bear two terminal CO's and are bridged by a $Ph_2P^-$ unit that lies well out of the $Rh_3$ plane. The remaining Rh atom bears a single CO, and the two other $\mu$-$Ph_2P$ groups also lie in the $Rh_3$ plane. The Rh–Rh distances in this complex are all relatively short with respect to the elongated ones found in **2** (2.793 (1), 2.698 (1), and 2.806 (1) Å). It is only with the heptacarbonyl derivative $Rh_3(\mu\text{-}Ph_2P)_3(CO)_7$ that the Rh–Rh distances becomes comparable with those in **2** (3.124 (11), 3.223 (12), and 3.084 (11) Å).

## Experimental Section

All preparative chemistry was performed with standard inert-atmosphere techniques. Solvent preparation and NMR and IR spectra/instrumentation were as previously described.[4] Reliable microanalytical data for **2** could not be obtained due to the loss of CO (see text). $[Rh(\mu\text{-}t\text{-}Bu_2P)(CO)]_3$ (**1**) was prepared as previously described.[5] CO used was CP grade.

**Preparation of $Rh_3(\mu\text{-}t\text{-}Bu_2P)_3(\mu\text{-}CO)(CO)_4$ (2).** A deep red solution of $[Rh(\mu\text{-}t\text{-}Bu_2P)(CO)]_3$ (**1**) (0.20 g) in hexane (30 mL) was exposed to CO (1 atm) in a glass Schlenk vessel (5 min). The solution became an intense dark green and was concentrated (10 mL) by bubbling CO (1 atm) through it (*hood*). Cooling (−40 °C) for 12 h under a CO atmosphere (1 atm) gave dark crystals of **2** in quantitative yield. Crystals of **2** were isolated by decanting the supernatant liquid under a CO atmosphere. It may be stored at room temperature under a CO atmosphere but reverts slowly to **1** under vacuum or nitrogen in the solid state. **1** is re-formed rapidly by placing solutions of **2** under vacuum, and the cycle is reproducible. Mp: **2** loses CO at 100–105 °C, and the remaining material melts at 223–225 °C [the melting point of $[Rh(\mu\text{-}t\text{-}Bu_2P)(CO)]_3$ (**1**)]. IR (Nujol mull, KBr plates) ($cm^{-1}$): $\nu$(CO) 1963 m, 1945 s, 1915 w, 1832 m. $^1H$ NMR (in $C_6D_6$, ambient temperature relative to $Me_4Si$, $\delta$ 0.0): $\delta$ 1.45 (m, $t\text{-}Bu_2P$). $^{31}P\{^1H\}$ NMR (toluene-$d_8$, relative to 85% $H_3PO_4$(aq), $\delta$ 0.0): at ambient temperature $\delta$ 48.08 (m); at −80 °C $\delta$ 110.65 (m), 169.72 (m) (relative areas 2:1).

