Synthesis and Reactions of New Complexes of Nickel, Palladium, and Platinum with 1,2-Ethanedithiol, 2-(Methylthio)ethanethiol, and 2-(Methylthio)ethane Disulfide[1]

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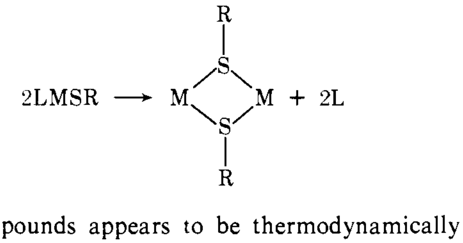
Abstract: 1,2-Ethanedithiol reacts with $Pt(PPh_3)_4$, $Pd(PPh_3)_4$, and $Ni(PPh_3)_4$ to give a monomer $Pt(SCH_2CH_2S)_2(PPh_3)_2$, dimer $Pd_2(SCH_2CH_2S)_4(PPh_3)_2$, and a dimer or polymer, respectively. The same compound can be obtained by treating the appropriate dihalo compound with 1,2-ethanedithiol in base. The palladium dimer cleaves with PMe_2Ph to give $Pd(SCH_2CH_2S)_2(PMe_2Ph)_2$. Monomers $Pd(SCH_2CH_2S)_2(diars)$ and $Ni(SCH_2CH_2S)_2(diphos)$ are obtained when the corresponding dichlorides are treated with 1,2-ethanedithiol. The addition of EtSH to $Pt(PPh_3)_4$ gives the unstable compound $PtH(SEt)(PPh_3)_2$. 2-(Methylthio)ethanethiol reacts with $Pt(PPh_3)_4$ to give the stable compound $PtH(SCH_2CH_2SMe)(PPh_3)$. The difference in stoichiometry and stability is a consequence of the chelate effect. With $Pd(PPh_3)_4$ and $MeSCH_2CH_2SH$ the product is the dimer obtained from 1,2-ethanedithiol and has arisen from a demethylation reaction. With $Ni(PPh_3)_4$ the nonchelated $Ni(SCH_2CH_2SMe)_2(PPh_3)_2$ is formed. Dimethyl disulfide does not react with $Pt(PPh_3)_4$ but $(MeSCH_2CH_2S)_2$ readily gives $Pt(SCH_2CH_2SMe)_2(PPh_3)$. This compound has one free and one coordinated *S*-methyl group, and its formation is a further example of chelate assisted addition. With $Pd(PPh_3)_4$ all the phosphines are displaced, and a polymer, $[Pd(SCH_2CH_2SMe)_2]_n$, is obtained. The polysulfides Me_2S_3 and Me_2S_4 react with $Pt(PPh_3)_4$ to give $Pt(SMe)_2(PPh_3)_2$. Reaction sequences are presented and the palladium demethylation reaction is discussed with respect to its relevance to the Raney nickel desulfurization.

Organosulfur derivatives of the transition metals are receiving increasing attention because of the novel structures and chemical properties of the complexes formed. Metal thiolates represent the most common class of compounds of this type, and they possess two properties characteristic of divalent sulfur chemistry. Firstly, the thiolato group is very polarizable and as a result tends to function as a bridging ligand,[2] and secondly the divalent sulfur shows a marked ability to stabilize centers of high electron density in organic[3] and inorganic[4] compounds. The coordination chemistry of bivalent sulfur donors can be divided into three parts according to the structure about the donor group; these are the thiolate RS^-, thione $R_2C{=}S$,[5] and thioether R_2S[6] ligands. In addition there exists an extensive chemistry of the metal complexes of 1,2- and 1,1-dithiolene ligands, which can be considered as being intermediate between the thiolate and thione categories. In this work we have restricted our attention to thiolate and thioether ligands and have attempted to develop a broad understanding of the chemistry of the nickel triad of elements with these important ligands.

Transition metal thiolate complexes have been known for a considerable number of years, and the products are commonly bridged polymers because it is frequently favorable for a monodentate ligand, L, to be displaced by the incoming coordinated thiolate (eq 1). The formation of sulfur bridged compounds appears to be thermodynamically favored over the isolation of monomers, and, although a number of monomeric thiolates have recently been prepared, they will readily bridge to a second metal to give a dimeric complex[7,8] (eq 2). These examples of monomers can be rationalized on the basis that the η-Cp ligand will not undergo ready displacement, and bridged complexes will only be obtained if a ligand is present which will undergo facile replacement. A similar case exists with η-$CpFe(SCH_3)(CO)_2$ where the monomer is stable under ambient conditions, and only at 70° is CO eliminated to give [η-$CpFe(SCH_3)CO]_2$. Monomeric coordinately unsaturated thiolates are particularly uncommon and are generally restricted to aryl thiolates[10,11] or perfluoroalkyl thiolates[12] of platinum and palladium which are metals characteristically forming 16-electron compounds. The first monomeric coordinately unsaturated alkyl thiolate complexes have recently been prepared by the base elimination of HCl from $IrHCl(SR)CO(PPh_3)_2$ (R = Me, Et, *i*-Pr, *n*-Bu). The resulting compounds, $Ir(SR)CO(PPh_3)_2$, do not bridge either by coordination into the fifth position or by displacement of the CO or triphenylphosphine.[13]



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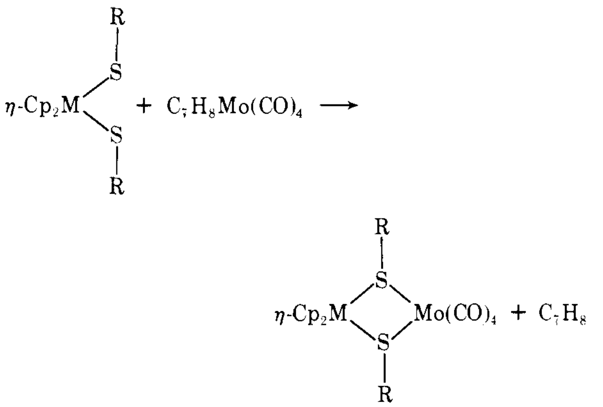


(2)

(M = Ti, Nb; R = Me, Ph)

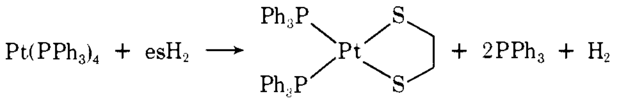
Thioether groups are much poorer ligands as evidenced by their lower coordinating ability toward platinum.[14] In view of our interest in the synthesis and chemistry of complexes of unsymmetrical chelates where the arms have a widely discrepant affinity for platinum metals,[15] we have prepared some mixed functional thioether-thiolates and investigated their chemistry with the nickel triad of elements.

