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π -Complexes of the Transition Metals. XIV. Acetylenic Condensations on Manganese(II) and Cobalt(II)^{1,2}

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The preparation of diphenylmanganese(II) and dimesitylcobalt(II) and the condensation of 2-butyne on these organometallic reagents are described. Bis-arene-manganese(I) and -cobalt(I) π -complexes are formed in these reactions and are isolable. The unique behavior of the aryl-cobalt derivative in catalytically trimerizing 2-butyne is reported also.

It has been shown previously that the cyclic condensation of 2-butyne with triphenylchromium(III) tetrahydrofuranate yields hexamethylbenzene and the bis-hexamethylbenzene-chromium π -complex, in addition to 1,2,3,4-tetramethylnaphthalene and its chromium π -complex.³ In the present study this method has been employed in the preparation of bis-arene complexes of manganese and cobalt which have been inaccessible either from the Grignard⁴ or Friedel–Crafts⁵ type reactions. These π -complexes, however, are obtained in minor yield; the trimer, *i.e.*, hexamethylbenzene, is the main product. Insofar as our experience goes, cobalt is unique among these transition metalorganics in catalytically trimerizing this acetylene.

The use of mesityl-instead of phenylmagnesium bromide in synthesizing a diaryl derivative of chromium(II) led to the successful preparation of the violet dimesitylchromium(II).² Dimesitylchromium, when treated with 2-butyne in tetrahydrofuran, yielded hexamethylbenzene and bishexamethylbenzene-chromium π -complex in much the same way as triphenylchromium cyclizes acetylenes. However, the *o*-methyl groups of the mesityl metal organics preclude the naphthalenic synthesis.

The reaction of mesitylmagnesium bromide and manganese(II) chloride (mole ratio 2:1) in tetrahydrofuran under nitrogen caused the precipitation of a beige solid which was considered to be dimesitylmanganese by analogy with the formation of dimesitylchromium, -cobalt and diphenylmanganese (vide infra) under similar conditions. However, the insolubility, sensitivity to air and moisture, and complete lack of reactivity of this solid toward 2-butyne in boiling tetrahydrofuran (decomposition to bimesityl) did not permit proof of structure. The chemical inertness of the mesitylmanganese derivative toward 2-butyne and the instability of diphenylchromium in tetrahydrofuran⁶ led us to investigate the possibility of the preparation of diphenylmanganese from phenylmagnesium bromide and manganese(II) chloride in the same solvent. light yellow-green precipitate was formed⁷ and this

(1) The subject matter of this paper was presented in Atlantic City, N. J., September, 1959; Abstracts, 136th Meeting, Amer. Chem. Soc., p. 93-P.

(2) Paper XIII, THIS JOURNAL, 82, 6255 (1960).

(3) H. Zeiss and W. Herwig, *ibid.*, **80**, 2913 (1958); W. Herwig, W. Metlesics and H. Zeiss, *ibid.*, **81**, 6203 (1959).

(4) H. Zeiss and M. Tsutsui, ibid., 79, 3062 (1957).

(5) E. O. Fischer and W. Hafner, Z. anorg. Chem., 286, 146 (1956).

- (6) M. Tsutsui and H. Zeiss, THIS JOURNAL. 81, 1376 (1959).
- (7) Diphenylmanganese also has been prepared from phenyllithium

too gave no reaction with 2-butyne at room temperature. However, on addition of 2 volumes of diethyl ether to the reaction mixture diphenylmanganese decomposed³ with the cyclization of 2-butyne proceeding to hexamethylbenzene and π -complex. The yields of these products were increased from 10 and 4%, respectively, to 31 and 10% when the entire reaction was performed in diethyl ether as solvent.

The structure in Fig. 1 of the manganese(I) π complex has been assigned on the basis of the properties of its tetraphenylboron salt. The infrared absorption of the bis-hexamethylbenzenemanganese cation is similar to that of the corresponding chromium(I) complex. Magnetic measurements showed the salt to be diamagnetic as required by the orbital and structural diagrams in Fig. 1.

