

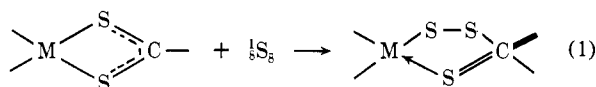
Sulfur Chelates. XV.¹ Sulfur Addition and Abstraction Reactions of Dithioaryl Acid Complexes of Zinc(II), Nickel(II), Palladium(II), and Platinum(II) and the X-Ray Crystal Structures of Bis(trithioperoxycumato)zinc(II) and Dithiocumato(trithioperoxycumato)nickel(II)

John P. Fackler, Jr.,* J. A. Fetchin, and David C. Fries

Contribution from the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106. Received March 15, 1972

Abstract: The single-crystal X-ray structures of Ni(*p*-dtc)₂S and Zn(*p*-dtc)₂S₂ (*p*-dtc = *p*-dithiocumate) are described. Five-membered disulfide (S-S bonds ~2.01 Å) containing chelate rings are found with planar NiS₄ and tetrahedral ZnS₄ coordination geometries. Mass spectroscopic studies of the sulfur addition reaction to Zn(dtb)₂ and Ni(dtb)₂ (dtb = dithiobenzoate) establish that sulfur atom scrambling occurs throughout all possible sites in Zn(dtb)₂. However, the addition of sulfur photochemically to Ni(dtb)₂ causes its appearance adjacent to the carbon atom rather than the metal. It is removed specifically from this position with triphenylphosphine. Kinetic studies of the reaction of triphenylphosphine with Ni(*p*-dtc)₂S establish that the sulfur abstraction occurs with a rate which is dependent on concentrations of both the complex and the phosphine. The $E_a = 7.8 \pm 1.0$ kcal/mol. Nuclear magnetic resonance studies establish the existence of an exceptional sulfur atom lability in the zinc sulfur-rich complexes. The activation energy for the sulfur atom exchange between dithiolate and perthiolate ligands is ~5.5 kcal/mol. The reaction is concentration dependent in such a way as to suggest that a rapid equilibrium exists between Zn(*p*-dtc)₂S₂, sulfur, and Zn(*p*-dtc)₂. This work suggests that other related zinc dithiolates such as the dithiocarbamates and xanthates activate sulfur in a similar manner.

Certain metal dithiolates react with sulfur or polysulfides²⁻⁵ to form products wherein chelate ring expansion occurs (eq 1). This reaction has been found



to occur with neutral⁴ dithioaryl acid-metal complexes and with anionic complexes² such as Ni(CS₃)₂²⁻. One or more "extra" sulfur atoms per atom of metal are found in the "oxidized" complex. Single-crystal X-ray data have firmly established the formation of the disulfide linkage⁶ in FeL₃S, where L is *p*-dithiotoluolate. Preliminary structural results^{7a} have been reported for the NiL₂S and ZnL₂S₂ complexes also, where L is *p*-dithiocumate. The details of these studies are described here. Bonamico, *et al.*,^{7b} recently described the structures of the dithiobenzoates NiL₂S₂ and ZnL₂S₂.

With the structures of the sulfur oxidative addition products now firmly established for nickel(II) and zinc(II) dithioarylates, the details of our investigations of the mechanism of sulfur addition and sulfur atom rearrangement can be presented. Some preliminary results which preceded the structural work have been reported.^{8,9} In view of the expanding interest in the chemistry of these sulfur-rich species, especially in

regard to similarities with the chemistry of nonheme iron proteins containing "inorganic sulfur,"^{10a} our studies of the sulfur atom lability in sulfur-rich zinc dithiolates also are presented, even though some important details remain obscure. These results bear upon studies of the mechanism by which chemically related species such as xanthates of zinc function as vulcanization catalysts.^{10b}

Experimental Section

All chemicals and solvents were used as received, unless otherwise specified. The isotopic enrichment of ³⁴S (37.2%) was obtained from Oak Ridge National Laboratory, Oak Ridge, Tenn. Ammonium sulfide solution (44% technical grade) was obtained from Matheson Coleman and Bell, and *p*-isopropylbenzaldehyde was obtained in technical grade from Eastman Organic Chemicals. Triphenylphosphine, received from Aldrich Chemical Co., was recrystallized. All analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. The products were checked for purity with thin layer chromatography.

Physical Measurements. Nuclear magnetic resonance measurements were obtained on Varian A-60A and HA-100 nuclear magnetic resonance spectrometers. All infrared spectra were recorded on Beckman IR-8 and IR-5A (CsBr optics) spectrophotometers. Visible spectra were recorded on the Cary 14 spectrophotometer. All melting points are uncorrected.

Purification of Toluene. Technical toluene (1800 ml) was stirred for 1 hr with 200 ml of concentrated H₂SO₄ in a 2000-ml beaker packed in ice. The organic layer was separated and stirred with 200 ml of 10% KOH solution for 30 min. After separating layers, the toluene was dried with Na₂SO₄, refluxed over sodium for 12-24 hr, and distilled through a packed column. The fraction at 110.5° was collected. Toluene was redistilled from potassium as needed.

Preparation of Complexes. The bis(perthioaryl acid) complexes with zinc(II) were prepared by a previously reported procedure.⁴ The bis(dithio- and the perthiodithioaryl acid) complexes of nickel(II), palladium(II), and platinum(II) were prepared from the potassium salt of the acid, using a slight modification of the procedure described by Bost and Shealy¹¹ for crude zinc(II) dithio acids.

(1) Part XIV: J. M. Andrews, D. Coucouvanis, and J. P. Fackler, *Inorg. Chem.*, **11**, 493 (1972).

(2) D. Coucouvanis and J. P. Fackler, Jr., *J. Amer. Chem. Soc.*, **89**, 1346 (1967).

(3) J. P. Fackler, Jr., and D. Coucouvanis, *ibid.*, **89**, 1745 (1967).

(4) J. P. Fackler, D. Coucouvanis, J. A. Fetchin, and W. C. Seidel, *ibid.*, **90**, 2784 (1968).

(5) D. Coucouvanis, *Progr. Inorg. Chem.*, **11**, 233 (1970).

(6) D. Coucouvanis and S. J. Lippard, *J. Amer. Chem. Soc.*, **90**, 3281 (1968).

(7) (a) D. C. Fries and J. P. Fackler, Jr., *Chem. Commun.*, 276 (1971);

(b) M. Bonamico, G. Dessy, V. Fares, and L. Scaramuzza, *J. Chem. Soc. A*, 3191 (1971).

(8) J. P. Fackler, Jr., J. A. Fetchin, and J. A. Smith, *J. Amer. Chem. Soc.*, **92**, 2910 (1970).

(9) J. Fackler, Jr., and J. A. Fetchin, *ibid.*, **92**, 2912 (1970).

(10) (a) See, for example, T. Kimura, Y. Nagata, and J. Tsyrgi, *J. Biol. Chem.*, **246**, 5140 (1971); (b) W. Hoffmann, "Vulcanization and Vulcanizing Agents," Garden City Press, Letchworth, England, 1967.

(11) R. W. Bost and O. L. Shealy, *J. Amer. Chem. Soc.*, **73**, 25 (1951).

Bis(*p*-perthiocumato)zinc(II), $Zn(p-dtc)_2S_2$. Sulfur (7 g) and 50 ml of $(NH_4)_2S$ (25% solution) in 50 ml of THF were added to a solution of 29.6 g of *p*-isopropylbenzaldehyde (0.2 mol) in 50 ml of THF. After the reaction mixture was boiled for 3 min, ice was added to cool it to room temperature. A solution of 15 g of $ZnCl_2$ in 100 ml of H_2O was added to the ligand mixture, and water was added to bring the total volume to approximately 500 ml. The red oil which formed was separated from the aqueous layer and triturated with methanol, which caused solidification. The methanol was decanted, and the orange-red precipitate was washed with 400 ml of 10% (v/v) HCl solution and several portions of methanol. Upon drying in the air, 36.9 g (71% yield) was obtained. The product was recrystallized several times from $CHCl_3$ -*n*-pentane, yielding small red-orange crystals, mp 121–123°.

Anal. Calcd for $C_{20}H_{22}S_6Zn$: C, 46.78; H, 4.32. Found: C, 45.41; H, 4.67.

Bis(*p*-dithiocumato)zinc(II), $Zn(p-dtc)_2$. A solution of triphenylphosphine in $CHCl_3$ in slight excess of stoichiometric requirements was added to a hot $CHCl_3$ solution of $Zn(p-dtc)_2S_2$. After cooling the solution with cold water, anhydrous ether was added, and crystals precipitated out. (The triphenylphosphine sulfide produced stays in solution.) Recrystallization was accomplished by dissolving the complex in a minimum amount of $CHCl_3$ and adding *n*-pentane, mp 169–170°.

Anal. Calcd for $C_{20}H_{22}S_4Zn$: C, 52.68; H, 4.86. Found: C, 53.01; H, 5.55.

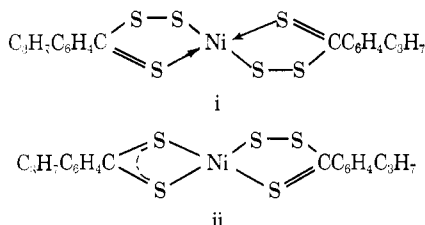
Bis(*p*-perthiocumato)nickel(II), $Ni(p-dtc)_2S_2$. To a solution of 2.00 g of $Zn(p-dtc)_2S_2$ (3.84×10^{-3} mol) in 50 ml of THF was added a solution of 1.00 g of $NiCl_2 \cdot 6H_2O$ (in slight excess) in 25 ml of MeOH. After 2 min, water was added to the solution, and the precipitate was filtered, washed with water, and air-dried. The crude yield, 1.85 g (94% yield), was dissolved in $CHCl_3$, and *n*-pentane was added. Dark blue violet crystals, which gave a red-brown chloroform solution, were obtained, mp 150–151°.

