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π-Complexes of the Transition Metals. I. Hein's Polyaromatic Chromium Compounds[1,2]

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The essential steps of Hein's methods for the preparation of polyphenylchromium compounds have been reproduced. The products of the chemical reduction of these compounds have led to a reformulation of their structures in terms of a bisarene cation. This biconoidal structure is then discussed with respect to the formerly anomalous behavior reported for these complexes and the new chemistry which may now evolve.

Sidgwick's brief summary of the phenylchromium compounds[4a] provided the impetus for this introductory study of the transition metal complexes. The new experimental facts relating to the anomalous behavior and properties exhibited by these compounds and the concept of a new and fertile borderland of π-complexes between organic and inorganic molecules are now reported.

Repetition of the steps employed by Hein and his co-workers[4] in preparing the key compounds of the series, "pentaphenylchromium hydroxide" I, "tetraphenylchromium" iodide II and "triphenylchromium" iodide III, afforded these compounds, corresponding to their previous descriptions albeit in very small amounts. The basic reaction, formulated by Hein as (1), gave the amorphous, hygroscopic and impure "pentaphenylchromium bromide" which, with alcoholic potassium hydroxide (2), gave rise to "pentaphenylchromium hydroxide," which crystallized in the form of golden orange plates from water–chloroform mixture.

$$5C_6H_5MgBr + 4CrCl_3 \longrightarrow$$

$$\text{“}(C_6H_5)_5CrBr\text{”} + CrCl_2 + MgBr_2 + MgCl_2\ \text{(Hein)} \quad (1)$$

$$\text{“Raw bromide”} + KOH \longrightarrow$$

$$\text{“}(C_6H_5)_5CrOH\cdot 4H_2O\text{”} + KBr \quad (2)$$

$$\text{“}(C_6H_5)_5CrOH\text{”} + KI \longrightarrow$$

$$\text{“}(C_6H_5)_4CrI\text{”} + C_6H_5OH + KOH \quad (3)$$

The aqueous mother liquor, after concentration and cooling, deposited crystalline, orange "pentaphenylchromium carbonate," formulated as "$[(C_6H_5)_5Cr]_2CO_3\cdot 6H_2O$." The mother liquor resulting from this step consisted of a strongly alkaline, sirupy, water-soluble black mass which deposited orange-yellow plates of "triphenylchromium" iodide III when treated with aqueous potassium iodide; while a suspension of I in a mixture of aqueous potassium iodide and chloroform was transformed into an orange oil which slowly crystallized and was eventually obtained as golden orange plates of "tetraphenylchromium" iodide II (reaction 3).

The first series of anomalies is apparent from the reaction scheme just presented. Phenylmagnesium bromide is recognized to be a reducing agent but not one of oxidation. The separation of tetra-, penta- and hexavalent chromium compounds from the same solution (no free iodine formed) is unaccountable. The production of tetravalent II with the liberation of phenol by potassium iodide from pentavalent I is scarcely conceivable, and this difficulty is compounded by the fact that over 50 salts were prepared by Hein, *et al.*,[4] from I with organic and inorganic anions, of which upwards of 40 were formulated as *tetraphenyl*chromium derivatives. The remainder were written as pentaphenylchromium salts containing varying amounts of solvent of crystallization.

The second set of anomalies recognized at the time consisted of the uniform light absorption properties of these polyphenylchromium compounds. They were found to have similar color in the visible range (orange to yellow) and to exhibit similar chromium band absorption near 350 mμ in the ultraviolet region. In the only previous independent work on the Hein compounds Klemm and Neuber[5] measured the magnetic susceptibilities of representatives of each "valence class" and found them all to possess one free electron, *i.e.*, paramagnetic to the extent of 1.72 ± 5% Bohr magnetons. These authors suggested, therefore, that all of Hein's compounds were in the same valence state and that this state was probably Cr^V. We have confirmed this magnetic property also with our sample of II.[6] Unquestionably these observations cast serious doubt on the formulation of 5, 4 and 3 phenyl groups attached covalently to chromium.

