TABLE I

COUPLING CONSTANTS OF CYCLOALKENES, C.P.S.

Compound	J^{13}C-H	A ($= J_{23}$)	A' ($J \gtrless_{12}$)	A'' ($= J_{24}$)
Cyclohexene, $n = 2$	(157)	9.60 ± 0.10	3.60 ± 0.10^a	...
Cyclopentene, $n = 2$	160 ± 1	5.40 ± 0.10^b	3.70 ± 0.10	...
Norbornene, $n = 1$	174 ± 1	5.80 ± 0.10^c	2.95 ± 0.10^c	...
Bicycloheptadiene, $n = 1$	168 ± 1	5.05 ± 0.10^d	2.70 ± 0.10^d	0.95 ± 0.10^d

^{a} In agreement with ref. 4 and with E. W. Garbisch, Jr., *J. Org. Chem.*, **27**, 4243 (1962), for J olefinic–allylic when $\phi \cong 60°$. ^{b} $J_{23} = 5.58 \pm 0.02$ c.p.s. for the cyclopentenyl protons in indene; D. D. Elleman and S. L. Manatt, *J. Chem. Phys.*, **36**, 2346 (1962). ^{c} We have measured the J's in 5- and 5,6-substituted 2-norbornenes. The results, $J_{23} = 5.1$ to 6.0 c.p.s. and $J_{12} = 2.2$–3.3 c.p.s., show that coupling constants also depend significantly on the nature of substituents. ^{d} According to F. S. Mortimer, *J. Mol. Spectry.*, **3**, 528 (1959), $J_{12} = 2.9 \pm 0.1$, $J_{23} = 3.45 \pm 0.1$, $J_{13} = 0.95 \pm 0.1$. The separation of the two outer lines in the ^{13}C pattern, 8.60 ± 0.1 c.p.s., 1.3 c.p.s. in excess of the sum of Mortimer's J's and the structure of this multiplet make our values more likely.

(Table I), to 2.5–3.5 c.p.s. for substituted cyclobutenes[8] and *ca.* 0.5–1.5 c.p.s. for 3,3-dimethylcyclopropene (I)[9] illustrate the trend.[10]

Pople, Schneider and Bernstein have observed that J_{ortho} in aromatic hydrocarbons increased from 1–4 c.p.s. in five-membered carbocyclic rings to 5–9 c.p.s. in six-membered rings and to 10–13 c.p.s. in seven-membered aromatic rings.[11] More recent work has substantiated this generalization.[12,13] We show that olefinic J's follow a similar trend and that, for a given ring size, they are superior in magnitude to J_{ortho} in aromatic hydrocarbons. A variation of J_{ortho} in six-membered aromatic hydrocarbons with bond order has recently been reported.[14] Hence, vicinal coupling constants in unsaturated hydrocarbons are dependent both on ring size and on the aromatic character of the molecule. This phenomenon may be useful for detecting "aromaticity," supplementing the so-called ring current effect.[13]

To test this idea, we examined the ^{13}C patterns of the conjugated double bond in the five-membered fragment (positions 1 and 2) of acenaphthylene which yielded $J_{13\text{C-H}} = 174 \pm 1$ and $J_{12} = 5.2 \pm 0.1$ c.p.s. This latter coupling constant, slightly smaller than those of indene ($J = 5.58$ c.p.s.) and cyclopentene ($J = 5.4$ c.p.s.), but considerably larger than those observed for typical five-membered aromatics, indicates that the C_1-C_2 double bond in acenaphthylene has only a slight amount of arcmatic character, a conclusion in agreement with the known properties of the molecule.[15]

Acknowledgments.—A sample of 3,3-dimethylcyclopropene (I) from Dr. G. L. Closs, transmitted by Dr. J. I. Musher, was kindly provided. We wish to thank the Alfred P. Sloan Foundation for partial support of this research. Dr. L. C. Allen and Mr. R. M. Erdahl

(8) W. G. Dauben and R. L. Cargill, *Tetrahedron*, **12**, 186 (1961); J. D. Roberts, private communication; O. L. Chapman, *J. Am. Chem. Soc.*, **85**, 2014 (1963).