Anal. Calcd for $C_{20}H_{22}S_6Ni$: C, 46.18; H, 4.26. Found: C, 47.11; H, 4.57.

(*p*-Perthiocumato)(*p*-dithiocumato)nickel(II), $Ni(p-dtc)_2S$. To a solution containing 3.0 g of sulfur and 32 ml (44%) of ammonium sulfide was added 50 ml of EtOH. After all the sulfur dissolved, the resulting ammonium polysulfide solution was added to 29.6 g of *p*-isopropylbenzaldehyde in 150 ml of EtOH. The reaction mixture turned yellow, an oil formed, and sulfur precipitated. Upon heating, most of the oil went into solution. During a 3-min boiling period, the mixture turned dark red-brown. The reaction mixture was cooled to 0° by the addition of ice, which caused an amorphous yellow resin to form (sulfur) which was removed with a spatula. A solution containing 50 ml of concentrated HCl and 250 ml of H_2O was added to the reaction mixture, and the crude product was extracted into 400 ml of Et_2O . The ether layer was shaken with a solution of 13 g of KOH in 400 ml of H_2O , yielding a brown-red aqueous solution. After adjusting the pH to ~6–7 with dilute HCl, 6.0 g of $NiCl_2 \cdot 6H_2O$ dissolved in 100 ml of H_2O was added to the aqueous solution. The purple-blue precipitate formed was washed with EtOH (absolute) and *n*-pentane, yielding 4.6 g of mixed products. The crude product was extracted with Et_2O , producing a purple solution. After filtering, the Et_2O was evaporated, leaving 1.0 g of crude $Ni(p-dtc)_2S$. The material was recrystallized from absolute Et_2O -absolute EtOH, producing large violet needles, mp 141–142°.

Anal. Calcd for $C_{20}H_{22}S_5Ni$: C, 49.90; H, 4.61. Found: C, 49.75; H, 4.60.

(12) The formulation used to indicate a perthioaryl acid ligand is placement of S after the dithioaryl acid abbreviation. Therefore, $Ni(p-dtc)_2S_2$ refers to i, whereas $Ni(p-dtc)_2S$ would refer to ii. Abbreviations include Et = C_2H_5 ; *p*-dtc = $S_2CC_6H_4$ -*p*-(*i*- C_3H_7); dtb = $S_2CC_6H_5$; *p*-dtt = *p*- $CH_3C_6H_4CS_2$; tmdtb = 3,4,5-trimethoxydithiobenzoate.



viations include Et = C_2H_5 ; *p*-dtc = $S_2CC_6H_4$ -*p*-(*i*- C_3H_7); dtb = $S_2CC_6H_5$; *p*-dtt = *p*- $CH_3C_6H_4CS_2$; tmdtb = 3,4,5-trimethoxydithiobenzoate.

Bis(*p*-dithiocumato)nickel(II), $Ni(p-dtc)_2$. The blue, Et_2O -insoluble material (3.6 g) obtained from the preparation of $Ni(p-dtc)_2S$ described above was recrystallized from $CHCl_3$ -*n*-pentane, yielding dark blue needles, mp 220–222°.

Anal. Calcd for $C_{20}H_{22}S_4Ni$: C, 53.46; H, 4.94. Found: C, 53.05; H, 4.93.

(*p*-Perthiocumato)(*p*-dithiocumato)palladium(II), $Pd(p-dtc)_2S$. A solution of the potassium salt of the perthio- and dithiocumate solution was obtained as described in the preparation of $Ni(p-dtc)_2S$. The pH of the potassium solution was adjusted to 7 with HCl (d), and 100 ml of the ligand solution (0.025 mol, assuming theoretical conversion of the aldehyde to the dithio- and perthiocumate species) was added to 1.00 g of K_2PdCl_4 in 50 ml of H_2O . A dark brown-violet precipitate developed almost immediately. After standing at room temperature about 1 hr, the solution was filtered, washed with EtOH, air-dried, and washed with Et_2O , which dissolved the soluble $Pd(p-dtc)_2S$ species. (The $Pd(p-dtc)_2S$ product was insoluble.) After evaporation of the Et_2O solution, the product was recrystallized from $CHCl_3$ -*n*-pentane in a Dry Ice-acetone bath, yielding small orange red crystals, mp 177–179°. The supernatant solution was evaporated at room temperature, yielding large dark red-orange crystals embedded in amorphous material. The amorphous contaminant was washed into *n*-pentane, leaving red-orange crystals behind. Slow evaporation from Et_2O and $CHCl_3$ yielded large red-orange crystals, mp 179–180°.

Anal. Calcd for $C_{20}H_{22}S_5Pd$: C, 45.40; H, 4.19. Found: C, 45.81; H, 4.24.

Bis(*p*-dithiocumato)palladium(II), $Pd(p-dtc)_2$. The Et_2O -insoluble material obtained in the $Pd(p-dtc)_2S$ preparation was dissolved in $CHCl_3$ and filtered and *n*-pentane was added. Small purple crystals were obtained when the *n*-pentane- $CHCl_3$ solution was put in a Dry Ice-acetone bath; slow dec ~245°, melting at 260°. The *n*-pentane- $CHCl_3$ supernatant solution was evaporated slowly, yielding large violet crystals; dec ~259°, melting at 263–265°. Slow evaporation from $CHCl_3$ yielded large violet needles, mp 264–266°.

Anal. Calcd for $C_{20}H_{22}S_4Pd$: C, 48.33; H, 4.46. Found: C, 48.27; H, 4.13.

(*p*-Perthiocumato)(*p*-dithiocumato)platinum(II), $Pt(p-dtc)_2S$. To a solution containing 14.8 g (0.1 mol) of *p*-isopropylbenzaldehyde in 75 ml of EtOH were added 1.5 g of sulfur and 16 ml (44%) of $(NH_4)_2S$ in 30 ml of EtOH. The procedure outlined in the preparation of $Ni(p-dtc)_2S$ was followed to the point of obtaining the acid solution in 400 ml of Et_2O . This was shaken with 8.0 g of KOH in 100 ml of water, and the separated water solution was acidified with HCl until the pH was 6. To this solution, which was heated to boiling, was added 2.00 g of K_2PtCl_4 in 50 ml of H_2O , which was also heated to boiling. After the combined solution cooled to room temperature for 1 hr, a brown product was filtered off and washed with H_2O , EtOH, and finally *n*-pentane, yielding 3.2 g of brown-orange powder. The powder was extracted into Et_2O , leaving behind a brown product.

The Et_2O -soluble product was obtained by evaporating the Et_2O , washing with *n*-pentane, and dissolving in $CHCl_3$. Upon slow evaporation of $CHCl_3$, dark red needles, dec ~179°, were obtained. Further purification (column chromatography on silica gel) yielded a product which decomposed at ~184°. The ether-insoluble product was eluted with a CS_2 -*n*-hexane (1:1, v/v mixture) solution; the brown-orange band (the first band), when evaporated and recrystallized from $CHCl_3$ -*n*-pentane (in a Dry Ice-acetone bath) and redissolved and slowly evaporated in $CHCl_3$, yielded needles of $Pt(p-dtc)_2S$, dec 184–192°.

Anal. Calcd for $C_{20}H_{22}S_5Pt$: C, 38.88; H, 3.59. Found: C, 38.61; H, 3.58.

Bis(*p*-dithiocumato)bis- μ -(*p*-dithiocumato)-diplatinum(II), $[Pt(p-dtc)_2]_2$. A green-brown band remained on the silica gel column from which $Pt(p-dtc)_2S$ had been obtained. Elution with CS_2 produced a greenish brown powder. Evaporation from CS_2 produced dark green-brown crystals, dec above 100°; mol wt, calcd 1171; found osmometrically in $CHCl_3$, 1090.

Anal. Calcd for $C_{40}H_{44}S_8Pt_2$: C, 41.01; H, 3.79; S, 21.90. Found: C, 43.19; H, 4.40; S, 21.73.

Bis(*p*-dithiolumato)palladium(II), $Pd(p-dtt)_2$. To a solution of 1.0 g of $Zn(p-dtt)_2$ in 200 ml of hot THF was added 0.812 g of K_2PdCl_4 (2.5 mmol) in 25 ml of hot H_2O . A precipitate formed immediately. Upon cooling the product (45% yield) was removed by filtration and washed with EtOH and *n*-pentane. Small violet crystals were obtained, mp 305–307° from *n*-pentane- CS_2 .

Anal. Calcd for $C_{16}H_{14}S_4Pd$: C, 43.59; H, 3.20. Found: C, 43.23; H, 3.06.

Bis(*p*-dithioloato)bis- μ -(*p*-dithioloato)-diplatinum(II), [Pt(*p*-dt)₂]₂. This product was prepared in a manner identical with that for the palladium derivative, mp 288–289°. Its infrared spectrum suggests bridging and terminal dithiolate ligands indicative of dimer formation.

Anal. Calcd for C₁₆H₁₄S₄Pt: C, 36.27; H, 2.65. Found: C, 37.52; H, 2.82.

Bis(dithiobenzoato)nickel(II), Ni(dtb)₂, and **Dithiobenzoatoperthiobenzoatonickel(II)**, Ni(dtb)₂S. Ni(dtb)₂ and Ni(dtb)₂S were prepared by previously reported methods.⁴

Sulfur-34 Addition to Bis(dithiobenzoato)nickel(II). Two methods were used to achieve sulfur addition to Ni(dtb)₂. In each method, a sample containing 37.2% sulfur-34 was used as received from the Atomic Energy Commission, Oak Ridge National Laboratory.