The difficulties attending the synthesis of the polyphenylchromium compounds by the Hein procedure induced us to attack the structural problem imposed by degradation methods. At this stage

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(1) The subject matter of this paper was presented in 1954, Abstr., 126th Meeting, Amer. Chem. Soc., p. 29-0, Sept., 1954, and also submitted to THIS JOURNAL as a preliminary Communication. The paper, however, was rejected by the referees chiefly on the grounds of insufficient evidence for our (with Professor L. Onsager) proposal of the π-complexed biconoidal structure. In 1955 a portion of our results was published in abbreviated form, *Yale Sci. Mag.*, **29**, 14 (1955); *Angew. Chem.*, **67**, 282 (1955); and in more complete form by F. A. Cotton, *Chem. Revs.*, **55**, 551 (1955). A series of lectures on this subject were also presented during June-July, 1955, at Heidelberg, Tübingen, Munich and Zürich, *Handbook, XIVth International Congress of Pure and Applied Chemistry*, p. 262. We have been informed (private discussion with Dr. E. O. Fischer) that the preparation of bis-benzenechromium from benzene, E. O. Fischer and W. Hafner, *Z. Naturforsch.*, **10b**, 665 (1955), was first realized after the above dates. This chronology is given here in an attempt to reduce the confusion which has arisen and is not to be construed as a detraction from the elegant method of preparation and structural proofs devised by Dr. Fischer and his colleagues.

(2) Taken from the doctoral dissertation of M. Tsutsui, Yale University, 1954, and supported by Contract No. DA-19-059-ORD-1494 between the Office of Ordnance Research, U. S. Army, and Yale University.

(3) Monsanto Chemical Co., Dayton 7, Ohio.

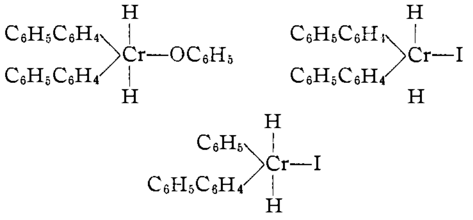
(4) (a) N. V. Sidgwick, "The Chemical Elements and Their Compounds," Oxford Univ. Press, New York, N. Y., 1950, p. 1001. For a modern review of Fr. Hein's original work see (b) F. A. Cotton, *Chem. Revs.*, **55**, 551 (1955); and also (c) H. J. Emeleus and J. S. Anderson, "Modern Aspects of Inorganic Chemistry," 1st Ed., D. Van Nostrand Co., Inc., New York, N. Y., p. 419.

(5) W. Klemm and A. Neuber, *Z. anorg. Chem.*, **227**, 261 (1936).

(6) We are indebted to Mr. R. Johnston of the Naval Research Laboratory, Wash., D. C., for this determination.

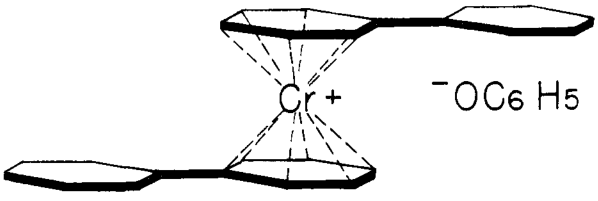
it was discovered that biphenylmercury was reduced smoothly in ether to benzene by lithium aluminum hydride without formation of biphenyl.[7] A similar reduction of "pentaphenylchromium bromide" demonstrated its grossly impure nature, for the organic product consisted of benzene, biphenyl, terphenyl and higher boiling polyphenyls. Reductions of I, II and III were next performed on a semi-quantitative basis owing to the small amounts of these substances available. "Tetraphenylchromium" iodide II on reduction gave biphenyl as the *sole* organic product and this in the amount of *two* mole equivalents. The degradation of "triphenylchromium" iodide III gave *both* benzene and biphenyl, each estimated to be present in a 1:1 mole ratio. Finally, "pentaphenylchromium hydroxide" I was reduced to a mixture of biphenyl and *phenol*, the molar ratio of which amounted to 2:1. Failure to detect benzene spectroscopically either from the hydride reduction of I or II clearly rendered the Hein formulation inadmissible. Also, the reappearance of phenol as a product from I, as it was in the reaction of I with potassium iodide, compelled the conclusion that I is a phenoxide rather than an hydroxide.