The coordination chemistry of chelates of this type has received only minimal study,[16] especially with respect to the addition reactions of thiols and disulfides. From this current work we wish to develop a comparative understanding of the addition and substitution reactions of these ligands and thereby to control by synthesis the structure and chemistry of the product.

Results

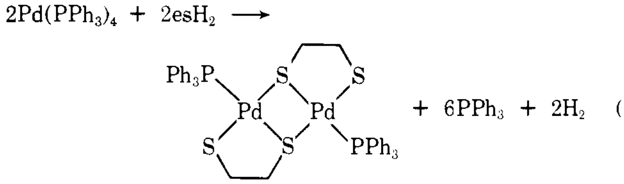
Reactions of 1,2-Ethanedithiol.[17] This difunctional mercaptan reacts rapidly with the zerovalent compounds $M(PPh_3)_4$ (M = Pt, Pd, Ni) to give products which are structurally different for each of the three metals. For platinum this chelating agent yields a monomer, for palladium a dimer, and for nickel a polymer.

The compound $Pt(PPh_3)_4$ reacts rapidly in benzene solution to yield the yellow monomer, $Pt(es)(PPh_3)_2$ (**1**). The ^1H NMR spectrum of **1** shows the es backbone methylenes as a sharp singlet at τ 7.33 with ^{195}Pt satellites separated by 46 Hz. The reaction most likely proceeds via a hydride intermediate which then reacts with the second thiol group to yield **1**, with the liberation of H_2. Compound **1** can also be prepared by treating either *cis*-$PtCl_2(PPh_3)_2$ or *trans*-$PtHCl(PPh_3)_2$ with esH_2 in the presence of base. In the latter reaction an impure hydrotriphenylphosphineplatinum intermediate (ν_{PtH} 2110 cm^{-1}; τ_{PtH} 19.1; J_{PH} = 22 Hz) can be isolated, which is probably $PtH(SCH_2CH_2SH)(PPh_3)_n$ (n = 1 or 2). We have been unable to obtain this compound in a pure state for complete characterization.



1 (3)

With $Pd(PPh_3)_4$ and esH_2 a rapid reaction again occurs and a bright red complex **2** is formed, which can be crystallized from CH_2Cl_2 and acetone (eq 4). Osmometric measurements show the compound to be dimeric, and the stoichiometry shows that an unusual reaction has occurred leading to the displacement of three PPh_3 molecules rather than the anticipated two, which is common as for the oxidative addition reactions of $Pd(PPh_3)_4$. The compound (**2**) can also be prepared by treating $PdCl_2(PPh_3)_2$ or $Pd(CN)_2(PPh_3)_2$ with esH_2 in the presence of base. The displacement of cyanide from the latter compound demonstrates the strong coordinating ability of dithiolates to the metal. The ^1H NMR spectrum of **2** shows two broad resonances in the region of τ 7.0 and 8.0 due to the nonequivalent methylene hydrogens in the backbone. This broad resonance for the es backbone is not due to an exchange process since the ^1H NMR spectrum of **2** is invariant in the range 35 to −60°. This compound **2** reacts with PMe_2Ph to yield the yellow monomer $Pd(es)(PMe_2Ph)_2$ (**3**) (eq 5). The product **3** arises from both a bridge cleavage reaction and the displacement of PPh_3. The ^1H NMR spectrum of **3** shows a sharp singlet at τ 8.0 for the dithiolato backbone, in agreement with this structure having equivalent methylenic hydrogens. The methyl resonances (τ 8.45) appear as a multiplet and the pattern (see Figure 1) is diagnostic of a moderate J_{P-P} coupling constant. This pattern is unexpected since the presence of a chelate causes the phosphines necessarily to be mutually cis. The integration of the resonances correspond to that anticipated for structure **3**.



2 (4)

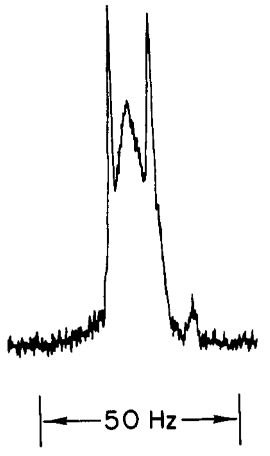
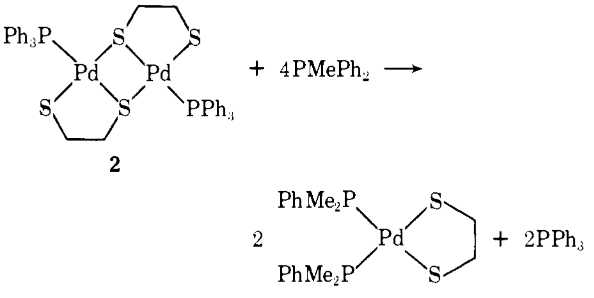


Figure 1. ^1H NMR spectrum of the methyl region of $Pd(es)(PMe_2Ph)_2$.