Thermal Method A. Equal molar amounts of enriched sulfur (1.485 mg) and Ni(dtb)₂ (16.327 mg) were heated to reflux in 7 ml of dimethylformamide for an additional 30 sec after a color change from green-brown to purple was observed. Upon the addition of 100 ml of H₂O, Ni(dtb)₂³⁴S precipitated. The product was filtered, washed with H₂O, and air-dried. Part of this product was treated with triphenylphosphine (2× excess) in boiling CHCl₃. The triphenylphosphine sulfide was removed from the insoluble Ni(dtb)₂ with Et₂O.

Photolytic Method B. A deaerated 50 ml of CHCl₃ solution (under nitrogen), containing 2.037 mg of sulfur-34 and 22.671 mg of Ni(dtb)₂, was irradiated for 20 hr with a mercury uv source. Approximately 50% of the Ni(dtb)₂ did not dissolve and remained unreacted at the bottom of the quartz tube. The purple solution was filtered, air evaporated, and redissolved in an Et₂O–CHCl₃ solution, in order to separate the more soluble Ni(dtb)₂³⁴S from unreacted S₈ and Ni(dtb)₂. The solvent was evaporated in air, yielding Ni(dtb)₂S. A portion of the product was treated as above with triphenylphosphine in boiling CHCl₃. The solution was cooled quickly and absolute EtOH was added. The blue Ni(dtb)₂ precipitate was washed with absolute EtOH and anhydrous Et₂O. A solution containing Ni(dtb)₂ but no sulfur produced no reaction under identical photolysis conditions.

Sulfur-34 Addition to Bis(dithiobenzoato)zinc(II). Sulfur-enriched 37.2% sulfur-34 was added to Zn(dtb)₂ in CHCl₃ by the photolytic procedure described above for Ni(dtb)₂.

Other Photolysis Reactions. When S₈ dissolved in CHCl₃ or toluene was irradiated with the mercury uv source at 2537 Å for 3–5 min, removed from the uv source, and mixed with blue Ni(dtb)₂ solutions, the solutions slowly turned violet. The violet product, identified by its melting point and visible spectroscopy, was Ni(dtb)₂S. Pd(dtb)₂S and Zn(dtb)₂S₂ were obtained by direct photolysis of degassed CHCl₃ solutions containing sulfur and the metal dithiobenzoate.

Mass Spectrometer Data. Solid samples of the various complexes studied here were introduced into a Varian M-66 mass spectrometer at probe temperatures between 150 and 160°. Ionization voltages near 60 eV were used with currents at ~40 μA and pressures between 4.0 and 14.0 × 10⁻⁷ Torr. Careful measurements were made of the effect of ionization voltage, probe temperature, and the time the sample remained in the probe on the reproducibility of the data.¹³ With the nickel and zinc dithiobenzoate derivatives, it was found that the *m/e* 122 peak intensity increased abnormally below ~17 eV ionization voltage. Since this *m/e* ratio can represent ⁵⁸Ni³²S₂⁺, the *m/e* 124 peak which reflects the formation of ⁶⁰Ni³²S₂⁺ was monitored. Above ~17 eV the intensity of this peak is negligible (<5% of *m/e* 122). Since the intensity of the *m/e* 122 peak gradually changes with the time the sample remains in the probe, some thermal decomposition of the sample probably occurs, leaving behind less volatile nickel sulfide materials. The results recorded are those obtained reproducibly for several runs and under the optimum conditions listed above.

Sulfur Abstraction from Ni(*p*-dtc)₂S with Triphenylphosphine. Kinetic data were obtained spectrophotometrically on a Cary Model 14 at a wavelength of 5300 Å. All solutions were prepared with purified toluene which was deoxygenated with dry N₂ prior to solution preparation. A constant-temperature bath was used to maintain the temperatures of the cell compartments and solutions of triphenylphosphine and Ni(*p*-dtc)₂S kept in the arms of a Y-tube prior to mixing. The time of each run was started after inversion of the Y-tube. The Y-tube was placed in the bath for at least 15 min prior to mixing. The decrease in absorbance was recorded as a function of time. Assuming Beer–Lambert law dependence

for the series absorbing at 5300 Å, and molar extinctions of 10,750 and 3560 M⁻¹ cm⁻¹ respectively for Ni(*p*-dtc)₂S and Ni(*p*-dtc)₂, the concentration of Ni(*p*-dtc)₂S was calculated. Rate constants and activation parameters were evaluated by standard procedures¹⁴ (Table VI).

Stock solutions of Pd(*p*-dtc)₂S in toluene were mixed with solutions of triphenylphosphine in toluene. Plots of absorbance vs. equivalents of triphenylphosphine were made at various wavelengths.⁴

Kinetic Studies of Sulfur Lability by Nmr Line-Shape Analysis. Mixtures of Zn(*p*-dtc)₂S₂ and Zn(*p*-dtc)₂ corresponding to various labile sulfur-to-zinc ratios were obtained by dissolving weighed quantities of the two complexes in 1:1 (v/v) CS₂:Et₂O. Baker analyzed CS₂ and MCB anhydrous ether were used. Comparative proton nmr studies were made on solutions formed by adding triphenylphosphine to Zn(*p*-dtc)₂S₂. The phenyl proton resonances did not interfere with observation of the low-field AB doublet. Temperature stability was accomplished using Varian Model 1040 temperature control units.

X-Ray Crystallographic Structural Data. Crystals of both Ni(*p*-dtc)₂S and Zn(*p*-dtc)₂S₂ were grown from saturated chloroform–methanol (20/80, v/v) solutions by slow evaporation and obtained as large, well-faceted prismatic plates. (The crystals of Ni(*p*-dtc)₂S were elongated about the *c* axis.) Suitable crystals of each were mounted in glass capillaries for data collection. Cell constants were obtained from a least-squares analysis of the angles χ , ϕ , and 2θ ($2\theta \geq 40^\circ$) measured for 12 and 20 general reflections for Ni(*p*-dtc)₂S and Zn(*p*-dtc)₂S₂, respectively, on a Picker four-circle diffractometer using Cu K β radiation (λ 1.3922 Å).

Crystal Data for Ni(*p*-dtc)₂S. C₂₀H₂₂S₅Ni: formula weight 481.43; deep violet triclinic prism 0.13 × 0.21 × 0.55 mm³; *a* = 14.166 (4), *b* = 13.128 (4), *c* = 6.408 (1) Å; α = 106.21 (1)°, β = 85.78 (1)°, γ = 108.82 (1)°; *V* = 1084 Å³; *D*_m = 1.46 (1) (measured by flotation); *z* = 2; *D*_x = 1.47 g/cm³; μ (Cu K α) = 55.3 cm⁻¹; space group *P* $\bar{1}$, demonstrated by structure refinement utilizing 2776 unique reflections observed with *I* < 2 σ (*I*), corrected for absorption.

Crystal Data for Zn(*p*-dtc)₂S₂. C₂₀H₂₂S₆Zn: formula weight 520.15; red-orange monoclinic prism, 0.42 × 0.42 × 0.19 mm³; *a* = 25.262 (6), *b* = 8.065 (2), *c* = 21.047 (5) Å; β = 147.49 (2)°; *V* = 2305 Å³; *D*_m = 1.49 (1) (measured by flotation); *z* = 4; *D*_x = 1.49 gm/cm³; μ (Cu K α) = 63.9 cm⁻¹; space group *C*2/*c* demonstrated by structure refinement utilizing 1754 unique reflections observed with *I* < 2 σ (*I*) and corrected for absorption.

Structure Determination and Refinement. The structures were determined using standard heavy atom techniques. The metal and sulfur atoms were located in an origin-removed Patterson synthesis and subsequent cycles of structure factor–Fourier calculations led to the location of all nonhydrogen atoms. Hydrogen atoms were included at calculated positions during the latter stages of refinement.

Structure refinement was achieved utilizing full-matrix least-squares routines, attributing anisotropic thermal parameters to all nonhydrogen atoms and uniform isotropic thermal parameters to all hydrogen atoms. The refinements were considered converged and, hence, terminated when the maximum shift in any given parameter did not exceed one-tenth the estimated standard error of that parameter.

The atomic form factors used throughout the refinements were those of Cromer and Waber^{15a} for the nonhydrogen atoms and Stewart, Davidson, and Simpson^{15b} for hydrogen. Anomalous dispersion corrections¹⁶ of the form $f = f_0 + \Delta f' + i\Delta f''$ were applied to the metal and sulfur form factors during the final cycles of refinement.

Refinement of Ni(*p*-dtc)₂S converged at *R*₁ and *R*₂ values of 0.061 and 0.065, respectively. The final weighting scheme utilized in the refinement was of the form: $w = [a + b|F_0| + c|F_0|^2]^{-1}$, where *a* = 4.49, *b* = 0.085, and *c* = 0.0004, the values being derived during the latter stages of refinement from a plot of the mean error, $|\Delta F|$, vs. the magnitude of *F*, $|F_0|$. The final atomic positional parameters are presented in Table I together with their estimated standard deviations in Table II.¹⁷

(14) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, Wiley, New York, N. Y., 1961.

(15) (a) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965); (b) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

(16) D. T. Cromer, *Acta Crystallogr.*, **18**, 17 (1965).

(13) We thank Dr. James A. Smith for making these measurements.

