likely to become more comparable, and the inherently higher sensitivity of the band gap to the metal–ligand distances indicated in Figure 5 could indeed be responsible for the reversal in the conductivity *vs.* pressure curve observed for MGS above *ca.* 100 kbars.

Another structural parameter which could change as a function of pressure, yet not produce a major structural rearrangement, is the angle between the Pt–N and Pt–Cl bond directions in the adjacent complex ions. To determine what effect this might have upon the electronic structure of MGS, a calculation was also carried out on $Pt(NH_3)_4PtCl_4$ in the completely staggered configuration (*i.e.*, $\theta = 45°$ in Figure 2), in which the degree of interionic ligand–ligand interaction should be at a minimum. The interionic distance in this calculation was set at 2.80 Å. As might be expected in view of the axial symmetry of most of the platinum–platinum interactions, very little change in the energy of the d-like molecular orbitals relative to those in the $\theta = 28°$, 2.80-Å metal–metal distance case was found and the overall Pt–Pt interaction, as measured by the Mulliken bond order, was essentially the same. It is interesting that even in this optimal configuration, no δ bonding involving the d_{xy} and $d_{x^2-y^2}$ orbitals on the platinum atoms was evidenced at this interionic separation, thus effectively ruling out this type of interaction as a significant factor in determining the physical properties of MGS at any reasonable pressure.

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Magnetic Behavior of Metal Derivatives of Substituted Benzeneazo-5-pyrazolones

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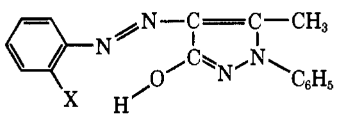
Received August 5, 1970

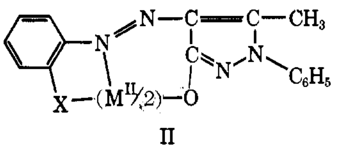
The synthesis and room-temperature magnetic moments of nickel(II), cobalt(II), and copper(II) complexes of substituted benzeneazo-5-pyrazolones and -3,5-pyrazolidinediones are reported. Cobalt(II) complexes which contain an $-SCH_3$ group in the ortho position to the azo linkage give anomalous moments, while those which contain either an $-OCH_3$ or an $-N(CH_3)_2$ group give normal, high-spin moments. Nickel(II) complexes of bidentate ligands were isolated as either high-spin or low-spin compounds depending upon the method of preparation. Anomalous moments were obtained for nickel(II) compounds which contained either a bromo or an iodo group ortho to the azo linkage. It is tentatively suggested that the coordination for nickel(II) is either tetrahedral or planar and that the ortho-bromo and ortho-iodo compounds contain both structures.

Introduction

In a rather extensive study of the coordination of divalent metal ions with azo derivatives of 3-pyrazolone[2] (I) it was shown that when $X = OCH_3$ or SCH_3 the resulting molecule is a terdentate ligand (II),



I



II

and the stability of the complex is greater than when X = H. However, when $X = F, Cl, Br, I, NO_2, CH_3$, or C_2H_5, the compounds behave like bidentate ligands, and the stability of the resulting metal complex is decreased for divalent nickel, cobalt, zinc, and cadmium while copper(II) compounds are not affected. Similar behavior was observed for the azo derivatives of 4-pyrazolone[3] and 5-pyrazolone.

It was suggested that the overall coordination reaction is

$$M(H_2O)_6^{2+} + 2HCh = M(Ch)_2(H_2O)_2 + 2H^+$$

and that the noncoordinating ortho substituents in the bidentate ligands interfered with the retention of water molecules. Thus, as the size of X increases, the water–metal bond length increases and the stability of the resulting complex decreases. The formation constants of divalent nickel, cobalt, zinc, and cadmium for the ortho-substituted benzeneazo-3- and -4-pyrazolones decrease in the order F, Cl, Br, I. Copper(II) complexes are insensitive to this steric effect and are therefore essentially not solvated in solution. Although the ortho-substituted azo-5-pyrazolones were too insoluble to study by potentiometric measurements, qualitative results showed the same steric effect.

Herein we report the synthesis and room-temperature magnetic moments of nickel(II), cobalt(II), and copper(II) complexes of substituted benzeneazo-5-pyrazolones (III) and -3,5-pyrazolidinediones (IV).

