sidered. It is apparent again that such an effect, which is most likely due to a more favorable entropy term, is operating in the rare earth complexes so that there is a small stabilization of about 0.4 log K unit for the chelates of the heavier (smaller) rare earth ions.

The magnitude of the stability constants for the 2:1 complexes leaves no doubt as to the fact that all of the groups are coordinated to the metal ion. The existence of only very weak 2:1 complexes with divalent metal ions again points to the larger effective coordination number of the rare earths since the rigidity of the ligand favors coordination of all four donor groups. It is very interesting that the stability constants for the 2:1 complexes show a uniform increase with atomic number. For all other quadridentate ligands of the substituted ammonia type which have been studied, the log K_2 values have decreased rather markedly at some point in the heavy-earth region.[12] (The only exception to this behavior with any quadridentate ligand is with ethylenediamine-N,N′-diacetic acid,[13] and since it is not of the trisubstituted ammonia type, it has rather different steric requirements). This is somewhat surprising since it might have been expected that the bulkiness of the piperidine ring would have led to increased steric factors and thus to a rather marked decrease in log K_2 values somewhere in the heavy-earth region before dysprosium. It should, however, be noted that with 2,6-piperidinedicarboxylic acid,[14] also a molecule with rigid geometric requirements, the log K_2 values for the rare earth ions were larger than expected when compared to those of iminodiacetic acid, a much more flexible molecule. In the 2,6-dicarboxypiperidineacetic acid it appears that the geometric arrangement of the donor groups in an eight-coordinate (or larger) structure is such that the two ligands do not suffer any serious steric hindrance and the normal trend is observed. The lack of steric interference is also shown by the fact that the difference in log K_1 and log K_2 across the series remains nearly constant, as expected for a ligand in which there is no particular steric effect as the size of the metal ion decreases.

Whether or not such steric considerations are the basis for the difference in properties of NTA and 2,6-dicarboxypiperidineacetic acid must, of course, in the final analysis be settled by a direct structure determination. An examination of molecular models of 2,6-dicarboxypiperidineacetic acid and NTA indicates that the former should more readily accommodate the dodecahedral configuration because its basic chelating arrangement is required to form chelating rings of two different sizes. In aqueous solution this would lead to a more favorable entropy term for complexes of this ligand compared to complexes of NTA.

Acknowledgments.—This work was supported by PHS Research Grant GM-08394 from the Division of General Medical Studies, Public Health Service.

[12] L. C. Thompson, B. L. Shafer, J. A. Edgar, and K. D. Mannila in "Chemistry of the Lanthanide and Actinide Elements," Advances in Chemistry Series, American Chemical Society, Washington, D. C., in press.

[13] L. C. Thompson, *J. Inorg. Nucl. Chem.*, **24**, 1083 (1962).

[14] L. C. Thompson, *ibid.*, **25**, 819 (1963).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF GEORGIA, ATHENS, GEORGIA 30601

Organosulfur Derivatives of the Metal Carbonyls. X. Some Transition Metal Derivatives Containing Both π-Cyclopentadienyl and *cis*-1,2-Ethylenedithiolate Ligands[1,2]

BY R. B. KING[3] AND C. A. EGGERS[4]

Received September 26, 1967

Reaction between $(C_5H_5)_2MCl_2$ and disodium ethylenedithiolate gives the complexes $(C_5H_5)_2MS_2C_2H_2$ (M = Ti, green-black; M = Zr, orange) suggested to be bis(cyclopentadienyl)metal(IV) ethylenedithiolate complexes from the nmr chemical shifts of the $H_2C_2S_2$ resonances. Reaction between $C_5H_5CoCOI_2$ and disodium ethylenedithiolate gives the volatile purple complex $C_5H_5CoS_2C_2H_2$. Similarly reaction between $[C_5H_5RhBr_2]_n$ and disodium ethylenedithiolate gives the volatile red-green dichroic complex $C_5H_5RhS_2C_2H_2$. The proton nmr chemical shifts of the $H_2C_2S_2$ protons in the $C_5H_5MS_2C_2H_2$ complexes of cobalt and rhodium indicate them to be cyclopentadienylmetal(I) dithioglyoxal complexes. Reaction between $C_5H_5Fe(CO)_2Cl$ and disodium ethylenedithiolate in aqueous methanol gives the black derivative $[C_5H_5Fe(CO)_2]_2S_2C_2H_2$ with a bridging ethylenedithiolate ligand. Reaction between $C_5H_5W(CO)_3Cl$ and disodium ethylenedithiolate gives the purple anion $[C_5H_5W(S_2C_2H_2)_2]^-$ isolable as its tetraphenylarsonium salt.

Introduction

The syntheses of numerous novel metal complexes containing the bis(trifluoromethyl)ethylene dithiolate[5-7] or maleonitriledithiolate[8,9] ligand have been investigated in considerable detail. However, syntheses of similar metal complexes containing the unsub-

---

[1] Portions of this work were presented at the 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967.

[2] Part IX: R. B. King and M. B. Bisnette, *Inorg. Chem.*, **6**, 469 (1967).

[3] Fellow of the Alfred P. Sloan Foundation, 1967–1969.

[4] Postdoctoral Research Associate, Jan–Oct 1967.

[5] R. B. King, *J. Am. Chem. Soc.*, **85**, 1587 (1963).

[6] R. B. King and M. B. Bisnette, *Inorg. Chem.*, **6**, 469 (1967).

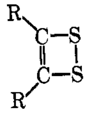
[7] (a) A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *J. Am. Chem. Soc.*, **85**, 2029 (1963); (b) *ibid.*, **86**, 2799 (1964); (c) A. Davison, D. V. Howe, and E. T. Shawl, *Inorg. Chem.*, **6**, 458 (1967).

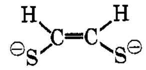
[8] J. Locke and J. A. McCleverty, *Chem. Commun.*, 102 (1965).