The pentavalent structures suggested by Klemm and Neuber[5] were next considered in the light of the new evidence. Rationalization of these structures with the experimental facts led to the following hydride structures for I, II and III. However, the relative stability of these compounds toward water, dilute acid and base, not being a typical property of metal–hydride bonds, invited considerable scepticism; and so an isotopic reduction method for testing the Klemm–Neuber structures was devised. A sample of II was reduced with lithium aluminum hydride and then hydrolyzed with deuterium oxide. As previously found, no benzene was formed; but the biphenyl was collected and burned to carbon dioxide and water. This water was reduced with zinc to hydrogen which was observed to be free of deuterium in the mass spectrometer.[8] This result of course eliminated a reduction mechanism which involved a displacement of biphenyl anion by aluminum hydride from chromium. But when II was reduced with lithium aluminum deuteride, the biphenyl produced contained 5.0 D% or one atom of deuterium per molecule of II or 2 molecules of biphenyl. It was supposed that the Klemm–Neuber structure for II would lead to biphenyl containing 10 D% or one atom of deuterium per molecule of biphenyl if reductive attack occurred on carbon as the previous experiment indicated. Deuteride reduction of III gave biphenyl containing 6.7 (6.55) D%,[9] or two-thirds of the amount predicted for the Klemm–Neuber structure. The benzene deuterium content was not determined. A sample of reagent biphenyl was subjected to the action of lithium aluminum deuteride in ether under the same conditions of time and temperature without becoming deuterated. While these isotopic results did not unequivocally dispose of the hydride structures, they did render them most unlikely.



$$\begin{array}{lcl} & \mathrm{H} & \\ \mathrm{C_6H_5C_6H_4}\diagdown & | & \\ & \mathrm{Cr{-}OC_6H_5} & \\ \mathrm{C_6H_5C_6H_4}\diagup & | & \\ & \mathrm{H} & \end{array} \qquad \begin{array}{lcl} & \mathrm{H} & \\ \mathrm{C_6H_5C_6H_4}\diagdown & | & \\ & \mathrm{Cr{-}I} & \\ \mathrm{C_6H_5C_6H_4}\diagup & | & \\ & \mathrm{H} & \end{array}$$

$$\begin{array}{lcl} & \mathrm{H} & \\ \mathrm{C_6H_5}\diagdown & | & \\ & \mathrm{Cr{-}I} & \\ \mathrm{C_6H_5C_6H_4}\diagup & | & \\ & \mathrm{H} & \end{array}$$



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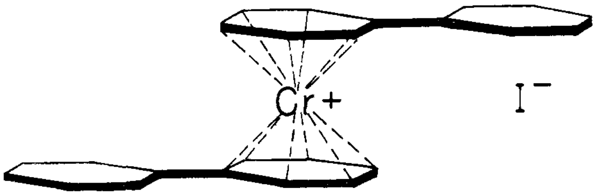

II

In the course of a number of discussions which ensued after the results of the lithium aluminum hydride reductions became known, Professor L. Onsager proposed the bis-aromatic structure for II as shown below. It was reasoned that the chromium atom, atomic number 24, requiring 12 electrons to fill its 4s, 3d and 4p shells to reach the stable krypton level, could do so by the donation of 6 π-electrons each from two aromatic rings, thus becoming a bis-aromatic-chromium[0] complex of considerable stability. It was recalled too that Hein in his early work had reduced both I and II electrolytically in liquid ammonia to, strangely enough, the *same* compound, formulated as "*tetraphenylchromium.*" Also, III could be reduced, both electrolytically and by sodium metal in the same solvent, to "*triphenylchromium.*" The corresponding cation, therefore, would arise by the loss of one electron, leaving the chromium atom with one unpaired electron and therefore paramagnetic. At the outset we were reluctant to believe that aromatic π-electrons could be donated in this manner and that the loss of resonance energy accompanying this process would be offset by the stability associated with the inert-gas configuration achieved. However, the weight of the

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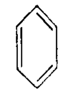
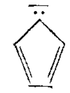
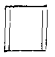
(7) In footnote 2, p. 569, of reference 4b there is a statement of misconception of the purpose of this experiment. It was meant to show that *if* the polyphenylchromium compounds possessed chromium–phenyl covalent bonds, such as exist in biphenylmercury and as suggested by Hein, then benzene would be produced by this ionic reduction and biphenyl could not arise by a free radical process. The importance of this observation, therefore, lay in testing the Hein formulation and not in determining others. The fact that the experiment showed the absence of biphenyl groups in biphenylmercury was gratuitous.

