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Synthesis and Chemistry of New Nickel, Palladium, and Platinum Complexes of 1,2-Ethanedithiol, 1,3-Propanedithiol, 1,4-Butanedithiol, 1,4,8-Trithianonane, and 1,4,8,11-Tetrathiaundecane^{1,2}

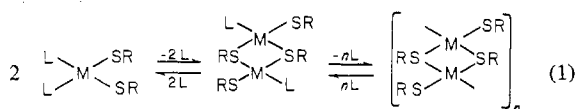
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Monomers of general formulas $M(\text{SPh})_2\text{L}_2$ ($M = \text{Ni, Pd, Pt, L} = \text{PMe}_2\text{Ph, DPPE, } c\text{-HxNC}$; $M = \text{Pd, Pt, L} = \text{DIARS}$) and $M(\text{SCH}_2\text{CH}_2\text{S})\text{L}_2$ ($M = \text{Ni, Pd, Pt, L} = \text{PMe}_2\text{Ph}$; $M = \text{Ni, L} = \text{DPPE}$; $M = \text{Pd, L} = \text{DIARS}$) have been prepared by cleavage of the polymers $[\text{M}(\text{SPh})_2]_n$ and $[\text{M}(\text{SCH}_2\text{CH}_2\text{S})]_n$ with the appropriate ligand. Anomalous $^1\text{H NMR}$ spectra are observed for complexes $\text{M}(\text{SCH}_2\text{CH}_2\text{S})(\text{PMe}_2\text{Ph})_2$. Complexes $\text{Pt}[\text{S}(\text{CH}_2)_3\text{S}]\text{L}_2$ ($\text{L} = \text{PPh}_3, \text{PMePh}_2$) and $\text{Pt}[\text{S}(\text{CH}_2)_3\text{S}](\text{L-L})$ ($\text{L-L} = \text{DPPE, } v\text{-DPPE}$), having six-membered rings, and $\text{Pt}[\text{S}(\text{CH}_2)_4\text{S}](\text{DPPE})$ having a seven-membered ring, have been prepared. The compound $\text{HS}(\text{CH}_2)_2\text{S}(\text{CH}_2)_3\text{SMe}$ and its coupled product with 1,3-dibromopropane, $\text{MeS}(\text{CH}_2)_3\text{S}(\text{CH}_2)_2\text{S}(\text{CH}_2)_3\text{S}(\text{CH}_2)_2\text{S}(\text{CH}_2)_3\text{SMe}$, have been isolated. The former reacts with $\text{Pt}(\text{PPh}_3)_3$ to give the compound $\text{PtH}[\text{S}(\text{CH}_2)_2\text{S}(\text{CH}_2)_3\text{SMe}]\text{PPh}_3$, in which the terminal thioether group is uncoordinated. The trimeric oligomer $[\text{Ni}_3[\text{S}(\text{CH}_2)_2\text{S}(\text{CH}_2)_3\text{S}(\text{CH}_2)_2\text{S}]]_n(\text{BF}_4)_2$ has been synthesized. The complex shows intense absorptions at 498 nm (ϵ 3700), 424 nm (ϵ 8500), and 293 nm (ϵ 23 200). In acetonitrile solution two polarographic waves are observed at -300 and -700 mV.

In a previous article³ we described some of our work directed at developing specific synthetic routes to monomers, dimers, and short-chain oligomers within the nickel triad of elements. The work was limited to the bidentate ligands 1,2-ethanedithiol and 2-(methylthio)ethanedithiol. In order to further pursue this problem one must appreciate that the coordination chemistry of simple thiols is complicated by two features: oligomer formation through strong thiolato bridges and oxidation of thiol to disulfide by metals in high oxidation states, with a concomitant reduction of the metal center. The second feature does not occur to any appreciable extent with metals of the nickel triad, but formation of thiolato bridges does frequently lead to polymeric materials which are difficult to purify and characterize. Oligomer formation in these systems arises from the initially formed terminal thiolate undergoing a substitution reaction with a ligand L on a second metal to give a bridged thiolate dimeric aggregate. Successive substitutions in this manner lead to the development of long-chain oligomer (eq 1). One aspect of this current work is to identify the salient



properties of metal M, substituent R, and ligand L which govern the conditions for interconversions between long-chain oligomers and monomers in the nickel triad.

A second aspect of this work is to extend our study on complexes of 1,2-ethanedithiol (esH_2) to those of dithiols having longer methylene chains. The es complexes contain a five-membered chelate ring, and in this paper we describe the results of our investigations leading to the isolation of similar complexes having six- and seven-membered chelate rings.

The final section of this article is devoted to considerations regarding specific synthetic routes to complexes containing two and three metal atoms. A number of investigators have reported compounds having a pair of nickel, palladium, or platinum atoms bridged by thiolato groups, but there appears to be only one group of comparable complexes having three nickel atoms. Thiolato-bridged complexes of type shown in eq 1, which have either two palladium or platinum atoms, have been reported for the case where L is a phosphine ligand.³⁻⁵ Brubaker has reported the synthesis of a series of thiolato-bridged nickel dimers where the ligand is a Schiff base type,⁶ and Busch in a series of papers has made a detailed study of

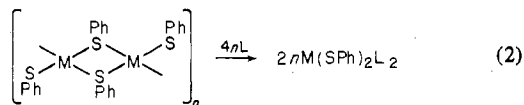
nickel oligomers with 2-aminoethanedithiol and related ligands.⁷⁻¹⁰ A nickel dimer has also been prepared using the tridentate dithiol bis(2,2'-ethanedithiol) sulfide.¹¹ The structure of this complex has been solved and shows that the thiolato bridge groups fold to allow the nickel atoms to closely approach each other.^{12,13} Little previous effort appears to have been devoted toward the specific synthesis of trimetallic oligomers, except for a report by Busch et al. describing the successful insertion of a third metal atom between two monomeric units of the complexes from 2-aminoethanedithiol.^{7,8} Bridging between the metals occurs via the thiolato groups and a crystal structure of $[\text{Ni}[\text{Ni}(\text{NH}_2\text{CH}_2\text{CH}_2\text{S})_2]_2]\text{Cl}_2$ has been solved.¹⁴ In this article we describe our results from a study of the coordination chemistry of 1,4,8,11-tetrathiaundecane with divalent nickel and discuss the reasons that we consider this ligand to be particularly promising for use in the directed synthesis of trimetallic oligomers.

