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Cyclopentadienyl Compounds of Chromium, Molybdenum and Tungsten

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A new preparative method for neutral bis-cyclopentadienyl compounds of the transition elements is the direct reaction of cyclopentadiene with the metal carbonyl. Bis-cyclopentadienylchromium(II) is described. Cyclopentadienyl carbonyls of molybdenum and tungsten are described and a structure involving bridging carbon monoxide groups is suggested.

Bis-cyclopentadienyl compounds of various transitional elements have been prepared by two methods. Firstly, the reaction of cyclopentadienylmagnesium halides with metal halides,[1,3] or acetylacetonates[2,3] leads to compounds of the type $[(C_5H_5)_2M^n]X_{n-2}$, where $n = 2$ to 5 is the oxidation state of the metal M, and X is a halogen, *e.g.*, $(C_5H_5)_2Ni^{II}$, $(C_5H_5)_2Rh^{III}Br$, $(C_5H_5)_2Ti^{IV}Br_2$, $(C_5H_5)_2Nb^{V}Br_3$; in the cases of $FeCl_3$ and Ru(III)-acetylacetonate, reduction to the neutral compound $(C_5H_5)_2M$ occurs. A modification of this method is the reaction of hexaminenickel(II) thiocyanate with cyclopentadienylpotassium in liquid ammonia solution to form $(C_5H_5)_2Ni$.[4] Secondly, the direct reaction of cyclopentadiene with an iron catalyst at 375° forms $(C_5H_5)_2Fe$[5]; no other applications of this preparative method have been reported.

A third preparative method has been found in the vapor phase reaction of cyclopentadiene with metal carbonyls at elevated temperatures.

On passing chromium hexacarbonyl vapor and cyclopentadiene in nitrogen through a tube at 280–340°, scarlet crystals of bis-cyclopentadienylchromium(II) are obtained in approximately 30% yield.

With molybdenum hexacarbonyl the main product of the reaction, which is obtained in about 30% yield at temperatures above 240°, is a molybdenum cyclopentadienyl carbonyl, $C_5H_5Mo(CO)_5MoC_5H_5$. In the reaction of tungsten hexacarbonyl with cyclopentadiene at temperatures above ~280° a cyclopentadienyl carbonyl, $C_5H_5W(CO)_6WC_5H_5$, is obtained.

Both of these cyclopentadienyl compounds are quite stable. Molecular weight determinations show them to be binuclear, and they are diamagnetic. The infrared absorption spectra (Fig. 1) of the two compounds are strikingly similar. Both show a single C–H stretching band, and have other bands in positions similar to those characteristic of bis-cyclopentadienyl compounds.[2a,6] In addition they have two intense bands in the C–O stretching region; for the molybdenum compound there is a sharp band at 1960 cm.$^{-1}$ and a broader one of comparable intensity at 1916 cm.$^{-1}$, while for the tungsten compound the analogous bands are at 1959 and 1911 cm.$^{-1}$, respectively. In the case of iron enneacarbonyl, $Fe_2(CO)_9$, the presence of two C–O frequencies has been attributed[7] to the presence in the molecule of two types of carbon monoxide groups, one non-bridging, the other in bridge positions between the metal atoms. The striking similarity of the molybdenum and tungsten cyclopentadienyl carbonyls, particularly in view of the difference in their stoichiometry, makes a similar interpretation for the existence of two C–O frequencies in these compounds difficult to accept.

The structures of these cyclopentadienyl carbonyls are, perhaps, best formulated as "triple decker sandwiches." A cyclopentadienyl ring is bonded to each metal atom and there are five and six bridging carbonyl groups in the molybdenum and tungsten compounds, respectively. The molybdenum compound, for example, is then formulated as bis-(cyclopentadienyl)-μ-pentacarbonmonoxide-bi-molybdenum(I). The diamagnetism of the compounds can be accounted for. The cyclopentadienyl ring is taken to be bound to the metal by a two electron delocalized bond resulting from the interaction of the unpaired π-electron of the cyclopentadienyl radical with a d-electron of the neutral metal atom as in the bis-cyclopentadienyl compounds.[8] Bonding of the cyclic carbon monoxide system follows from the furnishing by this system of, on the average, three electrons to each metal atom, three of the d-orbitals of the metal being used; the fifth d-orbital (or s-d hybrid orbital) is filled and not involved in bonding. With this arrangement, partial bonding between the carbon atoms of the carbon monoxide groups seems implied, and may provide an explanation for the observed C–O frequencies. The fact that the sharp band at 1959 or 1960 cm.$^{-1}$ is essentially unchanged in both compounds, and that this frequency is almost identical with the C–O frequency in the hexacarbonyls themselves, is consistent with the idea that on the average, the electrons of only three of the carbon monoxide groups are being disturbed in bonding to the metal. The second, broader C–O band may arise from interactions between adjacent C–O groups.