Table I. Fractional Atomic Coordinates and Their Estimated Standard Deviations for Ni(*p*-dtc)₂S

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	$\sigma(x/a)$	$\sigma(y/b)$	$\sigma(z/c)$
Ni	-0.07064	0.83450	-0.08014	0.00010	0.00011	0.00021
S(1)	-0.18838	0.90615	0.07600	0.00018	0.00020	0.00035
S(2)	-0.08765	0.93151	-0.29930	0.00018	0.00019	0.00038
C(1)	-0.17842	0.96153	-0.13719	0.00057	0.00062	0.00123
C(2)	-0.23650	1.02807	-0.17134	0.00059	0.00061	0.00130
C(3)	-0.31708	1.04001	-0.04135	0.00069	0.00077	0.00015
C(4)	-0.37288	1.10278	-0.07698	0.00074	0.00090	0.00159
C(5)	-0.35169	1.15434	-0.24471	0.00070	0.00072	0.00148
C(6)	-0.27160	1.14277	-0.37332	0.00067	0.00074	0.00147
C(7)	-0.21545	1.07974	-0.34122	0.00067	0.00074	0.00142
C(8)	-0.41134	1.22466	-0.28499	0.00085	0.00099	0.00197
C(9)	-0.47699	1.25723	-0.11107	0.00106	0.00123	0.00247
C(10)	-0.46552	1.17300	-0.49550	0.00231	0.00239	0.00310
S(1')	0.03373	0.76766	-0.28320	0.00016	0.00017	0.00033
S(2')	0.01181	0.65400	0.06511	0.00019	0.00019	0.00033
S(3')	-0.07578	0.75210	0.16572	0.00020	0.00020	0.00036
C(1')	0.06312	0.68067	-0.16988	0.00061	0.00063	0.00121
C(2')	0.12815	0.61517	-0.27611	0.00057	0.00061	0.00120
C(3')	0.12550	0.57237	-0.50061	0.00062	0.00068	0.00124
C(4')	0.18275	0.50618	-0.59775	0.00068	0.00074	0.00137
C(5')	0.24007	0.47472	-0.48398	0.00071	0.00078	0.00150
C(6')	0.24852	0.52408	-0.25459	0.00084	0.00093	0.00161
C(7')	0.19247	0.59105	-0.15510	0.00052	0.00078	0.00137
C(8')	0.29566	0.39588	-0.60193	0.00092	0.00103	0.00200
C(9')	0.32539	0.33510	-0.47129	0.00091	0.00101	0.00227
C(10')	0.36903	0.43951	-0.74831	0.00121	0.00136	0.00263

Table II. Anisotropic Thermal Parameters^a for Ni(*p*-dtc)₂S

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ni	0.0081 (2)	0.0079 (2)	0.0303 (2)	0.0042 (2)	0.0033 (2)	0.0062 (2)
S(1)	0.0101 (3)	0.0112 (3)	0.0326 (3)	0.0063 (3)	0.0055 (3)	0.0090 (3)
S(2)	0.0091 (3)	0.0104 (3)	0.0424 (3)	0.0063 (3)	0.0083 (3)	0.0112 (3)
S(1')	0.0083 (3)	0.0088 (3)	0.0333 (3)	0.0051 (3)	0.0041 (3)	0.0088 (3)
S(3')	0.0121 (3)	0.0114 (3)	0.0295 (3)	0.0070 (3)	0.0055 (3)	0.0081 (3)
S(2')	0.0108 (3)	0.0104 (3)	0.0268 (3)	0.0061 (3)	0.0024 (3)	0.0074 (3)
C(1)	0.006 (1)	0.007 (1)	0.028 (1)	0.003 (1)	0.002 (1)	0.004 (1)
C(2)	0.007 (1)	0.006 (1)	0.032 (1)	0.003 (1)	0.002 (1)	0.003 (1)
C(3)	0.008 (1)	0.011 (1)	0.035 (1)	0.005 (1)	0.006 (1)	0.009 (1)
C(4)	0.009 (1)	0.015 (1)	0.037 (1)	0.007 (1)	0.007 (1)	0.010 (1)
C(5)	0.009 (1)	0.009 (1)	0.035 (1)	0.005 (1)	0.0093 (1)	0.004 (1)
C(6)	0.008 (1)	0.011 (1)	0.037 (1)	0.005 (1)	0.002 (1)	0.008 (1)
C(7)	0.008 (1)	0.010 (1)	0.035 (1)	0.005 (1)	0.004 (1)	0.008 (1)
C(8)	0.011 (1)	0.015 (1)	0.054 (1)	0.008 (1)	0.005 (1)	0.012 (1)
C(9)	0.014 (2)	0.020 (2)	0.073 (2)	0.011 (2)	0.005 (2)	0.014 (2)
C(10)	0.053 (2)	0.054 (2)	0.065 (2)	0.048 (2)	-0.021 (2)	-0.012 (2)
C(1')	0.008 (1)	0.007 (1)	0.026 (1)	0.003 (1)	0.001 (1)	0.006 (1)
C(2')	0.006 (1)	0.007 (1)	0.026 (1)	0.003 (1)	-0.001 (1)	0.006 (1)
C(3')	0.007 (1)	0.009 (1)	0.026 (1)	0.004 (1)	-0.0001 (1)	0.005 (1)
C(4')	0.009 (1)	0.010 (1)	0.030 (1)	0.005 (1)	-0.001 (1)	0.003 (1)
C(5')	0.008 (1)	0.011 (1)	0.040 (1)	0.005 (1)	0.001 (1)	0.008 (1)
C(6')	0.012 (1)	0.105 (1)	0.038 (1)	0.009 (1)	0.0005 (1)	0.009 (1)
C(7')	0.010 (1)	0.011 (1)	0.028 (1)	0.006 (1)	-0.002 (1)	0.004 (1)
C(8')	0.012 (1)	0.015 (1)	0.052 (1)	0.009 (1)	0.003 (1)	0.006 (1)
C(9')	0.011 (2)	0.014 (2)	0.074 (2)	0.008 (2)	0.003 (2)	0.012 (2)
C(10')	0.018 (2)	0.024 (2)	0.080 (2)	0.016 (2)	0.017 (2)	0.022 (2)

^a β 's conform to the expression $T = \exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. Estimated standard deviations are 2×10^{-4} for Ni, 3×10^{-4} for S atoms, 1×10^{-3} for C(1)–C(8) and C(1')–C(8'), and 2×10^{-3} for C(9)–C(10) and C(1')–C(10').

Refinement of Zn(*p*-dtc)₂S₂ converged at *R*₁ and *R*₂ values of 0.065 and 0.078, respectively. Weighting was of the form $w = [a + b|F_o| + c|F_o|^2]^{-1}$, where $a = 2.41$, $b = 0.004$, $c = 0.0015$, the values derived as above. Final positional parameters are listed in Table III with their estimated standard deviations in Table IV.¹⁷

(17) Calculated and observed structure factors for both Ni(*p*-dtc)₂S and Zn(*p*-dtc)₂S₂ are included with the microfilm edition of this paper. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number JACS-72-7323. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche.

Results

Synthesis. The complexes of nickel(II), palladium(II), and platinum(II) containing a *p*-dithiocumate and *p*-perthiocumate ligand, M(*p*-dtc)₂S, were obtained by the reaction of metal salts with the potassium salts of perthio- and dithiocumic acids in acidic aqueous solution. Complexes of the type M(*p*-dtc)₂S are ether soluble and easily separated from the M(*p*-dtc)₂ species. However, no complex corresponding to Pt(*p*-dtc)₂ was found in the ether-insoluble crude product after Pt(*p*-dtc)₂S was removed. Bis(*p*-perthiocumato)zinc(II) was

Table III. Fractional Atomic Coordinates and Their Estimated Standard Deviations for $\text{Zn}(p\text{-dtc})_2\text{S}_2$

Atom	x/a	y/b	z/c	$\sigma(x/a)$	$\sigma(y/b)$	$\sigma(z/c)$
Zn	0.00000	0.18999	0.25000	0.00000	0.00013	0.00000
S(1)	0.08570	0.34594	0.41157	0.00011	0.00018	0.00012
S(2)	-0.03357	0.10928	0.37049	0.00011	0.00020	0.00012
S(3)	-0.09504	0.04195	0.22545	0.00013	0.00023	0.00014
C(1)	0.05093	0.26418	0.44540	0.00040	0.00068	0.00046
C(2)	0.09733	0.31752	0.55258	0.00040	0.00067	0.00046
C(3)	0.05035	0.30279	0.56362	0.00048	0.00084	0.00055
C(4)	0.09955	0.34328	0.66861	0.00047	0.00082	0.00055
C(5)	0.19626	0.39996	0.76671	0.00045	0.00071	0.00049
C(6)	0.24210	0.41909	0.75437	0.00048	0.00088	0.00056
C(7)	0.19431	0.37781	0.65021	0.00047	0.00089	0.00055
C(8)	0.25437	0.43696	0.88536	0.00053	0.00083	0.00058
C(9)	0.19060	0.47474	0.87843	0.00072	0.00169	0.00075
C(10)	0.32493	0.29477	0.97173	0.00085	0.00169	0.00084

Table IV. Anisotropic Thermal Parameters^a for $\text{Zn}(p\text{-dtc})_2\text{S}_2$

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Zn	0.00526	0.01624	0.00561	0.00000	0.00485	0.00000
S(1)	0.0065	0.0175	0.0069	-0.0032	0.0061	-0.0024
S(2)	0.0059	0.0192	0.0070	-0.0037	0.0058	-0.0033
S(3)	0.0070	0.0234	0.0075	-0.0056	0.0064	-0.0053
C(1)	0.0048	0.0139	0.0064	0.0001	0.0048	0.0005
C(2)	0.0047	0.0139	0.0061	0.0003	0.0046	0.0005
C(3)	0.0053	0.0205	0.0071	-0.0016	0.0053	-0.0017
C(4)	0.0058	0.0213	0.0077	-0.0010	0.0060	-0.0007
C(5)	0.0056	0.0143	0.0073	-0.0004	0.0056	-0.0007
C(6)	0.0055	0.0239	0.0074	-0.0029	0.0055	-0.0038
C(7)	0.0056	0.0223	0.0080	-0.0022	0.0061	-0.0024
C(8)	0.0072	0.0178	0.0082	-0.0009	0.0067	-0.0014
C(9)	0.0090	0.0409	0.0090	0.0049	0.0080	0.0010
C(10)	0.0073	0.0324	0.0076	0.0028	0.0061	0.0022

^a β 's conform to the expression $T = \exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. Estimated standard deviations are 1×10^{-4} for Zn and S, 4×10^{-4} for C(1)–C(8), and 6×10^{-4} for C(9) and C(10).

prepared in tetrahydrofuran (THF) by methods previously outlined.⁴ Metathesis of $\text{Zn}(p\text{-dtc})_2\text{S}_2$ with $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ in THF–MeOH yielded $\text{Ni}(p\text{-dtc})_2\text{S}_2$.

