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Nucleophilic Attack on η^2 -Coordinated Dithio Acids by Hydride Ion. A Preliminary Step in the Formation of a Variety of Nickel Complexes

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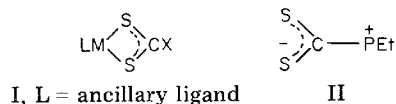
Received June 14, 1982

The nickel(II) complexes [(triphos)Ni(S₂CPEt₃)](BPh₄)₂, [(triphos)Ni(S₂CSMe)]BPh₄, [(triphos)Ni(S₂COEt)]BPh₄, and [(triphos)Ni(S₂CNEt₂)]BPh₄ (triphos = 1,1,1-tris((diphenylphosphino)methyl)ethane) react with NaBH₄ to give the complexes [(triphos)Ni(S₂C(H)PEt₃)]BPh₄, [(triphos)Ni(π -CS₂)], [(triphos)Ni(CO)], and [(triphos)Ni(SH)], respectively. The formation of all of these compounds is suggested to proceed via nucleophilic attack by the hydride ion from NaBH₄ on the electrophilic CS₂ carbon atom, followed by rearrangement of the resultant adduct. In some cases the reaction is accompanied by a lowering of the metal oxidation state by one or two units.

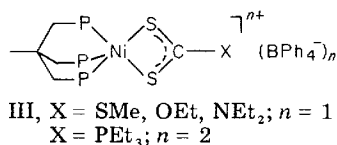
Introduction

Increasing attention has been directed recently toward the reactivity of (η^2 -dithio acid)metal complexes (I) with nucleophiles. Reactions of η^2 -metal-linked S₂C-X groups include ligand substitution to give complexes with different dithio acid ligands,¹⁻³ and nucleophile addition to give 1,1-dithiolate complexes.^{4,5} The η^2 -coordination of dithio acid ligands enhances the electrophilicity of the CS₂ carbon atom, which consequently can be attacked by nucleophiles.

In recent papers were showed that the hydride ion from NaBH₄ attacks the metal-coordinated S₂C-PEt₃ zwitterion (II) and transforms it into the dithioformate or the phosphonium adduct of dithioformate.^{1,4}



Now we show that the reactivity of (η^2 -dithio acid)metal complexes with NaBH₄ is in general a chemical feature of these disulfido ligands. The reactions of a number of nickel(II) complexes of formula [(triphos)Ni(S₂C-X)](BPh₄)_n (III) and NaBH₄ are summarized in Scheme I.



The product obtainable from each of these reactions depends on the nature of the X substituent. Beside addition reactions, the hydride ion may cause the fragmentation of the chelated dithioacid, thus generating metal complexes with a variety of smaller ligands such as CS₂, CO, and HS⁻. These reactions are often accompanied by a decrease of the metal oxidation number by one or two units.

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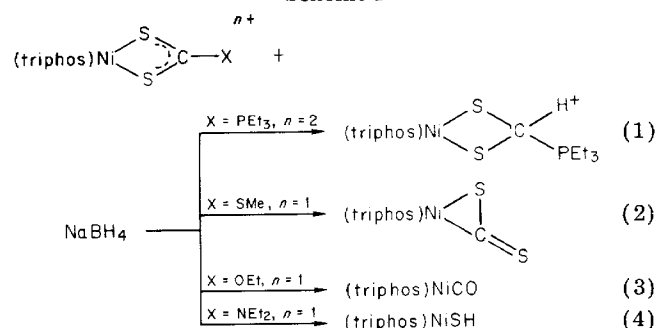
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Scheme I