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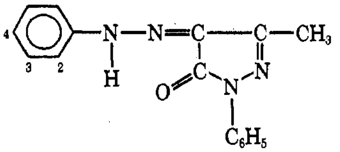
[1] Participants, NSF Undergraduate Research Participation Program—1966. Taken in part from senior honors dissertations, Franklin and Marshall College, 1967.

[2] F. A. Snavely, D. A. Sweigart, C. H. Yoder, and A. Terzis, *Inorg. Chem.*, **6**, 1831 (1967).

[3] F. A. Snavely, N. M. Rosenblum, P. S. Danielson, and R. R. Rill, *J. Inorg. Nucl. Chem.*, **33**, 455 (1971).

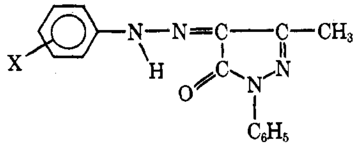
TABLE I

NICKEL COMPOUNDS WITH THE AZO DERIVATIVES OF 5-PYRAZOLONE[a]

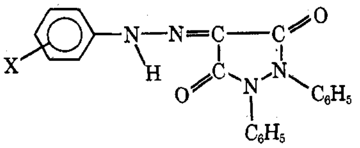


Preparative method	Azo[b] compd	Mp,[c] °C	% carbon Calcd	% carbon Found	% hydrogen Calcd	% hydrogen Found	% nitrogen Calcd	% nitrogen Found
B	4-Br-I	280–283	49.84	49.47	3.14	3.00	14.54	14.21
A	4-Br-II	280–283	49.84	49.85	3.14	3.34	14.54	14.65
C	4-NO_2-I	288–289	54.64	54.23	3.44	3.64	19.92	20.10
B	4-NO_2-II	288–289	54.64	54.64	3.44	3.48	19.92	19.55
B	3-NO_2-I	273–275	54.64	54.40	3.44	3.67	19.92	20.10
A	3-NO_2-II	273–277	54.64	54.22	3.44	3.67	19.92	19.59
A	3-Br	205–206	49.84	49.90	3.14	3.15	14.54	14.45
A	2-CH_3-4-NO_2	291–295	55.83	55.42	3.82	3.97	19.15	18.95
C	4-CH_3	281–283	64.22	63.72	4.64	4.76	17.21	17.72
A	4-OC_2H_5	277–281	61.65	61.70	4.85	4.98	15.98	15.65
A	4-Cl	276–279	56.33	56.40	3.55	3.45	16.43	16.18
A	4-I	266–269	44.42	44.65	2.80	2.87	12.96	13.15
A	3-OCH_3	268–270	60.64	60.46	4.49	4.48	16.64	16.84
C	3-F	245–247	59.19	58.24	3.73	3.71	17.23	17.02
A	3-I	145–146	44.42	44.18	2.80	2.88	12.96	12.68
A	2-F	300–302	59.19	59.36	3.73	3.90	17.23	17.25
B	2-Cl	287–290	56.33	56.16	3.55	3.45	16.43	16.50
B	2-Br	232–233	49.84	47.64	3.14	2.90	14.54	15.28
A	2–I	264–268	44.42	44.12	2.80	3.06	12.96	13.00
B	2-NO_2	260–263	54.64	54.35	3.44	3.34	19.92	19.68

[a] Analysis on samples dried at 110°, $M(Ch)_2$, where Ch^- is the chelate ion. [b] Roman numerals refer to the same compound prepared by different methods. [c] Most of the compounds melt with decomposition.



III



IV

Experimental Section

Preparation of Azo Compounds.—The azo compounds were prepared by coupling the appropriate diazonium salt to 1-phenyl-3-methyl-5-pyrazolone and 1,2-diphenyl-3,5-pyrazolidinedione and most of them have been reported[4] elsewhere. Neutralization equivalents were measured for the new azo compounds, and results agreed within 0.2% of calculated values.

Preparation of Metal Derivatives. Method A.—The azo compound was added to hot 95% ethanol and slightly less than the equivalent amount of 1 *N* sodium hydroxide was added. Enough ethanol was used so that a solution resulted after the addition of the base. To the boiling solution the stoichiometric amount of 1 *M* metal nitrate solution was added dropwise with stirring. In most cases the metal derivative precipitated within a few minutes and was filtered, washed with cold ethanol, and dried at room temperature.