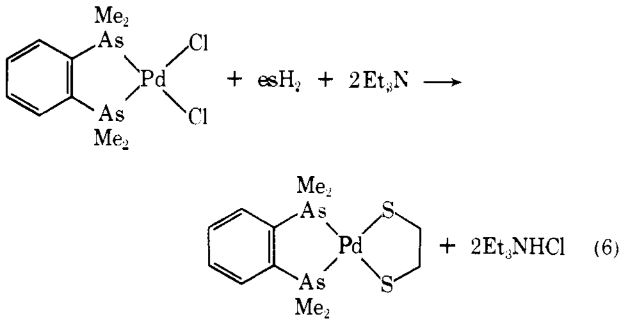


3 (5)

The reaction of esH_2 with either $NiCl_2(PPh_3)_2$ in ethanol or with $Ni(PPh_3)_4$ in benzene yields the chocolate brown, halocarbon soluble compound $[Ni(es)PPh_3]_2$ (**4**). The structure of **4** is analogous to that of **2** since the ^1H NMR spectrum shows broad resonances for the methylene backbone of the chelating dithiolate. The sharp lines for both the triphenylphosphine and reference signals precludes appreciable paramagnetism. Chemical evidence for the stoichiometry of **4** follows from two pieces of data: the formation of **4** from $NiCl_2(PPh_3)_2$ is accompanied by the loss of 1 equiv of PPh_3, which has been isolated and characterized; and furthermore **4** reacts with 1 equiv of diphos to yield the very stable complex Ni(es)diphos (**7**).

In the absence of excess PPh_3, complex **4** decomposes to yield a black insoluble powder which is similar to the one obtained from the reaction of $NiCl_2{\cdot}6H_2O$ with 1 equiv of esH_2. The stoichiometry and insolubility of this compound **5** indicates it to be the polymeric Ni(es). The black decomposition product from **4** is slightly different since it contains a small amount of PPh_3 which probably caps the ends of the Ni(es) polymers. Compound **4** can be recrystallized from excess PPh_3 without appreciable decomposition.

The occurrence of a dimer with palladium and a polymer with nickel prompted us to attempt the synthesis of monomeric 1,2-ethanedithiolate complexes of these metals. It appears probable that in each case the initial formation of $M(es)(PPh_3)_2$ occurs. When M = Pd or Ni, phosphine dissociation occurs which is followed by coordination of the thiolate sulfur atoms to a second metal. If the sole remaining phosphine also undergoes facile dissociation (M = Ni) polymer formation occurs. We have found that *monomers* are readily obtained when the neutral ligands (L) are replaced by a chelate; thus when $PdCl_2$(diars) or $NiCl_2$(diphos) are treated with esH_2 in the presence of base the monomers Pd(es)(diars) (**6**) and Ni(es)(diphos) (**7**) are obtained (eq 6 and 7). The ^1H NMR spectrum of **6** shows resonances at τ 7.1 (SCH_2) and 8.26 ($AsMe_2$) and that of **7** at τ 7.26 (SCH_2) and 7.8 (J_{PH} = 17 Hz) (PCH_2). It is necessary, however, to use a strongly coordinating chelate ligand in order to obtain monomers since when $PdCl_2$(bipy), $PdCl_2$(DTH), or $PdCl_2$(PN) is treated with esH_2 in base, a polymeric product, $[Pd(es)]_n$, is obtained. The same compound is also formed on treating $PdCl_2$(COD) or $NaPdCl_4$ with esH_2 in the presence of base.



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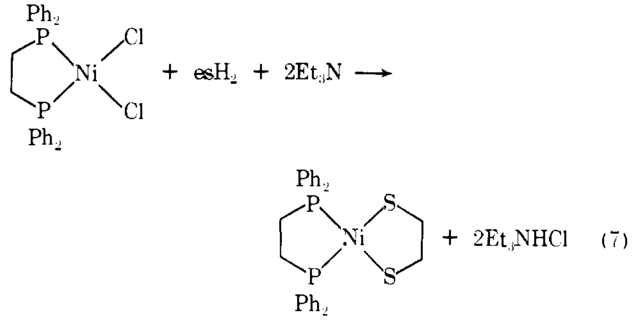
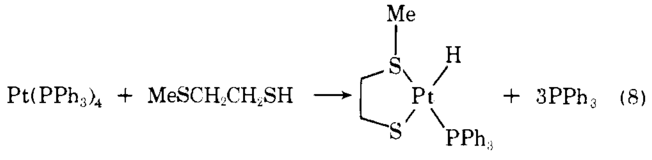


7

Reactions of 2-(Methylthio)ethanethiol. 2-(Methylthio)ethanethiol (bp 76.5–78° (23 mm); lit. 69.5° (26 mm)) (nmr τ 2.05 (Me), 2.66, 2.60 (CH_2), 1.58 (SH)) was prepared by the calcium reduction[18] of 1,3-dithiolene[19] in anhydrous ammonia. The compound reacts with $Pt(PPh_3)_4$ to give the hydroplatinum complex $PtH(SCH_2CH_2SMe)(PPh_3)$ (**8**) (eq 8). The ir spectrum shows a medium band at 2120 cm^{-1} for ν_{PtH}. The stereochemistry of **8** is confirmed by the ^1H NMR spectrum which shows a hydride resonance at τ 20.8 as a doublet due to coupling with a cis PPh_3 (J_{PH} = 20 Hz, J_{PtH} = 1200 Hz). The methyl resonance at τ 8.4 is also split into a doublet due to coupling with the phosphine (J_{PMe} = 1 Hz, J_{PtMe} = 14 Hz), and this nonzero value strongly implies that the *S*-methyl group and the PPh_3 are mutually trans. This reaction is one of the first examples of the oxidative addition of a chelating ligand and its significance will be stressed in the discussion section.

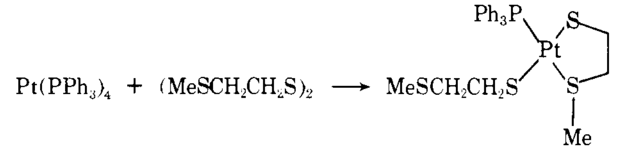


8

When $Pd(PPh_3)_4$ is treated with $MeSCH_2CH_2SH$ the dimer **2** is obtained. The reaction must proceed via a palladium hydride intermediate which undergoes the S-demethylation reaction to produce the identical complex obtained from esH_2. The compound $Ni(PPh_3)_4$ reacts with $MeSCH_2CH_2SH$ with a vigorous effervescence to give a brown oil. The product is probably $Ni(SCH_2CH_2SMe)_2(PPh_3)_2$ although complete characterization was not possible. The ^1H NMR spectrum shows resonances in the range τ 2.0–3.0 for the methyl and methylene hydrogens, the integration against the phenyl hydrogens confirming the stoichiometry of the complex.