[9] J. Locke and J. A. McCleverty, *Inorg. Chem.*, **5**, 1157 (1966).

stituted *cis*-1,2-ethylenedithiolate ligand[10] have received less attention. Several derivatives containing only *cis*-1,2-ethylenedithiolate ligands have been reported[11,12] including the neutral trigonal prismatic derivatives $M(S_2C_2H_2)_3$ (M = V, Cr, Mo, and W), the neutral square-planar derivative $Ni(S_2C_2H_2)_2$, some of the anionic reduction products of these compounds, and other isoelectronic anions such as $[Cu(S_2C_2H_2)_2]^-$. However, no compounds containing both π-cyclopentadienyl and ethylenedithiolate[13] ligands have yet been described in the literature.

The known bis(trifluoromethyl)ethylenedithiolate complexes have been obtained from metal carbonyl derivatives and bis(trifluoromethyl)dithietene (I, R = CF_3). Analogous synthetic methods are not applicable for unsubstituted ethylenedithiolate derivatives owing to the unavailability of the presumed unstable unsubstituted dithietene (I, R = H). However, the ethylenethiolate anion (II, R = H) is available in the form of its disodium salt.[10] Reactions of this salt with cyclopentadienylmetal halide derivatives appeared to be a possible synthetic method for the preparation of compounds containing both π-cyclopentadienyl and ethylenedithiolate ligands. Since Locke and McCleverty[9] have synthesized similar maleonitriledithiolate derivatives using cyclopentadienylmetal halides and disodium maleonitriledithiolate, their synthetic methods were adopted for the initial phases of this study and then extended to derivatives of other metals.


I


II

Experimental Section

Microanalyses were performed by Pascher Mikroanalytisches Laboratorium, Bonn, Germany. Molecular weight determinations were carried out with a Mechrolab vapor pressure osmometer in benzene solution by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. Infrared spectra were generally taken in potassium bromide pellets and recorded on a Perkin-Elmer Model 421 or 621 spectrometer with grating optics. Proton nmr spectra (Table I) were taken in chloroform-*d* solution (unless otherwise indicated) and recorded on a Varian A-60 spectrometer. Ultraviolet spectra were taken in dichloromethane solution and recorded on a Cary Model 14 spectrometer. Melting and decomposition points were determined in capillaries and are uncorrected.

A nitrogen atmosphere was always provided for the three operations: (a) carrying out reactions, (b) handling all filtered solutions of metal complexes, and (c) admitting to evacuated flasks.

Reagents.—Benzyl mercaptan and *cis*-1,2-dichloroethylene were purchased from Columbia Organic Chemicals, Inc., Columbia, S. C. The compounds $(C_5H_5)_2MCl_2$ were purchased from Arapahoe Chemical Co., Boulder, Colo. The compounds $C_5H_5CoCOI_2$, $C_5H_5Fe(CO)_2Cl$, and $C_5H_5W(CO)_3Cl$ were prepared by published procedures[14] or minor modifications thereof. The rhodium compound $[C_5H_5RhBr_2]_n$, described by Angelici and Fischer,[15] was prepared by reaction between bromine and $C_5H_5RhC_8H_{12}$[16] in dichloromethane solution.[17] The ultimate starting materials such as $Fe(CO)_5$, $W(CO)_6$, $(C_5H_5)_2Co$, and $Rh(H_2O)_3Cl_3$ were obtained from the usual commercial sources.[18]

TABLE I

PROTON NMR SPECTRA OF NEW COMPOUNDS DESCRIBED IN THIS PAPER

Compound	$\tau(C_5H_5)$	$\tau(S_2C_2H_2)$
$(C_5H_5)_2TiS_2C_2H_2$	4.04	2.57
$(C_5H_5)_2ZrS_2C_2H_2$	4.00	2.89
$C_5H_5CoS_2C_2H_2$	4.68	1.12
$C_5H_5RhS_2C_2H_2$	4.51	1.50[a]
$[C_5H_5Fe(CO)_2]_2S_2C_2H_2$	5.55	2.79
$[(C_6H_5)_4As][C_5H_5W(S_2C_2H_2)_2]$[b]	4.65	b

[a] Doublet, J(RhH) = 5 cps. [b] Additional resonance at τ 2.40 due to the 20 protons of the tetraphenylarsonium cation and the four $S_2C_2H_2$ protons.

Preparation of Disodium Ethylenedithiolate.—The method of Schroth and Peschel[10] was modified to take advantage of the commercial availability of benzyl mercaptan at reasonable prices.

A mixture of 139 g (1.12 moles) of benzyl mercaptan, 300 g (5.4 moles) of potassium hydroxide, and 1200 ml of ethanol was refluxed 3 hr under nitrogen with stirring and then treated dropwise at the boiling point over 75 min with 74.3 g (0.77 mole) of *cis*-1,2-dichloroethylene. After about half of this material was added, a precipitate began to form. After all of the *cis*-1,2-dichloroethylene was added, the mixture was refluxed for 7 hr. The reaction mixture was then cooled *slightly* and filtered. The filtrate was treated with about 750 ml of cold water which dissolved the potassium salts and precipitated the desired *cis*-1,2-bis(benzylthio)ethylene. The product was filtered and dissolved in boiling ethanol. Insoluble impurities were removed by filtration while hot. Cooling the filtrate precipitated most of the product. After filtering off this product, additional crops were obtained by adding water to the mother liquors. The total yield of white crystalline *cis*-1,2-bis(benzylthio)ethylene was 148 g (71% based on *cis*-1,2-dichloroethylene).