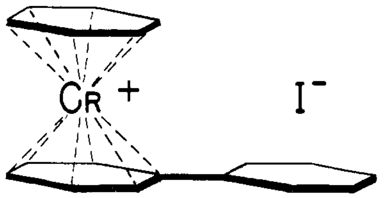
(8) We wish to express our appreciation for the assistance given us by Mr. J. Graff of the Department of Biochemistry, and by Dr. J. H. Wang, Department of Chemistry, Yale University, in the combustions and spectrometric determinations.

(9) The figure given here in parentheses was obtained several weeks after the first result with the remaining portion of biphenyl.

TABLE I

	Atomic no.	Group	1	2		3			4		
		Subgroup	*s*	*s*	*p*	*s*	*p*	*d*	*s*	*p*	
Cr	24		2	2	6	2	6	5	1		2 
Mo								(5)	(1)	(6)	
W											
Fe	26		2	2	6	2	6	6	2		2 
Ru								(4)		(6)	
Os											
Ni	28		2	2	6	2	6	8	2		2 
Pd								(2)		(6)	
Pt											
Kr	36		2	2	6	2	6	10	2	6	

evidence became compelling. Reformulating I in terms of the bis-arene structure permitted an explanation of the formation of II and the numerous other salts from I in terms of simple *metathetical* reactions. The formation of the same compound, now formulated as $[C_6H_5C_6H_5]_2Cr^0$, *bis-biphenyl-chromium*, by reduction of I and II was explicable, as well as the reduction of III to *benzene–biphenyl-chromium*^{0}, $[C_6H_6][C_6H_5C_6H_5]Cr$. Extrapolation of the solubilities of the bis-biphenyl- and benzene-biphenyl-chromium^I salts as well as the variation in the aromatic components of the complexes led to the prediction that the bis-benzene-chromium^I cation had also been formed in the course of the Grignard reaction, that it would be quite water-soluble and hence had been consistently missed. These predictions have since been confirmed.[10] More recently our views concerning the structures of the polyphenyl-chromium compounds have been corroborated by Hein[11] and also by Fischer and Seus.[11]



III

Reductions of II and III with lithium aluminum deuteride gave biphenyl in each case containing one-half and two-thirds of the deuterium, respectively, expected from a displacement by aluminum deuteride on carbon in the hydride structures. If, however, the assumption is made that the aromatic rings of the bis-arene structures for II and III are equivalent in reactivity and that the attack of one deuteride ion on any one aromatic ring is sufficient to cause the reductive collapse of the complex, then the fractional results are understandable on a statistical basis. Thus, a random collision with any of the four phenyl groups of II by a deuteride ion collapses the complex with expulsion of a non-deuterated biphenyl molecule and the formation of one monodeutero-biphenyl molecule per molecule of II with evolution of hydrogen. Since only biphenyl was measured for deuterium from the reduction of III, random distribution of deuterium by indiscriminate deuteride reduction at either benzene or biphenyl sites in the complex introduces deuterium two out of three effective reactions in biphenyl, or 6.7 D% in biphenyl. In terms of a nucleophilic displacement mechanism, this interpretation requires of course a 100% isotope effect as well as reliance on the deuterium analyses.[9] However, as long as the reactions of odd-electron, aromatic complexes are incompletely explored, an unforeseen reaction seems not as significant as an unexpected inhibition.

The resemblance of the bis-arene-chromium^1 complex to that of the ferricinium ion, and of the bis-arene-chromium^0 to ferrocene, is more than superficial, for the same reasoning regarding the ability of the iron atom, atomic number 26, to reach a krypton configuration by accepting 10 π-electrons from two cyclopentadienyl anions has been advanced.[12] Extension of these considerations to nickel (see Table I) and its 8 π-electron requirement for a stable krypton configuration permits the prediction of the eventual capture of cyclobutadiene in a complex such as bis-cyclobutadiene-nickel^0 or its cation.[1] Longuet-Higgins and Orgel[13] have now applied the molecular orbital theory to the possible existence of such a complex with favorable results. More broadly, this new concept of transition metal complexes may be expected to lead to significant advances in the theory of catalysis.