Much interest has recently been shown in the synthesis and chemistry of multimetallic compounds of Fe, Co, and Mo with thiolato ligands because of their importance in biological systems. Our choice of the nickel triad was made because the compounds obtained can be anticipated to be either tetra-coordinate or square planar and to be kinetically inert. Even though octahedral complexes would be expected to behave in a similar manner, a greater number of ligands could be substituted by thiolato groups, and bridge formation could lead to three-dimensional rather than two-dimensional oligomers. This consequently causes an increase in the number of possible isomers and hence in the complexity of the system.

Results and Discussion

Bridge Cleavage. The chemistry of homoleptic transition metal thiolates is dominated by the tendency of this class of compounds to aggregate through sulfur bridges.¹⁵⁻¹⁷ Our recent work leading to the synthesis of monomeric metal thiolates by reductive elimination of HCl from compounds of the type $\text{IrHCl}(\text{SR})\text{CO}(\text{PPh}_3)_2$ ¹⁸ or by chelate-assisted oxidative addition reactions³ has prompted us to search for general convenient synthetic routes to discrete monomeric transition metal thiolates. A method which has proven to be of good success is the cleavage of thiolato-bridged polymers by strongly coordinating ligands. When halides of the nickel triad are treated with thiols, the thiolato-bridged polymer is formed in quantitative yield. These thermally stable materials have previously been regarded as unreactive and of little synthetic value. Treating these polymers with substituted

phosphines, arsines, or isocyanides has led to the isolation of monomers in a number of cases. Indeed it will be shown that, for several of the new complexes which have been prepared, this method of preparation is the preferred synthetic route. The complexes prepared by this route are shown in eq 2 and

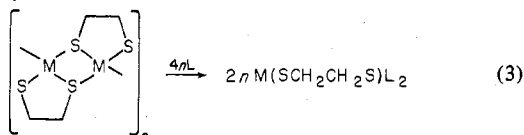


M = Ni; L = PMe_2Ph ,¹⁵ DPPE,¹⁵ c-HxNC

M = Pd; L = PMe_2Ph , DPPE,¹⁵ DIARS,¹⁹ c-HxNC

M = Pt; L = PMe_2Ph ,²⁰ DPPE,¹⁹ DIARS, c-HxNC

3. The polymers derived from 1,2-ethanedithiol $[\text{M}(\text{es})]_n$ (M



M = Ni; L = PMe_2Ph , DPPE³

M = Pd; L = PMe_2Ph ,³ DIARS³

M = Pt; L = PMe_2Ph

= Ni, Pd, Pt)²¹ react with PMe_2Ph in refluxing CH_2Cl_2 to yield monomeric complexes $\text{M}(\text{es})(\text{PMe}_2\text{Ph})_2$. The oligomers $[\text{Ni}(\text{es})]_n$ and $[\text{Pd}(\text{es})]_n$ can also be cleaved with DPPE and DIARS, respectively, to give $\text{Ni}(\text{es})(\text{DPPE})$ and $\text{Pd}(\text{es})(\text{DIARS})$. The platinum polymer is more inert to cleavage. When an electron-withdrawing group such as phenyl is used as substituent on the thiolate, the bridge is more easily cleaved. By treating the compound $[\text{M}(\text{SPh})_2]_n$ with the appropriate ligand the following monomers have been prepared: $\text{M}(\text{SPh})_2(\text{PMe}_2\text{Ph})_2$ [M = Ni, Pd, Pt], $\text{M}(\text{SPh})_2(\text{DPPE})$ [M = Ni, Pd, Pt], and $\text{M}(\text{SPh})_2(\text{DIARS})$ [M = Pd, Pt] (eq 2). The greater facility for cleavage of $[\text{M}(\text{SPh})_2]_n$ over $[\text{M}(\text{es})]_n$ is apparent since only PMe_2Ph of the above ligands will cleave $[\text{M}(\text{es})]_n$. The higher reactivity of the benzenethiolate oligomers $[\text{M}(\text{SPh})_2]_n$ is further shown by their ready cleavage with cyclohexyl isocyanide, a reaction not observed with $[\text{M}(\text{es})]_n$. When the compounds $[\text{M}(\text{SPh})_2]_n$ (M = Ni, Pd, Pt) are treated with cyclohexyl isocyanide the monomers $\text{M}(\text{SPh})_2(\text{c-HxNC})_2$ are obtained in high yield (M = Ni, ν_{NC} 2200 cm^{-1} ; M = Pd, ν_{NC} 2218 cm^{-1} ; M = Pt, ν_{NC} 2200, 2225 cm^{-1} , as solutions in CH_2Cl_2). The bright green nickel compound dissociates in solution and must be recrystallized from excess ligand. These complexes represent the first examples of thiolato complexes with isocyanide ligands. The ready isolation of these compounds shows the potential value of such a synthetic route to metal thiolates since alternative routes to such complexes are restricted by the reactivity of coordinated isocyanides toward nucleophiles (ROH, RSH, R_2NH) to yield imido ester derivatives.²²

The ^1H NMR spectra of complexes $\text{M}(\text{es})(\text{PMe}_2\text{Ph})_2$ show unexpected features. Complexes of type $\text{M}(\text{es})\text{L}_2$ must necessarily have mutually cis L groups, and when L = PMe_2Ph , this should cause the methyl resonance in the ^1H NMR spectrum to appear as a double doublet. In our previous paper³ we have reported that the observed pattern for the methyl resonance in $\text{Pd}(\text{es})(\text{PMe}_2\text{Ph})_2$ could only be interpreted on the basis of J_{PP} being larger than anticipated for two mutually cis phosphines. We have now prepared $\text{Ni}(\text{es})(\text{PMe}_2\text{Ph})_2$ and $\text{Pt}(\text{es})(\text{PMe}_2\text{Ph})_2$. The spectra of these compounds resemble that of the palladium analogue (the spectrum of $\text{Pt}(\text{es})(\text{PMe}_2\text{Ph})_2$ is shown in Figure 1) in that a separated triplet is not observed and virtual coupling occurs to a significant extent.^{23,24} The spectral data for all thiolato complexes with PMe_2Ph are collected in Table I. The ^1H NMR spectra of complexes $\text{M}(\text{SPh})_2(\text{PMe}_2\text{Ph})_2$ (M = Pd, Pt) in the methyl region show a triplet arising from virtual

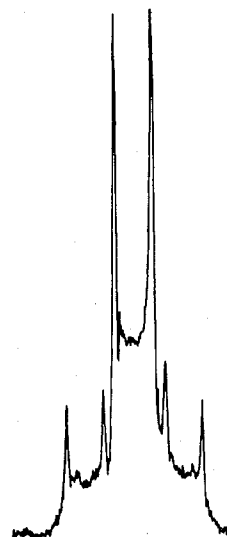


Figure 1. Methyl region of the ^1H NMR spectrum for $\text{Pt}(\text{es})(\text{PMe}_2\text{Ph})_2$.

