The Reaction of Carbon Monoxide with Organometallic Compounds.* X. The Reaction of Carbon Monoxide with Phenyl Derivatives of Transition Metals**

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In a previous communication¹⁾ it was reported that the phenylcobalt compound prepared from the reaction between phenylmagnesium bromide and cobalt(II) chloride in diethyl ether reacted with carbon monoxide at a low temperature (-35—-10°C) and 1 CO atm., giving benzophenone (22%) and benzoin (12.5%) at -25°C, and benzoin (35%) at -35°C. The formation of benzophenone was explained as resulting from the reaction of carbon monoxide with the phenyl radical which was formed from a homolytic fission of the carbon-cobalt bond in the phenylcobalt compound, while benzoin was assumed to be produced by the dimerization, followed by the hydrolysis, of the benzoylcobalt compound.

This reaction had a few curious and suggestive points for carbon monoxide-insertion reactions. Furthermore, since many transition metal compounds have been used in the synthetic application of carbon monoxide as catalysts and since sometimes the formation of organic derivatives of transition metals as the reaction intermediates were supposed,²⁾ it was felt desirable to clarify the reaction of carbon monoxide with organic derivatives of transition metals as a unit reaction in some detail, and also to discuss the effects of the variation of transition metals on the reactivities of the organic derivatives of transition metals with carbon monoxide.

This report will deal with the reaction of carbon monoxide with phenyl derivatives of transition metals and also with the relation between various transition metals and their behavior in carbon monoxide-insertion reactions. Moreover, the assumption on benzophenone formation, proposed in the previous communication, will be further discussed. The metals used in this work were divided into two groups: A: chromium, nickel and cobalt, which can form metal carbonyls by the action of carbon monoxide, and B: copper and cadmium, the carbonyls of which have not yet been isolated.

Results and Discussion

The phenyl derivatives of transition metals were prepared by the reaction between metal halides and phenylmagnesium bromide. Although most transition metal halides react with alkyl and aryl Grignard or organolithium compounds under ordinary conditions, isolable organometallic compounds are frequently not obtained. Moreover, the major successes in the preparation of sigma-bonded transition metal alkyls and aryls have mostly resulted from close attention to experimental conditions (e. g., low temperature reactions) or, more commonly, from the use of the coordination of donor solvents or ligands.³⁻⁵⁾

Therefore, the preparation of the phenyl

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* Part IX: M. Ryang, T. Hashimoto and S. Tsutsumi, This Bulletin, 37, 1704 (1964).

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1) M. Ryang and S. Tsutsumi, This Bulletin, **34**, 1341 (1961).

2) C. W. Bird, *Chem. Revs.*, **62**, 283 (1962).

3) G. E. Coats and F. Glockling, "Organometallic Chemistry," A. C. S. Monograph No. 147., Ed. by H. Zeiss, Reinhold Publishing Corp., New York (1961), p. 426.

4) J. Chatt et al., *J. Chem. Soc.*, **1960**, 1718; **1961**, 285.

5) W. Herwig and H. Zeiss, *J. Am. Chem. Soc.*, **81**, 4798 (1959).

TABLE I. EXPERIMENTAL RESULTS

	Reaction condition				Reaction product,* Yield,** %			
Metal	Temp. °C	Pres. CO atm.	Solvent	Time hr.	Biphenyl	Benzoin	Benzo-phenone	Triphenyl-carbinol
Co	−35	1	Et_2O	2	30	35	trace	5
	−25	1	Et_2O	2	44	12.5	22	12
	−10	1	Et_2O	1	80	trace	5.5	trace
Cr	−25[a)]	1	THF	5	15		38	
	−25[b)]	1	Et_2O	5	20		20	
Ni	0	1	THF	5	19	19	11.5	5
	12	1	Et_2O	3	17	23		6
	21	1	Et_2O	3	60			
Cu	− 5***	1	Et_2O	5	39			
	32	1	Et_2O	4	42			
	−20	7	Et_2O	5	29			
Cd	15	1	THF	3	8			
	30	7	THF	3	2			

* In addition to these products, benzoic acid and other carbonyl compounds were obtained, for example, diphenylbenzoylmethane was obtained in 10% yield from a and in 14% yield from b.

