ing temperature and prolonged retention time tended to pyrolyze, yielding additional unidentified peaks.

(26) As the sample aged, the ratio of the relative peak areas A:B increased; therefore, we assign production of 1-phenylcyclopentene to an isomerization reaction of 1-*p*-methoxybenzylcyclobutyl acetate. Such ready conversion of tertiary esters to alkenes has been previously observed.[15]

(27) The δ 6.32 value is consistent with that observed[20] for vinylic protons in β,β-dimethyl-*p*-nitrostyrene (a model for 1-*p*-nitrobenzalcyclobutane) and contrasts with the δ 5.97 value observed[20] for the vinylic protons in α,β-dimethyl-*p*-nitrostyrene (a model for 1-*p*-nitrophenylcyclopentene).

(28) The presence of the tropylium cation is consistent with a 1-*p*-nitrobenzalcyclobutane fragmentation reaction.

(29) O. Kamm and A. O. Matthews, "Organic Syntheses", Collect. Vol. I, Wiley, New York, N.Y., 1932, p 385.

(30) The NMR spectrum was consistent with that of authentic *p*-nitrobenzoic acid.

(31) R. V. Lemieux and E. von Rudloff, *Can. J. Chem.*, **33**, 1701, 1710 (1955).

1-Alkyl- (or aryl-) amino-2-methylpropane-2-thiols. Some Bi- and Tetradentate Nitrogen–Sulfur Ligands from Schiff's Base Disulfides

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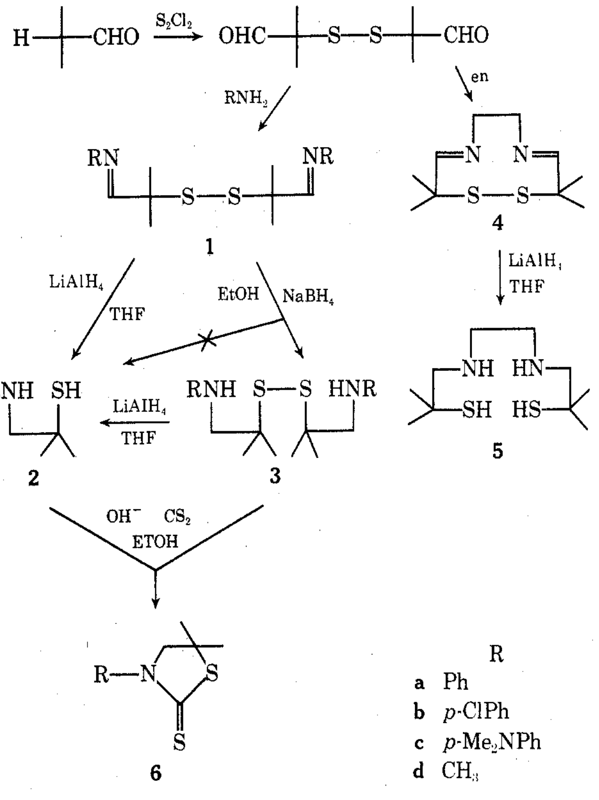
Repetition of a published procedure for the preparation of several N-substituted 1-amino-2-methylpropane-2-thiols (**2a–d**) for use as bidentate ligands indicated that the products characterized therein were not thiols, but the corresponding disulfides (**3a–d**). Preparation of the authentic thiols was accomplished by reduction of the intermediate Schiff's bases (**1a–d**) with $LiAlH_4$ in refluxing tetrahydrofuran. The novel tetradentate **5** was also synthesized from **4** using the same procedure. The chelating ability of **5** was demonstrated by formation of a neutral Ni(II) complex. It was also shown that the 3-arylamino-5,5-dimethylthiazolidine-2-thiones (**6**) were obtained from both the thiols and disulfides, indicating that formation of this derivative does not prove the presence of a thiol function.