The following is a typical preparation. Ten millimoles of 1-phenyl-3-methyl-4-(4-bromophenylazo)-5-pyrazolone (3.57 g) was dissolved in 130 ml of boiling 95% ethanol to which had been added 11 ml of 0.86 *N* NaOH. Five milliliters of 1.0 *M* $Ni(NO_3)_2$ solution was added dropwise to the boiling, well-stirred solution. The nickel compound started to precipitate before all of the metal nitrate was added. After the addition of the metal nitrate, the solution was heated for 5 min, suction filtered hot, washed with cold 95% ethanol, and air dried; yield 3.56 g of $Ni(CH)_2 \cdot 5H_2O$, about 90%.

Method B.—To a 50:50 mixture of 1 *M* metal nitrate solution and 95% ethanol concentrated ammonia was added in excess to form the ammine complex. The ammine complex was added dropwise to the boiling solution of the azo compound in 95% ethanol or mixtures of 95% ethanol and dioxane which may have contained aqueous ammonia.

Method C.—The azo compound is dissolved in boiling 95% ethanol or ethanol–dioxane mixtures and the metal nitrate solution is added. The sodium hydroxide is then added at a slow rate. The preparation is continued as in method A.

The elemental analysis and the method of preparation of the nickel(II) compounds of the azo derivatives of 5-pyrazolone are given in Table I. The analysis was done by G. Weiler and F. B. Strauss, Oxford, England.

Magnetic Measurements.—Magnetic susceptibilities were determined by the Gouy method. The magnet and sample holder were calibrated using an aqueous solution of $NiCl_2$.[5] Magnetic dilution was assumed and magnetic moments were calculated using Curie's law. Susceptibilities were measured for samples which contained water or ammonia of coordination and for the samples dried to constant weight at 110°. Molar susceptibilities of the metal chelates were corrected for diamagnetism by using the measured susceptibility of the appropriate chelating agent and by using the known diamagnetic contribution of the metal ion core.[6]

The susceptibilities of samples which contained either water or ammonia were corrected both for the diamagnetism and for the contribution to the molecular weight made by the water or ammonia.

Results and Discussion

Terdentate Azo Compounds.—The moments for the azo derivatives which contain a coordinating group in the 2 position are given in Tables II and III. These metal derivatives contained no water or ammonia of coordination regardless of the method of preparation.

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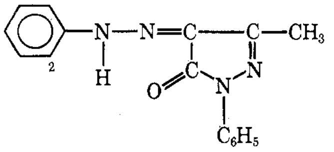
[4] (a) F. A. Snavely, W. C. Fernelius, and B. P. Block, *J. Amer. Chem. Soc.*, **79**, 1028 (1957); (b) F. A. Snavely, B. D. Krecker, and C. G. Clark, *ibid.*, **81**, 2337 (1959); (c) F. A. Snavely and B. D. Krecker, *ibid.*, **81**, 4199 (1959); (d) F. A. Snavely, W. S. Trahanovsky, and F. H. Suydam, *J. Org. Chem.*, **27**, 994 (1962); (e) F. A. Snavely, C. H. Yoder, and F. H. Suydam, *Inorg. Chem.*, **2**, 708 (1963); (f) F. A. Snavely and D. A. Sweigart, *J. Inorg. Nucl. Chem.*, **31**, 2277 (1969).

[5] B. N. Figgis and J. Lewis, "Techniques of Inorganic Chemistry," Vol. IV, Wiley, New York, N. Y., 1965, p 230.

[6] L. N. Mulay, "Magnetic Susceptibility," Wiley, New York, N. Y., 1963, p 1782.

TABLE II

MAGNETIC MOMENTS OF 2-SUBSTITUTED AZO DERIVATIVES OF 5-PYRAZOLONE AT 27–28°[a]

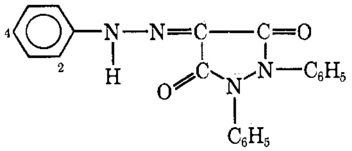


Compd	Magnetic moment, BM	Compd	Magnetic moment, BM
2-OCH_3-Cu	1.85	2-$N(CH_3)_2$-Cu	1.85
2-OCH_3-Ni	3.14	2-$N(CH_3)_2$-Ni	3.20
2-OCH_3-Co	4.55	2-$N(CH_3)_2$-Co	4.60
2-OCH_3-Zn	*b*	2-$N(CH_3)_2$-Zn	*b*
2-SCH_3-Cu	1.85	2-OCH_2-Cu (1:1)[c]	1.85
2-SCH_3-Ni	3.16	2-SCH_3-Cu (1:1)[c]	1.88
2-SCH_3-Co	2.78	2-$N(CH_3)_2$Cu (1:1)[c]	1.82