Table I. ^1H NMR Spectral Data in the Methyl Region for Complexes $\text{M}(\text{es})(\text{PMe}_2\text{Ph})_2$ and $\text{M}(\text{SPh})_2(\text{PMe}_2\text{Ph})_2$ (M = Ni, Pd, Pt)

Compd	Chem shift (methyl), τ	Multiplicity
$\text{Ni}(\text{es})(\text{PMe}_2\text{Ph})_2$	8.35 ($J_{\text{PH}} = 7$ Hz)	Doublet
$\text{Pd}(\text{es})(\text{PMe}_2\text{Ph})_2$	8.45	Ref 3
$\text{Pt}(\text{es})(\text{PMe}_2\text{Ph})_2$	8.37 ($J_{\text{PH}} = 10$ Hz, $J_{\text{PtH}} = 26$ Hz)	Doublet
$\text{Ni}(\text{SPh})_2(\text{PMe}_2\text{Ph})_2$	8.63	Singlet
$\text{Pd}(\text{SPh})_2(\text{PMe}_2\text{Ph})_2$	8.42 ($J_{\text{PH}} = 3.5$ Hz)	Triplet
$\text{Pt}(\text{SPh})_2(\text{PMe}_2\text{Ph})_2$	8.32 ($J_{\text{PH}} = 3.5$ Hz, $J_{\text{PtH}} = 27$ Hz)	Triplet

coupling. This could be regarded as evidence in favor of a trans stereochemistry for these benzenethiolato complexes. Nevertheless caution should be exercised since data from the complexes $\text{M}(\text{es})(\text{PMe}_2\text{Ph})_2$ have indicated that in these thiolato complexes the values of $J_{\text{PP}}(\text{cis})$ are larger than anticipated and we have no reliable assessment of $J_{\text{PP}}(\text{trans})$. Furthermore the methyl region in $\text{Ni}(\text{es})(\text{PMe}_2\text{Ph})_2$ gives rise to a sharp singlet. We believe this could be the first example of a case where cancelation of coupling constants leads to the observation of a single sharp resonance in the ^1H NMR spectrum. Such a situation has been reported in virtually coupled AXX' spin systems when investigated by ^{13}C NMR spectroscopy²⁵ but not to our knowledge in the ^1H NMR case. An alternative explanation, however, is that the single line results from conditions of exchange,²⁶ and the precise reason for this observed spectrum is being further investigated.

Six- and Seven-Membered Rings. Our work to date on dithiolato complexes of the nickel triad has been confined to the five-membered ring compounds derived from 1,2-ethanedithiol. We have now extended this study to the preparation of the six- and seven-membered ring compounds from 1,3-propanedithiol and 1,4-butanedithiol. The complexes all have platinum as the metal atom, since this metal is the one in the nickel triad most likely to form monomers.³ From 1,3-propanedithiol we have prepared the following complexes: $\text{Pt}(\text{ps})(\text{PPh}_3)_2$, $\text{Pt}(\text{ps})(\text{DPPE})$, $\text{Pt}(\text{ps})(\text{v-DPPE})$, and $\text{Pt}(\text{ps})(\text{PMePh}_2)_2$. The first three complexes of this series have been prepared by the addition of 1,3-propanedithiol and Et_3N to the appropriate dichloroplatinum(II) complex, and the final complex of the series has been prepared by cleavage of $[\text{Pt}(\text{ps})]_n$ with PMePh_2 . The yellow complexes are soluble in halocarbons.

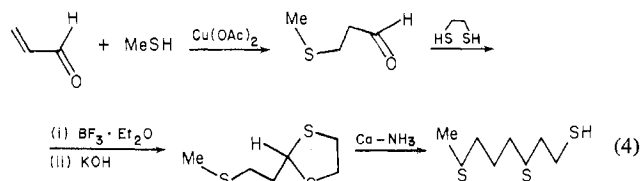
The ^1H NMR spectra give useful information regarding stoichiometry, as well as chemical shift and coupling constant

information. The methylene resonance on the central CH₂ group of the propane chain of 1,3-propanedithiol appears as a quintet ($J_{\text{HH}} = 7$ Hz). In the uncoordinated dithiol free rotation occurs, but upon coordination of the terminal thiolates this rotation is restricted and the propane backbone is locked into a puckered arrangement. Consequently this leads to a geometric arrangement where the two hydrogen atoms on the central methylene group became magnetically nonequivalent and can therefore have slightly different coupling constants to the terminal methylene hydrogens of the propane group. In the ¹H NMR spectrum of Pt(ps)(PPh₃)₂ this chemical shift difference is not resolvable and the spectrum appears as a slightly broadened quintet centered at τ 8.00 ($J_{\text{HH}} = 7$ Hz). The terminal methylenes in Pt(ps)(PPh₃)₂ appear as two overlapping triplets ($J_{\text{HH}} = 7$ Hz) with additional coupling to platinum ($J_{\text{PtH}} = 60$ Hz). These resonances are centered at τ 7.14 and 7.06 and arise from the sets of inequivalent terminal methylenic hydrogens. This inequivalence is a consequence of the rigid puckering of the methylenic backbone. The molecule does not have a symmetry plane through the four ligating atoms, and hence the hydrogens on the terminal methylenic group which lie above and below the plane are magnetically inequivalent. The ¹H NMR spectrum of Pt(ps)(DPPE) is closely analogous to that of Pt(ps)(PPh₃)₂ with the methylenic resonances from the 1,3-propanedithiolato backbone being centered at τ 7.95 (quintet, $J_{\text{HH}} = 7$ Hz), τ 7.07 (triplet, $J_{\text{HH}} = 7$ Hz, $J_{\text{PtH}} = 50$ Hz), and τ 7.00 (triplet, $J_{\text{HH}} = 7$ Hz, $J_{\text{PtH}} = 50$ Hz). Additionally there is a doublet ($J_{\text{PH}} = 17$ Hz) from the methylene backbone of DPPE centered at τ 7.87. For Pt(ps)(PMePh₂)₂ the additional resonances for the methyl group are centered at τ 8.30 with coupling to phosphorus ($J_{\text{PH}} = 9$ Hz) and platinum ($J_{\text{PtH}} = 27$ Hz).