X-Ray diffraction studies[9] have confirmed the stoichiometry of these compounds, and the results of a preliminary analysis for the molybdenum compound are consistent with the structure suggested above.

The carbonyl method is applicable to the preparation of neutral bis-cyclopentadienyl compounds of

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(1) T. J. Kealy and P. L. Pauson, *Nature*, **168**, 1039 (1951).

(2) (a) G. Wilkinson, THIS JOURNAL, **74**, 6146 (1952); (b) **74**, 6148 (1952).

(3) G. Wilkinson, P. L. Pauson, J. M. Birmingham and F. A. Cotton, *ibid.*, **75**, 1011 (1953).

(4) E. O. Fischer and R. Jira, *Z. Naturforschung*, **8b**, 217 (1953).

(5) S. A. Miller, J. A. Tebboth and J. F. Tremaine, *J. Chem. Soc.*, 632 (1952).

(6) E. R. Lippincott and R. D. Nelson, *J. Chem. Phys.*, **21**, 1307 (1953).

(7) *Cf.* R. K. Sheline and K. S. Pitzer, THIS JOURNAL, **72**, 1107 (1950).

(8) (a) W. E. Moffitt, Harvard University, in course of publication; (b) *cf.* also J. D. Dunitz and L. E. Orgel, *Nature*, **171**, 121 (1953); H. H. Jaffe, *J. Chem. Phys.*, **21**, 156 (1953).

(9) D. P. Shoemaker, Massachusetts Institute of Technology, private communication.