A solution of 40.7 g (0.15 mole) of this *cis*-1,2-bis(benzylthio)ethylene in 150 ml of ethanol was heated with an oil bath to 105° (bath temperature) and then treated with 30 g (1.3 moles) of sodium spheres over a period of 20 min. While maintaining the bath at 105°, 250 ml of ethanol was added and the bath temperature then increased to 130° for 45 min. After cooling the mixture to room temperature, the disodium ethylenedithiolate was precipitated by the addition of 250 ml of toluene. The product was filtered rapidly, washed with about 250 ml of diethyl ether in several portions, and then dried at 25° (0.1 mm). The yield of white solid disodium ethylenedithiolate was about 17.5 g (86% based on the *cis*-1,2-bis(benzylthio)ethylene; 61% over-all yield for the two steps).

Disodium ethylenedithiolate liquefied with decomposition upon exposure to air for more than a few minutes. For this reason and because of the reported fire hazard[19] this material was stored in an evacuated flask.

Preparation of $(C_5H_5)_2TiS_2C_2H_2$.—A mixture of 2.49 g (10 mmoles) of $(C_5H_5)_2TiCl_2$, 1.36 g (10 mmoles) of disodium ethyl-

---

[10] W. Schroth and J. Peschel, *Chimia*, **18**, 171 (1964).

[11] E. Hoyer and W. Schroth, *Chem. Ind.* (London), 652 (1965).

[12] G. N. Schrauzer and V. P. Mayweg, *J. Am. Chem. Soc.*, **87**, 3585 (1965); **88**, 3235 (1966).

[13] For brevity the *cis*-1,2-ethylenedithiolate dianion will be hereafter designated simply as "ethylenedithiolate."

[14] For the preparations of these materials see the following references. $C_5H_5CoCOI_2$: R. B. King, *Inorg. Chem.*, **5**, 82 (1966). $C_5H_5Fe(CO)_2Cl$ and $C_5H_5W(CO)_3Cl$: T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **3**, 104 (1956).

[15] R. J. Angelici and E. O. Fischer, *J. Am. Chem. Soc.*, **85**, 3733 (1963).

[16] J. Chatt and L. M. Venanzi, *J. Chem. Soc.*, 4735 (1957).

[17] For a closely related preparation of $[C_5H_5RhI_2]_n$ from $C_5H_5RhC_8H_{12}$ and iodine see A. Kasahara, T. Isumi, and K. Tanaka, *Bull. Chem. Soc. Japan*, **40**, 699 (1967).

[18] The following commercial sources were used: $Fe(CO)_5$, Antara Division of General Aniline and Film, New York, N. Y.; $W(CO)_6$, Pressure Chemical Corp., Pittsburgh, Pa.; $(C_5H_5)_2Co$, Arapahoe Chemicals, Inc., Boulder, Colo.; $Rh(H_2O)_3Cl_3$, Englehard Industries, Newark, N. J.

[19] W. Schroth and J. Peschel, *Z. Chem.*, **4**, 271 (1964).

enedithiolate, and about 30 ml each of methanol and acetone was stirred for 14 hr at room temperature. Immediate reaction occurred. The reaction mixture became brown-black and then more gradually green-black during the reaction period. Solvent was removed under vacuum at room temperature. A total of 1.34 g (50% yield) of green-black $(C_5H_5)_2TiS_2C_2H_2$, mp 177–179°, was obtained from the resulting residue by sublimation at 110–120° (0.1 mm) and by crystallization from mixtures of dichloromethane and hexane. The analytical sample was sublimed, recrystallized, and then resublimed. *Anal.* Calcd for $C_{12}H_{12}S_2Ti$: C, 53.7; H, 4.5; Ti, 17.8; S, 23.9; mol wt, 268. Found: C, 54.0; H, 4.3; Ti, 18.5; S, 23.5; mol wt, 283.

Infrared spectrum: ν(CH) bands at 3109 (vw), 3083 (vw), and 3065 (vw) cm^{-1}; other bands at 1431 (m), 1363 (vw), 1133 (vw), 1070 (vw), 1025 (vw, sh), 1015 (vw, sh), 1008 (m), 940 (w), 923 (vw), 910 (vw), 848 (m), 830 (m), 822 (s), 810 (s), 800 (s, sh), 721 (s, sh), and 691 (s) cm.$^{-1}$

Preparation of $(C_5H_5)_2ZrS_2C_2H_2$.—A mixture of 1.46 g (5 mmoles) of $(C_5H_5)_2ZrCl_2$ and 0.68 g (5 mmoles) of disodium ethylenedithiolate was stirred for only 10 min at room temperature in a mixture of ~30 ml each of degassed methanol and acetone. Solvent was removed as rapidly as possible from the resulting yellow-orange reaction mixture at room temperature under vacuum. Sublimation of the residue at 100–140° (0.15 mm) gave 0.19 g (12% yield) of yellow-orange $(C_5H_5)_2ZrS_2C_2H_2$. The analytical sample, mp 183–186°, was sublimed two additional times at 100–125° (0.2 mm).

Increasing the time of the reaction between $(C_5H_5)_2ZrCl_2$ and disodium ethylenedithiolate caused the original yellow-orange color of the reaction mixture to fade to white. No $(C_5H_5)_2ZrS_2C_2H_2$ could be isolated from this reaction mixture. Similarly no $(C_5H_5)_2HfS_2C_2H_2$ could be obtained from the reaction between $(C_5H_5)_2HfCl_2$ and disodium ethylenedithiolate. Even with a short reaction time of a few minutes, a white reaction mixture was obtained from which nothing could be isolated by sublimation or crystallization. *Anal.* Calcd for $C_{12}H_{12}S_2Zr$: C, 46.2; H, 3.9; S, 20.6; Zr, 29.3. Found: C, 45.9; H, 3.7; S, 20.8; Zr, 29.3.

Infrared spectrum: ν(CH) at 3100 (w) and 3066 (w) cm^{-1}; other bands at 1443 (w), 1432 (m), 1366 (w), 1358 (w), 1261 (vw), 1165 (w), 1073 (w, sh), 1065 (w), 1055 (w, sh), 1017 (s, sh), 1008 (s), 925 (w, sh), 917 (w, sh), 910 (w), 839 (s, sh), 803 (vs), 795 (vs, sh), 736 (vs), 674 (m), and 553 (w) cm^{-1}.