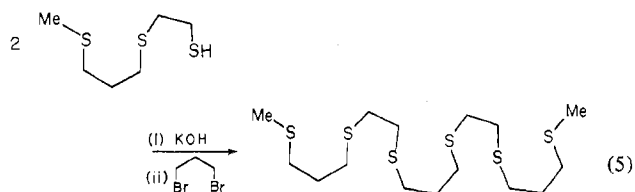
The seven-membered ring 1,4-butanedithiolato complex has been obtained by treating PtCl₂(DPPE) with 1,4-butanedithiol and Et₃N. The yield of monomer is considerably worse than was realized with the six-membered ring 1,3-propanedithiolato compound, and the tendency to form long chain oligomer considerably enhanced. Since this oligomerization proceeds by a mechanism involving substitution of the phosphine by the coordinated thiolate, the only satisfactory manner in which the monomeric platinum complex with a seven-membered ring can be isolated is by using the chelating DPPE ligand. Assignments of individual lines in the ¹H NMR spectrum to specific methylenic hydrogens were not attempted because of considerable overlapping. We have been unsuccessful in isolating significant amounts of monomer from higher dithiolates. Oligomerization appears to be very facile, and in cases where the polymer cleavage reaction is somewhat successful, the product has a tendency to rapidly revert back to polymer in the absence of excess phosphine.

Multidentate Thiolato-Thioether Ligands. In our previous paper³ we reported that addition of 2-(methylthio)ethanethiol, HSCH₂CH₂SMe, to Pt(PPh₃)₃ gave the hydroplatinum(II) complex PtH(SCH₂CH₂SMe)(PPh₃). A comment was made³ that this reaction represented an unusual type, since in all other reports of reactions involving addition of HX to Pt(PPh₃)₃ the product has a stoichiometry corresponding to either PtHX(PPh₃)₂ or [PtH(PPh₃)₃]X.²⁷ In the earlier paper we termed this reaction a "chelate-assisted oxidative addition". We conceive this reaction as proceeding by initial addition of the S-H bond to the zerovalent platinum moiety, followed by subsequent displacement of the additional triphenylphosphine by the thioether group held in close proximity. Chelation doubtless plays a significant role in governing the stoichiometry of the final product; nevertheless it should be stressed that the primary step is oxidative addition. This leads to the conclusion that this type of chelate-assisted oxidative addition reaction

can result in enhancement of subsequent steps in a reaction sequence (such as replacement of triphenylphosphine by thioether) but cannot be used to significantly increase the equilibrium constant of the initial oxidative addition step. We have prepared 1,4,8-trithianonane, HS(CH₂)₂S(CH₂)₃SMe, in order to investigate whether this displacement of triphenylphosphine by thioether can be extended one step further. The chosen synthetic route is shown in eq 4. The ¹H NMR

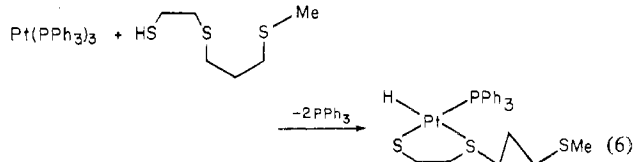


spectrum of the compound shows the anticipated resonances. Numbering from the thiol end of the molecule, the following assignments can be made: τ_{SH} 8.32 (broad), $\tau_{\text{CH}_2(1)}$ 7.32 (singlet), $\tau_{\text{CH}_2(2)}$ 7.25 (singlet), $\tau_{\text{CH}_2(3)}$ 7.43 (triplet, $J_{\text{HH}} = 7$ Hz), $\tau_{\text{CH}_2(4)}$ 8.17 (quintet, $J_{\text{HH}} = 7$ Hz), $\tau_{\text{CH}_2(5)}$ 7.35 (triplet, $J_{\text{HH}} = 7.5$ Hz), τ_{CH_3} 7.93 (singlet). It should be noted that the assignments for $\tau_{\text{CH}_2(1)}$ and $\tau_{\text{CH}_2(2)}$, and also for $\tau_{\text{CH}_2(3)}$ and $\tau_{\text{CH}_2(5)}$, may be reversed. 1,4,8-Trithianonane reacts with 1,3-dibromopropane in the presence of sodium ethoxide to give 2,6,9,13,16,20-hexathiaheneicosane MeS(CH₂)₃S(CH₂)₂S(CH₂)₃S(CH₂)₂S(CH₂)₃SMe (eq 5). Isolation of this col-



orless derivative, mp 33–36 °C, by treatment of 1,4,8-trithianonane in this manner with 1,3-dibromopropane, gives further support for our claimed preparation of 1,4,8-trithianonane. The ¹H NMR spectrum of 2,6,9,13,16,20-hexathiaheneicosane can be interpreted on the basis of the following assignments (it should be noted that the molecule is symmetrical about C(8)): τ_{Me} 8.00 (singlet), $\tau_{\text{CH}_2(1)}$ 7.37 (triplet, $J_{\text{HH}} = 7.5$ Hz), $\tau_{\text{CH}_2(2)}$, $\tau_{\text{CH}_2(8)}$ 8.07 (quintet, $J_{\text{HH}} = 7$ Hz), $\tau_{\text{CH}_2(3)}$, $\tau_{\text{CH}_2(6)}$ 7.44 (triplet, $J_{\text{HH}} = 7$ Hz), $\tau_{\text{CH}_2(4)}$, $\tau_{\text{CH}_2(5)}$ 7.33 (singlet).

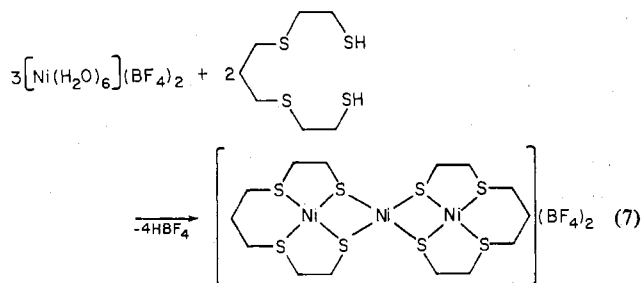
When Pt(PPh₃)₃ is treated with HS(CH₂)₂S(CH₂)₃SMe, a pale yellow hydroplatinum(II) complex PtH[S(CH₂)₂S(CH₂)₃SMe](PPh₃) is formed (eq 6). Although the complex



