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Complexes Derived from Strong Field Ligands. XX. The Effect of Extraplanar Ligands on the Properties of Transition Metal 4,4',4'',4'''-Tetrasulfophthalocyanines

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The influence of such extraplanar ligands as pyridine, nitrite, thiocyanate, cyanide, imidazole, benzimidazole, 2-methylimidazole, and histidine on the magnetic and spectral properties and on the relative stabilities of the +2 and +3 oxidation states of cobalt 4,4',4'',4'''-tetrasulfophthalocyanine has been investigated. While none of the ligands alters the ground state of the cobalt(II) complex from the doublet observed in the presence of water alone, the strong ligands, cyanide and imidazole, facilitate oxidation of the compound by atmospheric oxygen to cobalt(III) derivatives. The product from imidazole solutions contains two moles of coordinated imidazole while the cyanide is destroyed during oxidation. Ferricyanide oxidation produces cyanocobalt(III) tetrasulfophthalocyanine. The nickel(II) and copper(II) complexes appear to be unaffected even by such strong ligands as cyanide and imidazole, thus implying a very great ligand field strength on the part of the cyclic ligand.

Introduction

It has long been known that metals are the active sites in many naturally occuring substances containing macrocycles, such as metalloporphyrins, and that their biological funtions often are determined by the nature of, or the exchange of, labile extraplanar ligands, or by the variable oxidation states of the metal.[1] To show the validity of the assumptions and interpretations made concerning the complicated natural systems, there is a need to clarify the behavior of relatively simple materials that do not share the multifold structural complexity and diverse sites of reactivity with such substances as the hemoproteins and vitamin B_{12}. Studies of this kind should help define those relationships that produce the delicate balance of properties required for a complex to perform some specific function in a dynamic system. The complexes of 4,4',4'',4'''-tetrasulfophthalocyanine (see structure I, ref. 2) offer the possibility of this type of investigation. The syntheses in high purity and the magnetic properties of the copper(II), nickel(II), cobalt(II), iron(III), and manganese(II) derivatives have recently been reported.[2] Observations are summarized here on the interactions of some of these complexes with extraplanar ligands and the influence of these monodentate ligands on autoxidation.

Experimental

Materials.—Imidazole and benzimidazole were obtained from Matheson Coleman and Bell, and L-(+)-histidine was obtained from Eastman Organic Chemicals. All were used without further purification. Other chemicals were of reagent grade.

Solution Magnetic Measurements.—Magnetic moments were determined for samples in solution at room temperature by the Gouy method at a field strength of 19 kgauss. Demineralized, doubly-distilled water was used as a standard. The precision of measurement and method of estimating diamagnetic corrections were as reported earlier.[2] Magnetic susceptibility values were calculated from solution measurements using the equation

$$\chi_M{}^1 = (\Delta WR - \chi_g{}^L/W_L - \chi_g{}^E W_E - \chi_g{}^S W_S)(Z/W_C)$$

The subscripts or superscripts C, L, E, and S refer to the metal, ligand, extraplanar ligand, and solvent, respectively. The symbols $\chi_M{}^1$ and χ_g refer to the atomic susceptibility of the metal, after diamagnetic corrections, and gram susceptibility, respectively. The tube constant is denoted by R and ΔW is the change in weight of the solution (corrected for the contribution from the sample tube) for field "on" minus field "off." Z represents the atomic weight of the metal and W represents the weight of each component of the solution.

Tetrasodium Salt of Bis(imidazole)cobalt(III) 4,4',4'',4'''-Tetrasulfophthalocyanine 7-Hydrate.—Cobalt(II) tetrasulfophthalocyanine (0.612 g., 0.625 × 10^{-3} mole) was added to 10 ml. of 0.125 M imidazole (0.0850 g., 1.25 × 10^{-3} mole) in a 25-ml. volumetric flask, and the flask was filled to the mark with distilled water. Air was bubbled through the sample for about 60 hr. until a constant magnetic moment of 0.6 to 0.7 B.M. was obtained. The solution was evaporated to dryness under vacuum in a rotary evaporator. The sample was extracted for 3.5 hr. in a Soxhlet extractor containing 175 ml. of absolute alcohol. The remaining blue-green solid was dried overnight *in vacuo* over P_2O_5.