Reactions of 2-(Methylthio)ethane Disulfide. This new compound has been prepared by the iodine oxidation of $MeSCH_2CH_2SH$. When $Pt(PPh_3)_4$ is treated with this polyfunctional disulfide a yellow complex, $Pt(SCH_2CH_2SMe)_2PPh_3$ (**9**), is formed. The complex is monomeric and has both free (τ 8.0) and coordinated (τ 8.2) *S*-methyl groups. The methylene backbone shows a complex multiplet between τ 7.0 and 7.6 in the ^1H NMR spectrum because of the different sets of nonequivalent methylene hydrogens. The complex is robust and heating for 12 hr in benzene causes no displacement of the triphenylphosphine by the thioether group. Similarly the coordinated thioether group is not displaced by CO or PF_3. With $Pd(PPh_3)_4$ all the triphenylphosphines are substituted, and the apparently polymeric compound $[Pd(SCH_2CH_2SMe)_2]_n$ (**10**) is formed. The difference between platinum and palladium in these reactions is due to the weaker bonding between triphenylphosphine and the latter metal.

$$2\mathrm{MeSCH_2CH_2SH} + \mathrm{I_2} \longrightarrow (\mathrm{MeSCH_2CH_2S})_2 + 2\mathrm{HI} \quad (9)$$



9 (10)

$$n\mathrm{Pd(PPh_3)_4} + n(\mathrm{MeSCH_2CH_2S})_2 \longrightarrow [\mathrm{Pd(SCH_2CH_2SMe)_2}]_n + 4n\mathrm{PPh_3} \quad (11)$$

10

$$\mathrm{Pt(PPh_3)_4} \underset{\mathrm{PPh_3(-EtSH)}}{\overset{\mathrm{EtSH(-PPh_3)}}{\rightleftharpoons}} \mathrm{PtH(SEt)(PPh_3)_2} + 2\mathrm{PPh_3} \quad (12)$$

11

Reactions of Nonchelating Organosulfur Compounds with $Pt(PPh_3)_4$. As a result of the paucity of knowledge on the addition reactions of simple alkyl thiols, disulfides, and polysulfides with metals of the nickel triad, we have studied their reaction with $Pt(PPh_3)_4$ in order to obtain a basis for understanding the chemistry of the chelating ligands. This consideration is developed more fully in the discussion section where the importance of the comparison between the monodentate and polydentate ligands is shown. $Pt(PPh_3)_4$ reacts rapidly with EtSH to form a compound $PtH(SEt)(PPh_3)_2$ (**11**). Compound **11** is quite unstable since it cannot be recrystallized, it darkens on exposure to air, and it reverts back to $Pt(PPh_3)_4$ upon treatment with excess PPh_3. The compound reacts with CCl_4 to give $CHCl_3$ which was detected by GLC. The ir and NMR data confirm the formation of a hydride complex for which ν_{PtH} 2098 cm^{-1} and τ_{PtH} 18.25. The hydride resonance is a single line and shows no ^{31}P–H coupling. The instability of

$PtH(SEt)(PPh_3)_2$ is consistent with a similar observation on the arylthiol analogs.[20] The wide disparity in the stability of the compounds formed by the addition of $MeSCH_2CH_2SH$ and EtSH to Pt(0) is a consequence of the chelate effect.

When $Pt(PPh_3)_4$ is refluxed for 30 min with Me_2S_2 or Et_2S_2 no reaction occurs. In the case of Me_2S_2 though, a slow reaction is observed where less than 10% $Pt(SMe)_2(PPh_3)_2$ is formed in 6 hr. This shows further evidence for the importance of chelation in the oxidative addition reaction since $(MeSCH_2CH_2S)_2$ underwent facile addition at room temperature. The failure to observe significant addition with Me_2S_2 cannot be due to the thermodynamic unstability of the product since $Pt(SMe)_2(PPh_3)_2$ (**12**) can be readily isolated in high yield from the reaction of $Pt(PPh_3)_4$ with either Me_2S_3 or Me_2S_4. The ^1H NMR spectrum of **12** shows a singlet at τ 9.24 (J_{PtH} = 44 Hz).

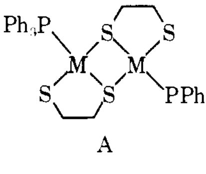
Discussion

The literature abounds with examples of transition metal 1,2-dithiolene complexes,[21] but there is a paucity of work on the reactions of 1,2-ethanedithiol with transition metal compounds. Two reported complexes with esH_2 are $[Fe(CO)_3]_2(es)$, formed in 0.27% yield from the reaction of esH_2 with $Fe(CO)_5$,[22] and the anions $Ni(es)_2^{2-}$ and $Ni_2(es)_3^{2-}$.[23] In addition Green[24] has reported the monomeric complexes η-$Cp_2M(es)$ (M = Mo, W). The nickel complexes were proposed on the basis of spectrophotometric measurements, but isolation for complete characterization was not attempted. We have found that esH_2 is very reactive toward compounds of the nickel triad and that the complexes formed can be isolated and characterized if the starting compounds are correctly chosen. The nature of the product depends on the metal; with platinum a monomer is formed, and with palladium and nickel a dimer, the latter being unstable with respect to polymerization. We have considered both the addition reaction to the zerovalent compound and the substitution reaction with the divalent halo complex and have found that the product obtained is the same from each. The initial product in each case is probably $M(es)(PPh_3)_2$. If the PPh_3 strongly coordinates to the metal, as is the case with Pt, the monomer will be isolated from the reaction. In the case of Pd one of these triphenylphosphines is readily displaceable by sulfur and the dimer (**2**) is the final product. For nickel the bonding to triphenylphosphine is weaker and the dimer decomposes to polymeric materials as shown in the reaction scheme.

$$\begin{tikzcd}
M(PPh_3)_4 + esH_2 \arrow[r, "-H_2", "-2PPh_3"'] & {} \\
 & \begin{matrix} M(es)(PPh_3)_2 \\ (M = Pt) \end{matrix} \arrow[r, "-PPh_3"] & {[M(es)(PPh_3)]_2\ (M = Pd)} \arrow[d, "-nPPh_3"] \\
 & & \begin{matrix} [M(es)]_n \\ (M = Ni) \end{matrix}
\end{tikzcd}$$

The strong coordinating ability of esH_2 is shown by the observation that it will displace cyanide from $Pd(CN)_2(PPh_3)_2$ to give compound **2**.