**X-ray Crystal Structure of $Rh_3(\mu\text{-}t\text{-}Bu_2P)_3(\mu\text{-}CO)(CO)_4$ (2).** Data were collected on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Mo K$\alpha$ radiation. Data were collected by the $\omega/2\theta$ scan technique at 23 ± 2 °C. Details of the standard data collection methods are similar to those outlined in ref 6. All calculations were performed on a PDP 11/44 computer using the Enraf-Nonius software package SDP PLUS.[7] Crystals of **2** were grown from hexane solutions under a CO atmosphere at (−40 °C). These were mounted in thin-walled glass capillaries under nitrogen (1 atm). Unit cell parameters were determined from 25 carefully centered reflections ($26.0° > 2\theta > 30.0°$). Crystal data for **2**: dark green prisms with metallic luster, maximum crystal dimensions 0.24 × 0.25 × 0.28 mm, triclinic, $P\bar{1}$ (No. 2), $C_{29}H_{54}O_5P_3Rh_3$, $M_r = 884.39$, $a = 11.578$ (1) Å, $b = 11.749$ (1) Å, $c = 15.502$ (1) Å, $\alpha = 98.815$ (1)°, $\beta = 94.457$ (1)°, $\gamma = 117.070$ (2)°, $V = 1829.3$ (5) Å$^3$, $D_c = 1.606$ g cm$^{-3}$, $Z = 2$, $\lambda$(Mo K$\alpha$) = 0.71073 Å (graphite monochromator), $\mu = 14.786$ cm$^{-1}$; scan width (0.8 + 0.35 tan $\theta$)°; range of indices (*hkl*) 0 to +13, −13 to +9, −18 to +18; standard reflections $4\bar{3}8$, $27\bar{1}$; decay of standards 9.8%. Data were corrected for Lorentz and polarization effects, and linear decay correction was applied. The structure was solved using MULTAN,[8] followed by successive cycles of difference Fourier maps and then least-squares refinement. All nonhydrogen atoms were refined anisotropically; hydrogen atoms were not located. A non-Poisson contribution weighting scheme with an experimental instability factor $P$[9] was used in the final stages of refinement ($P = 0.04$). Full-matrix least-squares refinement of 5258 reflections [$I > 3\sigma(I)$] out of 6082 unique observed ($3.0 < 2\theta < 50.0$) gave $R$ and $R_w$ values of 0.0336 and 0.0567, respectively. Number of variables = 361, data/parameter ratio = 14.565, shift to error ratio = 2.479, and esd of an observation of unit weight = 2.1356. The highest peak in the final difference Fourier was 0.667 e Å$^{-3}$. Supplementary material is available.[10]

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**Registry No.** 1, 104114-25-2; 2, 104114-26-3.

**Supplementary Material Available:** A complete ORTEP diagram of **2** and complete listings of bond lengths, angles, positional parameters, and temperature factors (8 pages); a complete listing of structure factors (53 pages). Ordering information is given on any current masthead page.

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(9) $P$ is used in the calculation of $\sigma(I)$ to downweight intense reflections in the least-squares refinement. The function minimized was $\sum w(|F_o| - |F_c|)^2$ where $w = 4(F_o)^2/[\sum(F_o)^2]_2$, where $[\sum(F_o)^2]^2 = [S^2(C + R^2B) + [P(F_o)^2]^2]/Lp^2$, where $S$ is the scan rate, $C$ is the total integrated peak count, $R$ is the ratio of scan time to background counting time, $B$ is the total background count, and $Lp$ is the Lorentz–polarization factor.

(10) See paragraph at end of paper regarding supplementary material.

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# Metal Complexes with Polydentate Sulfur-Containing Ligands. Crystal Structure of (2,6-Bis((ethylthio)methyl)pyridine)dibromozinc(II)

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The chemistry of transition-metal tridentate ligands containing N and/or O or tetradentates containing N and S as donor atoms is well known and documented, as indicated by the extensive studies on terpyridine (terpy),[1] pyridyl diimines,[2] $N_2S_2$ macrocycles,[3] or $N_2S_2$ open-chain ligands.[4] Quinquedentate ligands containing N and/or O have been less studied, probably due to the low availability of compounds of this kind; however, some ligands do exist such as 6,6″-bis($\alpha$-methylhydrazino)-4′-phenyl-2,2′:6′,2″-terpyridine = L, whose pentadenticity has been corroborated in $[SnMe_2L][PF_6]Cl$.[5] On the contrary, no structural information is available on tridentate $NS_2$ (S = thioether) and obviously on quinquedentate $N_xS_2O_{3-x}$ ligands. During the course of writing this paper, we became aware of a very recent paper by Lehn, Parker, and Rummer[6] in which are reported a ligand with the same $NS_2$ functionalities and its complexes with Rh and Pd, characterized only by spectroscopic methods.

In the course of studies on polynucleating macrocyclic sulfur-containing ligands derived from the condensation of 2,6-bis(bromomethyl)pyridine with thiol derivatives, it was found advantageous to examine the coordination chemistry of some related acyclic ligands. Here we describe the synthesis of a few of these ligands, their metal complexes, and the crystal structure of Zn(IIa)$Br_2$. To the best of our knowledge, there are only two other structural analyses of similar five-coordinate Zn complexes with one tridentate ligand and two monodentate ligands that have been reported in the literature. These have been reported by Einstein and Penfold[7] for $Zn(terpy)Cl_2$ and by Petersen, McCormick, and Nicholson[8] for $Zn(dapdH_2)Cl_2 \cdot H_2O$ where $dapdH_2$ is 2,6-diacetylpyridine dioxime. This, indeed, is the first example of a fully characterized complex with a tridentate acyclic ligand having thioether groups as coordinating agents.