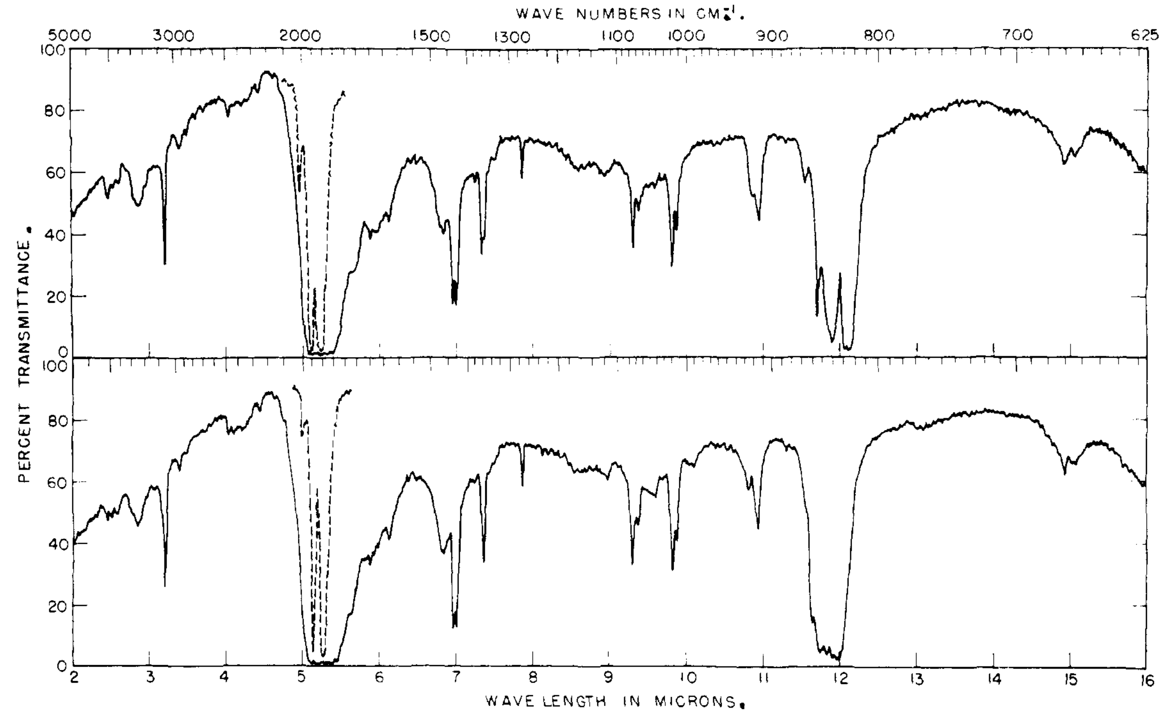

Fig. 1.—Infrared absorption spectra: top, molybdenum cyclopentadienyl carbonyl, full line 12.0 mg./1.5 g. KI, broken line 1.5 mg./cc. chloroform; bottom, tungsten cyclopentadienyl carbonyl, full line 19.0 mg./1.5 g. KI, broken line 2.4 mg./cc. chloroform. Band Double Beam Recording Spectrophotometer.

iron, cobalt and nickel using $Fe(CO)_5$, $Co_2(CO)_8$ and $Ni(CO)_4$, and is undoubtedly capable of further extension.

Experimental

Bis-cyclopentadienylchromium(II).—A slow stream of pure nitrogen or argon is passed through a bubbler of cyclopentadiene at room temperature, and then through a reaction tube. The tube contains chromium hexacarbonyl (5–10 g.) in a porcelain boat, and is held at 100–120° to give an appreciable vapor pressure of the carbonyl. The mixed vapors then pass through a reaction zone at 280–350°; bis-cyclopentadienylchromium is condensed from the gas stream by a water-cooled probe. The crude product, which is contaminated with finely divided metal from the thermal decomposition of the carbonyl is transferred to a vacuum apparatus for sublimation; all operations must be performed in an inert atmosphere box filled with either nitrogen or carbon dioxide, since the crude product is pyrophoric. Any unchanged $Cr(CO)_6$ is sublimed from the mixture at 50° and 0.1 micron pressure; the $(C_5H_5)_2Cr$ is then sublimed at 75–90°. Bis-cyclopentadienylchromium(II) forms scarlet crystals, m.p. 170–172°. *Anal.* Calcd.: C, 66.0; H, 5.53; Cr, 28.50. Found: C, 65.5; H, 5.4; Cr, 28.47. Analysis for chromium was made by the potassium iodide method,[10] after destruction of organic matter by fuming with perchloric acid; carbon and hydrogen analyses were made by combustion on the macroscale, a sample of $(C_5H_5)_2$-Cr being weighed out and transferred to the ignition tube in an inert atmosphere.

Bis-cyclopentadienylchromium(II) is thermally stable to at least 300°, but is exceedingly readily oxidized by air, being pyrophoric when finely divided. Attempts to obtain an infrared spectrum in carbon tetrachloride and carbon disulfide solution failed owing to extensive decomposition. Decomposition also occurred on grinding with nujol, and potassium bromide or iodide in an inert atmosphere. The magnetic susceptibility of the solid compound was measured by the Gouy divided tube method. The tube was filled with the ground solid in a gloved box which could be pumped out to 0.1 micron pressure, and then filled with specially purified nitrogen. [Seaford nitrogen, Air Reduction Sales, Inc., containing 0.002% water, 0.002% oxygen and 0.5% hydrogen was purified by passage over reduced copper at 650° to catalyze the combustion of oxygen; the treated gas was dried by passage through flake potassium hydroxide.] Water, $\kappa = 0.72 \times 10^{-6}$ c.g.s.u., and bis-cyclopentadienylnickel(II) ($\chi_{\text{mol}}^{298°\text{K.}} = +3348 \times 10^{-6}$ c.g.s.u.) which is known to follow Curie's law, were used as references. The molar susceptibility of $(C_5H_5)_2Cr$ at 298°K. was $+3450 \pm 50 \times 10^{-6}$ c.g.s.u., suggesting the presence of two unpaired electrons in the molecule.