Anal. Calcd. for $C_{38}H_{19}N_{12}O_{12}S_4Na_4Co \cdot 7H_2O$: C, 36.79; H, 2.68; N, 13.55; S, 10.33. Found: C, 36.54, 36.98; H, 3.22, 2.91; N, 13.28; S, 10.28.

Tetrasodium Salt of Hydroxocobalt(III) 4,4',4'',4'''-Tetrasulfophthalocyanine.—To an aqueous solution of cobalt(II) tetrasulfophthalocyanine (0.612 g., 0.625 × 10^{-3} mole) in a 25-ml. volumetric flask at pH 8 was added 10 ml. of 0.125 M sodium cyanide solution (0.0163 g., 1.25 × 10^{-3} mole). The volumetric flask was filled to the mark with distilled water. Air was bubbled through the solution for about 60 hr. until a constant magnetic moment in the range of 0.3 to 0.5 B.M. was obtained. The solution was evaporated to dryness under vacuum in a rotary evaporator, then was extracted for 3.5 hr. in a Soxhlet extractor containing 175 ml. of absolute alcohol. The remaining green solid was dried overnight *in vacuo* over P_2O_5.

Anal. Calcd. for $C_{32}H_{13}N_8O_{13}S_4Na_4Co$: C, 38.56; H, 1.31; N, 11.24; S, 12.87. Found: C, 38.80; H, 1.94; N, 11.19; S, 11.14.

Tetrasodium Salt of Cyanoaquocobalt(III) 4,4',4'',4'''-Tetrasulfophthalocyanine.—Cobalt(II) tetrasulfophthalocyanine (2.59 g., 2.64 × 10^{-3} mole) and potassium hexacyanoferrate(III) (0.870 g., 2.64 × 10^{-3} mole) were dissolved in 100 ml. of water and heated with stirring at 65° for 12 hr. After the solution was adjusted to pH 10, 200 g. of sodium perchlorate 1-

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(1) J. E. Falk and J. N. Phillips, "Chelating Agents and Metal Chelates," F. P. Dwyer and D. P. Mellor, Ed., Academic Press, New York, N. Y., 1964, Chapter 10.

(2) J. H. Weber and D. H. Busch, *Inorg. Chem.*, **4**, 469 (1965).

hydrate was added. The solution and undissolved material were briefly heated to 80° with stirring, cooled, and filtered at room temperature. The crude solid was twice refluxed for 4 hr. with 200 ml. of fresh absolute ethanol. After the second period of refluxing, the pure, blue-green product was filtered and dried overnight *in vacuo* over P_2O_5.

Anal. Calcd. for $C_{33}H_{12}N_9O_{12}S_4Na_4Co$: N, 12.32. Found: N, 12.49, 12.33.

Results and Discussion

Magnetic and spectral studies have been conducted on solutions of cobalt(II) tetrasulfophthalocyanine containing, as added ligands or salts, pyridine, sodium nitrite, sodium thiocyanate, potassium perchlorate, sodium cyanide, imidazole, benzimidazole, 2-methylimidazole, and histidine. The reactivity of the cobalt(II) in these systems toward atmospheric oxygen has been investigated. Less extensive studies have been conducted on solutions of nickel(II) and copper(II) tetrasulfophthalocyanines in the presence of sodium cyanide, pyridine, and imidazole. The behaviors of the cobalt(II) systems place them in two distinct categories and these are discussed separately below.

Many ligands do not greatly affect the value of the magnetic moment of the cobalt(II) tetrasulfophthalocyanine in solution. The value of 1.88 ± 0.05 B.M. obtained in pure water is nearly identical with the value (1.86 B.M. Table I) obtained in the presence of 2 moles of pyridine per mole of cobalt. Solutions containing nitrite ion, thiocyanate ion, or perchlorate ion exhibit slightly lower magnetic moments, 1.69 ± 0.04 B.M. (Table I). The visible spectrum of each of these solutions, including those containing pyridine, does not differ appreciably from that of cobalt(II) tetrasulfophthalocyanine in water alone. Equilibration by stirring with a stream of air causes no changes in the magnetic moments of these solutions, indicating that the divalent state of cobalt is stable under these conditions. Activity effects are probably responsible for the small changes observed in the magnetic moments upon the addition of salts. The alteration of the ionic character of the medium probably influences the constant for the monomer–dimer equilibrium.[3,4] In any event, the effect is small, as measured by magnetism. The measurement of the visible spectrum of dilute solutions containing 1000-fold excess of any of the salts produces the spectral changes expected for conversion of most of the complex into the so-called dimeric form[3]; *i.e.*, the band at 660 mμ is hardly detectable while the higher energy band at 630 mμ is very intense.