The failure of either the mesityl or phenyl derivatives of manganese to undergo reaction with 2butyne in tetrahydrofuran is evidence for an unusually stable organomanganese compound. However, weakening of its solvent coördination by the less basic diethyl ether permits an incorporation of acetylenic molecules in the complex and subsequent reaction by the mechanistic diagram previously described.³

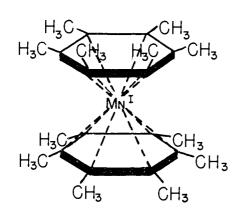
It is noted that naphthalenic synthesis did not occur by an interaction between a phenyl group on manganese with butyne. This phenomenon has only been observed when arylchromium(II or III) is used as the condensation reagent.³

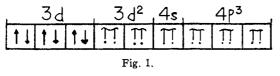
Dimesitylcobalt(II) was isolated under nitrogen as a light yellow-green powder, the reaction product of cobalt(II) chloride and mesitylmagnesium bromide (mole ratio, 1:2) in tetrahydrofuran.⁹ Dimesitylcobalt gradually decomposed at room temperature and therefore was kept in tetrahydrofuran below -10° . Such a slurry can be treated readily with 2-butyne at -30° . The trimerization of this acetylene proceeded smoothly under these conditions, the organocobalt system exhibiting catalytic activity as shown in Table I.

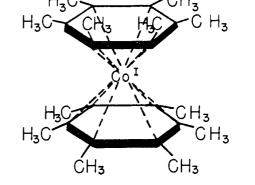
The π -complex formed halide, picrate, Reineckate and tetraphenylboron salts. The latter salt analyzed correctly for the structure shown in Fig. 2 and exhibited an infrared spectrum similar and manganous iodide: C. Beerman and K. Clauss, Angew. Chem., 71, 627 (1959).

(8) Triphenylchromium tri-tetrahydrofuranate is decomposed also by diethyl ether to π -complex; W. Herwig and H. Zeiss, *ibid.*, **79**, 6561 (1957); **81**, 4798 (1959).

(9) Dimesitylcobalt is cleaved by mercuric chloride to give mesitylmercuric chloride and cobaltous(II) ion in an experimentally determined ratio of 1.64:1.







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Fig. 2.

to those of the bis-hexamethylbenzene-chromium-(I) and -manganese(I) tetraphenylboron salts. Chemical evidence for the structure in Fig. 2 was provided by the decomposition of the cation with lithium aluminum hydride in ether which yielded 2 mole equivalents of hexamethylbenzene. Since the magnetic susceptibility examination of the cation showed it to be diamagnetic and on the assumption that the complex has octahedral geometry, one possible orbital configuration is given in Fig. 2. The electron complement of this complex as described is uncommon in the family of the bis-arene complexes in that it exceeds the inert gas configuration. It may well be that it is this unusual property which accounts for the singular capacity of cobalt to catalytically condense acetylenes in these reactions.

TABLE I

Cyclic	CONDENSATION	OF	2-BUTYNE	WITH	DIMESITYL					
COBALT										
2-Butyne, moles			8	10	20	40				
(Mes) ₂ Co, moles			1	1	1	1				

(CH₃)₆C₆(HMB).^a % 200480 50 153 1000 π -Complex, % % 2020 30 2020^a Yield based on cobalt, *i.e.*, one cobalt atom to produce 1 mole of HMB. ^b Bis-hexamethylbenzene-cobalt(I).

The fact that the yield of isolable π -complex in the trimerizations of 2-butyne by dimesitylcobalt (Table I) remains essentially constant while the amounts of hexamethylbenzene increase with greater mole ratios of butyne argues for a participation of the complex in the cyclization of the acetylene. However, these mechanisms are not clear and require further study.

Experimental¹⁰

Diphenylmanganese and 2-Butyne. To a slurried solu-tion of manganese(II) chloride (2.52 g., 0.02 mole) in 75 ml. of ether, 29 ml. of a 1.38 M solution of phenylmagnesium

bromide (0.04 mole) in ether was added dropwise. The reaction mixture was kept at -50° during the addition of Grignard reagent, then raised to -20° and stirred for about half an hour until no more solid precipitated. 2-Butyne (6.48 g., 0.012 mole) was added to the reaction mixture below -20° . The temperature was raised gradually to room temperature over a period of 4 hours after the addition of 2-butyne. After stirring overnight, the black reaction mixture was hydrolyzed with 50 ml. of water and then further diluted with 300 ml. of ether and 200 ml. of water. The brownish water layer was put aside. Removal of solvent from the ether extract left an oily material which with pieric acid gave a deep orange solid. This pierate of hexamethylbenzene was recrystallized from methanol to m.p. $173-175^{\circ}$, 2.5 g. (31.4%). The mixed melting point of this sample with authentic hexamethylbenzene picrate showed no depression and their infrared spectra were superimposable. The addition of aqueous sodium tetraphenylboron to the brown water solution put aside above precipitated a pinkish-white solid. Reprecipitation of the solid from methyl ethyl ketone solution by the addition of petroleum ether (b.p. 30-60°) yielded pinkishwhite crystals of bis-hexamethylbenzenemanganese(I) tetraphenylboron, 2.5 g. (10.8%) (gradually decomposed by heating to 350°).