[a] Compounds reported previously, 2:1, azo to metal: V. I. Mur, *J. Gen. Chem. USSR*, **24,** 585 (1954), **26,** 3577 (1956); F. A. Snavely, C. H. Yoder, and F. H. Suydam, *Inorg. Chem.*, **2,** 708 (1963); F. G. Schappell, Senior Disertation, Franklin and Marshall College, 1960. [b] Used to check corrections for chelate ion; $\chi_m \times 10^6$ is −366 for 2-OCH_3 and −395 for 2-$N(CH_3)_2$. [c] Formula is Cu(Ch)Cl where Ch^- is the chelate ion. % Cl for OCH_3: calcd, 8.7; found, 8.6. % Cl for SCH_3: calcd, 8.5; found, 8.3. % Cl for $N(CH_3)_2$: calcd, 8.4; found, 8.0.

TABLE III

MAGNETIC MOMENTS FOR THE METAL COMPOUNDS OF THE AZO DERIVATIVES OF 1,2-DIPHENYL-3,5-PYRAZOLIDINEDIONES AT 27–28°[a]



Compd	% mass loss (110°)	Magnetic moment, BM	Compd	% mass loss (110°)	Magnetic moment, BM
4-H-Cu	1.83[c]	1.92	2-OCH_3-Ni	None	3.09
4-Cl-Cu	2.04[c]	1.88	2-SCH_3-Ni	None	3.05
2-SCH_3-Cu	None	1.90	4-H-Ni(2H_2O)	*d*	3.14
2-OCH_3-Cu	None	1.90	4-F-Ni(2NH_3)	*d*	3.19
2-SCH_3-Cu (1:1)[b]	None	1.85	2-OCH_3-Co	None	4.65
2-OCH_3Cu (1:1)[b]	None	1.78	2-SCH_3-Co	None	2.83

[a] Compounds 2:1, azo to metal, reported previously: see ref 4f. Magnetic measurements made after complex was dried at 110°. [b] Formula is Cu(Ch)Cl where Ch^- is the chelate ion. [c] Temperature 150°. [d] Formulas are $Ni(Ch_2)(H_2O)_2$ and $Ni(Ch_2)(NH_3)_2$; air dried.

Formation constant work[4e,f] has shown these potentially terdentate ligands to form 2:1 ligand-to-metal complexes in solution.

The moments of the copper(II) complexes are all slightly higher than the spin-only value. These values are typical of four- and six-coordinate complexes of copper(II), in the absence of magnetic exchange, and consistent with the negative spin–orbit coupling constant.

A few moments of cobalt(II) are given for the terdentate ligands, and when the coordinating group is either OCH_3 or $N(CH_3)_2$, regular high-spin octahedral values are observed.

Cobalt(II) compounds with an SCH_3 group coordinated give room-temperature moments much lower than the expected value for octahedral high spin (4.7–5.2 BM) but too high for octahedral low spin (1.8–2.0 BM). The possibility of cobalt(III) being present as an impurity was ruled out by preparing the compounds by different methods and finding reproducible values. The temperature-dependent magnetic susceptibility was determined for the 2-SCH_3Co (Table II) derivative and the results are shown in Figure 1.[7] The results are indicative of a Boltzmann distribution between the high-spin (quartet) and low-spin (doublet) states.[8] The nickel(II) compounds with the terdentate ligands give routine moments for octahedral coordination.

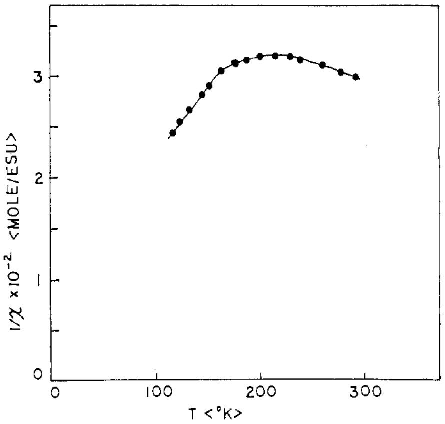


Figure 1.—The reciprocal molar magnetic susceptibility (corrected) *vs.* temperature for the Co(II) complex of 1-phenyl-3-methyl-4-(2-thiomethoxybenzeneazo)-5-pyrazolone. See Table II.