TABLE I

MOLAR SUSCEPTIBILITIES AND MAGNETIC MOMENTS FOR COBALT(II) TETRASULFOPHTHALOCYANINE (Co^{II}SPc) IN THE PRESENCE OF CERTAIN EXTRAPLANAR LIGANDS[a,b]

System	Diamag. cor. × 10^6	$\chi_M \times 10^6$ (complex)	μ_{eff}, B.M.
Co^{II}SPc + 2 py[c]	+660	+800	1.86 ± 0.005
Co^{II}SPc + 2 $NaNO_2$[d]	+594	+512	1.62 ± 0.05
Co^{II}SPc + 1 $NaNO_2$[d]	+572	+627	1.68 ± 0.03
Co^{II}SPc + 2 NaSCN[d]	+624	+644	1.73 ± 0.04
Co^{II}SPc + 2 $KClO_4$	+644	+584	1.72 ± 0.005

[a] 0.025 *M* MSPc in water at 20°. [b] No precautions were taken to protect samples from air. [c] py = pyridine. [d] μ_{eff} unchanged by 36-hr. aeration.

TABLE II

MOLAR SUSCEPTIBILITIES AND MAGNETIC MOMENTS OF COBALT TETRASULFOPHTHALOCYANINE (CoSPc) IN THE PRESENCE OF CYANIDE ION AND IMIDAZOLES[a,b]

System	Diamag. cor. × 10^6	$\chi_M \times 10^6$ (complex)	μ_{eff}, B.M.
Co^{II}SPc + 2 NaCN[c]	+590	+702	1.75 ± 0.03
CoSPc + 1 NaCN + air[d]	+570	−56	1.10 ± 0.09
Co^{II}SPc + 2 NaCN + air[d]	+590	−439	0.60 ± 0.12
Co^{III}SPc(OH)[e]	+562	−330	0.74 ± 0.16
Co^{II}SPc + 2 imid[c]	+600	+768	1.80 ± 0.05
CoSPc + 1 imid + air[d]	+575	+82	1.25 ± 0.05
Co^{II}SPc + 2 imid + air[d]	+600	−428	0.63 ± 0.10
CoSPc + 2 hist + air[d]	+644	−223	1.01 ± 0.06
CoSPc + 3 hist + air[d]	+691	−343	0.90 ± 0.04
Co^{II}SPc + 2 benz[f,g]	+668	+480	1.65 ± 0.03
Co^{II}SPc + 2 mimid[f,g]	+624	+492	1.62 ± 0.03

[a] 0.025 *M* CoSPc in water at 20°. [b] imid = imidazole, hist = histidine, benz = benzimidazole, mimid = 2-methylimidazole. [c] Air was carefully excluded from solutions. [d] Samples were aerated to constant μ_{eff} value. [e] Sample isolated from Co^{II}SPc + 2 NaCN system (μ_{eff} = 0.60 B.M.) and redissolved. [f] μ_{eff} unchanged by 36-hr. aeration. [g] μ_{eff} unchanged by 12-hr. aeration after adjusting solution to pH 10.

A very different behavior has been observed in the cases of the ligands cyanide and imidazole. When solutions containing 2 moles of cyanide ion or 2 moles of imidazole per mole of cobalt(II) tetrasulfophthalocyanine are carefully protected from the air, the magnetic moments exhibit consistent values of 1.75 and 1.80 B.M., respectively (Table II). The erratic behavior observed for unprotected solutions demonstrates that each of the two ligands promotes the oxidation of the cobalt(II) by the oxygen of the air.