(9) The ^{13}C pattern of compound I was observed as a single unresolved band of width at half height = 4.8 c.p.s. The vinyl protons of this molecule are known to be coupled to the six equivalent methyl hydrogens by 0.7 c.p.s. (G. L. Closs, *Proc. Chem. Soc.*, 152 (1962)), hence, the width at half height should be 4.2 c.p.s. due to this factor alone. It is clear that the magnitude of olefinic–olefinic coupling in I must be very small.

(10) G. V. Smith and H. Kriloff, *J. Am. Chem. Soc.*, **85**, 2016 (1963) and O. L. Chapman (ref. 8), also have found the ring size effect.

(11) J. A. Pople, W. G. Schneider and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., New York, N. Y., 1959, p. 193.

(12) H. J. Bernstein, J. A. Pople and W. G. Schneider, *Can. J. Chem.*, **35**, 65 (1957); K. L. Rinehart, A. K. Frerichs, P. A. Kittle, L. F. Westman, D. H. Gustafson, R. L. Pruett and J. E. McMahon, *J. Am. Chem. Soc.*, **82**, 4111 (1960); M. Rosenblum, A. K. Banerjee, N. Danieli and L. D. Herrick, *Tetrahedron Letters*, **No. 10**, 423 (1962); T. J. Katz and M. Rosenberger, *J. Am. Chem. Soc.*, **84**, 865 (1962); R. E. Bozak and K. L. Rinehart, *ibid.*, **84**, 1589 (1962).

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(14) N. Jonathan, S. Gordon and B. P. Dailey, *J. Chem. Phys.*, **36**, 2443 (1962).

(15) D. C. Morrison, *J. Org. Chem.*, **25**, 1665 (1960); K. Fukui, T. Yonezawa and C. Nagata, *Bull. Chem. Soc. Japan*, **34**, 37 (1961); M. A. Ali and C. A. Coulson, *Mol. Phys.*, **4**, 65 (1961).

developed the time integration method utilized here. We are indebted to the Mnemotron Corp. for the loan of the CAT computer.

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A New Class of Double-Bridged Coördination Polymers Based on Chromium(III)

Sir:

Earlier reports from this laboratory have concerned the preparation of coördination polymers of types which we write symbolically as $[M(AB)X_2]_n$[1] and $[MX_2]_n$[2] where AB represents a uninegative bidentate ligand and X represents a uninegative bridging group. We now wish to report a third class, $[M(a)(b)X_2]_n$, where a represents a neutral unidentate ligand and b a uninegative ligand. The preparation of this new class differs in method from that in the earlier series and appears to lead to polymers with substantially higher molecular weight than we have found for the other two types. The non-bridging ligands a and b are inorganic, so that this material is an example of a coördination polymer which in addition to its inorganic backbone has inorganic blocking groups in the repeating unit.

The synthesis is a two-step process in which chromium-(II) acetate is treated with a potassium phosphinate ($KOPR_2O$) to yield the corresponding chromium(II) phosphinate ($R = C_6H_5$, I). The latter is then oxidized with air in the presence of water to yield the composition $Cr(H_2O)(OH)(OPR_2O)_2$ ($R = C_6H_5$, II) which has polymeric properties. II has been prepared by these reactions under a variety of conditions, but here we will only describe a set of conditions which gives a product exhibiting a high intrinsic viscosity in chloroform.