Preparation of $C_5H_5CoS_2C_2H_2$.—A mixture of 1.35 g (3.33 mmoles) of $C_5H_5CoCOI_2$, 0.45 g (3.33 mmoles) of disodium ethylenedithiolate, and about 30 ml each of methanol and acetone was stirred for 14 hr at room temperature. Vigorous gas evolution occurred upon adding the solvent to the reagents. The reaction mixture soon became a deep magenta-purple and remained that color.

After the reaction period was over, solvent was removed under vacuum at room temperature. The residue was extracted with 20 ml of dichloromethane and the filtered extracts were evaporated. Sublimation of the purple residue twice at 80–85° (0.1 mm) gave 0.44 g (62% yield) of purple flakes of $C_5H_5CoS_2C_2H_2$, mp 126–129°. *Anal.* Calcd for $C_7H_7CoS_2$: C, 39.3; H, 3.3; S, 29.9; Co, 27.5; mol wt, 214. Found: C, 39.7; H, 3.1; S, 29.6; Co, 27.5; mol wt, 219.

Infrared spectrum: bands at 1540 (w), 1409 (m), 1337 (w), 1278 (w), 1102 (w), 1042 (w), 994 (m), 843 (m), 827 (m), 747 (m), and 703 (s) cm^{-1}.

Preparation of $C_5H_5RhS_2C_2H_2$.—A mixture of 0.7 g (2.1 mmoles) of $[C_5H_5RhBr_2]_n$, 0.29 g (2.1 mmoles) of disodium ethylenedithiolate, and about 15 ml each of methanol and acetone was stirred 15 hr under nitrogen. The reaction mixture slowly became a pure deep red. After the reaction period was over, solvent was removed under vacuum at room temperature. A total of 0.4 g (73% yield) of red-deep green dichroic $C_5H_5RhS_2C_2H_2$ was obtained from the residue by sublimation at 90–150° (0.23 mm). The analytical sample, mp 164–166°, was sublimed a second time. The red-green product was insoluble in water but gave deep pure red solutions in organic solvents such as acetone and dichloromethane. *Anal.* Calcd for $C_7H_7RhS_2$: C, 32.6; H, 2.7; S, 24.8; Rh, 39.9. Found: C, 32.7; H, 2.8; S, 24.5; Rh, 39.7.

Infrared spectrum: bands at 1432 (m), 1409 (m), 1398 (m), 1339 (m), 1276 (m), 1108 (w), 1096 (m), 1043 (m), 1004 (m), 983 (m), 913 (w), 850 (w), 838 (m), 822 (s), 735 (m), 709 (s, sh), 700 (s), 617 (w), and 570 (w) cm^{-1}.

Preparation of $[C_5H_5Fe(CO)_2]_2S_2C_2H_2$.—A sample of 2.13 g (10 mmoles) of $C_5H_5Fe(CO)_2Cl$ was dissolved in a minimum of methanol. After addition of 75 ml of cold water, the mixture was treated with 0.68 g (5 mmoles) of solid disodium ethylenedithiolate. An immediate reaction occurred to give a deep green-black precipitate and a brown solution. After 5 min this precipitate was filtered under nitrogen. While maintaining the nitrogen atmosphere, this precipitate was washed with 100 ml of cold water in several portions followed by 5 ml of methanol. After drying at 25° (0.1 mm), 1.42 g (64% yield) of crude $[C_5H_5Fe(CO)_2]_2S_2C_2H_2$ was obtained.

This compound decomposes very readily in solution and thus is difficult to recrystallize. An analytical sample was finally obtained by dissolving some of the compound in benzene, filtering, evaporating the filtrate to ~3 ml under nitrogen, adding excess hexane, and finally evaporating further. The pure black crystals of $[C_5H_5Fe(CO)_2]_2S_2C_2H_2$, mp 106–108°, were filtered and dried in an inert atmosphere. The solid decomposes slowly even under N_2 at 0° over a period of 4–6 weeks. When heated in a sublimer $[C_5H_5Fe(CO)_2]_2S_2C_2H_2$ decomposes without sublimation. *Anal.* Calcd for $C_{16}H_{12}O_4Fe_2S_2$: C, 43.3; H, 2.7; Fe, 25.1. Found: C, 43.2; H, 2.8; Fe, 24.2.

Infrared spectrum: strong ν(CO) bands at 2018, 1966, and 1952 cm^{-1}; other bands at 1485 (m), 1425 (m), 1415 (m), 1360 (vw), 1286 (m), 1055 (m), 1011 (m), 998 (m), 862 (m), 840 (m, sh), 833 (m), 826 (m), 809 (s), 697 (m), 650 (m), 617 (s), and 570 (s) cm^{-1}. ν(CO) bands in C_6H_6 solution: 2023, 1964, and 1957 (br, sh) cm^{-1}.

Preparation of $[(C_6H_5)_4As][C_5H_5W(S_2C_2H_2)_2]$.—A mixture of 1.85 g (5 mmoles) of $C_5H_5W(CO)_3Cl$, 0.34 g (2.5 mmoles) of disodium ethylenedithiolate, and 15 ml of methanol was stirred for 30 min at room temperature. The resulting purple solution was filtered into a solution of 1 g (2.4 mmoles) of tetraphenylarsonium chloride in 5 ml of methanol. Solvent was then removed at room temperature under vacuum. The residue was extracted with degassed acetone and the magenta extracts were filtered. Degassed methanol was added to the filtrate and the product was crystallized by evaporation in a stream of nitrogen and cooling to 0°. The product was recrystallized once more from a mixture of acetone and methanol and then five times from a mixture of acetone and hexane to give ~0.5 g (24% based on disodium ethylenedithiolate) of deep purple flakes, mp 212–214°. *Anal.* Calcd for $C_{33}H_{29}AsWS_4$: C, 48.8; H, 3.8; S, 15.8; As, 9.2. Found: C, 48.4; H, 4.1; S, 15.5; As, 9.3.