The cyanide and imidazole solutions have been oxidized to constant magnetic moment values of 0.60 and 0.63 B.M., respectively. From theoretical calculations, a value of 0.6 B.M. is expected for spin-paired cobalt(III) complexes.[5] When only 1 mole of cyanide ion or imidazole is present per mole of cobalt(II) complex, air oxidation produces constant magnetic moment values corresponding to oxidation of about 50% of the cobalt(II). The calculated magnetic moment for a 50% Co(II)–Co(III) mixture, 1.3 B.M., agrees reasonably well with the observed values of 1.10 and 1.25 B.M. found for the cyanide and imidazole solutions, respectively. From this it is clear that 2 moles of a given extraplanar ligand is required for complete oxidation of 1 mole of cobalt(II) to cobalt(III).

In these systems, as air oxidation continues, changes in the visible spectra follow a parallel trend to that observed in changes in the magnetic moments. As the ratio of cobalt(III) to cobalt(II) increases in the imidazole system, the extinction coefficient of the lower energy band (662 mμ) increases relative to its higher

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(3) K. Bernauer and S. Fallab, *Helv. Chim. Acta*, **44**, 1287 (1961).

(4) H. Kobayashi, Y. Torii, and N. Fukada, *Nippon Kagaku Zasshi*, **81**, 694 (1960).

(5) J. S. Griffith and L. E. Orgel, *Trans. Faraday Soc.*, **53**, 601 (1957).

energy shoulder. In the imidazole system, the 662 mμ band increases from an extinction coefficient of 6.40×10^4 for the cobalt(II) species, through 6.70×10^4 for the 50–50 mixture, to 8.00×10^4 for the cobalt(III) complex. The intensity of the 630 mμ shoulder is only slightly altered in the series of solutions. The magnetic moment values corresponding to these three solutions are 1.88, 1.40, and 0.60 B.M., respectively. The extent of oxidation of cobalt(II) in the solution can also be monitored by observing the decreasing intensity of the absorption band near 320 mμ. The extinction coefficient changes from 6.6×10^4 for the cobalt(II) compound to 3.6×10^4 for the cobalt(III) complex.

The cobalt(III) compounds formed in the imidazole and cyanide ion solutions have been isolated and analyzed. The compositions of the complexes correspond to the tetrasodium salt of bis(imidazole)cobalt(III) tetrasulfophthalocyanine 7-hydrate and the tetrasodium salt of aquohydroxocobalt(III) tetrasulfophthalocyanine. Because of strong sulfophthalocyanine absorption, imidazole bands were not found in the infrared spectrum of the imidazole complex. The hydroxo complex, when dissolved in aqueous solution, gave a magnetic moment of 0.74 B.M.

Both the solution measurements and the synthetic work serve to show that the strong extraplanar ligands promote the autoxidation of the cobalt ion to the trivalent state. In turn, this indicates that the highest energy d-electron of the cobalt(II) species occupies an orbital that becomes increasingly antibonding as the strength of binding to the unidentate ligands increases.

It is a particularly interesting observation that the compound derived from autoxidation in the presence of cyanide ion contains none of that unidentate ligand. In fact, care has been taken to search for cyanide, cyanate, cyanogen, formamide, and ammonium formate in all parts of the reaction system. None of these substances is present. Also, blanks have been run by aeration of solutions of nickel(II) tetrasulfophthalocyanine containing cyanide ion. In this case the cyanide is readily detected polarographically or by its infrared spectrum. Although investigations are continuing, these results conclusively demonstrate that the air oxidation of the cobalt(II) tetrasulfophthalocyanine in the presence of cyanide results in destruction of that anion.

The absence of CN^- from the products of the reactions considered above cannot be attributed to the instability of cyanide derivatives of cobalt(III) tetrasulfophthalocyanine, for such a species has been prepared by a different reaction. In fact, the route leading to cyanocobalt(III) tetrasulfophthalocyanine is equally interesting for the process involves the transfer of cyanide from ferricyanide concomitantly with oxidation of the cobalt(II) to cobalt(III). The product has been isolated in crystalline form and its nature established by elemental analysis for nitrogen (the only sensitive analysis) and by assignment of the C≡N stretching frequency at 2040 cm.$^{-1}$ (very strong). In contrast, the reaction of the diaquocobalt(III) derivative of vitamin B_{12} with ferrocyanide, ferricyanide, and cobalticyanide ions is reported[6] to produce bridged complexes.