Nickel Compounds of the Bidentate Ligands.—The results with nickel(II) and the bidentate ligands are given in Table IV. With either water or ammonia in the coordination sphere, $Ni(Ch)_2(H_2O)_n$ (see also Table III), the moments observed are in agreement with an octahedral environment. Upon drying these com-

TABLE IV

MAGNETIC MOMENTS OF NICKEL(II) COMPLEXES OF AZO-5-PYRAZOLONES AT ROOM TEMPERATURE

Preparative method	Azo compd	Magnetic moment,[b] BM	% mass loss (110°)	Magnetic moment,[c] BM
B	4-Br-I	3.15 (29)[e]	3.50	3.27 (27)
A	4-Br-II	3.32 (22)	10.40	0 (22)
B	4-NO_2-I	. . . .	*d*	0 (27)
C	4-NO_2-II	3.28 (22)	11.20	3.07 (23)
B	3-NO_2	3.17 (24)	8.00	0 (27)
A	3-Br	3.28 (26)	10.40	0 (27)
A	2-CH_3-4-NO_2	3.44 (24)	7.84	0 (22)
C	4-CH_3[a]	3.19 (28)	7.63	3.29 (27)
A	4-OC_2H_5	3.24 (24)	11.60	3.24 (22)
A	4-Cl[a]	3.24 (26)	5.50	3.33 (28)
A	4-I	3.24 (24)	9.08	2.85 (22)
A	3-OCH_3	3.26 (23)	11.85	3.20 (24)
C	3-F	3.04 (26)	11.60	3.24 (26)
A	3-I	3.22 (26)	9.35	3.22 (25)
A	2-F[a]	. . .	Trace	3.35 (28)
B	2-Cl[a]	. . .	Trace	3.21 (27)
B	2-Br[a]	. . .	Trace	1.78 (28)
A	2-I	. . .	None	1.89 (21)
B	2-NO_2	. . .	*d*	3.26 (28)

[a] Recrystallized from benzene after drying at 110°. Analysis on the recrystallized sample. [b] Measured before drying at 110°. [c] Measured after drying at 110°. [d] Not measured. [e] Temperatures of measurements are given in parentheses.

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(7) Taken from the senior honors thesis of J. E. Scott, Franklin and Marshall College, 1970. The Faraday method was employed and will be described in a future publication.

(8) R. C. Stoufer, D. W. Smith, E. A. Clevenger, and T. E. Morris, *Inorg. Chem.*, **5**, 1167 (1966); D. L. Williams, D. W. Smith, and R. C. Stoufer, *ibid.*, **6**, 590 (1967).

pounds at 110° or in a few cases at a slightly higher temperature, the water and ammonia are lost. A few of the nickel(II) complexes after drying are diamagnetic which is consistent with a square-planar arrangement of the two bidentate ligands.

The 4-Br and 4-NO_2 chelates of nickel(II) were each prepared by two methods. (Table I shows that after being dried at 110°, they are of the same stoichiometry.) Table IV shows that drying at 110° yields a diamagnetic or paramagnetic complex depending on the method of synthesis. We are investigating this interesting phenomenon which will be the subject of a future publication.

In no case where an electron-rich group in the ortho position is present (F, Cl, etc.) were diamagnetic compounds obtained. The nickel(II) compounds with halide in the 2 position contained little or no water or ammonia of coordination. This is consistent with the steric effect of the ortho substituent reported previously.[2,3] It is tempting to suggest that these groups occupy the fifth and sixth coordination sites yielding tetragonally distorted octahedral coordination as suggested by Zacharias, *et al.*[9] However, the ortho-substituent coordination does not explain the anomalous moments for the 2-Br and the 2-I derivatives. Preliminary results show that both compounds obey the Curie–Weiss law from 295 to 120°K. Hence the possibility of the tetragonal field being such that several states can be thermally populated, *i.e.*, $^1A \rightleftarrows {}^3B$ in D_{4h} microsymmetry as found for some nickel complexes,[10] can be eliminated. Likewise the ortho-substituted coordination does not explain the paramagnetic results obtained with the compounds which do not contain an electron-rich group in the 2 position.

