**, 103817-36-3; **5**, 103817-37-4; **7**, 78667-04-6; **8**, 103817-38-5; **9**, 103817-39-6; **10**, 103817-40-9; $[Zn(plaz)]ClO_4$, 103817-42-1; $[Co(plaz)]ClO_4$, 103817-44-3; $[Co(plaz)]BPh_4$, 103817-45-4; $[Cu(plaz)]BPh_4$, 103817-47-6; $[Cu(CH_3CN)_4]ClO_4$, 14057-91-1; $ClCH_2CN$, 107-14-2; 3,4-dihydro-2*H*-pyran, 110-87-2; thioacetic acid, 507-09-5; 1-methylimidazole, 616-47-7; mercaptoacetic acid, 68-11-1.

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Spectroscopic Study of the Effect of Methyl and Phenyl Substituents on the Basicity of Phosphine Ligands in Tungsten Carbonyl Derivatives

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The He I photoelectron spectra of diphosphine ligands (LL = $Me_2PCH_2PMe_2$, dmpm; $Me_2PCH_2CH_2PMe_2$, dmpe; $Ph_2PCH_2PPh_2$, dppm; $Ph_2PCH_2CH_2PPh_2$, dppe; $Et_2PCH_2PEt_2$, depm; $Et_2PCH_2CH_2PEt_2$, depe) and of the complexes $[W(CO)_4(LL)]$ and $[W(CO)_5(PMe_{3-n}Ph_n)]$ have been measured. In all cases the first ionization energies are lower both for the free phosphine ligands (lone pair on P) and for the complexes (tungsten 5d) when the phosphine has phenyl, rather than methyl or ethyl, substituents. These results are interpreted to indicate that the phenyl groups increase the donor ability of the phosphine ligands compared to the methyl or ethyl groups. The IR and ^{13}C NMR spectra have also been measured, but the Cotton-Kraihanzel force constants and the trends in the coupling constant $^1J(^{183}W-^{13}C)$ for the carbonyls trans to phosphine indicate that the basicity differences between the methyl- or phenyl-substituted phosphines are too small to be detected by these methods.

Introduction

The basicity of tertiary phosphine ligands has been studied by various spectroscopic methods. Infrared spectroscopy of phosphine-substituted metal carbonyls has enabled the study of carbonyl stretching frequencies and force constants, and on the basis of their trends, the donor strengths of various ligands have been compared.[1-5] From ^{13}C NMR studies it has been found that the replacement of one or more carbonyl ligands with tertiary phosphines in $M(CO)_n$ complexes leads to a deshielding of CO resonances for the remaining CO.[6] This implies that $\delta(^{13}CO)$ depends on the occupation of the antibonding orbital in CO, and the observation of a linear correlation between $\nu(CO)$ and $\delta(^{13}CO)$ has extended this idea.[7] More recently, the study of the coupling constants $[^1J(^{183}W-^{13}C)_{trans}]$ for the tungsten-carbonyl group trans to phosphorus in the complexes $[W(CO)_5L]$, where L = a tertiary phosphine ligand, had led to the formulation of a trans-influence series.[8] ^{31}P NMR spectroscopy studies the M-P bond more directly than IR and ^{13}C NMR studies, but it has been demonstrated that bond angle variations, or the differences in the hybridization of the unshared electrons of the phosphorus, is important in determining ^{31}P chemical shifts and coupling constant.[9-12] This leads to a greater difficulty in interpretion of these parameters.

Gas-phase ultraviolet photoelectron spectroscopy (UPS) is in principle the most direct method of investigating the electronic

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