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 $\pi$ -Complexes of the Transition Metals. XIV. Acetylenic Condensations on Manganese(II) and Cobalt(II)<sup>1,2</sup>

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The preparation of diphenylmanganese(II) and dimesitylcobalt(II) and the condensation of 2-butyne on these organo-metallic reagents are described. Bis-arene-manganese(I) and -cobalt(I)  $\pi$ -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  $\pi$ -complex, in addition to 1,2,3,4-tetramethylnaphthalene and its chromium  $\pi$ -complex.<sup>3</sup> 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 Grignard<sup>4</sup> or Friedel-Crafts<sup>5</sup> type reactions. These  $\pi$ -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 metal-organics 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).<sup>2</sup> Dimesitylchromium, when treated with 2-butyne in tetrahydrofuran, yielded hexamethylbenzene and bis-hexamethylbenzene-chromium  $\pi$ -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 tetrahydrofuran<sup>6</sup> led us to investigate the possibility of the preparation of diphenylmanganese from phenylmagnesium bromide and manganese(II) chloride in the same solvent. A light yellow-green precipitate was formed<sup>7</sup> and this

too gave no reaction with 2-butyne at room temperature. However, on addition of 2 volumes of diethyl ether to the reaction mixture diphenylmanganese decomposed<sup>8</sup> with the cyclization of 2-butyne proceeding to hexamethylbenzene and  $\pi$ -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)  $\pi$ -complex has been assigned on the basis of the properties of its tetraphenylboron salt. The infrared absorption of the bis-hexamethylbenzene-manganese 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 2-butyne in tetrahydrofuran is evidence for an unusually stable organomanganese compound. However, weakening of its solvent coordination by the less basic diethyl ether permits an incorporation of acetylenic molecules in the complex and subsequent reaction by the mechanistic diagram previously described.<sup>3</sup>

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.<sup>3</sup>

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.<sup>9</sup> Dimesitylcobalt gradually decomposed at room temperature and therefore was kept in tetrahydrofuran below  $-10^{\circ}$ . Such a slurry can be treated readily with 2-butyne at  $-30^{\circ}$ . The trimerization of this acetylene proceeded smoothly under these conditions, the organocobalt system exhibiting catalytic activity as shown in Table I.

The  $\pi$ -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  $\pi$ -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.

(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

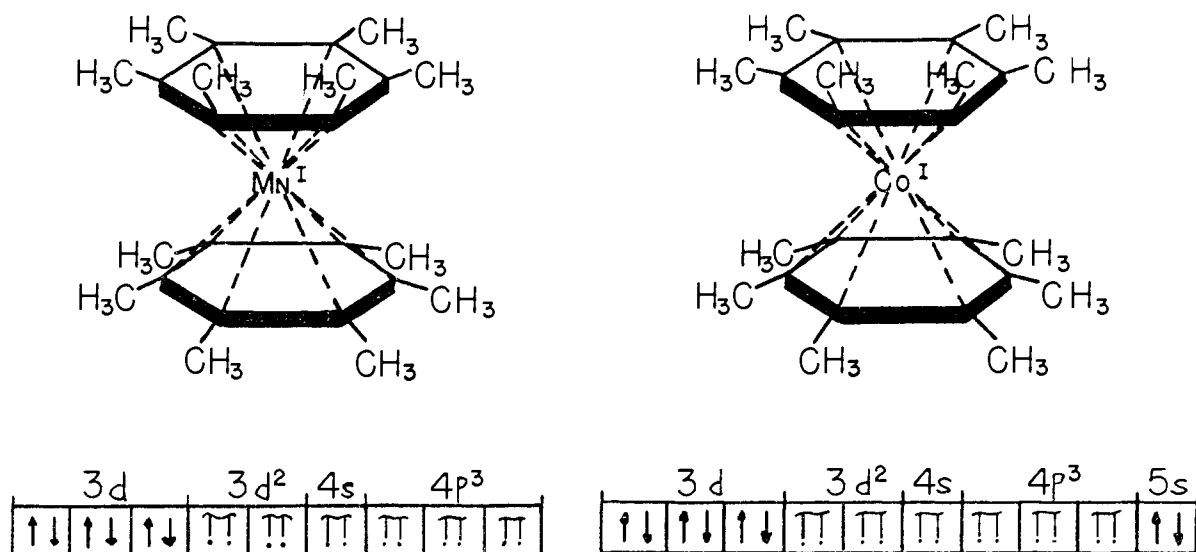


Fig. 1.

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.

2-Butyne, moles	6	8	10	20	40
(Mes) <sub>2</sub> Co, moles	1	1	1	1	1
(CH <sub>3</sub> ) <sub>6</sub> C <sub>6</sub> (HMB), <sup>a</sup> %	50	153	200	480	1000
π-Complex, <sup>b</sup> %	20	20	30	20	20

<sup>a</sup> Yield based on cobalt, *i.e.*, one cobalt atom to produce 1 mole of HMB. <sup>b</sup> 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.

#### Experimental<sup>10</sup>

**Diphenylmanganese and 2-Butyne.** To a slurried solution 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  $-50^{\circ}$  during the addition of Grignard reagent, then raised to  $-20^{\circ}$  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  $-20^{\circ}$ . 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 picric acid gave a deep orange solid. This picrate 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.  $30-60^{\circ}$ ) yielded pinkish-white crystals of bis-hexamethylbenzenemanganese(I) tetraphenylboron, 2.5 g. (10.8%) (gradually decomposed by heating to  $350^{\circ}$ ).

*Anal.* Calcd. for C<sub>48</sub>H<sub>56</sub>MnB: 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 tetrahydrofuran, 21 ml. of mesitylmagnesium bromide (0.95 molar, 0.02 mole) was added dropwise while keeping the reaction temperature below  $-50^{\circ}$ . 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  $-50^{\circ}$  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,  $159-162^{\circ}$ , yield 50–1000% (Table I). The addition of tetraphenylboron-water solution to the orange-red water layer yielded a deep orange-red precipitate of bis-hexamethylbenzene-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 Kofler hot-stage and are corrected. G. E. lamp-grade nitrogen was used throughout.