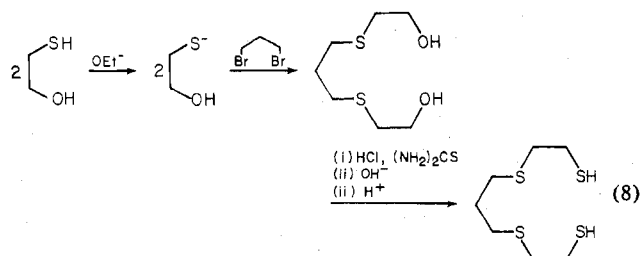
can be isolated as pale yellow plates, it is quite unstable and begins to decompose to a dark yellow solid in a matter of a few hours. Furthermore the complex is quite unstable to reductive displacement of the thiol by PPh₃. Consequently the isolation procedure must be effected in the presence of excess 1,4,8-trithianonane in order to avoid contamination with Pt(PPh₃)₃. The existence of a hydroplatinum(II) complex is evident from the observation of a band in the ir spectrum at 2140 cm⁻¹ and a doublet resonance ($J_{\text{PH}} = 18$ Hz) in the ¹H NMR spectrum centered at τ 20.6. The low-field portion of the ¹H NMR spectrum can be readily interpreted on the basis of a four-coordinate complex with the terminal thioether group uncoordinated. The following assignments can be made, numbering from the methylene group of the coordinated

thiolate: $\tau_{\text{CH}_2(1)}$, $\tau_{\text{CH}_2(2)}$ 8.10 (singlet), $\tau_{\text{CH}_2(3)}$ 7.17 (unresolved), $\tau_{\text{CH}_2(4)}$ 8.58 (quintet, $J_{\text{HH}} = 7$ Hz), $\tau_{\text{CH}_2(5)}$ 7.44 (triplet, $J_{\text{HH}} = 7$ Hz), τ_{Me} 7.90 (singlet). Comparison with the ^1H NMR spectrum of the free ligand shows that there are significant chemical shift differences for the methylenes adjacent to a coordinated sulfur atom, but further inspection shows that the resonances for both the $\text{CH}_2(5)$ and the methyl group are unshifted from their free ligand positions. This comparison is consistent with the terminal thioether group remaining uncoordinated because of the failure of the final triphenylphosphine molecule to undergo replacement.

Throughout this paper we have clearly defined the features required of the ligand system for the specific synthesis of thiolato monomers in the nickel triad. Specific synthetic routes to dimers are more difficult to develop. Our previous discovery that a dimer $[\text{Pd}(\text{es})\text{PPh}_3]_2$ was the sole product from treating $\text{PdCl}_2(\text{PPh}_3)_2$ with esH_2 and Et_3N showed that judicious ligand choice could be used to effect the partial ligand replacement necessary for dimer formation. Nevertheless in order to exploit this method considerable experimentation with each individual system will be necessary. A more viable choice of ligand for dimer synthesis is the compound bis(2,2'-ethanethiol) sulfide or ligands containing functional groups providing considerable steric hindrance.¹⁰ Use of bis(2,2'-ethanethiol) sulfide leads to dimers with sulfur groups in each coordination site. The compound TTU, $\text{HS}(\text{CH}_2)_2\text{S}(\text{C}-\text{H}_2)_3\text{S}(\text{CH}_2)_2\text{SH}$, can be potentially useful for the specific synthesis of trimers with sulfur groups in all ligating positions. If complete substitution occurs about the metal ion, the resulting monomer will have a pair of nonbridging cis thiolato groups, and hence two of these monomers should readily aggregate through a third metal ion to give a trimer. This reaction occurs with nickel. Treatment of $[\text{Ni}(\text{H}_2\text{O})_6](\text{BF}_4)_2$ with TTU leads to the formation of a trimer with sulfur as ligating atoms and two double thiolate bridges (eq 7).



The ligand TTU has been previously prepared by Busch et al. as an intermediate in the synthesis of a tetradentate macrocyclic ligand.²⁸ Their reported preparation commenced with 1,3-propanedithiol. We have found that an alternate route starting from 2-thioethanol can also be used as a convenient preparation of this material (eq 8).²⁹ The nickel complex of



TTU is a deep red color when in the bulk form but has a sheen similar to metallic copper when the material is allowed to precipitate onto a surface. The electronic spectrum of the complex in acetonitrile solution exhibits three broad intense bands at 498 nm (ϵ 3700), 424 nm (ϵ 8500), and 293 nm (ϵ 23 200). The spectrum in the solid state is closely similar. By

comparison the electronic spectrum of $[\text{Ni}(\text{SCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{S})_2]$ shows absorptions at 685 nm (ϵ 155), 510 nm (ϵ 1780), 388 nm (ϵ 2230), 303 nm (ϵ 16 000), and 259 nm (ϵ 22 400).¹¹ Assignments of transitions in multimetallic square-planar complexes of Ni(II) are difficult to perform with any confidence; however, it appears that the absorptions in $[\text{Ni}_3(\text{TTU})_2](\text{BF}_4)_2$ closely resemble those in mononuclear nickel(II) complexes with sulfur donor ligands.^{30,31}

The compound $[\text{Ni}_3(\text{TTU})_2](\text{BF}_4)_2$ is diamagnetic and shows no detectable ESR signal. The complex dissolves in acetonitrile to give a deep red solution. The square-planar geometry shown by this complex correlates well with previous studies on similar materials, where it has been found that sulfur ligands favor square-planar over tetrahedral geometry for divalent nickel²⁸ and that addition of additional ligands such as pyridine into the octahedral positions is unfavorable.⁷ The structure of $[\text{Ni}_3(\text{TTU})_2](\text{BF}_4)_2$ has not been elucidated but a number of predictions can be made with a high degree of confidence. The molecule will have a square-planar geometry about each nickel atom, but the overall geometry will be puckered because of the dihedral angles of the nickel planes through the bridging sulfurs. There exists the possibility that the conformation could be either a chair form or a boat form; however confirmation that $[\text{Ni}_3(\text{SCH}_2\text{CH}_2\text{NH}_2)_4]\text{Cl}_2$ exists in the chair conformation¹⁴ makes that structure the anticipated one. The boat form has been observed with $[\text{Ni}(\text{Set})_2]_6$,³² but this is probably a forced conformation due to the cyclic structure of this hexamer.

The complex $[\text{Ni}_3(\text{TTU})_2](\text{BF}_4)_2$ in acetonitrile solution does not undergo electrolytic oxidation up to a potential of 1.2 V. On reduction, however, two polarographic waves are observed. The first reduction occurs at -300 mV, and the second at -700 mV. The first wave is characteristic of an irreversible one-electron reduction, and by comparison of the relative wave heights it is apparent that the second wave also represents a single electron reduction. By comparison it should be noted that $[\text{Ni}(\text{SCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{S})_2]$ does not undergo reduction until -860 mV. This potential is higher since the second molecule is not positively charged, and there are only two, rather than three, nickel atoms for possible conjugation. Further work is in progress on the electrochemistry of these and related compounds.