Bis-cyclopentadienylchromium(II) reacts only very slowly with water, but dilute mineral acids cause rapid effervescence, liberating cyclopentadiene and forming a dark blue solution. This solution shows none of the reactions characteristic either of the chromous ion, or of a bis-cyclopentadienyl cation; thus, for example, it does not reduce mercuric chloride and does not give a precipitate with silicotungstic acid. It gives a blue precipitate of indefinite composition with the ferrocyanide ion, and with the thiocyanate ion forms an ether extractable blue complex. The nature of these blue substances has not been established at the present time.

Bis-(cyclopentadienyl)-μ-pentacarbonmonoxide-bi-molybdenum(I) and Bis-(cyclopentadienyl)-μ-hexacarbonmonoxide-bi-tungsten(I).—The vapor of molybdenum or tungsten hexacarbonyl is passed with cyclopentadiene through a heated tube, as in the above reaction with chromium hexacarbonyl. With molybdenum hexacarbonyl, the reaction to form the cyclopentadienyl carbonyl begins at about 250°; the cyclopentadienyl carbonyl remains in the heated portion of the tube. With tungsten hexacarbonyl, the reaction begins about 280°, the optimum temperature being about 320°. There is no evidence for the formation of bis-cyclopentadienyl compounds. The cyclopentadienyl carbonyls form within the tube as long needle crystals, admixed with metal from the thermal decomposition of the hexacarbonyl; they are crystallized first from chloroform and then from carbon tetrachloride. In both cases, the yield is about 30% based on the hexacarbonyl.

Molybdenum cyclopentadienyl carbonyl forms dark purple-red crystals. *Anal.* Calcd.: C, 38.95; H, 2.16; Mo, 41.45. Found: C, 38.85; H, 2.14; Mo, 41.40, m.p. 215–217° with decomposition. At 0.1 micron pres-

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[10] "Scott's Standard Methods of Analysis," 5th Edition, Vol. I, D. Van Nostrand Co., New York, N. Y., p. 288.

sure the compound volatilizes only slowly above 150°; it is readily soluble in chloroform, rather less soluble in carbon tetrachloride, alcohol, carbon disulfide, benzene and sparingly soluble in ligroin. It is insoluble in and unaffected by dilute acids or bases and aqueous oxidizing agents such as ceric sulfate. On treatment with nitric acid, 6 *N* or stronger or with bromine water, the compound is decomposed with evolution of carbon monoxide. There is no evidence for the formation of any complex cyclopentadienyl ions. The molecular weight was determined by cryoscopy using benzene as solvent; a value of 455 ± 20 was obtained, the calculated value being 461.0. The measured molar susceptibility was $\chi_{\text{mol}}^{298^\circ\text{K.}} = -210 \pm 5 \times 10^{-6}$ c.g.s.u.

Tungsten cyclopentadienyl carbonyl is also a purple-red crystalline substance having a m.p. 240–242° with decomposition. *Anal.* Calcd.: C, 28.86; H, 1.50; W, 55.25. Found: C, 28.94; H, 1.68; W, 55.23. The compound is readily soluble in chloroform, but rather less soluble than its molybdenum analog in other organic solvents, and is insoluble in ligroin. It is unaffected by dilute acids, bases and aqueous oxidizing agents except 6 *N* nitric acid or bromine, which cause decomposition. The molecular weight by cryoscopy in benzene was 650 ± 20 (calculated 666.0). The compound is diamagnetic, $\chi_{\text{mol}}^{298^\circ\text{K.}} = -220 \pm 5 \times 10^{-6}$ c.g.s.u.

The low solubility of both the molybdenum and tungsten cyclopentadienyl carbonyls in carbon disulfide or carbon tetrachloride allows only the infrared C–O frequencies to be observed using these solvents; solutions 1 mg./ml. concentration in carbon tetrachloride were used for high resolution in the C–O region with a Perkin–Elmer single beam instrument. The spectra over the 650–4000 cm.$^{-1}$ region were obtained using 1 inch diameter wafers formed under 40,000 lb. pressure from 1.5 g. of potassium iodide and a few mg. of the compound intimately ground together.

Analyses of molybdenum were made by the lead molybdate method (ref. 10, p. 589) and of tungsten by the cinchonine-tungstic oxide procedure (ref. 10, p. 1011); in both cases, organic material was first destroyed by oxidation with perchloric acid.