There are two likely structures for the palladium complex **2** and the nickel complex **4**, one with C_{2h} symmetry (A) and the other belonging to the C_{2v} point group (B). Both of these structures represent four-coordinate palladium(II) complexes, and interconversion is unlikely since the ^1H NMR spectrum of the complex is invariant down to −60°. The structure A is similar to the ones proposed for the products obtained by treating nickel chloride with $HSCH_2CH_2SCH_2CH_2SH$[25] and $[PdCl_2(PBu_3)]_2$ with 4-chlorobenzene-1,2-dithiol[26] (**13** and **14**), respectively. Support for structure A comes from the reaction of the complexes **2** and **6** with PMe_2Ph and diphos, respectively. In the case of Pd, the formation of the monomer is a consequence of the stronger coordinating power of PMe_2Ph to Pd(II), and in the case of Ni the monomer is formed because of the chelating ability of diphos. The ^1H NMR spectrum of **3** is characteristic of an $X_3AA'X'_3$ (X = ^1H, A = ^{31}P) system (Figure 1) where $J_{AA'}$ is intermediately coupled compared to J_{AX} and $J_{A'X'}$.[27] The observation of this spectrum is unexpected since mutually cis methylphosphines are expected to lead to a doublet spectrum in the methyl region. Control of the degree of polymerization by the strength of coordination of the phosphine ligand is definitively shown by the isolation of monomers **4** and **5**. For diars or diphos the strong bonding and chelate effect ensures that the species M(es)(chelate) will not undergo further substitution with the formation of dimers or polymers. It is nevertheless important that the chelate strongly coordinates to the metal since treating $PdCl_2(DTH)$, $PdCl_2(COD)$, or $PdCl_2(bipy)$ with esH_2 leads to a polymeric product of composition $[Pd(es)]_n$ (**15**). This material resembles the compounds of varying states of aggregation obtained from treating halopalladium compounds with simple thiols.[28,29]



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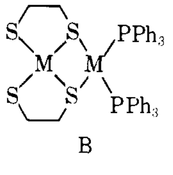

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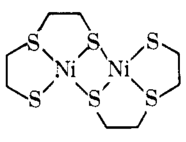

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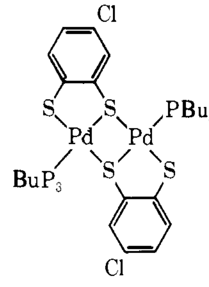
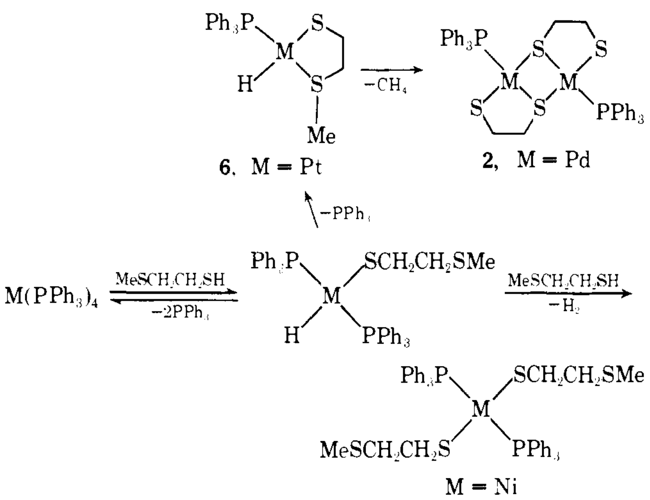


14

The reaction between $MeSCH_2CH_2SH$ and the zerovalent complexes of the nickel triad shows considerable differences from that expected from previous work on HX addition to these complexes.[30] The explanation for the difference is related to $MeSCH_2CH_2SH$ being both a protonic acid and a potential chelate. The rationalization of the products is shown below. The initial step is the addition of the thiol to form an unstable intermediate hydride $MH(SCH_2CH_2SMe)(PPh_3)_2$. Displacement of a triphenylphosphine with coordination of the *S*-methyl group leads to a compound having structure **6**, and in the case of platinum this compound is the one isolated from the reaction. In the case of palladium S-demethylation occurs leading to dimer formation by donor coordination of a sulfur atom from the resultant 1,2-ethanedithiolate to a second palladium atom. In the case of nickel, chelation does not occur before the initially formed hydride reacts with a second molecule of the thiol to give $Ni(SCH_2CH_2SMe_2)_2(PPh_3)_2$. These reactions are shown in Scheme I. Compound **6** is significant because of its remarkable stability to reductive elimination. We have also prepared the hydride $PtH(SEt)(PPh_3)_2$ (**9**) by addition of EtSH to $Pt(PPh_3)_4$. Complex **6** is stable in the solid state for months whereas **9** is partially decomposed after several days. In solution the difference is more marked since **6** can be readily recrystallized and is unaffected by excess PPh_3, whereas in solution **9** rapidly decomposes and