It seems probable that with the ortho-substituted derivatives, as well as the others listed in Table IV (after drying), the paramagnetism is due to either tetrahedral structures or pseudooctahedral coordination through intermolecular association in the crystal lattice.[11] As the latter seems unlikely with the ortho-substituted complexes, we tentatively suggest that, in the absence of solvent, the compounds listed in Table IV are either tetrahedral or square planar. With the 2-Br and 2-I compounds we suggest that the solid contains both structures.[12]

Electronic spectra are of little help in distinguishing the various structural possibilities because strong charge-transfer bands obscure the d–d bands, which would be of limited value anyway due to the rather low real symmetry of the compounds reported here.

A complete investigation of the temperature dependency of the magnetic susceptibilities reported above is in progress.

[9] P. S. Zacharias, B. Behera, and A. Chakravorty, *J. Amer. Chem. Soc.*, **90**, 7363 (1968).

[10] G. A. Melson and D. H. Busch, *ibid.*, **86**, 4830 (1964); S. L. Holt, R. J. Bouchard, and R. L. Carlin, *ibid.*, **86**, 519 (1964).

[11] E. K. Barefield, D. H. Busch, and S. M. Nelson, *Quart. Rev., Chem. Soc.*, **22**, 457 (1968).

[12] B. T. Kilbourn, H. M. Powell, and J. A. C. Darbyshire, *Proc. Chem. Soc., London*, 207 (1963).

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Reactions of Several Cationic Organometallic Isocyanide Complexes with Sodium Borohydride

BY P. M. TREICHEL,* J. P. STENSON, AND J. J. BENEDICT

Received October 5, 1970

Reactions of borohydride ion with $C_5H_5Fe(CO)(CNCH_3)_2^+$, $C_5H_5Mo(CO)_2(CNCH_3)_2^+$, and $C_5H_4CH_3Mn(NO)(CNCH_3)_2^+$ occur with addition of BH units across the two C≡N bonds in the coordinated isocyanide ligands. With borohydride ion and $C_5H_5Fe(CNCH_3)_3^+$ addition of BH units to the three isocyanide ligands occurs. Reaction of $C_5H_5Fe(CO)(CHNCH_3)_2BH_2$ and $C_5H_4CH_3Mn(NO)(CHNCH_3)_2BH_2$ with $(C_6H_5)_3C^+BF_4^-$ leads to substitution by fluorine of the two terminal boron hydride protons in these complexes, giving $C_5H_5Fe(CO)(CHNCH_3)_2BF_2$ and $C_5H_4CH_3Mn(NO)(CHNCH_3)_2BF_2$, respectively. All products were characterized by analyses, mass spectra, and nmr (^1H and ^{11}B) and infrared spectra.

Reduction of cationic transition metal organometallic complexes with borohydride ion is most often accompanied by hydride transfer to the metal or to one of the ligand groups. The π-hydrocarbon ligands are particularly well known to add hydride ion in these reactions. Among the earliest work in this area is the reduction of the cobalticinium and rhodicinium ions to give the uncharged cyclopentadienylcyclopentadienemetal complexes[1] and the reduction of cycloheptatrienylchromium tricarbonyl cation to cycloheptatrienechromium tricarbonyl.[2] More recently π-arene ligands have been shown to add a hydride ion to give cyclohexadienylmetal complexes,[3,4] and π-olefin-metal complexes have been converted to σ-alkylmetal complexes with borohydride.[5] Although in the initial cobalticinium and rhodicinium work[1] it was suggested that the hydride ion became attached to the ring in the endo position, there now seems to be ample evidence, including finally an X-ray crystallographic study,[6] that this is incorrect; substitution occurs in the exo position only. The same stereochemistry is

[1] M. L. H. Green, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 3759 (1959).

[2] J. D. Munro and P. L. Pauson, *ibid.*, 3475 (1961).

[3] G. Winkhaus, L. Pratt, and G. Wilkinson, *ibid.*, 3807 (1961).

[4] M. L. H. Green, L. Pratt, and G. Wilkinson, *ibid.*, 989 (1960).

[5] M. L. H. Green and P. L. I. Nagy, *J. Organometal. Chem.*, **1**, 58 (1963).

[6] P. H. Bird and M. R. Churchill, *Chem. Commun.*, 777 (1967).