Experimental Section

Benzenethiol, 1,2-ethanedithiol, 1,3-propanedithiol, and 1,4-butanedithiol were commercial samples and not purified prior to use. Potassium tetrachloroplatinate and sodium tetrachloropalladate were purchased from Engelhard Inc. Microanalyses were carried out by Galbraith Laboratories, Inc. Triphenylphosphine, 1,2-bis(diphenylphosphino)ethane, 1,2-bis(diphenylphosphino)ethylene, and 1,2-bis(dimethylarsino)benzene were commercial samples. Methylidiphenylphosphine and dimethylphenylphosphine were prepared by treating the Grignard reagent from methyl iodide with distilled chlorodiphenylphosphine and dichlorophenylphosphine, respectively, with subsequent purification by vacuum distillation. ^1H NMR spectra were obtained on Varian T-60 and Jeol MH 100 spectrometers. Electronic spectra were obtained on a Cary 14 spectrometer. Infrared spectra were measured on Perkin-Elmer Model 457 and 700 spectrometers as Nujol mulls. Conductivities were measured using an Industrial Instruments Model RC 1682 conductivity bridge. All synthetic operations were carried out under an atmosphere of nitrogen.

Bis(thiophenolato)bis(cyclohexyl isocyanide)nickel(II), $\text{Ni}(\text{SPh})_2(\text{c-HxNC})_2$. A suspension of $[\text{Ni}(\text{SPh})_2]_n$ (276 mg) in CH_2Cl_2 (20 ml) was refluxed with cyclohexyl isocyanide (0.3 ml) for 3 min. The solution was allowed to cool and the complex precipitated by addition of hexane. After two recrystallizations from $\text{c-HxNC}-\text{CH}_2\text{Cl}_2$ -hexane, grass green crystals were eventually obtained by dissolving the material in CH_2Cl_2 (~5 ml), slowly adding hexane (30 ml), passing nitrogen over the solution to remove a portion of the CH_2Cl_2 , and finally cooling the solution at 0 °C for 2 h; mp 128-132 °C. Anal. Calcd for $\text{C}_{26}\text{H}_{32}\text{NiN}_2\text{S}_2$: C, 63.1; H, 6.47; N, 5.65. Found: C, 62.1; H, 6.53; N, 6.20. The initial yield was essentially

quantitative. The analytical data indicate slight contamination with $[\text{Ni}(\text{SPh})_2]_n$.

Bis(thiophenolato)bis(dimethylphenylphosphine)palladium(II), Pd(SPh)₂(PMe₂Ph)₂. Using a similar procedure as above with $[\text{Pd}(\text{SPh})_2]_n$ (162 mg) and PMe₂Ph (0.15 ml), the complex was obtained as orange crystals; yield 270 mg (90%); mp 154 °C dec. Anal. Calcd for C₂₈H₃₂PdP₂S₂: C, 56.0; H, 5.32; S, 10.7. Found: C, 56.0; H, 5.42; S, 11.0.

Bis(thiophenolato)-1,2-bis(dimethylarsino)benzenepalladium(II), Pd(SPh)₂(DIARS). Again using a similar procedure with $[\text{Pd}(\text{SPh})_2]_n$ (108 mg) and DIARS (0.07 ml), the complex was obtained as large orange crystals; yield 188 mg (93%); mp 174–176 °C. Anal. Calcd for C₂₂H₂₆As₂PdS₂: C, 43.3; H, 4.26; S, 10.5. Found: C, 43.2; H, 4.27; S, 10.6.

Bis(thiophenolato)bis(cyclohexyl isocyanide)palladium(II), Pd(SPh)₂(c-HxNC)₂. Again using a similar procedure with $[\text{Pd}(\text{SPh})_2]_n$ (162 mg) and cyclohexyl isocyanide (0.4 ml), with a reflux time of 15 min, the complex was obtained as orange crystals; yield 252 mg (93%); mp 120 °C dec. Anal. Calcd for C₂₆H₃₂N₂PdS₂: C, 57.5; H, 5.90; N, 5.16. Found: C, 57.2; H, 5.90; N, 5.10.

Bis(thiophenolato)-1,2-bis(diphenylphosphino)ethaneplatinum(II), Pt(SPh)₂(DPPE). A suspension of $[\text{Pt}(\text{SPh})_2]_n$ (207 mg) in CH₂Cl₂ was refluxed for 5 h with DPPE (200 mg). Precipitation with hexane, followed by two recrystallizations from CH₂Cl₂-hexane, gave the complex in pure form; yield 320 mg (80%); mp 228–232 °C. Anal. Calcd for C₃₈H₃₄P₂PtS₂: C, 56.2; H, 4.20; S, 7.90. Found: C, 56.0; H, 4.30; S, 7.91.

Bis(thiophenolato)-1,2-bis(dimethylarsino)benzeneplatinum(II), Pt(SPh)₂(DIARS). Using the procedure for the previous complex with $[\text{Pt}(\text{SPh})_2]_n$ (207 mg) in CH₂Cl₂ and 1,2-dimethyl(arsino)benzene (300 mg), the complex was obtained after precipitation with hexane. Purification was effected by three recrystallizations from CH₂Cl₂-hexane; yield 300 mg (61%); mp 196–198 °C. Anal. Calcd for C₂₂H₂₆As₂PtS₂: C, 37.8; H, 3.72; S, 9.17. Found: C, 37.9; H, 3.44; S, 9.14.

Bis(thiophenolato)bis(cyclohexyl isocyanide)platinum(II), Pt(SPh)₂(c-HxNC)₂. A suspension of $[\text{Pt}(\text{SPh})_2]_n$ (207 mg) in CH₂Cl₂ was refluxed for 10 min with excess (~15 drops) cyclohexyl isocyanide. The compound was precipitated by addition of hexane and recrystallized twice from CH₂Cl₂-hexane; yield 250 mg (59%); mp 149–152 °C. Anal. Calcd for C₂₆H₃₂N₂PtS₂: C, 49.5; H, 5.07; N, 4.44. Found: C, 49.3; H, 4.85; N, 4.54.

1,2-Ethanedithiolatobis(dimethylphenylphosphine)nickel(II), Ni(es)(PMe₂Ph)₂. $[\text{Ni}(\text{es})]_n$ (300 mg) was suspended in refluxing CH₂Cl₂ (20 ml) and PMe₂Ph (0.28 ml) was added. Dissolution occurred, and after 20 min the solution was allowed to cool to room temperature. The compound was precipitated with hexane and recrystallized from CH₂Cl₂-hexane in the presence of a little added PMe₂Ph. Large lustrous dark brown crystals formed; yield 460 mg (80%); mp 164 °C. Anal. Calcd for C₁₈H₂₆NiP₂S₂: C, 50.6; H, 6.09. Found: C, 50.1; H, 6.30.