Scheme I



cannot be recovered. This difference is not due to the greater volatility of EtSH since it has been reported that the more acidic and less volatile p-$CH_3C_6H_4SH$ forms $PtH(p$-$CH_3C_6H_4S)(PPh_3)_2$, which is also quite unstable to dissociation of the thiol in solution.[19] We believe that these results add a new dimension to the consideration of oxidative addition reactions. Previously it has been shown that the ability of a metal center to add a substrate is dependent on the basicity of the metal[31] and on the steric requirements of the ligands.[32] In working with multifunctional ligands which can undergo chelate addition it is apparent that there is also a chelate assistance to the oxidative addition reaction. This feature will obviously only occur for compounds which can, by addition or displacement, coordinate the three or more groups of the substrate. Chelate assistance to the oxidative addition reaction is even more dramatically shown for the addition of disulfides. The addition of diphenyl disulfide to $M(PPh_3)_4$ (M = Pt, Pd)[33] had been recently reported; however, we find that Et_2S_2, like t-Bu_2S_2,[33] will not oxidatively add to $Pt(PPh_3)_4$. The tetrafunctional disulfide, however, undergoes facile addition even at room temperature to give $Pt(SCH_2CH_2SMe)_2PPh_3$ (**7**). This result shows the enhanced reactivity of disulfides when simultaneous chelation can occur. A further consequence of this work is that it gives a useful comparison between the relative reactivity of thiols and disulfides toward addition. This greater reactivity of thiols is also shown by the observation that $IrCl(CO)(PPh_3)_2$ reacts with $MeSCH_2CH_2SH$ at room temperature but is unchanged after refluxing in benzene with $(MeSCH_2CH_2S)_2$ for 12 hr.[34]

Although the compound $Pt(SMe)_2(PPh_3)_2$ (**10**) cannot be prepared by the addition of Me_2S_2 to $Pt(PPh_3)_4$, the desired product is readily obtained with Me_2S_3 or Me_2S_4. The isolation of compound **10** is important since it shows that the inability of simple dialkyl disulfides to add is not caused by the instability of the addition product. The extrusion of sulfur in the reactions of polysulfides with transition metal complexes has been previously reported in the formation $[CF_3C(S)CF_3C(S)][Fe(CO)_3]_2$ from $CF_3CSSSSCCF_3$ and pentacarbonyliron.[21]

The reaction of $MeSCH_2CH_2SH$ with $Pd(PPh_3)_4$ to give the S-demethylated compound **2** merits further comment. In an earlier reaction scheme we have considered that the intermediate $PdH(SCH_2CH_2SMe)PPh_3$ undergoes dimerization with loss of methane. To our knowledge this is the first example of an S-demethylation reaction occurring with a metal hydride compound. The S-demethylation reaction of methyl sulfides to yield thiolate complexes has been previously studied for the elimination of a methyl halide from the ligand and a halotransition metal compound.[35-39] The reaction bears strong resemblance to the SN2 displacement of an alkyl group from an alkylsulfonium ion (R_3S^+) by a nucleophile (X^-), and the S-demethylation reaction occurs with palladium and not platinum complexes because of the considerable hydridic character of palladium hydrides.[30] The observation of this S-demethylation reaction has considerable relevance to the reported heterogeneous desulfurization of organic thioethers and thiols with Raney nickel.[40]

Table I

Compound	Color	C(%)	H(%)	S(%)	Mol wt
$Pt(es)(PPh_3)_2$ (1)	Yellow	55.4 (56.2)^c	4.08 (4.19)	8.05 (7.90)	735^a (811)
$[Pd(es)(PPh_3)]_2$ (2)	Red	52.3 (52.1)	4.09 (4.12)	14.0 (13.9)	830^a (920)
$Pd(es)(PMe_2Ph)_2$ (3)	Yellow	45.7 (45.5)	5.54 (5.48)	13.7 (13.5)	453^a (474)
$[Ni(es)(PPh_3)]_2$ (4)	Brown	57.2 (58.2)	4.60 (4.69)	15.7 (15.5)	Unstable
$[Ni(es)]_n$ (5)	Black	16.3 (15.9)	2.60 (2.65)		Insoluble
Pd(es)(diars) (6)	Yellow	29.7 (29.8)	4.13 (4.09)	13.2 (13.4)	440^b (480)
Ni(es)(diphos) (7)	Orange	61.4 (61.2)	4.95 (5.10)	12.0 (11.7)	
$PtH(SCH_2CH_2SMe)PPh_3$ (8)	Pale yellow	44.9 (44.6)	4.12 (4.07)	11.7 (11.3)	579^a (565)
$(MeSCH_2CH_2S)_2$	Colorless	33.4 (33.6)	6.28 (6.53)	60.0 (59.8)	
$Pt(SCH_2CH_2SMe)_2PPh_3$ (9)	Yellow	42.9 (42.9)	4.27 (4.32)	19.24 (19.09)	639^b (671)
$[Pd(SCH_2CH_2SMe)_2]_n$ (**10**)	Yellow	22.9 (22.4)	4.21 (4.36)	39.9 (40.0)	Insoluble
$PtH(SEt)(PPh_3)_2$ (11)	Pale yellow	58.4 (57.5)	4.61 (4.52)		Unstable
$Pt(SMe)_2(PPh_3)_2$ (12)	Yellow	55.8 (56.1)	4.48 (4.42)	8.18 (7.88)	
$[Pd(es)]_n$ (15)	Orange	12.7 (12.1)	2.00 (2.00)		Insoluble

^{a} $CHCl_3$. ^{b} C_6H_6. ^{c} Theoretical values in parentheses.

On this basis the desulfurization under hydrogenation conditions may occur through surface intermediates of the type shown in eq 13.

$$\mathrm{HNi} \xrightarrow{\mathrm{R_2S}} \mathrm{HNiSR_2} \xrightarrow{\mathrm{-RH}} \mathrm{NiSR} \xrightarrow{\mathrm{-RH}} \mathrm{NiS} \qquad (13)$$

Conclusions

The aim of this work was to investigate the behavior of chelating alkyl thiols and thioethers with compounds of the nickel triad. Emphasis was placed on the addition reaction to the low-valent compounds, and the following results have been obtained which we believe may be of general importance to this area of transition metal chemistry. (1) Bifunctional thiols and disulfides show considerably enhanced reactivity because of chelation, and this effect can lead to products of different stoichiometry and structure. (2) The bifunctional ligand esH_2 will readily form discrete complexes with this triad, and, by using a strongly coordinating chelate on the complex to be reacted, a directed synthesis of monomers can be achieved. The work shows that by using ligands of strong, medium, or weak coordinating ability on the initial compound, one can effect directed syntheses of monomers, dimers, and polymers, respectively. (3) Mercaptans are more reactive toward addition than are disulfides. (4) Tri- and tetrasulfides show promise as reactive precursors to bisthiolate complexes. (5) A homogeneous model for the Raney nickel desulfurization reaction has been suggested which is indicative of a likely reaction sequence.