Nitrogen- and sulfur-donor ligand systems[1] are of continuing interest in coordination chemistry, and at our laboratory we are especially interested in complexes of molybdenum[2] and iron.[3] Recently, interesting properties have been found for complexes with tertiary thiol groups such as 3-mercaptovaline (penicillamine).[2c,4] We sought to synthesize a variety of such tertiary thiols (**2a–d**), and a straightforward route for these compounds had recently appeared in this journal.[5] This involved Schiff's base formation using α,α'-dithiodiisobutyraldehyde followed by reduction with $NaBH_4$ (Scheme I), and no difficulty was anticipated. This same route also appeared suitable for the novel tetradentate **5**, because the cyclic Schiff's base **4** was a known compound.[6] However, our attempts to repeat this synthetic sequence failed, and the preparation and characterization of these compounds by a revised procedure is the subject of this paper.

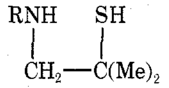
Scheme I



Attempts to make **2a** gave the viscous, pale yellow, nondistillable liquid previously described.[5] However, only 1–2% thiol was found (I_2 titration), and ir and NMR showed NH, but no SH. Molecular weight data were consistent with a dimer, which we assign as the disulfide **3a.** This is a surprising result because the reaction and subsequent work-up were conducted under argon. Neither diselenide-catalyzed hypophosphorous acid reduction[7] nor more vigorous $NaBH_4$ treatment (2 hr in refluxing acetonitrile) would cleave **3a.** The literature reveals tertiary disulfides to be fairly resistant to reduction; e.g., di-*tert*-butyl disulfide is resistant to $LiAlH_4$ in refluxing ether, but is reduced in refluxing tetrahydrofuran (THF),[8] and while penicillamine disulfide is little affected by $NaBH_4$ (50°),[9] it can be cleaved by Na–NH_3.[10] Treatment of either **3a** or its precursor **1a** with $LiAlH_4$ in THF gave the desired thiol as a distillable, mobile liquid (Table I), which exhibited an SH peak (NMR, ir) and the correct molecular weight, and consumed 2 equiv of iodine, a characteristic of some tertiary thiols (sulfenyl iodide formation).[11]

It was apparent that the previous report[5] of **2a** was in error, and that the others (**2b–d**) of interest to us were probably disulfides (**3b–d**) also. In order to test this, we repeated the synthesis of "**2b**", "**2c**", and "**2d**", reported to be a viscous, nondistillable liquid, a crystalline solid (mp 82–83°), and a volatile liquid [bp 113–114° (0.75 Torr)], respectively. Again the $NaBH_4$ reduction gave products with these same properties. These compounds were shown to be the disulfides **3b–d** by an analogous process. When these Schiff's bases (**1b–d**) were reduced with $LiAlH_4$ in THF,

Table I
Properties of the 1-Amino-2-methylpropane-2-thiols[a]



$$\begin{array}{cc} RNH & SH \\ | & | \\ CH_2 & \!\!\!\!-\!\!\!-C(Me)_2 \end{array}$$

R	Bp, °C (Torr)	% yield	Mol wt (theory)	NMR, ppm (Me)$_2$	CH$_2$	NH/SH[b]	ArH	Other
Ph (**2a**)	90–92 (0.7)[c]	64	180[d] (181)	1.38	3.08	3.88 (b) 1.71	6.4–7.3 (m)	
p-ClPh (**2b**)	111–114 (0.1)[c]	63	216[d] (216)	1.42	3.10	4.07 (b) 1.72	6.4–7.3 (m)	
p-Me$_2$NPh (**2c**)	135–137 (0.15) (mp 50–51.5)[e]	67	224[d] (224)	1.40	3.09	3.60 (b) 1.79	6.7 (m)	2.80 (Me$_2$N)
Me (**2d**)	47 (20)[f]	20	117[g] (119)	1.37	2.54	1.56 1.56		2.47 (MeN)
Ethylene (**5**)	101–103 (0.07)[c]	50	230[g] (236)	1.37	2.62	1.76 1.76		2.78 (CH$_2$CH$_2$)

[a] Satisfactory C, H, N analyses were obtained for the new compounds **2a–c** and **5**. [b] Both protons exchangeable with D_2O. [c] Mobile liquid, solidifying in the freezer. [d] VPO in 1,2-dichloroethane. [e] Recrystallized from hexane. [f] Hydrochloride mp 229.5–230° dec (lit.[12] 222–224° dec). [g] Cryoscopy in benzene.

the authentic thiols summarized in Table I were obtained. The *N*-methyl compound (**2d**) has been isolated before as the hydrochloride,[12] but this is the first report of the free base. In view of the low yield we obtained (20%), this compound is probably better prepared (79%) by the route described in ref 12.