Experimental[14]

"Pentaphenylchromium Bromide."[15]—Phenylmagnesium bromide solution prepared from 25 g. of magnesium, 150 g. of bromobenzene and 200 ml. of ether was treated with 40 g. of anhydrous chromium trichloride[16] according to Hein from which *ca.* 12 g. of orange-brown resinous solid was obtained from the chloroform layer. In only 3 out of over 50 runs did we obtain "raw bromide" from which "pentaphenyl-chromium hydroxide" could be prepared. We attribute these failures to our subsequent care in excluding oxygen from the Grignard flasks (no phenol formed). Many varia-

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[10] H. H. Zeiss and W. Herwig, THIS JOURNAL, **78**, 5959 (1956).

[11] Fr. Hein, *Chem. Ber.*, **89**, 1816 (1956); E. O. Fischer and D. Seus, *ibid.*, **89**, 1809 (1956).

[12] E. Ruch and E. O. Fischer, *Z. Naturforsch.*, **7b**, 676 (1952).

[13] H. C. Longuet-Higgins and L. E. Orgel, *J. Chem. Soc.*, 1969 (1956).

[14] All m.p.'s are corrected. Combustion analyses were performed by the Schwarzkopf Microanalytical Laboratories, Woodside 77, N. Y.

[15] Fr. Hein, *Ber.*, **54**, 1905 (1921).

[16] Fr. Hein, *ibid.*, **54**, 2708 (1921).

tions of time, temperature, reagent concentrations, added reactants and chromium trichloride purity were tried without success. In one run out of 3 using chromyl chloride in place of the trichloride, we obtained "raw bromide" of the "correct" composition.

"Pentaphenylchromium Hydroxide."[15]—The "raw bromide" (27 g.) was transformed into the "hydroxide" in ethanol with potassium hydroxide (7 g.), which was crystallized from water as large, deep orange plates, 2 g. These crystals were very hygroscopic and lost water of hydration when dried *in vacuo* over Drierite. Their color changed too to a deep olive-gray, m.p. 102–104°, as described by Hein. In water the orange color of the crystals returned and they absorbed at 248 and 345 mμ in the ultraviolet region in 95% ethanol.

"Tetraphenylchromium" Iodide.[16]—A solution of 0.05 g. of "pentaphenylchromium hydroxide" in chloroform was shaken with 1 ml. of a saturated solution of potassium iodide in water, and the chloroform solution was then washed with water. Petroleum ether was now added to the chloroform solution to incipient turbidity, and the mixture was then put aside in the cold. The orange-yellow flakes of "tetraphenylchromium" iodide (0.005 g.) which had crystallized were separated by centrifugation and washed thrice with ether, m.p. 160–165°. These were crystallized from chloroform as orange-red plates containing solvent of crystallization and this chloroform was removed by heating at 55° *in vacuo* for 7 hr. The pure iodide, m.p. 177–178°, was yellow-orange in color and absorbed at 250 and 342 mμ (log ϵ 4.01 and 3.39, resp., 0.0001 M in ethanol).

Anal. Calcd. for $C_{24}H_{20}ICr$: C, 59.13; H, 4.52; I, 26.07; Cr, 10.68. Found: C, 58.82; H, 4.46; I, 26.13; Cr, 10.58.

The *density* of the iodide was determined by suspending the solid in a mixed solution of iodobenzene and carbon tetrachloride: 1.6170 (16°). Its *molecular weight* was determined cryoscopically using *m*-dinitrobenzene as solvent and was found to be 482 (487) in dilute solution, *i.e.*, 0.00233 g. of iodide in 0.04898 g. of solvent. This value was reproducible so long as solutions of comparable concentration were employed. However more concentrated solution gave erratic results as would be expected for ionic compounds.