Experimental Section

^{1}H NMR spectra were recorded on Varian T-60 and A-60 spectrometers. Infrared spectra were recorded on a Perkin-Elmer Model 457 spectrometer. Molecular weight measurements were determined on a Hitachi-Perkin Elmer Model 115 molecular weight apparatus standardized with benzil. Carbon and hydrogen analyses were performed on a Perkin-Elmer Model 240 elemental analyzer, and sulfur analyses by Galbraith Laboratories (Table I). Melting and decomposition points were measured in evacuated sealed tubes. All reactions involving $Ni(PPh_3)_4$, $Pd(PPh_3)_4$, and $Pt(PPh_3)_4$ were carried out under a nitrogen atmosphere in nitrogen saturated solvents. $Ni(PPh_3)_4$ was prepared by the reduction of $Ni(acac)_2$ with $NaBH_4$ and PPh_3 in methanol. $Pd(PPh_3)_4$ and $Pt(PPh_3)_4$ were prepared as described previously. Dimethyl tetrasulfide was prepared from MeSH and S_2Cl_2[41] and its ^{1}H NMR spectrum corresponded with that previously reported.[42]

2-(Methylthio)ethane Disulfide ($(MeSCH_2CH_2S)_2$). This compound was routinely prepared by the iodine oxidation of $MeSCH_2CH_2SH$ in a two-phase benzene–water system containing excess Na_2CO_3 (to consume the HI evolved). After complete oxidation, as evidenced by a persistent purple coloration, the phases were separated, and the organic layer was washed with $Na_2S_2O_3$ and dried over $MgSO_4$. Benzene was removed in vacuo and the residue distilled to give the compound: bp 160–162° (<0.5 mm).

1,2-Ethanedithiolatobis(triphenylphosphine)platinum (1). From $PtCl_2(PPh_3)_2$. To a suspension of $PtCl_2(PPh_3)_2$ (200 mg) in dry THF (15 ml) was added esH_2 (0.5 ml). The mixture was refluxed to evolve HCl. The yellow solution was evaporated to an oil, diluted with ethanol (10 ml), and allowed to cool. The complex was filtered and dried in vacuo: 160 mg (78%); mp 244–246°.

From $PtHCl(PPh_3)_2$. To a solution of $PtHCl(PPh_3)_2$ (100 mg) in CH_2Cl_2 was added excess esH_2. Upon addition of triethylamine the solution eventually became yellow (2 hr). The solvent was removed and the product recrystallized from CH_2Cl_2 and ethanol.

From $Pt(PPh_3)_4$. To a solution of $Pt(PPh_3)_4$ (1.0 g) in CH_2Cl_2 (30 ml) was added excess esH_2. The color of the solution faded. Hexane (20 ml) was added and the volume of the solvent reduced to 5 ml. Trituration with ether gave the complex.

Bis(1,2-ethanedithiolato)bis(triphenylphosphine)dipalladium (2). From $PdCl_2(PPh_3)_2$. An excess of esH_2 was added to $PdCl_2(PPh_3)_2$ (1.5 g) in dry THF. Triethylamine was added dropwise until no further Et_3NHCl was liberated. The solution was heated to reflux, evaporated to a volume of 2 ml, diluted with CH_2Cl_2, and filtered. The filtrate was diluted with acetone (20 ml) and the CH_2Cl_2 removed under vacuum until the total volume was 15 ml. Cooling to −5° for 12 hr gave the complex as red crystals which were filtered, washed with acetone and ether, and dried by heating in vacuo for 24 hr at 110° to remove the acetone: 1.03 g (63%); mp 236°. The compound can be prepared in an analogous manner from $Pd(CN)_2(PPh_3)_2$.

From $Pd(PPh_3)_4$. An excess of 1,2-ethanedithiol was added to $Pd(PPh_3)_4$ (1.2 g) in CH_2Cl_2 (50 ml). After stirring for 2 min the mixture was filtered and diluted with acetone (20 ml) and the volume reduced to 10 ml. The solution was cooled and the complex collected: 0.38 g (48%).

From $MeSCH_2CH_2SH$. To a solution of $Pd(PPh_3)_4$ (350 mg) in benzene (15 ml) was added $MeSCH_2CH_2SH$ (0.5 ml). The mixture was refluxed for 10 min and then allowed to cool to room temperature. The precipitate was washed with methanol and dissolved in a minimum volume of CH_2Cl_2. Filtration, followed by addition of acetone gave the complex: 64 mg (46%).

1,2-Ethanedithiolatobis(dimethylphenylphosphine)palladium (3). To a solution of **2** (210 mg) in CH_2Cl_2 (20 ml) was added PMe_2Ph (ca. 0.3 ml). Within 15 min the solution became lemon yellow in color. After 45 min hexane (30 ml) was added and the solvent volume reduced to 10 ml under a stream of N_2. The yellow crystals which formed were filtered and recrystallized from CH_2Cl_2 and hexane. The compound was dried in vacuo: 168 mg (78%); mp 158–160°.

Bis(1,2-ethanedithiolato)bis(triphenylphosphine)dinickel (1). From $Ni(PPh_3)_4$. The procedure was identical with that for the preparation of $Pt(es)(PPh_3)_2$ from $Pt(PPh_3)_4$.

From $NiCl_2(PPh_3)_2$. $NiCl_2(PPh_3)_2$ (758 mg) and esH_2 (109 mg) were stirred for 3 hr in ethanol (50 ml of 95%). The product was filtered and washed with ether (2 × 10 ml) to give the complex: 430 mg (90%). The filtrate was evaporated and extracted with ether, and the PPh_3 in the extract was crystallized from ethanol–water: 268 mg (88%).

(1,2-Ethanedithiolato)nickel (5). $NiCl_2 \cdot 6H_2O$ (474 mg) was dissolved in the minimum volume of water and diluted to 20 ml with ethanol. 1,2-Ethanedithiol (188 mg) in ethanol (5 ml) was added. After stirring for 30 min the black compound was filtered and washed with water and ether: 235 mg (78%).