The cyclic Schiff's base **4** was prepared and reduced ($LiAlH_4$) to give the new tetradentate **5** in reasonable yield. Its properties are described in Table I and its chelating ability demonstrated by formation of a neutral Ni(II) complex. Further studies of the coordination chemistry of **5** and **2a–d** are currently in progress.

The mass spectral evidence given previously[5] to support the formulation of "**2a**" can be attributed to the presence of a few percent of the authentic, more volatile thiol in the disulfide. The NMR evidence given[5] for thiol must be rejected. The SH was supposedly under the *gem*-dimethyl resonance for "**2a–c**", and our NMR data clearly show only six protons in this peak before and after D_2O exchange. Only one NH or SH proton was even listed for "**2d**", and this was no doubt the NH, as we see a sharp two-proton peak for these in **2d**. The formation of a crystalline thiazolidine-2-thione (**6c**) from **3c** remains to be explained, as this was used as further evidence of an SH. Upon examination, *both* the free thiol **2c** and the disulfide **3c** yielded this derivative on treatment with CS_2 and NaOH in ethanol. **2a** and **3a** behaved similarly, and thus, while providing crystalline derivatives (**6a–c**), their formation cannot be used as evidence of a thiol function. The differing yields of these derivatives (p-Me$_2$N > p-H > p-Cl) appears to reflect the varying basicity of the nitrogen atom.

The mechanism of formation of **6** from the disulfide is not clear, but may arise from small, equilibrium amounts of thiol formed by reaction with the xanthate or sulfide which must be present (from the CS_2, NaOH, and ethanol present). The lability of the S–S bond in the presence of RS^- types is well known.[13]

$$RSSR + R'S^- \rightleftarrows RSSR' + RS^-$$

Although it is beyond the scope of our interest to reexamine the remaining compounds reported as thiols in ref 5, it is reasonable to assume that they are also disulfides (**3**). Nevertheless, the general synthetic sequence reported there is still of value as long as $LiAlH_4$–THF is used in the reduction step and reductant-compatible substituents are present.

Experimental Section

NMR spectra were obtained with a Varian A-60 instrument (35°) with tetramethylsilane as the internal standard. Either a Hewlett-Packard 302B vapor pressure osmometer (37°) or an anaerobic cryoscopy cell[14] were used for molecular weight determinations. The H-P Model 185 CHN Analyzer was used for the elemental microanalyses, and infrared spectra were obtained on a Beckman IR20-A as KBr disks or as smears between salt plates. All evaporations were done at or near ambient temperature with a Swissco rotary vacuum evaporator. Thiol titrations with 0.05 *N* ethanolic I_2–KI (dead stop end point) were adapted from the literature.[15] Melting points were determined with a hot stage microscope and are corrected. α,α'-Dithioisobutyraldehyde was prepared according to the literature[6] [70%, bp 92–93° (0.3 Torr)], as was the cyclic Schiff's base **4**,[6] except that MeOH was used as a solvent (93%, mp 163–166°).

Bis[1-(N-substituted)imino-2-methyl-2-propyl] Disulfides (1a–d). Instead of the more complex published procedure,[5] the imines **1a–c** were more expeditiously prepared by refluxing the amine with α,α'-dithiodiisobutyraldehyde (30–60 min) in isopropyl alcohol (followed by H_2O washing and recrystallization from *i*-PrOH). The NMe compound **1d** was obtained[5] in 84% yield with a reaction period of 4 hr instead of the 4 days prescribed.