Experimental Section

All chemicals and solvents employed were reagent grade and were used without further purification. All the reactions described were carried out under an atmosphere of dry nitrogen. The solid complexes were collected on a sintered-glass frit and washed successively with ethanol and petroleum ether (bp 40–70 °C) before being dried in a stream of dry nitrogen. Infrared spectra were recorded with a Perkin-Elmer 283 spectrophotometer using samples milled in Nujol. ³¹P NMR spectra were taken on a Varian CFT 20 spectrometer. Chemical shifts are downfield (+) from external H₃PO₄. The methods used for the magnetic and molar conductance measurements and the recording of the UV-visible spectra have been described previously.⁶

Syntheses. [(triphos)Ni(S₂C(H)PEt₃)]BPh₄ (1). A solution of [(triphos)Ni(S₂CPEt₃)](BPh₄)₂⁴ (0.45 g, 0.3 mmol) in acetone (25 mL) was treated with NaBH₄ (0.02 g, 0.5 mmol) in ethanol (10 mL). There was an immediate color change from dark green to orange. By addition of *n*-butanol (20 mL) to the solution and partial evaporation an orange microcrystalline solid was obtained; yield 85%.

Anal. Calcd for C₇₂H₇₅BNiP₄S₂: C, 72.18; H, 6.31; Ni, 4.90; P, 10.34. Found: C, 71.97; H, 6.24; Ni, 4.85; P, 10.45.

[(triphos)Ni(π -CS₂)] (2). A solution of NaBH₄ in ethanol was added dropwise to a suspension of [(triphos)Ni(S₂CSMe)]BPh₄⁷ (0.34 g, 0.3 mmol) in acetone (30 mL) until the suspended compound dissolved to give a red brown solution. Ethanol (10 mL) then was added. Dark brown crystals precipitated in a short time; yield 90%; IR (cm⁻¹) ν (C=S) 1145, ν (CS) 630.

Anal. Calcd for C₄₂H₃₉NiP₃S₂: C, 66.41; H, 5.17; Ni, 7.73; S, 8.44. Found: C, 66.25; H, 5.14; Ni, 7.64; S, 8.35.

(6) Sacconi, L.; Bertini, I.; Mani, F. *Inorg. Chem.* 1968, 7, 1417.

(7) Unpublished results of this laboratory. The [(triphos)Ni(S₂CSMe)]BPh₄ complex was synthesized by treatment under nitrogen of a solution of [(triphos)Ni(S₂CS)] (0.5 mmol)² in CH₂Cl₂ (20 mL) with MeOSO₂F (0.55 mmol), followed by addition of NaBPh₄ (0.5 mmol) in ethanol (30 mL).

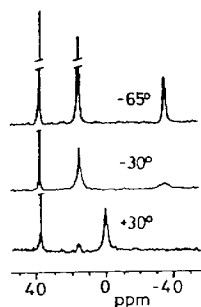


Figure 1. Variable-temperature $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of $[(\text{triphos})\text{Ni}(\text{S}_2\text{C}(\text{H})\text{PEt}_3)]\text{BPh}_4$ in acetone.

$[(\text{triphos})\text{Ni}(\text{CO})]$ (3). An acetone (30 mL) suspension of $[(\text{triphos})\text{Ni}(\text{S}_2\text{COEt})]\text{BPh}_4$ ⁸ (0.34 g, 0.3 mmol) was treated with a large excess of NaBH_4 in ethanol (20 mL) which caused the solid to dissolve, giving a yellow brown solution. When left standing for 1 h, the solution gave yellow crystals: yield 50%; IR (cm^{-1}) $\nu(\text{CO})$ 1890.

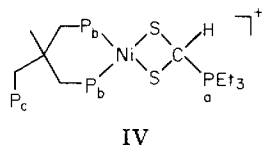
Anal. Calcd for $\text{C}_{42}\text{H}_{39}\text{NiOP}_3$: C, 70.91; H, 5.52; Ni, 8.25. Found: C, 70.81; H, 5.60; Ni, 8.19.