## Experimental Part

Unless specifically mentioned, all operations were performed under nitrogen atmosphere. Dehydrated and deoxygenated solvents were used to synthesize the ligands. MeOH was dehydrated with Mg, and benzene with Na/benzophenone. Solvents were placed under vacuum to eliminate the dissolved oxygen. In all cases this treatment was sufficient to operate the reaction. Sodium methoxide had been prepared from sodium metal

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and dehydrated MeOH. 2,6-Bis(bromomethyl)pyridine was prepared according to a reported procedure.[9] Ethanethiol, 2-mercaptoethanol, and cysteamine hydrochloride are commercially available and were used as received.

Microanalysis (C, H, N) were performed in our analtyical laboratory on a Perkin-Elmer 240-B. $^1$H NMR spectra were run on a Bruker WP 80SY. All compounds reported in this paper analyzed correctly. No attempt was made to analyze the ligands IIa, IIb, IIc, because the analyses of their complexes and $^1$H NMR of the Zn and Cd compounds were correct.

**Synthesis of 2,6-Bis((ethylthio)methyl)pyridine (IIa).** NaMeO (37.7 mmol) in methanol was stirred for 15 min with ethanethiol (37.7 mmol, 2.8 mL) (total volume of methanol ca. 20 mL). Then, this solution was added to a solution of 2,6-bis(bromomethyl)pyridine (18.9 mmol, 5 g) in methanol (50 mL). After 2 h under reflux, the solvent was removed under reduced pressure. The resulting residue was extracted twice with diethyl ether (150 mL), and the solid was discarded. The extract was washed twice with an aqueous solution of $Na_2CO_3$ and then twice with water (150 mL each time), dried ($MgSO_4$), and evaporated under vacuum. Yield: 79% (3.1 g).

**Synthesis of 2,6-Bis(((hydroxyethyl)thio)methyl)pyridine (IIb).** This compound was prepared from 2-mercaptoethanol by applying the procedure indicated for IIa except for some minor modifications: 2,6-Bis(bromomethyl)pyridine was dissolved in a mixture of methanol/benzene (1:2); the refluxing time was 3 h; extraction was achieved with $CH_2Cl_2$; the extract was dried with $Na_2SO_4$ for 8 h. Yield: 57% (2.8 g).

**Synthesis of 2,6-Bis(((aminoethyl)thio)methyl)pyridine (IIc).** NaMeO (76 mmol) in methanol was stirred for 30 min with cysteamine hydrochloride. The formed NaCl was filtered out, and the filtrate was added to a solution of 2,6-bis(bromomethyl)pyridine (18.9 mmol, 5 g) in methanol/benzene (1:3). After 3 h under reflux, the solvent was removed under reduced pressure. The workup procedure is analogous to that described for IIb.

**Synthesis of Ni(IIa)$Cl_2$·$H_2O$.** $NiCl_2$·$6H_2O$ (1.76 mmol, 0.42 g) in methanol (3 mL) was added to a solution of 2,6-bis((ethylthio)methyl)pyridine (1.76 mmol, 0.4 g) in a mixture of methanol/ethyl acetate (1:1, 10 mL). After the mixture was allowed to stand at room temperature for 1 day in a vessel open to the air, a green solid was obtained. This was filtered out, washed with cold methanol, and dried in vacuo. Yield: 46%.

Analogous procedures were employed for Co(IIa)$Cl_2$ (yield 36%), Co(IIa)$(NO_3)_2$ (38%), and Ni(IIa)$Br_2$ (39%).

**Synthesis of Zn(IIa)$Br_2$.** This compound was prepared in the same manner as for Ni(IIa)$Cl_2$·$H_2O$ except for some minor modifications: $ZnBr_2$ dissolved in methanol (5 mL); IIa in methanol (3 mL). After the mixture was allowed to stand at room temperature for 3 days in an open vessel, white crystals (0.4 g) suitable for X-ray analysis were obtained.