Bis[1-(N-substituted)amino-2-methyl-2-propyl] Disulfides (3a–d). The $NaBH_4$ reductions were performed as described,[5] but under argon, and the reactions worked up in the same way. Products with the reported physical appearance (**3a,b**), melting point (**3c**), or boiling point (**3d**) were obtained, but no thiol beyond 1–2% was found (titration). No SH could be found under the *gem*-dimethyl peak by NMR, the integration showing only six protons before or after D_2O exchange (see text). NH (ca. 3340–3420 cm^{-1}) was seen in the ir, but SH was absent. Molecular weight data (VPO, 1,2-dichloroethane) were consistent with the disulfide **3**: **3a**, 346 (theory 360); **3b**, 440 (theory 429); **3c**, 439 (theory 446); **3d**, 250 (theory 236).

1-Alkyl- (or aryl-) amino-2-methylpropane-2-thiols (2a–d) and Ethane-1,2-bis(*N*-1-amino-2-methylpropane-2-thiol) (5).[16] The appropriate Schiff's base, **1a–d** or **4** (0.10 mol), or disulfide (**3a**) was dissolved in dry THF (100–300 ml) and added with stirring (argon atmosphere) to $LiAlH_4$ (0.12 mol; 0.16 mol for **4**) in dry THF (100 ml) over 30–40 min. The reaction mixture was refluxed for 2 hr and hydrolyzed by the cautious addition of saturated NaK-tartrate solution (50–75 ml), and then ether (300 ml) added. The sludge was separated by decanting or filtration (Celite) and washed well with ether. The solvent was removed (a Vigreux column was used for **2d** because of its volatility), and the residual liquid subjected to simple distillation (in vacuo) to give the thiols described in Table I. The ir showed SH as a medium-weak to weak band at 2530–2550 cm^{-1}, and the NH as a medium to medium-strong band at 3340–3420 cm^{-1}. A separate SH was seen in the NMR for **2a–c**, but was pooled with the NH in **2d** and **5**. Titration with I_2 gave 97–100% of 2 equiv/thiol for **2a,b** and 1 equiv/thiol for **2d** and **5**.[17] A colored complex was formed between I_2 and **2c** and the end point was not distinct. The products were stored (frozen) in serum bottles under argon.

Preparation of 3-Aryl-5,5-dimethylthiazolidine-2-thiones (6a–c). The general method[5] was to reflux a mixture of the thiol (3.0 mmol) or disulfide (1.5 mmol), 10 *N* NaOH (0.30 ml), CS_2 (7 mmol), and ethanol (10 ml) for 24 hr (argon), add water (3–4 ml), and chill. The crystalline derivative was filtered, washed (cold MeOH, then H_2O), and recrystallized from the same ethanol–water mixture prior to analysis. The yields listed are for the crude products. Use of the disulfides **3a** and **3c** led to similar (or higher) yields of the identical **6** (melting point and mixture melting point).

3-Phenyl-5,5-dimethylthiazolidine-2-thione (6a): colorless plates (45%), mp 114–115°. Anal. Calcd for $C_{11}H_{13}NS_2$: C, 59.15; H, 5.86; N, 6.27. Found: C, 58.80; H, 5.87; N, 6.17.

3-(*p*-Chlorophenyl)-5,5-dimethylthiazolidine-2-thione (6b): colorless needles (34%), mp 111–111.5°. Anal. Calcd for $C_{11}H_{12}ClNS_2$: C, 51.25; H, 4.69; N, 5.43. Found: C, 51.34; H, 4.81; N, 5.81.

3-(*p*-Dimethylaminophenyl)-5,5-dimethylthiazolidine-2-thione (6c): pale yellow needles (79%), mp 156–157° (lit.[5] 157–158°).