$[(\text{triphos})\text{Ni}(\text{SH})]$ (4). NaBH_4 (0.05 g, 1 mmol) in ethanol (20 mL) was allowed to react with a solution of $[(\text{triphos})\text{Ni}(\text{S}_2\text{CNEt}_2)]\text{BPh}_4$ ⁸ (0.34 g, 0.3 mmol) in acetone (30 mL). Within a few minutes a light brown solution was obtained. Yellow crystals precipitated in a short time; yield 40%.

Anal. Calcd for $\text{C}_{41}\text{H}_{40}\text{NiP}_3\text{S}$: C, 68.73; H, 5.62; Ni, 8.19; S, 4.47. Found: C, 68.68; H, 5.58; Ni, 8.12; S, 4.39.

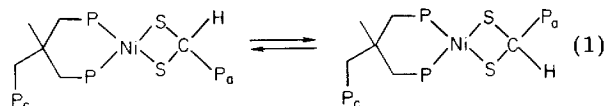
Results and Discussion

When NaBH_4 was reacted with $[(\text{triphos})\text{Ni}(\text{S}_2\text{CPEt}_3)](\text{BPh}_4)_2$ (triphos = 1,1,1-tris((diphenylphosphino)methyl)ethane) in acetone-alcohol, the color of the solution turns to orange and a microcrystalline orange solid of empirical formula $[(\text{triphos})\text{Ni}(\text{S}_2\text{C}(\text{H})\text{PEt}_3)]\text{BPh}_4$ (1) precipitates. This complex is diamagnetic and air stable in the solid state. It is soluble in all common organic solvents, in which it behaves as a 1:1 electrolyte (molar conductance in 10^{-3} nitroethane solution: $46 \text{ cm}^2 \Omega^{-1} \text{ mol}^{-1}$). The reflectance spectrum, with no band at frequencies $<15000 \text{ cm}^{-1}$, is typical of the square-planar nickel(II) complexes or of the low-spin square-pyramidal complexes, in which the metal atom undergoes a weak apical interaction.⁹ The IR spectrum shows no bands attributable to $\text{C}=\text{S}$ stretching modes. The structure of 1 has been unambiguously ascertained by means of variable-temperature ^{31}P NMR spectra. The ^{31}P NMR spectra for the temperature range $+30$ to -65°C are presented in Figure 1. At -65°C the spectrum indicates a "frozen" structure in which the triphos ligand is functioning as a bidentate ligand, one of the arms leading to a phosphine group being not coordinated to the metal. The most likely structure is illustrated in IV. The ^{31}P NMR assignments



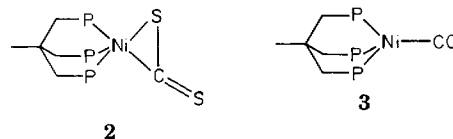
are as follows: $\delta(\text{P}_a)$ 38.90, $\delta(\text{P}_b)$ 16.72, and $\delta(\text{P}_c)$ -31.77. As the temperature increases, the uncoordinated Ph_2P group c begins to switch its position with the other two

arms of the tripod ligand as shown by the simultaneous broadening of the above resonances. At $+30^\circ\text{C}$ they give rise essentially to a broad absorption at ca. 1 ppm. The temperature increase induces only a very small high-field shift of the resonance due to the phosphorus atom of the PEt_3 group (from 38.90 ppm at -65°C to 38.03 ppm at $+30^\circ\text{C}$). Conversely when the temperature is decreased to -80°C (not shown), the resonance due to the uncoordinated phosphorus atom P_c and to the phosphorus atom P_a are split into two signals at 39.38 and 39.02 ppm and at 31.73 and 32.45 ppm, respectively. This splitting may be attributed to the presence of isomeric structures which at higher temperature rapidly interconvert as shown in eq 1. The phosphonium adduct of dithioformate $\text{S}_2\text{C}(\text{H})\text{PEt}_3$



has been recently found in the three complexes of general formula $[(\text{triphos})\text{MS}_2\text{C}(\text{H})\text{PEt}_3](\text{BPh}_4)_n$ ($\text{M} = \text{Fe}$,¹⁰ $n = 1$; $\text{M} = \text{Co}$,⁴ $n = 1$ or 2). These have been assigned a distorted square-pyramidal geometry around the metal center at variance with structure 1 where the triphos ligand acts as bidentate ligand. Likely, the latter compound receives extra stability from the well-known electronic factors which favor the formation of the low-spin d^8 square-planar complexes.