Anal. Caled. for C48H56MnB: C, 82.51; H, 8.08; Mn, 7.86; B, 1.55. Found: C, 82.64; H, 7.82; Mn. 8.16; B, 1.52.

Dimesitylcobalt and 2-Butyne.-To a slurried solution of cobalt(II) chloride (1.30 g., 0.01 mole) in 500 ml. of tetrabydrofuran, 21 ml. of mesitylmagnesium bromide (0.95 molar, 0.02 mole) was added dropwise while keeping the re-action temperature below -50° . A light yellow-green solid precipitated, and the reaction mixture almost solidified. The reaction mixture was shaken well to obtain a slurried solution. 2-Butyne (6-40 moles; see Table I) was added to the solution at the temperature of -50° causing instant decomposition of the yellowish-green material. The temperature was gradually raised to room temperature during 4 hours with efficient stirring, and the mixture was stirred at room temperature overnight. The reaction mixture was refluxed for 30 minutes, and tetrahydrofuran was then removed under reduced pressure. Ether (150 ml.) was added to the residue followed by hydrolysis with 50 ml. of water. The mixture then was diluted with 500 ml. of ether and 300 ml. of water. Removal of the solvent from the dried ether layer (anhydrous sodium sulfate) left crystalline hexamethylbenzene which was easily recrystallized to constant melting point, 159-162°, yield 50-1000% (Table I). The addition of tetra-phenylboron-water solution to the orange-red water layer yielded a deep orange-red precipitate of bis-hexamethylben-zene-cobalt(I) tetraphenylboron which was recrystallized with considerable difficulty from methyl ethyl ketone as rec-

⁽¹⁰⁾ Microanalyses are by Schwarzkopf Microanalytical Laboratory, Woodside 77, N. Y. Melting points were determined on a Koffer hot-stage and are corrected. G. E. lamp-grade nitrogen was used throughout.

tangular plates, m.p. 205-208° dec., yield 20-30% (for

Anal. Calcd. for C48H56CoB: C, 82.04; H, 8.03; Co, 8.39; B, 1.54. Found: C, 82.10; H, 8.17; Co, 8.19; B, 1.49.

The picrate of the π -complex was recrystallized from methyl ethyl ketone as large golden flakes, 210° dec.

Anal. Calcd. for C₂₀H₂₅CoN₂O₇: Co, 9.61; N, 6.85. Found: Co, 9.83; N, 6.76.

To the water layer separated from the hydrolyzed mixture, 10 g. of solum chloride was added. The solution was extracted with chloroform until colorless. After drying with anhydrous sodium sulfate the chloroform was removed under reduced pressure leaving a deep orange-red material. This residue was dissolved in 5 ml. of methyl ethyl ketone and then was filtered. The addition of 200 ml. of ether precipitated bis-hexamethylbenzene-ccbalt(I) chloride. Repetition of this precipitation gave a highly hygroscopic, fine, orange-red powder, yield 20-30%.

Anal. Calcd. for C24H36ClCo: Cl, 8.46. Found: Cl, 8.05.

Reductive Cleavage of Bis-hexamethylbenzenecobalt-(I) Chloride with Lithium Aluminum Hydride.-The reductive cleavage of the chloride was carried out in a manner similar to that employed with bis-biphenylchromium iodide.4 The chloride (0.2660 g.) was decomposed with 1 g. of Li-AlH in 2.51 g. of ether. After hydrolysis of the reaction mixture, the solvent was removed from ether solution leaving a white crystalline hexamethylbenzene, 0.200 g., m.p. 155–159°. This product formed a picrate, m.p. 170–173°, which was identified as hexamethylbenzene picrate by mixed melting point and infrared comparison with authentic sample; yield of hexamethylbenzene: calcd. 0.206 g., found 0.200 g. (97%).