Analogous procedures were employed for Co(IIa)$(SCN)_2$ (yield 42%), Ni(IIa)$(SCN)_2$ (29%), and Ni(IIc)$Br_2$·$H_2O$ (42%).

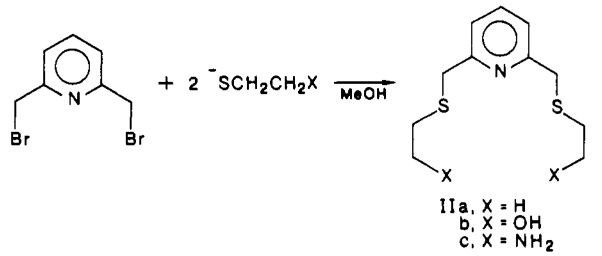
**Synthesis of Cu(IIb)$Cl_2$.** $CuCl_2$·$2H_2O$ (1.55 mmol, 0.26 g) suspended in THF (20 mL) was added to a solution of 2,6-bis(((hydroxyethyl)thio)methyl)pyridine (IIb) (1.55 mmol, 0.4 g) in THF (20 mL). The mixture was stirred for 1 h, and the resulting solid was filtered out, washed with cold THF, and dried in vacuo. Yield: 39%.

Analogous procedures were employed for Cd(IIb)$Cl_2$ (yield 31%), Ni(IIb)$Cl_2$ (40%), Ni(IIb)$(NO_3)_2$·$H_2O$ (42%), Co(IIb)$Cl_2$ (38%), Cd(IIc)$(NO_3)_2$ (23%); Cu(IIc)$Cl_2$ (36%), and Co(IIc)$Cl_2$ (38%).

**X-ray Structure Determination.** Colorless single crystals of $ZnBr_2$-$C_{11}NS_2H_{17}$ are monoclinic, space group $P2_1/n$, with $a = 12.622$ (7) Å, $b = 9.226$ (3) Å, $c = 15.033$ (4) Å, $\beta = 107.85$ (3)°, $V = 1666$ (1) Å$^3$, $Z = 4$, $D = 1.804$ g cm$^{-3}$, and $\mu = 64.8$ cm$^{-1}$.

X-ray diffraction data at 293 K were collected with an Enraf-Nonius CAD-4 four-circle diffractometer using graphite-crystal monochromated Mo K$\alpha$ radiation ($\lambda = 0.71069$ Å) on a 0.2 × 0.5 × 0.5 mm prismatic, crystal. The number of independent reflections collected by using the $\omega$–$2\theta$ technique and $2\theta < 50°$ was 2900. These are included within $-13 < h < 13$, $0 < k < 10$, and $0 < l < 17$. The nonunique data were averaged, and the resulting intensities were corrected for Lorentz and polarization effects. The reflections were measured at the azimuth position corresponding to a minimum absorption by using an imaginary crystal with finite but small thickness and infinitely large surface area (FLAT PSI MODE). The structure was solved by direct methods (MULTAN-82)[10] and refined by full-matrix least-squares methods (SHELX 1976).[11]

**Scheme I**



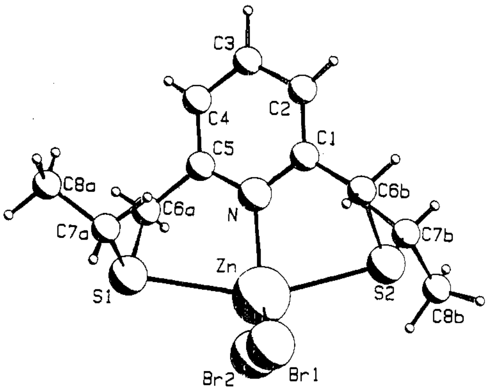


**Figure 1.** PLUTO drawing of Zn(IIa)$Br_2$. Selected bond lengths: Zn–N1 = 2.083 (5) Å, Zn–S1 = 2.741 (2) Å, Zn–S2 = 2.632 (2) Å, Zn–Br1 = 2.368 (1) Å, Zn–Br2 = 2.375 (1) Å. Selected bond angles: Br–Zn–Br = 125.3 (1)°; S–Zn–S = 157.0 (1)°, Br1–Zn–N1 = 120.3 (1)°, Br2–Zn–N1 = 114.3 (1)°.