1,2-Ethanedithiolatobis(dimethylphenylphosphine)platinum(II), Pt(es)(PMe₂Ph)₂. A suspension of $[\text{Pt}(\text{es})]_n$ in CH₂Cl₂ (20 ml) was refluxed for 90 min with PMe₂Ph (~12 drops). Filtration, dilution with heptane, and removal of CH₂Cl₂ on a rotary evaporator gave a colorless crystalline compound. Recrystallization from CH₂Cl₂-heptane gave the pure complex; yield 135 mg (72%); mp 175–179 °C. Anal. Calcd for C₁₈H₂₆P₂PtS₂: C, 38.4; H, 4.62; S, 11.4. Found: C, 38.1; H, 4.86; S, 10.5.

1,3-Propanedithiolatobis(triphenylphosphine)platinum(II), Pt(ps)(PPh₃)₂. To a suspension of *cis*-PtCl₂(PPh₃)₂ (100 mg) in CH₂Cl₂ (15 ml) was added excess 1,3-propanedithiol (2 drops) and Et₃N (4 drops). Evolution of Et₃N·HCl occurred and the solution changed from colorless to yellow. Ethanol was added and CH₂Cl₂ was removed on a rotary evaporator. The yellow precipitate was filtered, washed with a small quantity of water to remove Et₃N·HCl, and washed well with ethanol and diethyl ether; yield 93 mg (89%). The complex was recrystallized from CH₂Cl₂-ethanol; mp 220–225 °C. Anal. Calcd for C₃₉H₃₆P₂PtS₂: C, 56.7; H, 4.39; S, 7.77. Found: C, 56.8; H, 4.59; S, 7.90.

1,3-Propanedithiolatobis(diphenylphosphino)ethaneplatinum(II), Pt(ps)(DPPE). The complex PtCl₂(DPPE) was first prepared by refluxing a mixture of K₂PtCl₄ (0.96 g) and DPPE (1.00 g) in a solution of chloroform (17 ml) and ethanol (17 ml). After 8 h the mixture was cooled to room temperature and filtered. After being washed with water, the crude solid was heated at 80 °C in DMF (12

ml) until solution was complete. Slow addition of ether gave PtCl₂(DPPE) as colorless crystals which were filtered, washed with ether, and dried in vacuo; mp >300 °C. The compound is a non-conductor in chloroform. The conversion of this product into Pt(ps)(DPPE) followed the procedure used for the preparation of Pt(ps)(PPh₃)₂. The compound was recrystallized twice from chloroform-ethanol; mp 273–274 °C. TLC in CH₂Cl₂-acetone (10:1) on alumina showed a single spot. Anal. Calcd for C₂₉H₃₀P₂PtS₂: C, 49.8; H, 4.32. Found: C, 49.6; H, 4.12.

1,3-Propanedithiolatobis(diphenylphosphino)ethyleneplatinum(II), Pt(ps)(v-DPPE). The complex PtCl₂(PhCN)₂ was prepared by treating K₂PtCl₄ with benzonitrile for 32 days in aqueous solution. This compound was converted into PtCl₂(v-DPPE) by treatment with v-DPPE for 2 h in CH₂Cl₂. The compound PtCl₂(v-DPPE) (250 mg), excess 1,3-propanedithiol (5 drops), and Et₃N (6 drops) were stirred together in CH₂Cl₂ until the transient brown color of the solution had changed to yellow. The solution was filtered, hexane was added, and the volume of solution was reduced on a rotary evaporator until precipitation was effected. The compound was washed with water and diethyl ether. Recrystallization from CH₂Cl₂-diethyl ether gave the pure complex; yield 90 mg (34%); mp 271–274 °C. Anal. Calcd for C₂₉H₂₈P₂PtS₂: C, 49.9; H, 4.05. Found: C, 50.1; H, 3.92.

1,3-Propanedithiolatobis(methyldiphenylphosphino)platinum(II), Pt(ps)(PMePh₂)₂·1/2CH₂Cl₂. To a solution of K₂PtCl₄ (260 mg) in ethanol (8 ml) and water (8 ml) was added excess 1,3-propanedithiol (8 drops). The red-brown polymer $[\text{Pt}(\text{ps})]_n$ was removed by filtration. This compound was then suspended in CH₂Cl₂ and excess PMePh₂ (14 drops) was added. After 18 h the pale yellow solution was filtered and the volume of the solution was reduced to 1–2 ml. Addition of ether gave an oily precipitate which solidified after 48 h at 0 °C. This pale yellow precipitate (mp 120–138 °C) was recrystallized from CH₂Cl₂-diethyl ether; yield 282 mg (62%). Final purification was effected by dissolving the sample in a mixture of CH₂Cl₂-acetone (10:1) and eluting the material on a 10-ml column of neutral alumina. Addition of diethyl ether to the concentrated solution gave the complex as yellow crystals; final yield 170 mg (37%). The complex was dried in vacuo for 80 h at 50 °C; mp 140–141 °C. Anal. Calcd for C₂₉H₃₃ClP₂PtS₂: C, 47.8; H, 4.47. Found: C, 47.8; H, 5.00. The ¹H NMR spectrum of the dried sample showed the presence of CH₂Cl₂ in an amount corresponding to one-half molecule per molecule of platinum complex.

1,4-Butanedithiolatobis(diphenylphosphino)ethaneplatinum(II), Pt(bs)(DPPE). To a suspension of PtCl₂(DPPE) (100 mg) in CH₂Cl₂ (15 ml) was added excess 1,4-butanedithiol (2 drops) and Et₃N (2 drops). Evolution of Et₃N·HCl occurred and the reaction mixture became pale yellow. After stirring of the mixture for 5 h, it was filtered using filter aid. The volume of the solution was reduced to 1–2 ml, diethyl ether was added, and the mixture was allowed to stand for 12 h at 0 °C. The resulting precipitate was filtered, washed with a little water, and dried in vacuo. TLC in CH₂Cl₂-acetone (10:1) on alumina showed two spots, one of which had an R_f value of zero and was apparently the polymer $[\text{Pt}(\text{bs})]_n$. This crude product was purified by chromatography on silica (60–200 mesh) using CH₂Cl₂-acetone (10:1) as eluent. The volume of the solution was reduced by means of a rotary evaporator, and the complex isolated by addition of diethyl ether and cooling the solution to 0 °C. The complex was filtered and dried in vacuo at 50 °C for 48 h; yield 28 mg (18%); mp 227–228 °C. Anal. Calcd for C₃₀H₃₂P₂PtS₂: C, 50.5; H, 4.52; S, 8.99. Found: C, 50.4; H, 4.30; S, 8.74.