Infrared spectrum: ν(CH) band at 3030 (w) cm^{-1}; other bands at 1470 (m), 1430 (m), 1332 (vw), 1305 (vw), 1175 (vw), 1153 (vw), 1073 (m), 1015 (vw), 991 (m), 787 (m), 743 (m, sh), 736 (m, sh), 730 (m), 682 (s, sh), and 672 (s) cm^{-1}.

Ultraviolet and Visible Spectra. **A.** **$(C_5H_5)_2TiS_2C_2H_2$.**—Maxima were observed at 627 mμ (ϵ 1540), 516 mμ (ϵ 1340), 419 mμ (ϵ 2600), ~262 mμ (sh) (ϵ 16,000), ~235 mμ (sh) (ϵ 31,500), and 225 mμ (ϵ ~40,000) in dichloromethane solution (green-black).

B. **$(C_5H_5)_2ZrS_2C_2H_2$.**—Maxima were observed at ~600 mμ (ϵ 70), 530 mμ (ϵ 200), 347 mμ (ϵ 3320), 237 mμ (ϵ ~35,000), and 224 mμ (ϵ 46,000) in dichloromethane solution (yellow-orange).

C. **$C_5H_5CoS_2C_2H_2$.**—Maxima were observed at 737 mμ (ϵ 1200), 551 mμ (ϵ 8900), 410 mμ (ϵ 2000), 282 mμ (ϵ 30,400), and 233 mμ (ϵ 24,000) in dichloromethane solution (purple).

D. **$C_5H_5RhS_2C_2H_2$.**—Maxima were observed at 497 mμ (ϵ 6910), 410 mμ (sh) (ϵ 510), 303 mμ (ϵ 2240), and 243 mμ (ϵ 28,800) in dichloromethane solution (red).

E. **$[(C_6H_5)_4As][C_5H_5W(S_2C_2H_2)_2]$.**—Maxima were observed at 850 mμ (sh) (ϵ 160), 656 mμ (ϵ 1350), 542 mμ (ϵ 5330), 320 mμ (sh) (ϵ 5400), 293 mμ (sh) (ϵ 7450), 271 mμ (sh) (ϵ 23,600), 263 mμ (sh) (ε 26,700), and 225 mμ (ε ~80,000) in dichloromethane solution (bright purple).

F. **$[C_5H_5Fe(CO)_2]_2S_2C_2H_2$.**—This compound rapidly gave intractable tars in dichloromethane solution and was thus too unstable to run ultraviolet and visible spectra in this solvent. It was too insoluble in other appropriate solvents such as ethanol and saturated aliphatic hydrocarbons.

Discussion

Preparative Methods.—The dark green titanium compound $(C_5H_5)_2TiS_2C_2H_2$ obtained from $(C_5H_5)_2TiCl_2$ and disodium ethylenedithiolate appears to be closely related to the known likewise green compounds $(C_5H_5)_2TiS_2C_6H_4$ and $(C_5H_5)_2TiS_2C_2(CN)_2$ obtained by treatment of $(C_5H_5)_2TiCl_2$ with 1,2-benzenedithiol in the presence of base[20] and with sodium maleonitriledithiolate,[9] respectively. The orange zirconium compound $(C_5H_5)_2ZrS_2C_2H_2$ described in this paper appears to be more reactive toward hydrolysis and related processes than its titanium analog. It represents the first example of a zirconium derivative of this type. As described in the Experimental Section, a hafnium analog could not be prepared apparently owing to its instability to the reaction conditions.

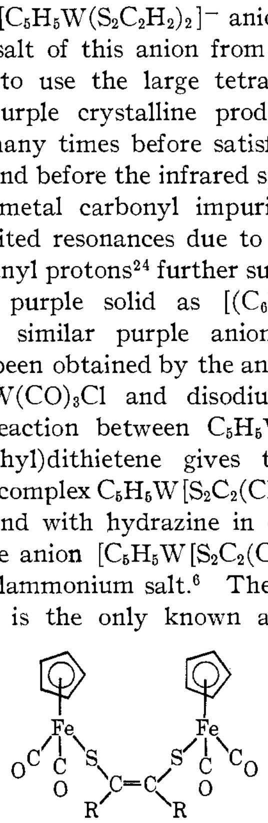
Locke and McCleverty[9] describe the reaction between disodium maleonitriledithiolate and $C_5H_5CoCOI_2$ to give the purple complex $C_5H_5CoS_2C_2(CN)_2$. The closely related reaction between disodium ethylenedithiolate and $C_5H_5CoCOI_2$ gave good yields of the completely analogous purple complex $C_5H_5CoS_2C_2H_2$. This compound is also closely related to the compound $C_5H_5CoS_2C_2(CF_3)_2$ obtained from $C_5H_5Co(CO)_2$ and bis(trifluoromethyl)dithietene (I, R = CF_3).[5] The new complex $C_5H_5CoS_2C_2H_2$ like its analogs appears to be air stable both in the solid state and in its purple solutions in organic solvents.