The non-methylic hydrogen atoms were located by difference Fourier synthesis and refined with global isotropic temperature factors; the remaining hydrogen atoms were introduced into calculated positions and refined with an independent global temperature factor. The final residuals, for 207 variables refined against 2183 data for which $I > 2\sigma(I)$, were $R = 0.058$, $R_\omega = 0.052$ ($w = 1/(\sigma^2(F) + 0.0001F^2)$). In a final difference Fourier synthesis, the maximum heights are near those of the Zn atom (1.5 e A$^{-3}$). The scattering factors are taken from ref 12.

## Results and Discussion

The synthetic route to these (alkylthio)pyridine ligands is indicated in Scheme I and consists of the frequently employed preparation of sulfides by treatment of alkyl halides with salts of mercaptans. Ligands that have been synthesized are shown in Scheme I.

Because of their extreme tendency to yield oils, ligands IIb and IIc were characterized through analyses and $^1$H NMR of their Zn or Cd complexes. For all cases, IIa–c, the results of the $^1$H NMR analyses are in agreement with the proposed structure.

Ligand IIa reacts easily at room temperature with salts of transition metals in a +2 formal oxidation state to yield compounds with stoichiometries M(IIa)$X_2$ (M = Co, Ni, Zn; X = Cl, Br, $NO_3$, SCN). In no case, thus far, has a 2:1 ligand to metal ratio been observed.

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**Table I.** Fractional Coordinates ($\times 10^4$) for Non-Hydrogen Atoms with Their Standard Deviations and Equivalent Temperature Factors

| | $x/a$ | $y/b$ | $z/c$ | $B_{eq}$, Å$^2$ |
|---|---|---|---|---|
| Zn1 | 2534 (1) | 3877 (1) | 9733 (1) | 4.24 |
| Br1 | 4183 (1) | 2691 (1) | 9693 (1) | 5.66 |
| Br2 | 811 (1) | 2717 (1) | 9594 (1) | 6.39 |
| S1 | 3005 (2) | 4038 (3) | 11635 (1) | 4.80 |
| S2 | 2157 (2) | 4849 (2) | 8017 (1) | 4.80 |
| N1 | 2531 (4) | 6106 (6) | 9955 (4) | 3.18 |
| C1 | 2724 (5) | 7027 (7) | 9336 (5) | 3.50 |
| C2 | 2680 (5) | 8512 (8) | 9444 (5) | 4.46 |
| C3 | 2437 (6) | 9061 (9) | 10211 (6) | 5.29 |
| C4 | 2246 (6) | 8113 (9) | 10837 (6) | 4.90 |
| C5 | 2296 (5) | 6648 (8) | 10713 (5) | 3.64 |
| C6a | 2064 (6) | 5573 (9) | 11381 (5) | 4.67 |
| C6b | 3023 (6) | 6363 (9) | 8531 (5) | 5.01 |
| C7a | 4358 (6) | 4927 (10) | 12126 (6) | 5.71 |
| C7b | 774 (6) | 5670 (9) | 7659 (6) | 5.94 |
| C8a | 4483 (7) | 5766 (11) | 13008 (7) | 7.24 |
| C8b | −75 (7) | 4583 (13) | 7085 (7) | 8.08 |

**Table II.** Structural Parameters

a. Bond Lengths (Å) with Standard Deviations

| | | | |
|---|---|---|---|
| Zn1-Br1 | 2.368 (1) | C1-N1 | 1.336 (8) |
| Zn1-Br2 | 2.375 (1) | C5-N1 | 1.358 (8) |
| S1-Zn1 | 2.741 (2) | C2-C1 | 1.383 (10) |
| S2-Zn1 | 2.632 (2) | C6b-C1 | 1.504 (10) |
| N1-Zn1 | 2.083 (5) | C3-C2 | 1.378 (11) |
| C6a-S1 | 1.812 (8) | C4-C3 | 1.359 (11) |
| C7a-S1 | 1.834 (8) | C5-C4 | 1.368 (10) |
| C6b-S2 | 1.796 (8) | C6a-C5 | 1.503 (10) |
| C7b-S2 | 1.826 (7) | C8a-C7a | 1.501 (13) |
| | | C8b-C7b | 1.527 (12) |