"Triphenylchromium" Iodide.[17]—One hundred ml. of the water layer remaining after the filtration of "pentaphenylchromium hydroxide" described above was concentrated to 50 ml. by freeze-drying (Hein performed this concentration at 40–45° also *in vacuo*). After standing in the refrigerator for one week, this solution had deposited red prisms which were separated by centrifugation and recrystallized from ethanol, m.p. 117–119°, and corresponding to the compound designated by Hein as *"pentaphenylchromium carbonate."* Four ml. of the deep-red filtrate was evaporated to dryness under freeze-dry conditions, leaving 0.82 g. of a yellow-brown, brittle resin whose chromium analysis corresponded to a trihydrate of *"triphenylchromium" hydroxide.* A solution of 0.75 g. of this hydroxide in 30 ml. of chloroform and 15 ml. of water was shaken with 2 ml. of a saturated aqueous solution of potassium iodide, and the aqueous layer was then extracted thoroughly with chloroform. The combined chloroform extracts, now red in color, were washed with water, poured over Drierite, filtered and then brought to turbidity with petroleum ether. After standing one week in the cold, the solution had deposited a red solid which after four recrystallizations from chloroform with tetrahydrofuran gave orange-yellow plates, m.p. 110–112°, when dried *in vacuo* at 60° for 9 hr. This "triphenylchromium" iodide is considerably more soluble in water than "tetraphenylchromium" iodide and absorbs weakly at 270 mμ and strongly at 343 mμ in 95% ethanol.

Anal. Calcd. for $C_{18}H_{15}ICr$: Cr, 12.64. Found: Cr, 11.88.

Its molecular weight was found to be 430 (theory 411) by cryoscopic measurement in *m*-dinitrobenzene. Fifteen similar recrystallizations of the iodide raised the m.p. to 146–148°, but the infrared spectrum of the iodide remained essentially unchanged. Analysis and molecular weight of the iodide, m.p. 112°, indicated that it was a monohydrate, but this was not confirmed.

Anal. Calcd. for $C_{18}H_{15}ICr{\cdot}H_2O$: C, 50.5; H, 4.24; I, 29.6; Cr, 12.1. Found: C, 50.6; H, 4.05; I, 27.3; Cr, 11.9.

$LiAlH_4$ Reduction of "Tetraphenylchromium" Iodide.—To a solution of 0.50 g. of lithium aluminum hydride in 50 ml. of ether previously distilled from $LiAlH_4$ was added 0.0102 g. of "tetraphenylchromium" iodide. Vigorous reaction occurred at the surface of the ether-insoluble iodide with evolution of gas, presumably hydrogen, and complete disappearance of the iodide within a few minutes. The solution became brown and, after standing for 4 hr. in the cold, it turned clear with the deposition of a white, amorphous precipitate. The cold reaction mixture was then hydrolyzed with 0.5 ml. of water, the ether layer was decanted and the precipitate was dissolved in dilute hydrochloric acid. The acid solution was extracted with ether, and the ether extracts were distilled in a simple distilling flask. The residue consisted of pure biphenyl whose identity was confirmed by its ultraviolet absorption, determined in ether and a 10-cm. cell path, to be at 248 mμ. The distilled ether likewise showed absorption at 248 mμ and contained biphenyl in the amount of 0.0027 g. as determined from the optical density of the solution. A total of 0.0049 g. was thus determined, or 76% of the theoretical amount based on two molecules of biphenyl per mole of the iodide. Both the absence of benzene and amount of biphenyl produced in this reduction precluded a Klemm–Neuber formulation for the iodide such as bis-phenyl-biphenyl-chromium iodide.

$LiAlH_4$ Reduction of "Triphenylchromium" Iodide.—The iodide (0.2034 g.) was reduced in one l. of ether with 1.00 g. of $LiAlH_4$ by the general procedure just described. However, in this case the ethereal solution was distilled through a 12″ Vigreux column, for it was found that while ordinary distillation permitted co-distillation of biphenyl with the ether, the column perfectly inhibited this complication. The ether distillate was free, therefore, of biphenyl but was now found to contain benzene in the amount of 0.0010 g. by spectrophotometric determination. The residue from the distillation amounted to 0.0480 g. and was shown to be biphenyl both by sublimation and mixed m.p. and by ultraviolet absorption. Based on the benzene-biphenyl-chromium iodide structure these yields constitute 63% of biphenyl and 3% of benzene. The low recovery of benzene prompted us to determine the maximum efficiency of the method by treating a solution of 0.0135 g. of benzene in 585 ml. of ether with 0.150 g. of $LiAlH_4$, allowing the mixture to stand for 8 hr. and then hydrolyzing the solution with 1 ml. of water. The solids were filtered and the ether solution was distilled through the Vigreux column used above. The amount of benzene recovered as determined spectrophotometrically was 0.0041 g. or 31%. In a similar experiment freshly prepared biphenylmercury (0.0144 g.) was reduced with 0.080 g. of lithium aluminum hydride in 70 ml. of ether over a period of 4 hr. The solution was then hydrolyzed with a small amount of water and filtered, and the precipitate was dissolved in dilute hydrochloric acid and extracted with ether. The combined ether extracts were distilled through the 12″ Vigreux column, and the ether distillate was found to contain 0.0020 g. of benzene, or 32% of the theoretical amount. The small quantity of residue remaining in the distillation flask contained neither biphenyl nor biphenylmercury.