Nickel(II) Complex of 5. A solution of **5** (1 mmol) in MeOH (4 ml) was added to a warm solution of $Ni(OAc)_2 \cdot 4H_2O$ (1 mmol) in MeOH (8 ml). The solid, which separated immediately, was filtered, washed (MeOH), and vacuum dried (1 hr at 50°) to give 188 mg (61.4%) of the tan-pink crystalline complex. Its ir spectrum exhibited bands at 3220 and 3270 cm^{-1} (sh) (coordinated NH). Anal. Calcd for $C_{10}H_{22}N_2S_2Ni \cdot \frac{1}{2}H_2O$: C, 39.75; H, 7.67; N, 9.27. Found: C, 39.67; H, 7.85; N, 9.59.

Registry No.—**1a,** 54410-19-4; **1b,** 54410-20-7; **1c,** 54410-23-0; **1d,** 57443-08-0; **2a,** 54410-26-3; **2b,** 54410-28-5; **2c,** 54410-33-2; **2d,** 54410-35-4; **3a,** 57443-09-1; **3b,** 57443-10-4; **3c,** 57443-11-5; **3d,** 57443-12-6; **4,** 57443-13-7; **5,** 57443-14-8; **5** Ni(II) complex, 57443-07-9; **6a,** 57443-15-9; **6b,** 57443-16-0; **6c,** 54410-36-5; α,α'-dithiodiisobutyraldehyde, 15581-80-3; aniline, 62-53-3; *p*-chloroaniline, 106-47-8; *N,N*-dimethyl-*p*-phenylenediamine, 99-98-5; methylamine, 74-89-5; $Ni(OAc)_2$, 373-02-4.

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(14) This apparatus will be described elsewhere.

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(16) No attempt was made to optimize yields.

(17) We have no explanation as yet for the uptake of less I_2 by those thiols containing aliphatic amino groups.

Ferrocene-1,1′-disulfonyl Azide and 2,4,6-Trimethylpyridinium Ferrocenesulfonyl Ylide. Synthesis and Decomposition

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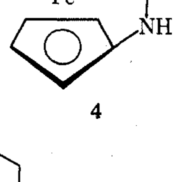
Photolysis of ferrocene-1,1′-disulfonyl azide in various solvents and at different wavelengths gave 1′-sulfamylferrocenesulfonyl azide and ferrocene-1,1′-disulfonamide. The thermolysis products depended on the solvent used. In cyclohexane, 1′-sulfamylferrocenesulfonyl azide, ferrocene-1,1′-disulfonyl azide, *N,N*′-dicyclohexylferrocene-1,1′-disulfonamide, 1′-(*N*-cyclohexylsulfamyl)ferrocenesulfonyl azide, and 1′-(*N*-cyclohexylsulfamyl)ferrocenesulfonamide were obtained. In benzene, products both of kinetic (azepine) and thermodynamic control (anilide) were formed but disubstitution did not occur. In mesitylene, the dimesitylamide was obtained. No intramolecular cyclization products were ever detected. 2,4,6-Trimethylpyridinium ferrocenesulfonyl ylide did not undergo photolysis but did thermolyze to ferrocenesulfonamide and *sym*-collidine. Again no ferrocenophane was formed.

The thermal and photochemical decomposition of ferrocenylsulfonyl azide (**1**) has led to some very interesting results.[1,2] Thermolysis in benzene led to a unusually high yield (for such reactions[3]) of hydrogen-abstraction product, ferrocenesulfonamide (**2**), and to a low yield of "substitution"[4] into the aromatic nucleus (**3**).[2] More solvent insertion and less hydrogen abstraction were observed in cyclohexane, but the yield of **2** was very high in cyclohexene. Photolysis of **1** led to quite different results. Thus, the main product formed in benzene was the novel bridged derivative **4**, [2]ferrocenophanethiazine 1,1-dioxide,[1] together with much smaller amounts of **2**. The same products were formed in cyclohexene, but now, for the first time, was observed what is probably the addition of a singlet sulfonyl

$FcSO_2N_3$
1

$FcSO_2NH_2$
2

$FcSO_2NHC_6H_5$
3



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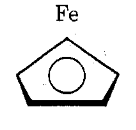

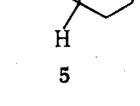

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