Sulfur addition to bis(dithioaryl acid)nickel(II) complexes has been reported by metathetical procedures⁴ as well as base-catalyzed reactions.^{4,5,18} Loss of sulfur from $\text{Zn}(p\text{-dtc})_2\text{S}_2$ to $\text{Ni}(\text{dtb})_2$ and $\text{Pd}(\text{dtb})_2$, forming $\text{Zn}(p\text{-dtc})_2$ and $\text{Ni}(\text{dtb})_2\text{S}$ or $\text{Pd}(\text{dtb})_2\text{S}$ (eq 2), was followed by nmr spectral changes. The shift in position of resonance from the perthiocumate ligand toward the dithiocumate ligand indicated bis(perthioaryl acid)-zinc(II) complexes act as sulfur addition agents.¹⁹

Elemental sulfur was added to bis(dithioaryl acid)-metal complexes by two methods. In the thermal method A, sulfur was added to the chelate ring of $\text{Ni}(\text{dtb})_2$ by heating stoichiometric amounts of complex and sulfur in dimethylformamide (DMF). Sulfur addition to $\text{Ni}(\text{dtb})_2$, as well as $\text{Pd}(p\text{-dtc})_2$ and $\text{Zn}(p\text{-dtc})_2$, occurred when chloroform solutions of the complex and elemental sulfur were photolyzed at 3500 Å by the photolytic method B.

Structures. A preliminary report of the structure of $\text{Ni}(p\text{-dtc})_2\text{S}$ has been communicated.^{7a} Figure 1 presents the structure of the complex along with selected

(18) W. Hieber and K. Bruck, *Z. Anorg. Allg. Chem.*, **269**, 13 (1952).

(19) Proton nmr studied (J. P. Fackler and I. Lin, to be published) of the reaction of ZnL_2S_2 with NiL'_2 , where L and L' are different dithiolates, have shown that LS transfer occurs as well as "S" transfer when L is *p*-dtc and L' is *p*-dtc. When $\text{Zn}(p\text{-dtc})_2\text{S}_2$ and $\text{Ni}(p\text{-dtc})_2\text{S}_2$ are mixed in chloroform-*d*, some $\text{Zn}(p\text{-dtc})_2\text{S}_2$ also is formed. See also A. Giuliani, *Inorg. Nucl. Chem. Lett.*, **7**, 1001 (1971).

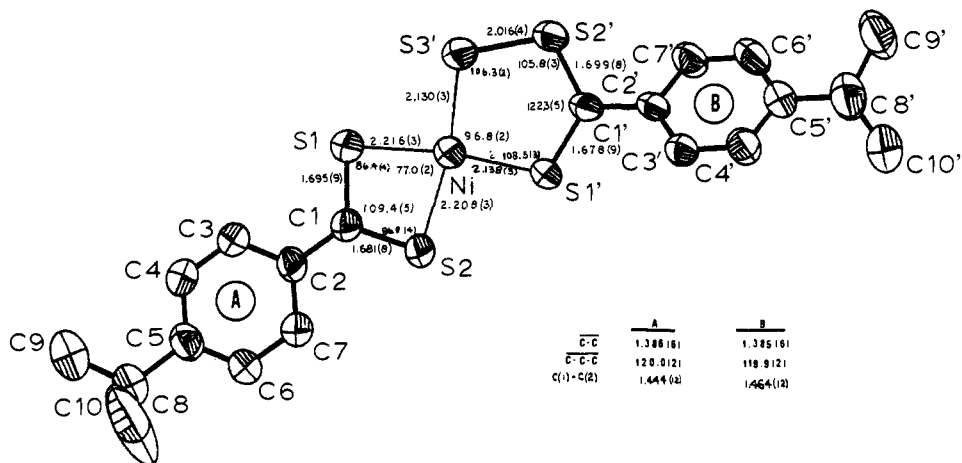
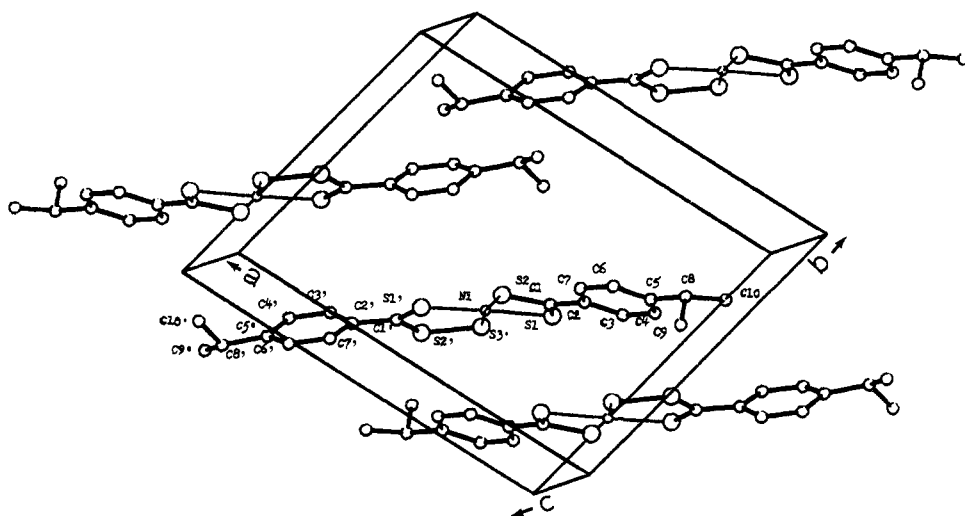
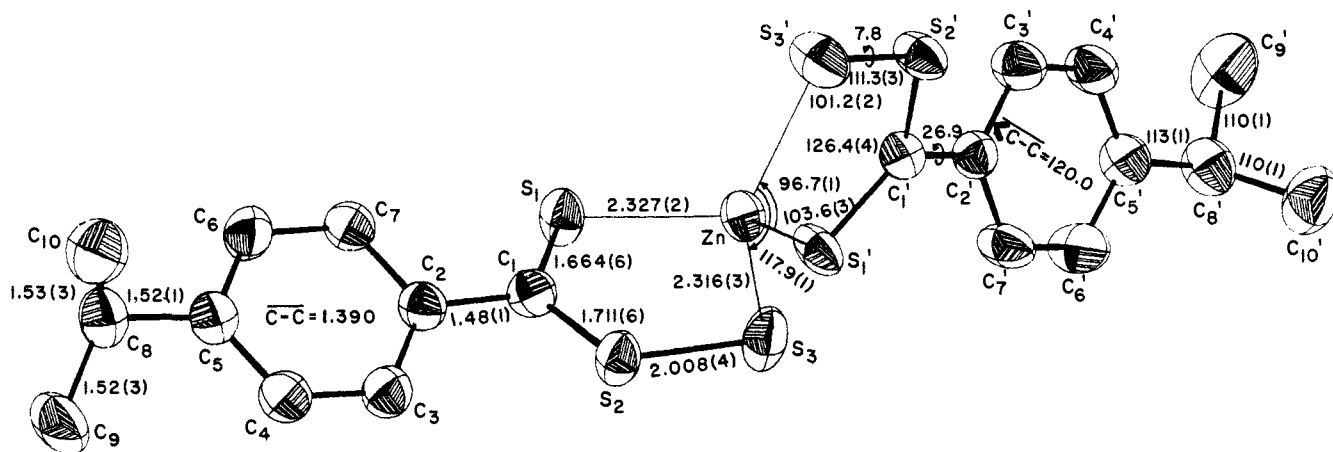
bond lengths and angles. Atom coordinates are given in Table I with the resultant thermal parameters presented in Table II. A description of the packing of this complex in the unit cell is given in Figure 2.

The structure of $\text{Zn}(p\text{-dtc})_2\text{S}_2$ is presented in Figure 3. Atom coordinates and thermal parameters are presented in Tables III and IV, respectively. The $\text{Zn}(p\text{-dtc})_2\text{S}_2$ crystallizes in a manner similar to that reported^{7b} for $\text{Zn}(\text{dtb})_2\text{S}_2$.

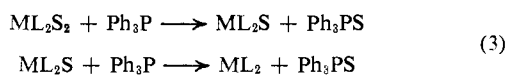
Mass Spectroscopy. Mass spectra of $\text{Zn}(\text{dtb})_2$, $\text{Zn}(\text{dtb})_2\text{S}_2$, $\text{Ni}(\text{dtb})_2$, and $\text{Ni}(\text{dtb})_2\text{S}_2$ were obtained under a variety of conditions as indicated. The time-dependent character of the spectra of heated samples suggests that a slow thermal decomposition does occur in the probe. However, the spectra reported, which were obtained as quickly as possible upon insertion of the probe into the spectrometer, appear to reflect a primary degradation of the complexes by electron bombardment. A set of typical traces for $\text{Ni}(\text{dtb})_2$ and $\text{Ni}(\text{dtb})_2\text{S}$ has been presented.²⁰

Spectra were recorded for samples obtained by adding elemental sulfur containing a 37.2% enrichment of ³⁴S. In particular, the $\text{C}_6\text{H}_5\text{CS}^+$ region, 120–123 amu, reflects the presence of ³⁴S added to a position adjacent to the carbon atom in the complex. Assuming the sum of the intensities of 121, 122, and 123 amu peaks reflects the total of $\text{C}_6\text{H}_5\text{CS}^+$ produced, the ratio of 123 to the sum, I_{123}/I_{tot} , indicates the enrichment of this fragment in ³⁴S. Table V lists the experimental results obtained for the various compounds.