$LiAlH_4$ Reduction of "Pentaphenylchromium Bromide."—To a solution of 5.0000 g. of lithium aluminum hydride in 5 l. of ether was added 1.000 g. of "raw bromide" with evolution of gas. Shortly after the addition of the sample, it dissolved with a development of brown color in the ether solution. After 8 hr. in the refrigerator and occasional shaking, the solution became clear and yielded a white precipitate. This mixture was hydrolyzed with 20 ml. of water in the cold, the ether layer was decanted and the precipitate was dissolved in dilute hydrochloric acid and extracted with ether. The ether solutions were next distilled from an ordinary distilling flask, and the residue was separated into methanol-soluble (0.3108 g.) and insoluble (0.065 g.) fractions. A portion of the former fraction was first sublimed and then crystallized from methanol to give pure biphenyl, m.p. 68–69°, which melted undepressed with an authentic sample and which absorbed at 248 mμ in ether. The methanol-insoluble fraction was recrystallized from 95% ethanol as plates of *p*-biphenylbenzene, m.p. 210–212°, 0.007 g., melting undepressed with a reagent sample. The ether distillate now amounting to 4240 ml. was redistilled through the 12″ Vigreux column, leaving 0.3246 g. of biphenyl as residue. The ether distillate contained 0.0259 g. of benzene as determined spectroscopically.

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(17) F. Hein, *Ber.*, **54**, 2727 (1921).

$LiAlH_4$ Reduction of "Pentaphenylchromium Hydroxide."—The "hydroxide" (0.0031 g.) was reduced with 0.020 g. of $LiAlH_4$ in 40 ml. of ether according to the general procedure previously described in detail. The reaction mixture was hydrolyzed with 0.5 ml. of water after the solution had come clear with the formation of the white precipitate. This precipitate, after separation by filtration, was dissolved in 1 ml. of dilute hydrochloric acid. This solution was saturated with sodium chloride and then extracted with 20 ml. of ether. The ether extract was combined with the ether filtrate, this solution washed with 3% sodium hydroxide twice, and the resultant ether solution was then distilled through the Vigreux column. No benzene was detected in the distillate, but biphenyl was left as residue, 0.0010 g., or 47% of the theoretical amount based on the bis-biphenylchromium phenoxide formulation. The alkaline solution was acidified and extracted exhaustively with ether. This ether solution absorbed at 273 mμ and was estimated to contain 0.0003 g. of phenol, or 47% of the theoretical amount.

$LiAlD_4$ Reduction of "Tetraphenylchromium" Iodide.—A solution of 0.0945 g. of the iodide was reduced with 0.200 g. of lithium aluminum *hydride* in 500 ml. of ether for 7 hr. and then hydrolyzed with 2 g. of *deuterium oxide*. After handling this mixture as already described, the ether solution was distilled, and no benzene was detected in the distillate. Biphenyl, 0.0122 g., was obtained by sublimation of the residue, 0.0310 g. (52%) and contained 0.31 D%.[8]

In a completely similar experiment 0.0520 g. of the iodide was reduced with 0.1500 g. of lithium aluminum *deuteride* in 260 ml. of ether. This mixture was hydrolyzed with 1.5 g. of deuterium oxide. Again, no benzene was found in the ether distillate, and biphenyl, containing 5.0 D%,[8] was obtained, 0.0083 g. , by the sublimation of the residue, 0.021 g. (64%), from the distillation.