A suspension of 2.7 g. of freshly prepared $Cr(OAc)_2 \cdot H_2O$ in 125 ml. of deoxygenated water is refluxed under nitrogen with stirring for 1 hr. After the addition of a deoxygenated solution of $KOP(C_6H_5)_2O$ (prepared by the exact neutralization of 8.0 g. of $(C_6H_5)_2P(O)OH$ with 1 M KOH) without exposure to air, the refluxing is continued for 2–3 hr. under nitrogen. The precipitated intermediate I is then separated by filtration at room temperature and washed several times with deoxygenated water, all operations being conducted under nitrogen. I is next dispersed in 500 ml. of water and oxidized to II by exposure to the atmosphere. After crude II has been removed by filtration, washed thoroughly with water, and dried at 100°, it is dissolved

(1) B. P. Block, J. Simkin and L. R. Ocone, *J. Am. Chem. Soc.*, **84**, 1749 (1962).

(2) B. P. Block, S. H. Rose, C. W. Schaumann, E. S. Roth and J. Simkin, *ibid.*, **84**, 3200 (1962).

in benzene. The resulting solution is then separated from the small quantity of benzene insolubles (less than 0.3 g.) by filtration and evaporated at room temperature in a stream of nitrogen to yield II. Final drying is at 120°. *Anal.* Calcd. for $C_{12}H_{13}CrO_6P_2$: C, 55.25; H, 4.43; Cr, 10.0; P, 11.88. Found: C, 56.39; H, 4.36; Cr, 9.7; P, 11.93. Yields vary from 70 to 95%. The intrinsic viscosity of II prepared in this manner is 0.6 to 0.7 in chloroform. Less rigorously controlled conditions lead to polymers with intrinsic viscosities from 0.1 to 0.5. Even unfractionated samples with viscosities in the range 0.12 to 0.20 have number average molecular weights greater than 10,000 as determined by ebulliometry and vapor pressure osmometry in chloroform. Consequently, the higher-viscosity samples certainly have molecular weights of at least several tens of thousands.

Although any of the groups present in II could serve as bridging groups, the most probable structure contains a double-bridged backbone similar to that suggested for $Cr(AcCHAc)(OP(C_6H_5)_2O)_2$[1] except that a *cis* configuration is not required. The infrared spectrum of II contains absorption peaks characteristic of PO_2 stretching with virtually the same frequency and absorption profile as found for polymeric $Cr(AcCHAc)$-$(OP(C_6H_5)_2O)_2$.[1] This is strong evidence that the diphenylphosphinate anion is functioning in the same way in both polymers. Furthermore, the hydroxyl group and the water O–H stretching vibrations can be identified separately at frequencies which suggest they are normally coördinated groups. Thus infrared indicates that the hydroxyl groups are not bridging groups. The solubility of II in benzene or chloroform accompanied by marked swelling and the high intrinsic viscosity values are good evidence for the presence of linear chains as the predominating species with cross-linking only of minor importance. The indications are, then, that the repeat unit is
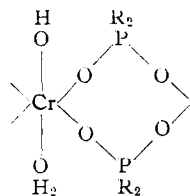
Thermogravimetric analysis of II shows initial weight loss at 375° with a step in the 410–430° region which corresponds to a 3–10% weight loss. No polymer melt temperature has been observed up to or well beyond the decomposition point. Surprisingly the polymer shows remarkable resistance to hydrolysis and other chemical degradation. For example, no change in intrinsic viscosity is oberved upon refluxing a suspension of the polymer in water for several hours. A cast film of high-viscosity II plasticized with 30% Aroclor 1254 has a tensile strength of over 1900 p.s.i.

In addition to the diphenyl species described here we have also been able to prepare the analogs with phenylmethylphosphinate, dimethylphosphinate and cacodylate bridging groups. The mechanism by which this kind of polymer forms is not clear. It would appear that the intermediate I could be a polymer somewhat analogous to the phosphinate polymers involving zinc, beryllium and cobalt.[2] The oxidation step then may serve to increase the oxidation state of the chromium and introduce the additional ligands. Alternatively polymerization may be involved in the oxidation step.