The analogous rhodium compound $C_5H_5RhS_2C_2H_2$ was prepared similarly by the reaction between disodium ethylenedithiolate and the π-cyclopentadienylrhodium derivative $[C_5H_5RhBr_2]_n$. This halide is more readily prepared than $C_5H_5RhCOI_2$.[21,22] This red-green dichroic volatile rhodium complex appears to be closely related to the bis(trifluoromethyl) derivative $C_5H_5RhS_2C_2(CF_3)_2$ obtained from $C_5H_5Rh(CO)_2$ and bis(trifluoromethyl)dithietene.[6]

Locke and McCleverty[9] describe the reaction between $C_5H_5Fe(CO)_2Cl$ and disodium maleonitriledithiolate in aqueous methanol to give $[C_5H_5Fe(CO)_2]_2S_2C_2(CN)_2$ (III, R = CN). Similar treatment of $C_5H_5Fe(CO)_2Cl$ with disodium ethylenedithiolate in aqueous methanol gives a black precipitate of the analogous $[C_5H_5Fe(CO)_2]_2S_2C_2H_2$ (III, R = H). This compound is very unstable in solution. In order to obtain satisfactory results in its preparation, it is necessary to select a solvent mixture in which the product is so insoluble that it precipitates immediately. Thus treatment of $C_5H_5Fe(CO)_2I$ with disodium ethylenedithiolate in a mixture of methanol and acetone (in which $[C_5H_5Fe(CO)_2]_2S_2C_2H_2$ is soluble) gave a complex reaction mixture from which neither $[C_5H_5Fe(CO)_2]_2S_2C_2H_2$ (III, R = H) nor any other cyclopentadienyliron organosulfur derivatives could be isolated.

Anionic metal derivatives of the $S_2C_2H_2$ system appear to be much less stable than analogous metal derivatives of the $S_2C_2(CN)_2$ and $S_2C_2(CF_3)_2$ systems presumably owing to the strong electron-withdrawing tendencies of the CN and CF_3 substituents which stabilize anions by removing negative charge from the metal atom. This stabilization of anions by substitution of a hydrogen atom in ethylenedithiolate complexes with either a CN or a CF_3 group is demonstrated by polarographic data[23] which show the dianions $[M(S_2C_2R_2)_2]^{2-}$ (M = Co or Ni) to be oxidized with increasing difficulty in the sequence R = H (most easily oxidized) < R = CF_3 < R = CN (most resistant to oxidation).

This instability of metal dithiolate anions containing H rather than CF_3 or CN substituents is consistent with our inability in most cases to isolate anionic derivatives containing both π-cyclopentadienyl and $S_2C_2H_2$ ligands. Reaction of $C_5H_5W(CO)_3Cl$ with disodium ethylenedithiolate gave a purple solution containing the $[C_5H_5W(S_2C_2H_2)_2]^-$ anion. In order to isolate a solid salt of this anion from this solution it was necessary to use the large tetraphenylarsonium cation. The purple crystalline product had to be recrystallized many times before satisfactory analyses were obtained and before the infrared spectrum showed freedom from metal carbonyl impurities. The nmr spectrum exhibited resonances due to the phenyl and π-cyclopentadienyl protons[24] further supporting formulation of this purple solid as $[(C_6H_5)_4As][C_5H_5W(S_2C_2H_2)_2]$. A similar purple anion $[C_5H_5W[S_2C_2(CN)_2]_2]^-$ has been obtained by the analogous reaction between $C_5H_5W(CO)_3Cl$ and disodium maleonitriledithiolate.[9] Reaction between $C_5H_5W(CO)_2NO$ and bis(trifluoromethyl)dithietene gives the dark green volatile neutral complex $C_5H_5W[S_2C_2(CF_3)_2]_2$; reduction of this compound with hydrazine in ethanol solution gives the purple anion $[C_5H_5W[S_2C_2(CF_3)_2]_2]^-$ isolable as its tetraethylammonium salt.[6] The anion $[C_5H_5W[S_2C_2(CF_3)_2]_2]^-$ is the only known anion containing



III

---

[20] H. Köpf and M. Schmidt, *J. Organometal. Chem.* (Amsterdam), **4**, 426 (1965).

[21] Preparation of $C_5H_5Rh(CO)I_2$ unlike the preparation of $[C_5H_5RhBr_2]_n$ requires $C_5H_5Rh(CO)_2$ as a starting material. The yields of $C_5H_5Rh(CO)_2$ from the reaction between $[Rh(CO)_2Cl]_2$ and sodium cyclopentadienide in petroleum ether are only ~25%.[22]

[22] E. O. Fischer and K. Bittler, *Z. Naturforsch.*, **16b**, 225 (1961).

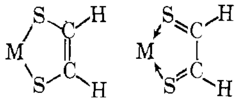
[23] For pertinent polarographic data see A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *Inorg. Chem.*, **3**, 814 (1964), and E. Hoyer, W. Dietsch, and W. Schroth, paper presented at the Ninth International Conference on Coordination Chemistry, St. Moritz, Switzerland, Sept 1966; Abstracts, p 316.

[24] The resonance from the four $H_2C_2S_2$ protons was apparently hidden under the much stronger resonance from the 20 tetraphenylarsonium protons.

both π-cyclopentadienyl and $S_2C_2(CF_3)_2$ ligands[25] but appears to be more stable (particularly in solution) than the unsubstituted anion $[C_5H_5W(S_2C_2H_2)_2]^-$ prepared in this work.

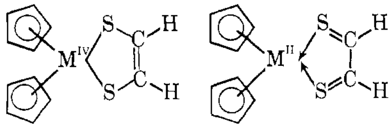
Spectra and Structure.—Complexes with the $H_2C_2S_2M$ chelate ring system IV can exist as a resonance hybrid involving the two structures IVa and IVb. Structure IVa is a metal complex of the ethylenedithiolate dianion. Structure IVb is a metal complex of the neutral dithioglyoxal. Because of the different charges on the ligands in the structures IVa and IVb the metal atom in the ethylenedithiolate derivatives IVa has a formal oxidation state two units higher than the metal atom in the dithioglyoxal derivatives IVb. The relative contributions of structures IVa and IVb to the actual resonance hybrid will depend upon the relative stabilities for the different oxidation states of the central metal atom.