(20) Reference 8, Figure 1.

Figure 1. The structure of Ni(*p*-dte)₂S.Figure 2. Packing geometry in the unit cell for Ni(*p*-dte)₂S.Figure 3. The structure of Zn(*p*-dte)₂S₂.

The complex reported to be Zn(dtb)₂S_{1.76} contains ~12% Zn(dtb)₂ with 88% Zn(dtb)₂S₂, as determined by a spectrophotometric titration using⁴ triphenylphosphine (eq 3) to extract the total excess sulfur. To date



we have not produced a crystalline mixed ligand ZnL₂S species. Solids with this stoichiometry can be obtained, but powder diffraction data suggest⁴ that ZnL₂ and ZnL₂S₂ are the dominant species.

Observation of the PS⁺ fragment in the mass spectrum of Ph₃PS formed in the abstraction of sulfur from Ni(dtb)₂S also can be used qualitatively to monitor the

Table V. Mass Spectral Results of Sulfur^a Addition

Complex	I_{123}/I_{tot}	n^b
Ni(dtb) ₂ —no enrichment	0.046 (1) ^c	12
Zn(dtb) ₂ —no enrichment	0.045 (2)	3
Sulfur Enriched in ³⁴ S Added		
Ni(dtb) ₂ S—thermal (A)	0.113 (4)	7
Ni(dtb) ₂ S—photolytic (B)	0.151 (1)	8
Zn(dtb) ₂ S _{1.76} —photolytic (B) ^d	0.170 (7)	10
Product after Removal of Excess Sulfur		
Ni(dtb) ₂ —thermal (A)	0.099 (8)	11
Ni(dtb) ₂ —photolytic (B)	0.054 (2)	17
Zn(dtb) ₂ —photolytic (B)	0.165 (2)	10

^a Sulfur 37.7% enriched in ³⁴S. ^b Number of spectral measurements on sample. ^c One standard deviation in parentheses for the last significant figure. ^d Product contains 12% Zn(dtb)₂ in Zn(dtb)₂S₂.

distribution of ³⁴S. The m/e 65 amu peak shows a relative increase in intensity when sulfur enriched in ³⁴S is incorporated into Ni(dtb)₂.

As seen in Table V, the ratio I_{123}/I_{tot} in a reference sample of Ni(dtb)₂ reflects the natural abundance²¹ (4.2%) of ³⁴S in sulfur. Since ⁵⁸Ni³²S₂⁺ (122 amu, a possible decomposition product of Ni(dtb)₂) would decrease I_{123}/I_{tot} , this material presumably is absent except in samples which remained several minutes at the 150° probe temperature, after which the 122-amu peak was found to increase in intensity. While several factors can produce as much as a 5–10% error in the intensity analysis, it is assumed that the ratio I_{123}/I_{tot} is a measure of the ³⁴S appearing in the C₆H₅CS⁺ fragment. Thus the maximum ratio of I_{123}/I_{tot} possible using 37.2% enriched ³⁴S is 0.37.

It is readily apparent from the results presented in Table V that ³⁴S addition to the zinc and nickel dithiobenzoates leads to ³⁴S incorporation in the C₆H₅CS⁺ fragment. The quantitative results are different for the two metals, however. For nickel, a dependence on the method used for sulfur addition is observed. Upon abstraction of the excess sulfur with triphenylphosphine, the data show that ³⁴S remains incorporated in the zinc complex and the nickel to which sulfur was added by heating, but very little ³⁴S remains in the nickel species to which the sulfur has been added by method B, the photolysis procedure. Thus a scrambling of sulfur atoms occurs in the zinc complex and in the thermal addition of sulfur to NiL₂. But *sulfur addition and abstraction with the nickel complex using the photolysis addition procedure takes place with nearly complete positional specificity.*

Sulfur Abstraction Kinetics with Triphenylphosphine.

The abstraction of excess sulfur with triphenylphosphine from Ni(*p*-dte)₂S in toluene is slow enough to be studied by conventional spectrophotometric techniques. With Ni(*p*-dte)₂S₂ and Pd(*p*-dte)₂S the abstraction occurs too rapidly to be followed by conventional mixing procedures. With the former compound a stepwise abstraction of sulfur is observed. By recording the absorbance at 18,870 cm⁻¹ as a function of time, second-order kinetic data are obtained (Figure 4) for the abstraction of sulfur from Ni(*p*-dte)₂S, at 25.0, 30.5, and 41.3°. Average values of the rate constant, k (M⁻¹ sec⁻¹), and activation parameters are presented in Table VI.

(21) G. Friedlander and J. W. Kennedy, "Nuclear and Radiochemistry," Wiley, New York, N. Y., 1955, p 417.

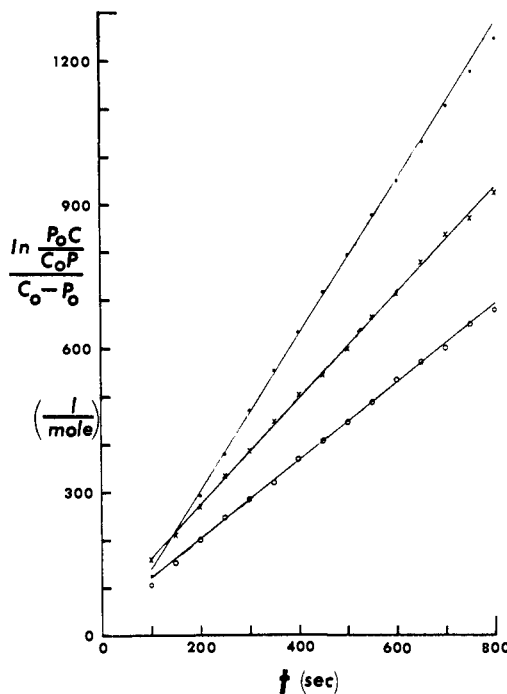


Figure 4. Second-order plots as a function of temperature for the reaction of triphenylphosphine with Ni(*p*-dte)₂S: $C_0 = 9.14 \times 10^{-4}$ M; $P_0 = 5.24 \times 10^{-4}$ M; (· · ·) 41.3°, (× × ×) 30.5°, (000) 25.0°.

Table VI. Kinetic Results of the Reaction of Ni(*p*-dte)₂S with Triphenylphosphine

Temp, °C	Initial concentrations ($\times 10^4$)		k , M ⁻¹ sec ⁻¹
	Ni(<i>p</i> -dte) ₂ S	Ph ₃ P	
25.0 (1) ^a	9.26 (10) ^a	4.66 (10) ^a	0.79
		6.98 (10)	0.82
	9.30 (10)	6.98 (10)	0.83
30.5 (1)		7.91 (10)	0.86
		8.84 (10)	0.81
	9.14 (10)	5.24 (10)	0.80
	9.14 (10)	5.24 (10)	1.07
41.3 (1)	8.00 (10)	5.88 (10)	1.10
	9.14 (10)	5.24 (10)	1.62
	Av k , M ⁻¹ sec ⁻¹		
25.0	0.82 (4)	$E_a = 7.8 \pm 1.0$ kcal/mol	
30.5	1.09 (5)	$\Delta H^\ddagger(300^\circ\text{K}) = 6.6 \pm 1.0$ kcal/mol	
41.3	1.62 (8)	$\Delta S^\ddagger(300^\circ\text{K}) = -37 \pm 2$ eu	

^a Standard deviation in last figure given in parentheses.

Nmr Studies of Sulfur Exchange in Zn(*p*-dte)₂S₂. The doubled AB pattern appearing in the phenyl region between 7 and 8 ppm from TMS (Figure 1, ref 9) for Ni(*p*-dte)₂S, Pd(*p*-dte)₂S, and Pt(*p*-dte)₂S is expected based on the presence of two different ligands. For Zn(*p*-dte)₂S₂ or Zn(*p*-dte)₂S₂ (Figure 5), only one AB pattern appears⁹ at room temperature in CS₂. This spectrum is sulfur atom dependent with the doublet separation in the Zn(*p*-dte)₂ case being 65 Hz (at 60 MHz) for the Zn(*p*-dte)₂ and 35 Hz for Zn(*p*-dte)₂S₂. The separation of these doublets is a linear function of the value of x in ZnL₂S_x.