1,2-Ethanedithiolato-1,2-bis(dimethylarsino)benzenepalladium (6). $PdCl_2(diars)$ (195 mg) was suspended in acetone (10 ml) and esH_2 (0.5 ml) added. Triethylamine was added when the color changed to yellow with evolution of Et_3NHCl. After 15 min the compound was filtered and washed with water, methanol, and ether. The complex was recrystallized from CH_2Cl_2 and acetone: 194 mg (95%); mp 272–274°.

1,2-Ethanedithiolato-1,2-bis(diphenylphosphino)ethanenickel (7). Nickel chloride (1.2 g) was dissolved in water (3 ml) and the filtered solution diluted with ethanol (60 ml of 95%). Diphos (2.0 g) was added and the slurry refluxed with stirring for 20 min. Upon addition of esH_2 (0.5 ml) the solution darkened. Triethylamine (1 ml) was added and the mixture was kept at room temperature for 12 hr. The precipitate was filtered then dissolved in CH_2Cl_2. After extraction with saturated aqueous NaCl, the CH_2Cl_2 layer was dried over $MgSO_4$. Removal of CH_2Cl_2 and recrystallization from ethanol gave the complex: 2.1 g (78%); mp 210° (with decomposition).

Hydrido-2-(methylthio)ethanethiolatotriphenylphosphineplatinum (8). To a filtered solution of $Pt(PPh_3)_4$ (760 mg) in benzene (20 ml) was added $MeSCH_2CH_2SH$ (200 mg). The solution was stirred for 5 min, and after removal of the solvent a mixture of CH_2Cl_2 (2 ml) and ether (50 ml) added. After 12 hr at −10° the supernatant liquid was decanted and the complex washed with water (10 ml) and hexane (20 ml): 300 mg (87%); mp 124–135°.

Bis-2-(methylthio)ethanethiolatotriphenylphosphineplatinum (9). To a filtered solution of $Pt(PPh_3)_4$ (950 mg) in benzene (50 ml) was added $(MeSCH_2CH_2S)_2$ (200 mg). The solution was stirred until the color changed from orange to yellow (1 hr). The solvent was removed and the residue recrystallized twice from benzene–hexane. The complex was washed with ether and dried: 550 mg (100%); mp 133°.

Bis[2-(methylthio)ethanethiolato]palladium (10). To a benzene solution (10 ml) of $Pd(PPh_3)_4$ (400 mg) was added 2-(methylthio)ethane disulfide (75 mg). The solution was refluxed for 10 min, evaporated to an oil, and triturated with Et_2O (10 ml) to yield a yellow-orange powder which was washed with CH_2Cl_2 (10 ml), and Et_2O (10 ml), yield 105 mg (100%).

Hydridoethanethiolatobis(triphenylphosphine)platinum (11). $Pt(PPh_3)_4$ (520 mg) was dissolved in benzene (20 ml) and the solution filtered. Evaporation to a volume of 5 ml followed by addition of EtSH gave a pale solution. Hexane (25 ml) was slowly added and the mixture stirred for 30 min. The precipitate was filtered and washed with ether: 295 mg (90%); mp 125–128°.

Bis(methanethiolato)bis(triphenylphosphine)platinum (12). To a filtered solution of $Pt(PPh_3)_4$ (650 mg) in benzene was added Me_2S_4 or Me_2S_3 (0.5 ml). The solution was stirred for 2 hr. The solvent was removed and the residue recrystallized twice from CH_2Cl_2 and ethanol to give the complex: 210 mg (49%); mp 210° with decomposition.

(1,2-Ethanedithiolato)palladium (15). This material is most easily prepared by the reaction of $Pd(COD)Cl_2$ in CH_2Cl_2 solution with esH_2 (equal weight) followed by addition of Et_3N (equal weight). After stirring 1 hr the brown orange polymeric material is removed by filtration and washed sequentially with CH_2Cl_2, EtOH, H_2O, EtOH, and Et_2O. The yield is essentially quantitative.

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Acidolysis and Oxidative Cleavage Reactions of Benzylchromium Cations

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Abstract: The organometallic complex $[(H_2O)_5CrCH_2C_6H_5]^{2+}$ is oxidized in aqueous perchloric acid by Fe^{3+}, Cu^{2+}, $[Co(NH_3)_5Cl^{2+}]$, $[Co(NH_3)_5Br^{2+}]$, O_2, and H_2O_2 at an identical rate, independent of the nature and concentration of the oxidizing agent. The first-order rate constant is 10^3k_1 (sec^{-1}) = 2.63 ± 0.21 (25.0°, μ = 1.00 *M*). The organic products and Cr(III) products were determined. In certain instances, the reaction initiates polymerization of acrylonitrile but in other instances it does not. The rates of para-substituted derivatives correlate with the Hammett σ_p parameter, giving $\rho = -1.01$. The reactions are discussed in terms of a unimolecular homolysis of the Cr–C bond by the S_H1 mechanism, followed by rapid oxidation of one or both of the fragments so formed.

In studies of the reduction of organic molecules by metal ions, solutions of benzyl halides and Cr(II) were shown to generate (eventually) Cr(III) and an organic product which, under anaerobic conditions, is largely toluene.[2,3] In the course of those studies, separation and identification the benzylpentaaquochromium(III) cation, $[(H_2O)_5CrCH_2C_6H_5]^{2+}$ (**1**), were realized. Further, it was confirmed that **1** was formed quantitatively, and that its decomposition via the acidolysis reaction (eq 1) is responsible for the final products.

An intriguing puzzle attended the study[4] of the rate of reaction 1 in $HClO_4$ solutions in the absence of dioxygen: the kinetics showed not a first-order dependence upon [**1**], but (under a limited set of concentration conditions) approximated a half-order dependence.[5-9] A mechanism which accounts for the kinetic observations under these circumstances has not as yet been formulated, although a

$$\mathbf{1} + H_3O^+ = Cr(H_2O)_6^{3+} + C_6H_5CH_3 \qquad (1)$$