The chemical shifts of the $H_2C_2S_2$ hydrogen atoms in the nmr spectra of the complexes permit assessment of the relative contributions of structures IVa and IVb to the final resonance hybrid. In the ethylenedithiolate structure IVa the protons of the $H_2C_2S_2$ ligand are attached to ethylenic carbon atoms and would be expected to exhibit chemical shifts near the τ 3 value characteristic of ethylenic protons in olefins with somewhat electronegative substituents. However, in the dithioglyoxal structure IVb the protons of the $H_2C_2S_2$ ligand are attached to thioaldehyde carbon atoms and would be expected to exhibit chemical shifts near the τ 0 value characteristic of protons in the formyl group of aldehydes.


a b

IV

Table I gives the chemical shifts of the $H_2C_2S_2$ protons in the complexes prepared from sodium ethylenedithiolate. The $H_2C_2S_2$ protons in the compounds of the type $(C_5H_5)_2MS_2C_2H_2$ (M = Ti and Zr) are in the approximate region expected for the dithiolate derivatives $(C_5H_5)_2M^{IV}S_2C_2H_2$ (Va). In this structure the titanium or zirconium atom has the favored oxidation state +4. The relative contributions of the dithioglyoxal structures Vb with the titanium or zirconium atom in the rare +2 oxidation state appear to be very small. These dithioglyoxal structures Vb are closely related to the carbonyl derivatives $(C_5H_5)_2M(CO)_2$ with the metal atoms in likewise +2 formal oxidation states. The small contributions of the dithioglyoxal structures Vb to the $(C_5H_5)_2MS_2C_2H_2$ resonance hybrid may therefore be related to the instability of the titanium carbonyl derivative $(C_5H_5)_2Ti(CO)_2$[26] and the inability to prepare the analogous zirconium carbonyl derivative $(C_5H_5)_2Zr(CO)_2$.[26,27]

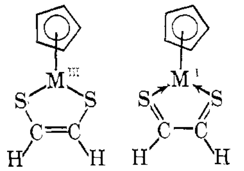


a b

V

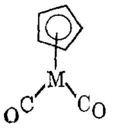
The $H_2C_2S_2$ protons in the $C_5H_5MS_2C_2H_2$ (M = Co and Rh) compounds exhibit much lower proton nmr chemical shifts (τ 1.0–1.5) than the corresponding protons in the $(C_5H_5)_2MS_2C_2H_2$ (M = Ti and Zr) compounds. This suggests that the major contributors to the $C_5H_5MS_2C_2H_2$ resonance hybrids are the dithioglyoxal structures VIb (M = Co and Rh). These structures are closely related to those of the fairly stable cyclopentadienylmetal dicarbonyls $C_5H_5M(CO)_2$ (VII) (M = Co[28] and Rh[22]). In both VIb and VII the metal atoms are in the +1 formal oxidation states. The dithioglyoxal structure VIb being the major contributor to the $C_5H_5MS_2C_2H_2$ compounds is also consistent with the recent X-ray study by Baird and White.[29] On the basis of the bond lengths and angles these workers prefer a dithioketone structure for the trifluoromethyl derivative $C_5H_5CoS_2C_2(CF_3)_2$. The corresponding ethylenedithiolate structures VIa (M = Co and Rh) for the $C_5H_5MS_2C_2H_2$ compounds have the metal atoms in the favored +3 formal oxidation state but with a very unfavorable coordination number of five for the +3 metal atom. By contrast the vast majority of the thousands of stable Co^{+3} and Rh^{+3} complexes have a coordination number of six.

Schrauzer and Mayweg[12] report the proton nmr spectra of the species $Ni(S_2C_2H_2)_2$ and $[V(S_2C_2H_2)_3]^-$ which contain only metal atoms and unsubstituted ethylenedithiolate ligands. In both cases resonances were observed around τ 0.8, indicative of dithioglyoxal structures as the major contributors. The dithioglyoxal derivatives $Ni^0(S_2C_2H_2)_2$ and $[V^{-I}(S_2C_2H_2)_3]^-$ are "isoelectronic" with the known relatively stable carbonyl derivatives $Ni(CO)_4$ and $V(CO)_6^-$.



a b

VI



VII

In general, the proton nmr resonances of the $H_2C_2S_2$ protons in the new compounds prepared from disodium ethylenedithiolate exhibit the expected singlets. An interesting exception is the proton nmr resonance of the $H_2C_2S_2$ protons in the rhodium compound $C_5H_5RhS_2C_2H_2$ where a doublet with a separation of about 5 cps is observed. This arises from coupling of the $H_2C_2S_2$

---

[25] In most cases attempts to prepare anions containing both cyclopentadienyl and bis(trifluoromethyl)ethylenedithiolate ligands result in expulsion of the cyclopentadienyl ligand leaving anions with just bis(trifluoromethyl)ethylenedithiolate ligands.[6]

[26] J. G. Murray, *J. Am. Chem. Soc.*, **83**, 1287 (1961).

[27] R. B. King, M. B. Bisnette, and K. H. Pannell, several unpublished unsuccessful attempts in the period 1965–1967.

[28] T. S. Piper, F. A. Cotton, and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **1**, 165 (1955); E. O. Fischer and R. Jira, *Z. Naturforsch.*, **10b**, 355 (1955).

[29] H. W. Baird and B. M. White, *J. Am. Chem. Soc.*, **88**, 4744 (1966).

protons with the ^{103}Rh nucleus ($I = 1/2$, 100% abundance). Strong interaction between these protons and the rhodium nucleus in the $H_2C_2S_2M$ chelate ring is indicated by the relatively high value of this J(Rh–H) coupling constant.[30]

Acknowledgment.—We are indebted to the U. S. Air Force Office of Scientific Research for partial support of this work under Grant AF-AFOSR-1211-67.

[30] For comparison the J(Rh–H) coupling constant in $C_5H_5Rh(CO)_2$ is only 0.5 cps.