The spectrum of a solution corresponding to Zn(*p*-dte)₂S in CS₂-ether (1:1, v/v) is presented in Figure 6 as a function of temperature. The single AB pattern ultimately becomes (below -90° at 60 mHz) the doubled AB pattern expected for nonequivalent ligands

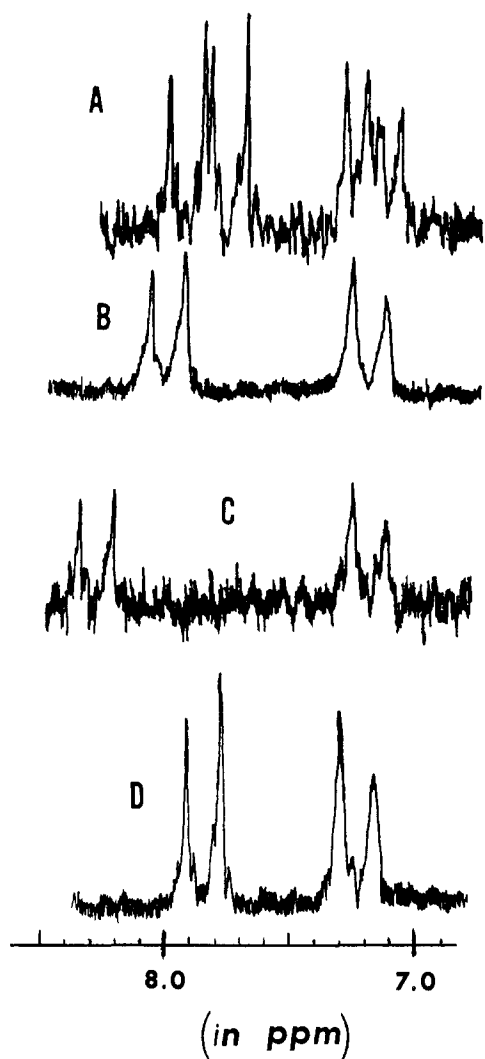


Figure 5. The phenyl region proton magnetic resonance spectrum of: A, $\text{Ni}(p\text{-dtt})_2\text{S}$; B, $\text{Zn}(p\text{-dtt})_2\text{S}$; C, $\text{Zn}(p\text{-dtt})_2$; D, $\text{Zn}(p\text{-dtt})_2\text{S}_2$.

in $\text{Zn}(p\text{-dtt})_2$ and $\text{Zn}(p\text{-dtt})_2\text{S}_2$. While the upfield doublet is not resolved even at -116° , the lower field doublet can be used to evaluate the rate of exchange process leading to magnetic equivalence. By integrating the resolved low-field doublets as a function of the x in $\text{Zn}(p\text{-dtt})_2\text{S}_x$, it is possible to show that the upper doublet, A (7.8 ppm), coming from the low-field AB doublet in the room temperature spectrum corresponds to the protons in $\text{Zn}(p\text{-dtt})_2\text{S}_2$, while the doublet, B, at 8.2 ppm belongs with $\text{Zn}(p\text{-dtt})_2$. Sulfur atom exchange is the only process by which the protons in each species may become magnetically equivalent.

The exchange rate of sulfur in " $\text{Zn}(p\text{-dtt})_2\text{S}_x$," an equimolar mixture of $\text{Zn}(p\text{-dtt})_2\text{S}_2$ and $\text{Zn}(p\text{-dtt})_2$, can be obtained from an approximate line-shape analysis of the temperature dependence of the low-field room temperature AB doublet (Figure 6). This doublet, which becomes a distinct quartet at sufficiently low temperature, presumably arises from the protons adjacent to the CS_2 portion of the molecule. The chemical shift of this doublet is most sensitive to the sulfur addition process wherein the phenyl ring loses its coplanarity (*vide infra*) with the metal chelate ring. Sulfur exchange rate data and activation energies obtained are presented in Table VII. While the precision of the data is rather

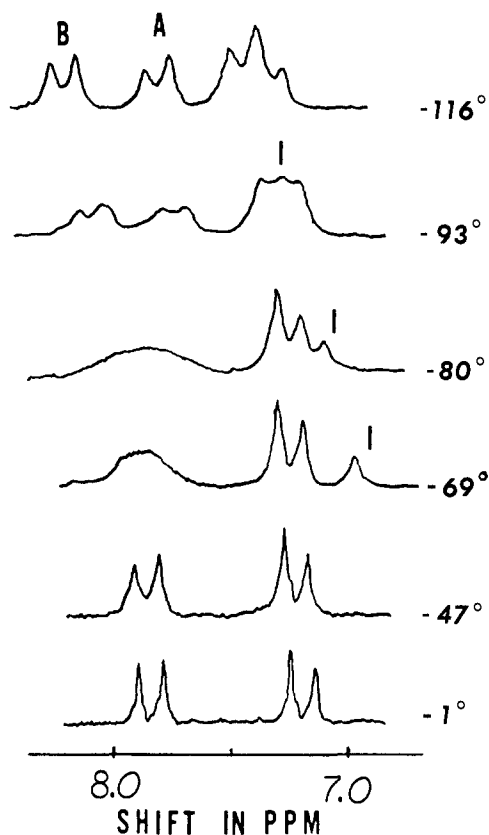


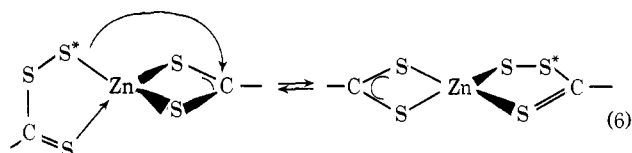
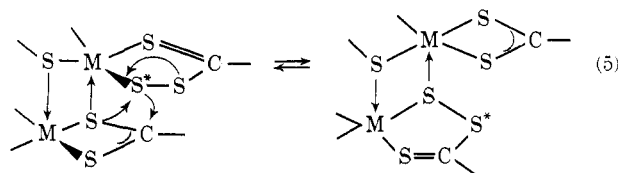
Figure 6. The temperature-dependent 60-MHz nmr spectrum of " $\text{Zn}(p\text{-dtt})_2\text{S}$ " in 1:1 CS_2 - $(\text{C}_2\text{H}_5)_2\text{O}$. TMS is the reference. A temperature-dependent impurity is noted by the vertical mark. A belongs with $\text{Zn}(p\text{-dtt})_2\text{S}_2$ and B with $\text{Zn}(p\text{-dtt})_2$.

poor owing to the difficulties associated with the line-shape analysis, the activation energy appears to be concentration independent and within a range of 4.9–5.9 kcal/mol. The rate itself clearly is concentration dependent. Attempts to evaluate the molecularity of the reaction to date have been unsuccessful. As can be seen from a plot of $\log(1/\tau)$ vs. $\log C$ (Figure 7), the apparent molecularity increases from one to something above two as the concentration is increased from $10^{-2} M$.

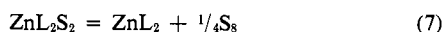
Discussion

The reaction of ^{35}S with $\text{Ni}(\text{S}_3\text{CS})_2^{3-}$ and the subsequent extraction of the radioactive sulfur in the resultant $\text{Ni}(\text{S}_3\text{CS})_2^{2-}$ with triphenylphosphine led Coucouvanis and Fackler² to suggest that sulfur addition occurs specifically to form a disulfide containing five-membered chelate ring in which the added sulfur atom resides adjacent to the carbon. However, this interpretation rested on the assumption that triphenylphosphine is somewhat nucleophilic in its reaction with the perthiocarbonate complex. Furthermore, the structure of $\text{Ni}(\text{S}_3\text{CS})_2^{2-}$ has not been firmly established, although there seems to be little doubt that anionic 1,1-dithiolates undergo a ring expansion upon addition of sulfur.

As reported here, the structures of $\text{Ni}(p\text{-dtt})_2\text{S}$ and $\text{Zn}(p\text{-dtt})_2\text{S}_2$ firmly establish the formation of five-membered chelate rings from sulfur addition to the four-membered chelate ring containing metal dithioarylates. This result also has been established^{7b} for $\text{Ni}(\text{dtt})_2\text{S}_2$ by single-crystal techniques.



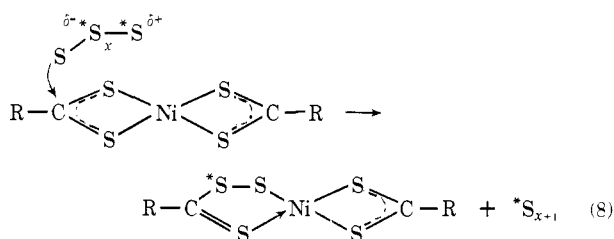
by eq 5 could lead to insertion of sulfur into the C-S bond. In the case of the zinc species, this process may even be intramolecular (eq 6), particularly at low concentrations of the complex (Table VII). It is also possible that an equilibrium exists between the Zn(dtb)₂S₂, Zn(dtb)₂, and sulfur in solution (eq 7), with the



“active” sulfur accepting nucleophilic sulfur²⁵ atoms from the complex and contributing the same to an insertion in the C-S bond of a complex. Regardless of the specific mechanism, however, carbon-sulfur bonds must be broken (and made) in the process.

The photolytic results with nickel are even more interesting, since addition and abstraction reactions do not produce a scrambling of sulfur. The mass spectral data establish the ³⁴S addition to be at the carbon rather than at the atom site adjacent to the metal.²⁶ Thus sulfur insertion in the C-S bond appears to be energetically more feasible than insertion into the Ni-S bond in this complex.

Based on the suggestion that “photosulfur”²⁷ is the active species produced on irradiation of hydrocarbon solutions containing sulfur, it is reasonable to suggest that this material nucleophilically adds to the metal dithiolate chelate ring by initial attack at the CS₂ carbons (eq 8). This result is seen to be consistent with the sulfur extraction data using triphenylphosphine.



The sulfur abstraction from molecular sulfur,^{28, 29} mono-, di-, and polysulfides,³⁰⁻³⁴ and carbamoyl di-

(25) W. A. Pryor, “Mechanisms of Sulfur Reactions,” McGraw-Hill, New York, N. Y., 1962, p 156 ff.

(26) Only the very unlikely specific rearrangement in the mass spectrometer in which the sulfur atom adjacent to the metal in the NiL₂S migrates to the carbon atom to produce C₆H₅CS⁻ could negate this conclusion.

(27) P. D. Bartlett, A. K. Colter, R. E. Davis, and W. R. Roderick, *J. Amer. Chem. Soc.*, **83**, 109 (1961).

(28) R. E. Davis, *J. Phys. Chem.*, **63**, 307 (1959).