b. Bond Angles in (deg) with Standard Deviations

| | | | |
|---|---|---|---|
| Br2-Zn1-Br1 | 125.3 (1) | C1-N1-Zn1 | 120.4 (4) |
| S1-Zn1-Br1 | 98.0 (1) | C5-N1-Zn1 | 120.6 (4) |
| S1-Zn1-Br2 | 90.9 (1) | C5-N1-C1 | 118.9 (6) |
| S2-Zn1-Br1 | 91.7 (1) | C2-C1-N1 | 121.8 (6) |
| S2-Zn1-Br2 | 100.5 (1) | C6b-C1-N1 | 116.5 (6) |
| S2-Zn1-S1 | 157.0 (1) | C6b-C1-C2 | 121.7 (7) |
| N1-Zn1-Br1 | 120.3 (1) | C3-C2-C1 | 119.2 (7) |
| N1-Zn1-Br2 | 114.3 (1) | C4-C3-C2 | 118.4 (7) |
| N1-Zn1-S1 | 77.9 (2) | C5-C4-C3 | 121.0 (7) |
| N1-Zn1-S2 | 79.2 (2) | C4-C5-N1 | 120.6 (7) |
| C6a-S1-Zn1 | 84.5 (2) | C6a-C5-N1 | 117.1 (6) |
| C7a-S1-Zn1 | 108.7 (3) | C6a-C5-C4 | 122.3 (6) |
| C7a-S1-C6a | 101.8 (4) | C5-C6a-S1 | 114.1 (4) |
| C6b-S2-Zn1 | 86.6 (2) | C1-C6b-S2 | 113.1 (5) |
| C7b-S2-Zn1 | 107.4 (3) | C8a-C7a-S1 | 114.8 (6) |
| C7b-S2-C6b | 101.8 (4) | C8b-C7b-S2 | 109.6 (6) |

The common stoichiometry presented by all these complexes suggested, as we had initially thought, that compound IIa behaves as a tricoordinated ligand, via the nitrogen and the sulfur atoms.

More confusing are the $^1$H NMR data of IIa and $\mathrm{Zn(IIa)Br_2}$ with regard to the denticity of the ligand. Because of the sulfur coordination to the zinc ion, an NMR shift of the sulfur-bonded methylene protons $\mathrm{CH_3C}H_2\mathrm{SC}H_2$py would be expected. This indeed happens for the bridging methylene between the sulfur and the pyridine moieties (3.8 ppm in IIa; 4.3 ppm in $\mathrm{Zn(IIa)Br_2}$), but it does not for the other group (2.5 ppm in IIa; 2.45 ppm in $\mathrm{Zn(IIa)Br_2}$). Since the observed spectroscopic properties were not sufficient to clearly determine the chelating capacity of ligand IIa, an X-ray crystal structure analysis of $\mathrm{Zn(IIa)Br_2}$ was undertaken.

As can be observed in Figure 1, which also shows the atom-labeling scheme, the coordination polyhedron about the zinc atom can be described as a trigonal bipyramid (TBP). The bromide ligands are cis and occupy two of the equatorial positions. The remaining sites are occupied by the sulfur atoms and the nitrogen of the tridentate chelating ligand (IIa). The angle between the normal of the mean planes defined by N-Zn-Br1-Br2 and Zn-S1-S2-N is 85.5°. The C6a and C6b atoms depart from the last mean plane 1.02 Å. In addition, these two planes depart from the pyridine plane −0.03 and +0.05 Å, respectively. Table I contains the final positional parameters. Table II contains the bond lengths and angles. It is interesting to comment on the slightly long S-Zn distances (average 2.7 Å), that could explain the small chemical shift $^1$H NMR variation of the $\mathrm{CH_3CH_2S}$ protons from noncoordinated to coordinated IIa.