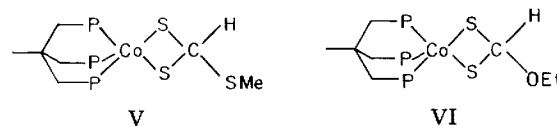
Reaction of $[(\text{triphos})\text{Ni}(\text{S}_2\text{CSMe})]\text{BPh}_4$ or $[(\text{triphos})\text{Ni}(\text{S}_2\text{COEt})]\text{BPh}_4$ with NaBH_4 produces dark brown or yellow crystals of $[(\text{triphos})\text{Ni}(\pi\text{-CS}_2)]$, 2, or $[(\text{triphos})\text{Ni}(\text{CO})]$, 3, respectively. Analytical and spectroscopic data



agree well with the representations given for 2 and 3. These compounds have been previously synthesized by different routes.^{11,12}

Both reactions which lead to the formation of 2 and 3 can be envisaged as involving in a first step the attack by the hydride ion from NaBH_4 on the electrophilic carbon atom of the CS_2 moiety of the methyl trithiocarbonate or xanthate ligands.

Nucleophilic attack by hydride ion on the CS_2 carbon atom of a 1,1-dithio ligand has been reported to occur in the reactions of NaBH_4 with metal complexes containing the chelated zwitterion $\text{Et}_3\text{P}-\text{CS}_2$ (see Introduction). More recently, we observed that NaBH_4 reacts with acetone solutions of the $[(\text{triphos})\text{Co}(\text{S}_2\text{CSMe})]\text{BPh}_4$, and $[(\text{triphos})\text{Co}(\text{S}_2\text{COEt})]\text{BPh}_4$ complexes to give the compounds V and VI, which can be isolated in good yield.¹⁰



The reaction mechanism for the formation of 2 may proceed by an initial attack of H^- on the CS_2 carbon atom of the trithiocarbonate complex to give an intermediate of type V. This intermediate could then interconvert directly to the final product by expelling methyl mercaptan, followed by a rearrangement of the CS_2 group. On

(8) Unpublished results of this laboratory. The $[(\text{triphos})\text{Ni}(\text{S}_2\text{CX})]\text{BPh}_4$ ($\text{X} = \text{OEt}$, NEt_2) complexes were synthesized by adding under nitrogen KS_2COEt or $\text{NaS}_2\text{CNEt}_2$ (1 mmol) in ethanol (10 mL) to a mixture of $\text{Ni}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ (1 mmol) in ethanol (20 mL), triphos (1 mmol) in CH_2Cl_2 (20 mL), and NaBPh_4 (1 mmol) in acetone (10 mL).

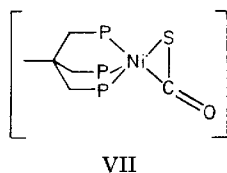
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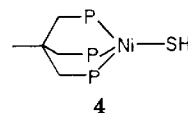
the basis of the above considerations, the reaction mechanism for compound 3 may be tentatively rationalized in terms of the formation of the unstable carbonyl sulfide, intermediate VII, which then converts to the carbonyl derivative 3. As a confirmation of this mechanism we



found that the nickel (0) complex $[\text{Ni}(\text{triphos})_2]$ reacts with COS to give 3 in good yield. Moreover, Werner et al. reported that the carbonyl complex $[(\text{C}_5\text{H}_5)\text{Co}(\text{PMe}_3)\text{CO}]$ is obtainable from the reaction of $[(\text{C}_5\text{H}_5)\text{Co}(\text{PMe}_3)_2]$ with COS via an unstable COS intermediate.¹³ The sulfur atom can be easily removed from the COS group by action of the phosphine ligand, a fact already ascertained in the reactions of some phosphine-rhodium compounds with COS, which give carbonyl complexes and phosphine sulfides.¹⁴ However, we have not been successful in isolating any phosphine sulfide.