1,4,8-Trithianone (TTN), HS(CH₂)₂S(CH₂)₃SMe. Methanethiol (25 g) was slowly added to a mixture of copper acetate (0.25 g) and stabilized acrolein. The reaction mixture was kept below 40 °C by an ice bath during the addition. The reaction mixture was stirred overnight and filtered, and the intermediate 3-(methylthio)propionaldehyde (36 g) was purified by distillation (bp 52 °C (11 mm)). This material was mixed with a solution of ethanedithiol (30 ml) in CHCl₃ (40 ml) and the solution was added to a mixture of BF₃·Et₂O (60 ml), CHCl₃ (200 ml), and acetic acid (100 ml). The mixture became hot and refluxed. The mixture was extracted with a 10% KOH solution (5 × 200 ml) and then water (200 ml). The organic layer was dried over MgSO₄. The filtered solution was reduced in volume to ~60 ml, and the orange oil was distilled (bp 114 °C (0.5 mm)); yield 46 g of the second intermediate (eq 4). This compound was added to anhydrous ammonia (1.5 l) and then diethyl ether (50 ml) was added. To the reaction mixture was added calcium (15% excess) and the ammonia was allowed to evaporate. After 18 h 1 N HCl (1

1.) was added, the mixture stirred, and a further portion (200 ml) of 1 N HCl added. The mixture was extracted with diethyl ether (4 × 150 ml), dried with MgSO₄, and purified by distillation (bp 119–121 °C (1.75 mm)); yield 32.7 g. Anal. Calcd for C₆H₁₄S₃: C, 39.5; H, 7.7; S, 52.9. Found: C, 39.5; H, 7.6; S, 53.1.

Hydro(1,4,8-trithianone)triphenylphosphineplatinum, PtH[(CH₂)₂S(CH₂)₃SMe](PPh₃)₃. To a filtered solution of Pt(PPh₃)₃ (2.09 g) in benzene (50 ml) was added excess TTN. The mixture was allowed to stand under nitrogen for 18 h. Benzene was removed on a rotary evaporator until the volume of the solution was ~5 ml, and diethyl ether, containing a little TTN, was added (50 ml). Cooling the solution at 0 °C gave large yellow crystals; yield 0.92 g (86%); mp 115–117 °C. Anal. Calcd for C₂₄H₂₉P₃S₃: C, 45.1; H, 4.57. Found: C, 44.8; H, 4.52.

1,4,8,11-Tetrathiaundecane (TTU). Sodium (4.6 g) was dissolved in ethanol (180 ml). The solution was cooled to 10 °C and 2-thioethanol (15.6 g) was added. To this solution was slowly added 1,3-dibromopropane (20.1 g) keeping the temperature below 15 °C. The NaBr formed was filtered and the volume of solution reduced. The intermediate, HO(CH₂)₂S(CH₂)₃S(CH₂)₂OH, was purified by distillation (bp 147–154 °C (1 mm)); yield 13.5 g. To this material was added thiourea (10.6 g) and concentrated HCl (36 ml). The mixture was refluxed 12 h. To the cooled solution was added KOH (23 g) in water (140 ml), and the mixture was further refluxed for 3 h. The compound^{28,29} was obtained by distillation after acidification of this reaction mixture.

Bis(1,4,8,11-tetrathiaundecane)trinickel Bis(tetrafluoroborate), [Ni₃(TTU)₂](BF₄)₂. To a solution of [Ni(H₂O)₆](BF₄)₂ (762 mg) in ethanol (30 ml) was added TTU (460 mg) in ethanol. The complex precipitated as a red-brown solid. The complex was filtered, washed with ethanol and diethyl ether, and dried in vacuo; yield 570 mg (100%). Anal. Calcd for C₁₄H₂₈B₂F₈Ni₃S₈: C, 21.0; H, 3.52; S, 32.0. Found: C, 21.5; H, 3.51; S, 31.7.

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Registry No. Ni(SPh)₂(c-HxNC)₂, 59738-09-9; Pd(SPh)₂(PMe₂Ph)₂, 59738-10-2; Pd(SPh)₂(DIARS), 59738-11-3; Pd(SPh)₂(c-HxNC)₂, 59738-12-4; Pt(SPh)₂(DPPE), 33971-06-1; Pt(SPh)₂(DIARS), 59765-76-3; Pt(SPh)₂(c-HxNC)₂, 59738-13-5; Ni(es)(PMe₂Ph)₂, 59738-14-6; Pt(es)(PMe₂Ph)₂, 59738-15-7; Pt(ps)(PPh₃)₂, 59738-16-8; Pt(ps)(DPPE), 59738-17-9; Pt(ps)(v-DPPE), 59738-18-0; Pt(ps)(PMePh₂), 59738-19-1; Pt(bs)(DPPE), 59738-20-4; PtH(S(CH₂)₂S(CH₂)₃SMe)(PPh₃), 59738-21-5; [Ni₃(TTU)₂](BF₄)₂, 59738-24-8; Ni(SPh)₂(PMe₂Ph)₂, 59738-22-6; Pt(SPh)₂(PMe₂Ph)₂, 59779-78-1; TTN, 59738-59-9; TTU, 25676-62-4; [Ni(SPh)₂]_n, 28210-32-4; [Pd(SPh)₂]_n, 59738-64-6; [Pt(SPh)₂]_n, 59738-65-7; [Pt(es)]_n, 59738-61-3; *cis*-PtCl₂(PPh₃)₂, 15604-36-1; PtCl₂(DPPE), 19998-23-3; PtCl₂(PhCN)₂, 14873-63-3; [Pt(ps)]_n, 59738-63-5; methanethiol, 74-93-1; acrolein, 107-02-8; 3-(methylthio)propionaldehyde, 3268-49-3; ethanedithiol, 26914-40-9; C₆H₁₂S₃, 59007-87-3;

Pt(PPh₃)₃, 13517-35-6; 2-thioethanol, 60-24-2; 1,3-dibromopropane, 109-64-8; HO(CH₂)₂S(CH₂)₃S(CH₂)₂OH, 16260-48-3; thiourea, 62-56-6.

References and Notes

- Presented in part at the 30th Northwest Regional Meeting of the American Chemical Society, Honolulu, June 1975, and the First Chemical Congress of the North American Continent, Mexico City, Dec 1975; see Abstracts, No. INOR 91.
- The following abbreviations are used: DPPE, 1,2-bis(diphenylphosphino)ethane; DIARS, 1,2-bis(dimethylarsino)benzene; v-DPPE, *cis*-1,2-bis(diphenylphosphino)ethylene; es, 1,2-ethanedithiolate; ps, 1,3-propanedithiolate; bs, 1,4-butanedithiolate; TTN, 1,4,8-trithianone; TTU, 1,4,8,11-tetrathiaundecane.
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