Compounds IIb and IIc react readily at room temperature with salts of transition metals in a +2 formal oxidation state, yielding compounds with stoichiometries $\mathrm{M(IIb)X_2}$ (M = Cd, Cu; X = $\mathrm{NO_3}$, Cl) or $\mathrm{M(IIc)X_2}$ (M = Ni, Cd; X = Cl, $\mathrm{NO_3}$). These complexes present, with respect to those of IIa, an enhanced solubility and, as their precursors do, a great tendency for oiling. This has precluded the growth of crystals suitable for X-ray analysis; however, some structural information can be obtained from the spectroscopic data.

The IR spectra of $\mathrm{M(IIc)X_2}$ compounds display N-H absorption bands at 3160 and 3260 cm$^{-1}$, 100 and 80 cm$^{-1}$ lower than the corresponding ones in IIc, clearly evidencing a M-N bond. Less evidence exists on the pyridine and/or sulfur coordination to the metal, since there are not any bands in the IR spectrum that unambiguously confirm it.

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**Registry No.** IIa, 103884-50-0; IIb, 103884-51-1; IIc, 103884-52-2; $\mathrm{Ni(IIa)Cl_2}$, 103884-35-1; $\mathrm{Co(IIa)Cl_2}$, 103884-36-2; $\mathrm{Co(IIa)(NO_3)_2}$, 103884-37-3; $\mathrm{Ni(IA)Br_2}$, 103884-38-4; $\mathrm{Zn(IIa)Br_2}$, 103884-39-5; $\mathrm{Co(IIa)(SCN)_2}$, 103884-40-8; $\mathrm{Ni(IIa)(SCN)_2}$, 103884-41-9; $\mathrm{Cu(IIb)Cl_2}$, 103884-43-1; $\mathrm{Cd(IIb)Cl_2}$, 103884-44-2; $\mathrm{Ni(IIb)Cl_2}$, 103884-45-3; $\mathrm{Ni(IIb)(NO_3)_2}$, 103884-46-4; $\mathrm{Co(IIb)Cl_2}$, 103980-73-0; $\mathrm{Ni(IIc)Br_2}$, 103884-42-0; $\mathrm{Cd(IIc)(NO_3)_2}$, 103884-47-5; $\mathrm{Cu(IIc)Cl_2}$, 103884-48-6; $\mathrm{Co(IIc)Cl_2}$, 103884-49-7; 2,6-bis(bromomethyl)pyridine, 7703-74-4; ethanethiol, 75-08-1; 2-mercaptoethanol, 60-24-2; cysteamine hydrochloride, 156-57-0.

**Supplementary Material Available:** Tables of positional parameters, bond distances to hydrogen atoms, and anisotropic thermal parameters (*U*'s) (3 pages); a table of observed and calculated structure factors (13 pages). Ordering information is given on any current masthead page.

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# Variable-Temperature Magic-Angle-Spinning $^{13}$C NMR of Solid $\mathrm{Fe_3(CO)_{12}}$

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Several years ago we reported that the room-temperature magic-angle-spinning (MAS) $^{13}$C NMR spectrum of solid $\mathrm{Fe_3(CO)_{12}}$ is consistent with rapid bridge-terminal exchange of carbonyls occuring in the solid state.[1] Broad-line NMR results for $\mathrm{Fe_3(CO)_{12}}$ were also reported to be consistent with a dynamic process in the solid state.[2] We have now obtained MAS $^{13}$C NMR spectra for $\mathrm{Fe_3(CO)_{12}}$ at temperatures down to −93 °C. These show, for the first time, a spectrum consistent with the static structure of $\mathrm{Fe_3(CO)_{12}}$.

## Experimental Section

Triiron dodecacarbonyl (Pressure Chemicals) was enriched in $^{13}$CO by stirring a methylene chloride solution of $\mathrm{Fe_3(CO)_{12}}$ under an atmosphere of enriched carbon monoxide in the presence of 10 mg of 5% Pd/C. The level of enrichment was determined by mass spectroscopy to be 18%. The enriched $\mathrm{Fe_3(CO)_{12}}$ was recrystallized from pentane prior to use.

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[1] Dorn, H. C.; Hanson, B. E.; Motell, E. *Inorg. Chim. Acta* **1981**, *74*, L71.

[2] Gleeson, J. W.; Vaughan, R. W. *J. Chem. Phys.* **1983**, *78*, 5384.

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