The reaction between hexacyanoferrate(III) and pentacyanocobaltate(II) ions provides a useful example in which both oxidation–reduction and bridge formation occur.[7] In this case the solid cyanide bridged

$$[Fe^{III}(CN)_6]^{3-} + [Co^{II}(CN)_5]^{3-} \longrightarrow [(CN)_5Co^{III}\text{–}NC\text{–}Fe^{II}(CN)_5]^{6-}$$

complex was isolated.

In the reaction between cobalt(II) tetrasulfophthalocyanine and hexacyanoferrate(III) ion, an unstable bridged intermediate presumably forms, followed by oxidation–reduction, cleavage of the bond between the bridging cyanide ion and iron, and, probably, by rearrangement of the cobalt isocyanide to cobalt cyanide.

The two unusual results observed during oxidation of the cobalt(II) complex in systems containing cyanide or ferricyanide may indicate that an accumulation of energy derived from the oxidation–reduction reaction is utilized in degradation of the instantaneous product of the primary reaction. This constitutes a promising class of energy-transfer reaction meriting further investigation.

The behavior of the imidazole-containing systems during oxidation of the cobalt(II) complex differs substantially. While appearing to be as effective as cyanide in facilitating the oxidation of the cobalt(II), the imidazole apparently survives the transformation unaltered and is retained in the coordination sphere of the cobalt(III) product. Although the strength of the imidazole as a ligand is perhaps best illustrated here, it has previously been reported that benzimidazole is the strongest ligand known to form tetrahedral cobalt(II) complexes.[8]

The three substituted imidazoles, 2-methylimidazole, histidine, and benzimidazole, differ substantially from the parent compound in their abilities to promote the autoxidation of cobalt(II) tetrasulfophthalocyanine. When the systems are equilibrated with air to constant magnetic moments (Table II), the values are such as to indicate mixtures of cobalt(II) and cobalt(III). Spectral changes are also consistent with this suggestion. Should this simple view prove to be true, the enhanced steric requirements of the substituted imidazoles must be credited with the effect. Other workers[9,10] have found it difficult or impossible to form iron(II) phthalocyanine complexes with imidazoles that are substituted at the 2 position (2-methylimidazole) or at positions 4 and 5 (benzimidazole).

The effects of cyanide and imidazole on the magnetic moments of copper(II) and nickel(II) tetrasulfophthalocyanines have been investigated (Table III). The copper(II) complex has absorption bands at 630 and 338 mμ while the nickel(II) complex absorbs at

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[6] P. George, D. H. Irvine, and S. C. Glauser, *Ann. N. Y. Acad. Sci.*, **88**, 393 (1960).

[7] W. P. Griffith, *Quart. Rev.* (London), **16**, 188 (1962).

[8] M. Goodgame and F. A. Cotton, *J. Am. Chem. Soc.*, **84**, 1543 (1962).

[9] H. Giesemann, *J. prakt. Chem.*, **4**, 169 (1956).

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TABLE III

MOLAR SUSCEPTIBILITIES AND MAGNETIC MOMENTS OF METAL TETRASULFOPHTHALOCYANINES (MSPc) IN THE PRESENCE OF CYANIDE ION, PYRIDINE, AND IMIDAZOLE[a,b]

System	Diamag. cor. × 10^6	$\chi_M \times 10^6$ (complex)	μ_{eff}, B.M.
$Ni^{II}SPc$	+550	−441	0.50 ± 0.04
$Ni^{II}SPc$ + 2 NaCN[c]	+590	−510	0.43 ± 0.08
$Ni^{II}SPc$ + 2 py	+660	−555	0.50 ± 0.10
$Ni^{II}SPc$ + 2 imid[c]	+600	−505	0.47 ± 0.02
$Cu^{II}SPc$	+550	+768	1.77 ± 0.05
$Cu^{II}SPc$ + 2 NaCN[c]	+590	+883	1.83 ± 0.07
$Cu^{II}SPc$ + 2 imid[c]	+600	+703	1.76 ± 0.06

[a] 0.025 *M* MSPc in water at 20°. [b] py = pyridine, imid = imidazole. [c] μ_{eff} does not change with 24-hr. aeration.