(29) P. D. Bartlett, E. F. Cox, and R. E. Davis, *J. Amer. Chem. Soc.*, **83**, 103 (1961).

(30) M. J. Boskin and D. B. Denney, *Chem. Ind. (London)*, 330 (1959).

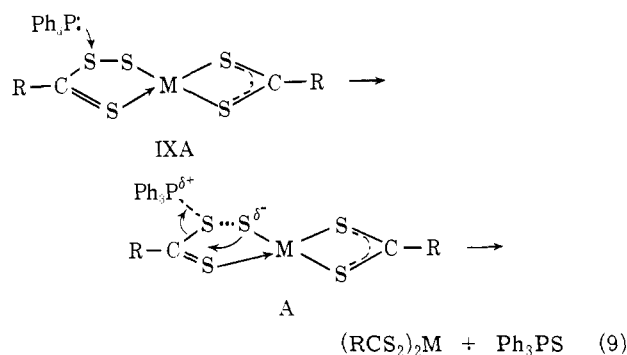
(31) D. B. Denney and M. J. Boskin, *J. Amer. Chem. Soc.*, **82**, 4736 (1960).

(32) C. G. Moore and B. R. Trego, *Tetrahedron*, **18**, 205 (1962).

(33) R. E. Davis, *Surv. Progr. Chem.*, **2**, 225 (1964), and references therein.

sulfides³⁵ has been extensively studied with triphenylphosphine and other phosphines. Nucleophilic attack by the phosphine on sulfur has been proposed in these organic systems. Reactions of sulfur abstraction from 1,1-dithiolate complexes^{2, 3} were postulated to occur in a similar manner, with removal of the sulfur atom adjacent to the carbon atom. The mass spectroscopic study of Ni(dtb)₂S using ³⁴S establishes the triphenylphosphine removal of a sulfur atom in the disulfide linkage of the chelate ring from the site adjacent to the carbon. This result is consistent with nucleophilic attack by the phosphine on this sulfur atom.

The activation parameters for desulfurization of Ni(*p*-dtc)₂S with Ph₃P are indicative of a bimolecular reaction. For Pd(*p*-dtc)₂S, the contrast in rate of sulfur removal was unexpected initially. If abstraction involved removal of sulfur adjacent to the metal, one might expect the weaker Ni-S bond to lead to a faster rate with the nickel complex. However, since sulfur is removed from the palladium complex within the time of mixing, palladium increases sulfur atom lability relative to nickel. This result can be rationalized if palladium activates the sulfur atom adjacent to the carbon (eq 9). The barrier to the formation of the activated complex or intermediate, A (~8 kcal/mol for the nickel complex), would depend on the metal's ability to delo-



calize negative charge into the π system of the dithio ligand or toward the thioketonic sulfur. This would suggest that a strong metal-sulfur bond could induce a fast rate of desulfurization at the site adjacent to carbon. A conclusion of this type is consistent with the work of Moore and Trego,³² who show that an ion pair or polarized complex must be involved to explain rearrangement in alkenyl-alkyl disulfides accompanying desulfurization.

The sulfur atom lability as deduced by nuclear magnetic resonance studies of Zn(*p*-dtc)₂S₂-Zn(*p*-dtc)₂ mixtures is striking. Extrapolated to room temperature, the data suggest sulfur atom exchange lifetimes of ~10⁻⁵ sec. Thus Zn(*p*-dtc)₂S₂ and other zinc(II) dithioaryl acid species can function as effective sulfur-atom transfer species. Indeed, Zn(*p*-dtc)₂S₂ and other ZnL₂S₂ species rapidly react with metal dithioarylates to form “sulfur-rich” complexes and ZnL₂. While some ligand exchange does appear to occur in this process,^{19a} sulfur atom transfer is also very important and clearly must be very rapid. In effect, ZnL₂ activates sulfur by forming a zinc complex containing a very labile disulfide sulfur atom. These results suggest that

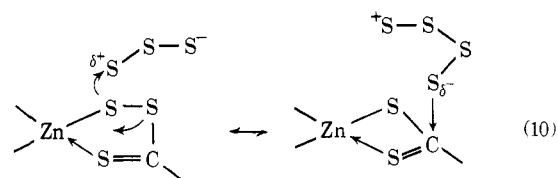
(34) D. N. Harpp, J. G. Gleason, and J. P. Snyder, *J. Amer. Chem. Soc.*, **90**, 4181 (1968).

(35) A. A. Watson, *J. Chem. Soc.*, 2100 (1964).

zinc dithiolates generally function as accelerators for sulfur addition to olefins by creating labile, nucleophilic (or electrophilic), active disulfide sulfur. While "sulfur-rich" metal xanthates or dithiocarbonates have not been isolated to date, there is no reason to believe that such materials cannot be formed.

As a final point, it is possible that the mass spectral results are directly related to the nmr kinetic data in the zinc dithiolate system. If the rapid sulfur atom exchange between ligands also produces the sulfur atom scrambling, it is apparent that the activation energy associated with the insertion of sulfur into the C-S bond of the dithiolate ligand is very small. The activation energy of ~ 5 kcal/mol for the exchange process is not very different from the activation energy of the reaction of NiL_2S with triphenylphosphine (~ 8 kcal/mol). This latter process requires P-S bond formation as well as C-S and S-S bond rupture leading to the transition state. The low activation energy suggests

that C-S bond formation also occurs (eq 9). A related



type of mechanism is possible for the sulfur atom exchange (eq 10), although the exchange may be intramolecular at low concentrations.

Acknowledgments. The support of the National Science Foundation, GP-11701, the National Institutes of Health, AM-13558, and the donors of the Petroleum Research Fund, PRF-3201-AC3, is gratefully acknowledged for various parts of this study. James A. Smith, Dominic Hunt, and Alex Avdeef also are recognized for their contributions to some of these studies.

π Groups in Ion Pair Bonding. Triphenylmethyl Lithium Tetramethylethylenediamine

J. J. Brooks and G. D. Stucky*

Contribution from the School of Chemical Sciences,
Department of Chemistry, and the Materials Research Laboratory,
University of Illinois, Urbana, Illinois 61801. Received January 10, 1972

Abstract: The stereochemistry of the triphenylmethyl carbanion has been determined in the crystalline complex, triphenylmethyl lithium tetramethylethylenediamine, $(\text{C}_6\text{H}_5)_3\text{C}^-\text{Li}^+(\text{CH}_3)_2\text{N}(\text{CH}_2)_2\text{N}(\text{CH}_3)_2$, from three-dimensional X-ray data collected by counter methods. The crystallographic parameters are: $a = 8.546$ (2), $b = 16.171$ (3), $c = 16.999$ (3) Å; $\beta = 106.75$ (2) $^\circ$ at 22 $^\circ$; $P2_1/c$, $Z = 4$ with a calculated density of 1.07 g/cc. Each lithium atom is coordinated to two nitrogen atoms of the bidentate chelate and to one π carbanion. The $(\text{C}_6\text{H}_5)_3\text{C}^-$ group has $\text{C}_6\text{H}_5\text{-C}(1)\text{-C}_6\text{H}_5$ bond angles of 117.0 (6), 122.8 (7), and 118.3 (6) $^\circ$, suggesting predominantly sp^2 hybridization for the central carbon atom, C(1). The twist angles of the phenyl rings depend on their interaction with the lithium atom, with the smallest twist angle being observed for the phenyl ring with the closest lithium-carbon atom contacts. Geometrical features are consistent with greater π -electron delocalization between the benzylic carbon atom and the two phenyl groups which exhibit smaller twist angles. The lithium atom is not located directly over C(1) but has four close contacts to the carbanion, 2.23 Å to C(1), 2.49 and 2.51 Å to two carbon atoms on one phenyl group, and one close contact of 2.54 Å to one carbon atom of a second phenyl group. A correlation is noted between carbanion stability and metal-nitrogen atom distances in organometallic complexes containing coordinated nitrogen base molecules.

The triphenylmethyl moiety can be stabilized as a carbonium ion, radical, or carbanion. The stabilization of these species is the result of delocalization attained through π -type interactions, with the maximum delocalization being obtained when the phenyl groups are coplanar with the methyl carbon atom. However, it is sterically impossible for the triphenylmethyl group to attain a planar conformation. Lewis and coworkers¹ and Seel² were the first to suggest twisted phenyl rings in triphenylmethyl and diphenylmethyl molecules. Two types of twisted geometries were suggested:¹ (1) the symmetrical propeller geometry in which each of the phenyl rings is twisted by some angle θ from the mean plane of the four central carbons, and (2) the nonsym-

metrical form in which one of the three rings is twisted in the opposite direction to the other two. The present consensus is that the propeller geometry is more favorable.

Calculations based on van der Waals radii^{2,3} and spectral evidence⁴ produced predictions of twist angles of from 20 to 30 $^\circ$ for the radical species. Vapor-phase electron diffraction studies⁵ of the triphenylmethyl radical showed a twist angle of approximately 45 $^\circ$. Crystallographic studies of the tri-*p*-nitrophenylmethyl radical⁶ gave twist angles of 40, 30, and 30 $^\circ$ for the phenyl rings.

(3) M. Szwarc, *Discuss. Faraday Soc.*, **2**, 39 (1947).

(4) F. C. Adam and S. I. Weissman, *J. Amer. Chem. Soc.*, **80**, 2057 (1958).

(5) P. Andersen, *Acta Chem. Scand.*, **19**, 629 (1965).

(6) P. Andersen and B. Klewe, *ibid.*, **21**, 2599 (1967).

(1) G. N. Lewis, T. M. Magel, and D. Lipkin, *J. Amer. Chem. Soc.*, **64**, 1774 (1942).

(2) F. Seel, *Naturwissenschaften*, **31**, 504 (1943).