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Isomerization of α -Hydroxysilanes to Silyl Ethers. III. Triphenylsilylcarbinol*

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Treatment of triphenylsilylcarbinol with sodium-potassium alloy gives not only the isomeric ether triphenylmethoxy-silane but also triphenylsiloxytriphenylsilylmethane and bis-(triphenylsilylmethoxy)-diphenylsilane. The formation of these latter products is explained as a nucleophilic attack by the anion of triphenylsilylcarbinol on itself with displacement of either hydroxymethyl or phenyl groups. Triphenylsilylmethyl formate was isolated from a preparation of triphenylsilylcarbinol.

It has been shown^{1,2} previously that practically all types of aliphatic or aromatic α -silylcarbinols are rearranged readily to the isomeric silyl ethers by treatment with sodium-potassium alloy or other reagents

$R_3SiCOHR'_2 \longrightarrow R_3SiOCHR'_2$ $\mathbf{R} = \text{Me or Ph}, \mathbf{R'} = \mathbf{H}, \text{Me or Ph}$

The sole exception to this general reaction appeared to be the primary alcohol triphenylsilylcarbinol (I), which reacted with sodium-potassium alloy to give an unidentified high-melting solid, but apparently none of the expected ether triphenyl-methoxysilane (II). Further investigation has shown that triphenylsilylcarbinol is no exception to the general reaction since triphenylmethoxysilane now has been isolated from the reaction mixture in about 20% yield along with two other products, triphenylsiloxytriphenylsilylmethane (III) and bis-(triphenylsilylmethoxy)-diphenylsilane (IV), and recovered carbinol.

$$\begin{array}{c} \text{Ph}_{s}\text{SiCH}_{2}\text{OH} \xrightarrow{\text{Na}/\text{K}} \text{Ph}_{s}\text{SiOMe} + \text{Ph}_{s}\text{SiOCH}_{2}\text{SiPh}_{s} + \\ \text{I} & \text{II}, 15\text{-}20\% & \text{III}, 10\text{-}20\% \\ \text{Ph}_{s}\text{SiCH}_{2}\text{OSiPh}_{2}\text{OCH}_{2}\text{SiPh}_{s} \\ \text{IV}, 25\text{-}40\% \end{array}$$

Treatment of the carbinol in ether at room temperature with 0.1 equivalent or less of sodiumpotassium alloy led to the evolution of a small quantity of gas (1.5%) of the total active hydrogen) and the slow formation over several hours of crystals of IV. After removal of the apparently unconsumed alloy and the crystalline precipitate,

* Presented in part at the 138th Meeting of the American Chemical Society, New York, N. Y., September, 1960.

(1) A. G. Brook, THIS JOURNAL, 80, 1886 (1958).

(2) A. G. Brook, C. M. Warner and M. E. McGriskin, ibid., 81, 981 (1959).

the oily material obtained on removal of the ether was worked up by fractional crystallization giving III and recovered I or by distillation giving II. Our failure to isolate II previously probably was due to the fact that II is hydrolyzed to triphenylsilanol during chromatography on alumina.

The identity of III and IV were established both by degradation and by synthesis. Thus on treat-ment with cold 1.5% potassium hydroxide in ethanol-pyridine-water, III gave triphenylsilanol and triphenylsilylcarbinol and IV gave diphenylsilanediol and two equivalents of triphenylsilylcarbinol. However at reflux temperature III gave only triphenylsilanol and IV gave diphenylsilanediol and triphenylsilanol, since at higher temperatures triphenylsilylcarbinol is hydrolyzed mainly to triphenylsilanol. Syntheses of III and IV were

$$(Ph_{3}SiCH_{2}O)_{2}SiPh_{2} \xrightarrow{KOH} 2Ph_{3}SiCH_{2}OH + Ph_{2}Si(OH)_{2}$$

$$1.5\% KOH$$
reflux Ph_{3}SiOH + Ph_{2}Si(OH)_{2}

accomplished by treatment of either triphenylchlorosilane or diphenyldichlorosilane with triphenylsilylcarbinol using ammonia as hydrogen chloride acceptor.

Some variation in the yields of the various products in different runs was observed (see Table I). Undoubtedly part of this is associated with difficulties of separation of the products, but part may be due to variations in reaction time or in quantity of alloy used, although no clear-cut trend was observed. The fact that the reaction mixtures were not stirred continuously and that the droplets of alloy often became encrusted with crystalline product undoubtedly led to variations in yield.