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Steric Effects and the Stability of Complex Compounds. II. The Chelating Tendencies of N,N'-Dialkylethylenediamines with Copper(II) and Nickel(II) Ions[1]

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The stepwise formation constants for $\mathrm{RHNCH_2CH_2NHR}$ (R = methyl, ethyl, *n*-propyl or *n*-butyl), with copper(II) and nickel(II) ions have been determined at 0° and 25°. The results show an appreciable steric effect in the case of the N,N'-dialkylethylenediamines compared to the N-alkylethylenediamines and unsubstituted ethylenediamine. N,N'-Diisopropylethylenediamine did not form normal complexes with copper(II) and nickel(II) ions.

While correlation of the stepwise formation constants of a metalammine with the base strength of the amine is usually good, there are several examples of irregularities that have been attributed to steric factors.[3] The magnitude of this effect has been determined in the case of N-alkylethylenediamines[4] and was found to increase with increasing alkyl size. This paper is the second in a series of investigations to determine the effect of steric hindrance on the stability of complex compounds.

Reported here are the results obtained on the chelating tendencies of N,N'-dialkylethylenediamines with copper(II) and nickel(II) ions in 0.50 *M* potassium nitrate as measured by the Bjerrum titration technique.[5] Since the N,N'-dialkylethylenediamines have approximately the same base strength,[6] any large difference in the formation constants of the chelate may be attributed to steric hindrance. Copper(II) and nickel(II) ions were chosen in order to study the effect of steric hindrance in complexes having a planar configuration as well as octahedral.

Experimental

Calculation of Formation Constants.—The concentration formation constants for equilibria of the type $[\mathrm{MA}_{(n-1)}] + \mathrm{A} \rightleftarrows [\mathrm{MA}_n]$ are designated by the expression $K_n = [\mathrm{MA}_n]/[\mathrm{MA}_{(m-1)}]\,[\mathrm{A}]$.

These constants may be found by measuring the *p*H of solutions containing known amounts of the metal ion plus hydrogen ion and a large amount of a non-complexing electrolyte. The maximum value of $\bar{n}$ for systems investigated here was 3 and the modified development previously reported[4] was applied. This method of calculation is valid only if the *p*H is higher than 4.5 as was the case in all of the titrations reported here. Each of the constants was measured at two temperatures, 0° and 25°. However, it has been observed since paper I in this series[4] that values of enthalpy and entropy derived from equilibrium data measured at only two temperatures can be greatly in error, therefore these values are not presented. Each titration was conducted at least twice, the formation constants for the two determinations not varying by more than ±0.02 log *K* unit.

Reagents.—The amines N,N'-diMeen, N,N'-diEten, N,N'-di-*n*-Pren and N,N'-di-*n*-Buen[7] were prepared by the method of Schneider.[8] N,N'-Di-*i*-Pren was obtained by a modification of the procedure of Zienty[9] using ethylene dibromide and isopropylamine. The preparation and properties of the amines used in this investigation have been described in a previous note.[6]

Standard Solutions.—The amines were diluted with distilled water until approximately 5 *M* and then standard-

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(1) This investigation was supported by a grant-in-aid from the National Institutes of Health, Grant No. G-3239.

(2) Abstracted in part from a thesis by R. Kent Murmann presented to the graduate faculty of Northwestern University in partial fulfillment of the requirements for the Ph.D. degree, 1954.

(3) J. Bjerrum, *Chem. Revs.*, **46**, 381 (1950).

(4) F. Basolo and R. K. Murmann, THIS JOURNAL, **74**, 5343 (1952).

(5) J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1941.

(6) F. Basolo, R. K. Murmann and Y. T. Chen, THIS JOURNAL, **75**, 1478 (1953).

(7) The diamines discussed here are designated as follows: N,N'-diMeen = N,N'-dimethylethylenediamine, N,N'-diEten = N,N'-diethylethylenediamine, N,N'-di-*n*-Pren = N,N'- di-*n*-propylethylenediamine, N,N'-di-*n*-Buen = N,N'-di-*n*-butylethylenediamine, and N,N'-di-*i*-Pren = N,N'-di-*i*-propylethylenediamine.

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(9) F. B. Zienty, THIS JOURNAL, **68**, 1388 (1946).