CONTRIBUTION FROM CYANAMID EUROPEAN RESEARCH INSTITUTE,
COLOGNY, GENEVA, SWITZERLAND

Carbon Monoxide Insertion Reactions. VI. The Mechanisms of the Reactions of Methylmanganese Pentacarbonyl and Acetylmanganese Pentacarbonyl with Triphenylphosphine

BY K. NOACK, M. RUCH, AND F. CALDERAZZO

Received August 29, 1967

The reaction of methylmanganese pentacarbonyl with triphenylphosphine yields the isomeric mixture of $CH_3COMn(CO)_4P(C_6H_5)_3$ (I). The *cis* and *trans* isomers, which give two distinct acetyl proton peaks in nmr spectra, have been separated by chromatography on silica and the infrared spectra of enriched chromatographic fractions were measured. The number of infrared C–O stretching vibrations is that expected for local C_s and C_{4v} symmetries for the *cis* and the *trans* isomers, respectively. The *cis* isomer is the initial product of the reaction. The rate of isomerization $cis \overset{k_i}{\rightleftharpoons} trans$ follows a first-order kinetic equation with $k_i = 2.5 \times 10^{-4}$ sec^{-1} at 30° in acetone. A dissociative intermolecular mechanism involving $\{CH_3COMn(CO)_4\}$ is proposed for the isomerization. This is confirmed by the finding that an isomeric mixture of $CH_3COMn(CO)_4P(C_6H_5)_3$ exchanges the phosphine ligand with $P(C_6D_5)_3$. The infrared study of the reaction between $CH_3{}^{13}COMn(CO)_5$ and triphenylphosphine has shown that the final product is the isomeric mixture of $CH_3{}^{13}COMn(CO)_4P(C_6H_5)_3$ with retention of ^{13}C labeling at the acetyl position. A dissociative mechanism is proposed for this reaction.

Introduction

The kinetics of the reactions

$$CH_3Mn(CO)_5 + P(C_6H_5)_3 \longrightarrow CH_3COMn(CO)_4P(C_6H_5)_3 \quad (1)$$

$$CH_3COMn(CO)_5 + P(C_6H_5)_3 \longrightarrow CH_3COMn(CO)_4P(C_6H_5)_3 + CO \quad (2)$$

have been studied[1,2] and it was found that both reactions are first order in the metal complex and independent of triphenylphosphine concentration in ether solvents.

Acetylmanganese tetracarbonyltriphenylphosphine(I) exists in solution as an equilibrium mixture of the *cis* and *trans* isomers, according to nmr measurements,[3,4] showing the presence of two peaks of unequal intensities between τ 7 and 8. Kraihanzel and Maples[4] suggested that the high-field peak was due to the *trans* isomer, whereas we did not specify any assignment.

By studying the reaction of $CH_3Mn(CO)_5$ with ^{13}CO we have shown[5] that *cis*-$CH_3COMn(CO)_4{}^{13}CO$ is formed by a mechanism of methyl migration.

From a mechanistic point of view, it is important to determine which geometrical isomer of $CH_3COMn(CO)_4P(C_6H_5)_3$ is formed initially in the course of reaction 1. Furthermore, two mechanisms, both consistent with the kinetic data,[1,2] have been proposed[6] for reaction 2. The first one involves the coordinately unsaturated intermediate $\{CH_3COMn(CO)_4\}$, while the second considers the slow preequilibrium of $CH_3COMn(CO)_5$ to $CH_3Mn(CO)_5$. Since previous work[6] had not distinguished between the two possibilities, it appeared interesting in this connection to investigate the reaction of $CH_3{}^{13}COMn(CO)_5$ with triphenylphosphine.

Experimental Section

Methylmanganese pentacarbonyl was prepared according to a method described previously.[7] Labeled acetylmanganese pentacarbonyl, $CH_3{}^{13}COMn(CO)_5$, was prepared from $NaMn(CO)_5$ and $CH_3{}^{13}COCl$; details of this preparation will be given in a forthcoming publication.[8] All of the reactions were carried out in an atmosphere of prepurified nitrogen. Fully deuterated triphenylphosphine was prepared by allowing phenyl-d_5-magnesium bromide to react with phosphorous trichloride. Benzene-d_6 was brominated with a solution obtained from bromine and silver nitrate in nitric acid according to a known procedure.[9]

The infrared spectra were measured with a Perkin-Elmer Model 521 spectrophotometer, modified in such a way that the grating order change was at 2200 cm^{-1} rather than at 2000 cm^{-1}. The spectral slit width in the 2200–1500-cm^{-1} region was between 1.0 and 1.4 cm^{-1} (slit program 700). The spectra were measured on an expanded abscissa scale (1 cm = 10 wavenumbers with scan speed 40 cm^{-1}/min).

The infrared measurements of the carbon monoxide evolved

---

[1] F. Calderazzo and F. A. Cotton, *Chim. Ind.* (Milan), **46**, 1165 (1964).

[2] R. J. Mawby, F. Basolo, and R. G. Pearson, *J. Am. Chem. Soc.*, **86**, 3994 (1964).

[3] F. Calderazzo and K. Noack, *J. Organometal. Chem.* (Amsterdam), **4**, 250 (1965).

[4] C. S. Kraihanzel and P. K. Maples, *J. Am. Chem. Soc.*, **87**, 5267 (1965).

[5] K. Noack and F. Calderazzo, *J. Organometal. Chem.* (Amsterdam), **10**, 101 (1967).

[6] F. Calderazzo and K. Noack, *Coord. Chem. Rev.*, **1**, 118 (1966).

[7] F. Calderazzo and F. A. Cotton, *Inorg. Chem.*, **1**, 30 (1962).

[8] K. Noack, *J. Organometal. Chem.* (Amsterdam), in press.

[9] D. H. Derbyshire and W. A. Waters, *J. Chem. Soc.*, 573 (1950).