An acetone solution of the dithiocarbamate complex $[(\text{triphos})\text{Ni}(\text{S}_2\text{CNET}_2)]\text{BPh}_4$ reacts with NaBH_4 , giving a light brown solution from which yellow crystals of empirical formula $[(\text{triphos})\text{Ni}(\text{SH})]$, 4, are precipitated. Compound 4 is air stable in the solid state but decomposes in solution even in an inert atmosphere. For this reason the compound has not been studied in solution. The room-temperature magnetic moment has a value of 2.11 μ_B , corresponding to a doublet ground state. The reflectance spectrum with absorption maxima at 8700 (sh), 10400, and 22200 cm^{-1} is comparable with those of distorted tetrahedral nickel (I) complexes.¹⁵ No band that could be attributed to the S-H stretching vibration has been detected in the IR spectrum. Indeed, this is rarely

observed, probably due to its low intensity.¹⁶ A preliminary X-ray analysis has confirmed the structure proposed for 4. The nickel atom is coordinated by the three



phosphorus atoms of the triphos ligand and by the sulfur atom, which form a distorted tetrahedral environment.

While we do not have enough information to propose a plausible mechanism for the formation of this thiol complex from the starting dithiocarbamate compound, it is useful to report the presence of some secondary products in the reaction mixture. Alkyl mercaptans and hydrogen sulfide are indeed detected when the $[(\text{triphos})\text{Ni}(\text{S}_2\text{C-X})]\text{BPh}_4$ ($\text{X} = \text{SMe, OEt, NEt}_2$) complexes are treated with NaBH_4 .

Indeed, tripod-like poly(tertiary phosphines) such as triphos can stabilize mercapto complexes of transition metals.¹⁷ In particular, the nickel complexes are limited to the μ -S dinuclear complex $[(\text{triphos})\text{Ni}(\mu\text{-S})\text{Ni}(\text{triphos})](\text{BPh}_4)_2$,¹⁸ obtained through reaction of nickel(II) aquocations with H_2S in the presence of triphos and NaBPh_4 . Up to date the dithiocarbamate reaction seems to be the only way of obtaining compound 4.

Acknowledgment. Thanks are expressed to Mr. F. Cecconi, F. Nuzzi, and D. Masi for technical assistance and to Mr. P. Innocenti for recording NMR spectra.

Registry No. 1, 83561-90-4; 2, 60294-99-7; 3, 14876-51-8; 4, 83561-91-5; $[(\text{triphos})\text{Ni}(\text{S}_2\text{CPEt}_3)](\text{BPh}_4)_2$, 83561-93-7; $[(\text{triphos})\text{Ni}(\text{S}_2\text{CSMe})]\text{BPh}_4$, 83561-95-9; $[(\text{triphos})\text{Ni}(\text{S}_2\text{COEt})]\text{BPh}_4$, 83561-97-1; $[(\text{triphos})\text{Ni}(\text{S}_2\text{CNET}_2)]\text{BPh}_4$, 83561-99-3; NaBH_4 , 16940-66-2; $(\text{triphos})\text{Ni}(\text{S}_2\text{CS})$, 83562-00-9; MeOSO_2F , 421-20-5; KS_2COEt , 151-01-9; $\text{NaS}_2\text{CNET}_2$, 148-18-5; $\text{Ni}(\text{BF}_4)_2$, 14708-14-6; triphos, 22031-12-5; NaBPh_4 , 143-66-8.

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