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The Electronic Structures of Square-Planar Metal Complexes. III. High-Spin Planar Cobalt(I) and Iron(I)[1,2]

Sir:

The reaction between toluene 3,4-dithiol and a number of divalent transition metal ions gives complexes which have the general formula
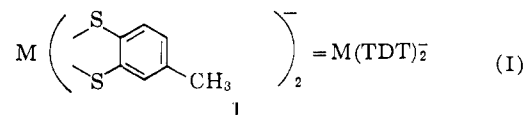
Formula I is established from analytical and conductance data in Table I. Magnetic susceptibility data in Table I indicate that the copper complex has $S = 0$, the nickel complex has $S = 1/2$, the cobalt complex has $S = 1$ and the iron complex has $S = 3/2$. The e.s.r. spectrum of an acetone solution of $Ni(TDT)_2^-$ gives $<g> = 2.08$; the $[(n\text{-}C_4H_9)_4N][Ni(TDT)_2]$ powder gives $g_\perp = 2.045$ and $g_{||} = 2.193$.[3] The g-values show that the unpaired electron is mainly localized on the nickel. Further, the anisotropy in the g tensor is consistent with a d^9 planar situation. For comparison, planar $Cu(acac)_2$ has $g_\perp = 2.075$ and $g_{||} = 2.254$.[4]

TABLE I

PROPERTIES $M(TDT)_2^-$ COMPLEXES

Complexes	Analytical	Calcd.	Found	μ_{eff} (B.M.)	Λ^a
$[(C_6H_5)_3As(CH_3)][Cu(TDT)_2]$	C	57.17	56.79		
	H	4.36	4.97	Diamagnetic	85
$[(C_6H_5)_3As(CH_3)][Ni(TDT)_2]$	C	57.57	57.49		
	H	4.39	4.37	1.89	91
$[(C_6H_5)_3As(CH_3)][Co(TDT)_2]$	C	57.55	57.00		
	H	4.39	4.58	3.27	96
$[(C_6H_5)_3As(CH_3)][Fe(TDT)_2]$	C	57.62	57.18		
	H	4.41	4.46	4.39	94

^{a} For $0.0001\ M$ solutions in nitromethane at 25°; expressed in cm.^{2} mole^{-1} ohm^{-1}.

The electronic spectra of the $M(TDT)_2^-$ complexes in acetonitrile show the following weak bands, which may be assigned to d–d transitions: M = Ni, 7300 cm.$^{-1}$ (ϵ 190); M = Co, 9300 cm.$^{-1}$ (ϵ 58), and a shoulder, indicative of a maximum at 11,300 cm.$^{-1}$ ($\epsilon \sim 100$); M = Fe, 7100 cm.$^{-1}$ (ϵ 45), 7900 cm.$^{-1}$ (ϵ 55), 9200 cm.$^{-1}$ (ϵ 65) and 10,300 cm.$^{-1}$ (ϵ 95). The X-ray powder patterns show that the $[(C_6H_5)_3As(Me)][M(TDT)_2]$ complexes are isomorphous.

We conclude from the above evidence that the complexes are planar and are composed of M^+ and two dithiolate radical anion moieties. The unpaired electron which each radical anion would possess must be paired

(1) Paper II: E. Billig, R. Williams, I. Bernal and H. B. Gray, *Inorg. Chem.*, in press.

(2) The support of the National Science Foundation is gratefully acknowledged.

(3) Details of these experiments and e.s.r. experiments on similar Cu^{2+} complexes will be published by H. B. Gray, E. Billig and I. Bernal.

(4) B. R. McGarvey, *J. Phys. Chem.*, **60**, 71 (1956). Also, planar Cu(salicylaldimine)₂ gives $g_x = 2.04$, $g_y = 2.05$ and $g_z = 2.20$: A. H. Maki and B. R. McGarvey, *J. Chem. Phys.*, **29**, 35 (1958).