630 and 334 mμ. Neither the absorption spectra nor the magnetic moments of these compounds are affected by the presence of either cyanide ion or imidazole. Further, extended aeration fails to alter either property.

The fact that the addition of ligands such as pyridine above and below the plane in such complexes as bis(salicylaldoxime)nickel(II) and bis(N-methylsalicylaldimine)nickel(II) converts those planar complexes into spin-free, essentially octahedral derivatives is well known.[11,12] Modern theory has been invoked to explain this effect,[13] in general, in the terms utilized in the discussion of the cobalt(II) case above. In these laboratories[14,15] the nickel(II) atom in other cyclic forced-planar complexes has been found to undergo the transformation from the singlet to the triplet state in the presence of extraplanar ligands weaker than cyanide. Consequently, the fact that nickel(II) tetrasulfophthalocyanine does not exhibit this behavior even in the presence of cyanide ion or imidazole demonstrates that the sulfophthalocyanine ligand exerts an unusually strong ligand field. This conclusion has been reached earlier in conjunction with a study of the magnetic moments of the tetrasulfophthalocyanines of Mn(II), Fe(III), Co(II), Ni(II), and Cu(II).[2] Since spin-paired Mn(II) occurs with only a very few ligands, including CN^-, RNC, and tetrasulfophthalocyanine, it was concluded that the ligand field strength of the latter is comparable to that of cyanide. A troublesome consideration follows from this notion. If the two ligands (CN^- and SPc) were of comparable strength, the addition of cyanide above and below the plane might be expected to produce a spin-free pseudooctahedral structure. The difficulty is most probably associated with the failure of such considerations to take into account the very great part the π-system plays in determining the coordinating ability of th ehighly conjugated cyclic ligand. The π-bonding molecular orbitals of e_g and a_{2u} symmetry probably play a major role both in determining the stability of the square-planar, spin-paired complex and in preventing its reaction with extraplanar ligands to form spin-free tetragonal complexes.[16]

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Reactions of Alkali Metal Derivatives of Metal Carbonyls. VI. Some Reactions of Anions Prepared from Indenylmolybdenum Tricarbonyl Dimer and Azulenedimolybdenum Hexacarbonyl[1]

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Indenylmolybdenum tricarbonyl dimer, $[C_9H_7Mo(CO)_3]_2$, is reduced by sodium amalgam in tetrahydrofuran to give a brown solution containing the $[C_9H_7Mo(CO)_3]^-$ anion. This solution reacts with methyl iodide to form the expected yellow-orange tricarbonyl $CH_3Mo(CO)_3C_9H_7$. However, allyl chloride and chloromethyl methyl sulfide react with the $[C_9H_7Mo(CO)_3]^-$ anion in tetrahydrofuran solution at room temperature to form the yellow dicarbonyls π-$C_3H_5Mo(CO)_2C_9H_7$ and π-$CH_3SCH_2Mo(CO)_2C_9H_7$, respectively, in unusually facile decarbonylation reactions. Treatment of $[C_9H_7Mo(CO)_3]_2$ with iodine in dichloromethane solution gives a brown dicarbonyl iodide $C_9H_7Mo(CO)_2I$ rather than the expected tricarbonyl iodide. Azulenedimolybdenum hexacarbonyl, $C_{10}H_8Mo_2(CO)_6$, reacts with sodium amalgam in tetrahydrofuran to give a yellow-brown solution which gives yellow dimeric $[C_{10}H_8Mo(CO)_3CH_3]_2$ on treatment with methyl iodide.

A. Indenyl Derivatives

Recently numerous organometallic compounds of interest have been obtained by treatment of various anionic cyclopentadienyl metal carbonyls, especially $[C_5H_5Fe(CO)_2]^-$ and $[C_5H_5M(CO)_3]^-$ (M = Mo or W), with various organic halides.[2] This paper describes

(1) For Part V of this series see R. B. King and M. B. Bisnette, *J. Organometal. Chem.*, **2**, 38 (1964).