Biphenyl (100 mg.) was treated with 500 mg. of lithium aluminum *deuteride* in 500 ml. of ether and hydrolyzed with 2.0 ml. of water. The sublimed biphenyl product contained 0.00 D%.[8]

$LiAlD_4$ Reduction of "Triphenylchromium" Iodide.—This iodide (0.300 g.) was reduced with 0.900 g. of lithium aluminum *deuteride* (97.8%) in 1500 ml. of ether and the solution hydrolyzed with 5 ml. of deuterium oxide. The ether solutions from the work-up procedure were distilled through the Vigreux column leaving 0.0890 g. of residue (79%) which gave 0.0470 g. of sublimed biphenyl. The ether distillate contained 0.0162 g. of benzene by spectrophotometric analysis, or 28% of the theoretical amount based on the benzene-biphenyl-chromium iodide structure. The biphenyl obtained above contained 6.7 D%. In a duplicate run made two weeks later the content was found to be 6.55 D%.[8]

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Infrared Absorption Spectra of *o*-Hydroxyazobenzene and its Metal Chelate Compounds

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The infrared absorption spectra of *o*-hydroxyazobenzene and its Cu, Ni and Co chelates are reported. Disappearance of the OH band in 3300 cm.$^{-1}$ region and the bathochromic shift of the carbonyl band in 1600 cm.$^{-1}$ region indicate the presence of a resonating system involving the azo linkage and the *o*-hydroxy group. The carbonyl band and the azo band shift to lower frequencies in the metal chelates, and the extent of shift is in the order of Cu > Ni > Co.

Introduction

In connection with an infrared absorption study of polyazobenzenes,[1] an investigation of a series of *o*-hydroxy azo compounds has been undertaken. In spite of the need for fundamental information on infrared absorption spectra of aromatic azo compounds, very little work has been reported in this field. It is the purpose of this investigation to study the infrared absorption spectra of *o*-hydroxyazobenzene, the simplest of the *o*-hydroxy aromatic azo compounds, and its Cu, Ni and Co chelates. The result of such a study should be of importance in connection with infrared analysis of *o*-hydroxy azo dyes of more complicated structures.

Experimental

Preparation of Samples.—*o*-Hydroxyazobenzene was prepared by coupling diazotized aniline with phenol according to the method of Bamberger[2] and was purified *via* copper chelate and recrystallized from ethanol (m.p. 82.5°).

The metal chelates were prepared by refluxing an ethanol solution of ligand and metal acetate for 10 minutes. After cooling, the metal chelates separated as needles, which were then recrystallized from ethanol. Although an attempt was made to prepare the cadmium chelate, only the ligand was recovered. The copper chelate was most easily prepared, while the nickel and cobalt complexes were prepared with increasing difficulty. The metal content of these chelate compounds was determined by complexometric titration after decomposing the samples with fuming nitric acid in a sealed tube,[3] and all the chelate compounds were found to contain 2 moles of ligand per mole of metal. The properties and the result of analyses are shown in Table I.

TABLE I

METAL CHELATES OF *o*-HYDROXYAZOBENZENE

Metal chelated	Color	Metal, %	
		Calcd.[a]	Found
Cu(II)	Brown	14.80	14.55
Ni(II)	Dark green	13.81	14.02
Co(II)	Dark blue	13.87	14.11

[a] Metal contents were calculated from the formula $(C_{12}H_9ON_2)_2M$, where M represented the metal chelated.

Infrared Spectra.—A Perkin-Elmer model 21 double beam spectrophotometer equipped with sodium chloride optics was used for the determination of infrared spectra, and samples were run both as Nujol mulls and as potassium bromide disks. For all the samples, these procedures gave almost identical spectra.

Results and Discussion

The significant absorption bands of these compounds below 1700 cm.$^{-1}$ are shown in Table II, along with assignments to group vibrations where possible.

The only absorption band observed in the 3300 cm.$^{-1}$ region is one due to the characteristic aromatic C–H stretching vibration at 3030 cm.$^{-1}$. This band is stable in position as well as in intensity when one goes from the ligand to the metal che-

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(1) K. Ueno, THIS JOURNAL, **79**, in press (1957).

(2) E. Bamberger, *Ber.*, **33**, 3191 (1900).

(3) P. J. McCarthy, R. J. Hovey, K. Ueno and A. E. Martell, THIS JOURNAL, **77**, 5820 (1955).