** The calculations of yields are based on the amounts of bromobenzene used to prepare phenylmagnesium bromide.

*** Phenyllithium was used to prepare phenylcopper.

derivatives of transition metals and the reaction with carbon monoxide were carried out at a low temperature in proper solvents (tetrahydrofuran or diethyl ether), and the isolation and identification of the reaction products were carried out by the ordinary methods.[6)] The results of the reaction of carbon monoxide with various phenyl derivatives of transition metals are summarized in Table I. Since the reaction of phenylmagnesium bromide with carbon monoxide at −10°C in diethyl ether (for 5 hr.) gave only small amounts of diphenylcarbinol (2%) and triphenylmethane (1%), and since benzene was obtained in about a 90% yield, the carbon monoxide-inserted products in Table I were assumed to be produced from the reaction between carbon monoxide and the phenyl derivatives of transition metals. Also, the hydrolysis of the reaction mixtures obtained from the reaction of phenylmagnesium bromide with transition metal halides in the absence of carbon monoxide gave biphneyl in yields analogous to the yields of biphenyl in the presence of carbon monoxide. (Table II)

TABLE II. THE YIELDS OF BIPHENYL FROM THE REACTION IN THE ABSENCE OF CARBON MONOXIDE

Metal	Temp. °C	Time hr.	Solvent	Yield %
Co	−25	4	Et_2O	55
Ni	0	4	THF	20
Cu	32	4	Et_2O	35
Cd	15	4	THF	10

As may be seen in Table I, the phenyl derivatives of transition metals known to form metal carbonyls, including chromium, nickel and cobalt, reacted with carbon monoxide at a low temperature under 1 CO atm. to give the reaction products derived from carbon monoxide insertion, while diphenylcadmium and phenylcopper were unreactive to carbon monoxide under several reaction conditions and no products derived from carbon monoxide insertion were obtained in isolable amounts. On the basis of the above results, the coordination of carbon monoxide to metals may be considered to be the first step in these reactions; then alkyl-acyl rearrangement[7)] occurs to form benzoyl derivatives of transition metals, which decompose to give benzophenone or dimerize to give benzoin.

In the previous communication, the formation of benzophenone was explained as resulting from the reaction of carbon monoxide with the phenyl radical. However, benzophenone was not isolated from the reaction between carbon monoxide and phenylcopper even at a somewhat higher reaction temperature and a more elevated carbon monoxide pressure, although biphenyl was formed in a good yield and the formation of phenyl radical was certain.

On the basis of these results, it may be considered improper to explain the mechanism of benzophenone formation by a simple radical mechanism. Therefore, benzophenone should

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6) M. Ryang and S. Tsutsumi, This Bulletin, **35**, 1121 (1962); **37**, 341 (1964).

7) T. H. Coffield, J. Kozikowski and R. D. Closson, *J. Org. Chem.*, **22**, 598 (1957).

be thought to be produced from the decomposition of thermally-unstable benzoyl derivatives of transition metal,8) which are dimerized and then hydrolyzed, to give benzoin at a lower reaction temperature.

The mechanical aspects of the ketone formation reaction and the studies of the factors which determine the course of benzophenone formation or benzoin formation will be presented in detail in a forthcoming paper.

Experimental

Materials.—*Bromobenzene.*—Commercial bromobenzene was purified by fractional distillation; b. p. 155°C, n_D^{20} 1.5602.

Metal Halides. — Commercial anhydrous metal halides (chromium(III) chloride, nickel chloride, cobalt(II) chloride, cuprous iodide and cadmium chloride) were dried by heating under reduced pressure.

Reactions.—*The Reaction of Carbon Monoxide with Diphenylnickel.*9)—The apparatus and procedure employed here were identical with those described in the previous paper.6) Twenty-six grams (0.2 mol.) of nickel chloride was added to a ethereal solution of phenylmagnesium bromide which had been prepared by using 31.4 g. (0.2 mol.) of bromobenzene, 5.4 g. (0.22 g. atm.) of magnesium and 150 ml. of anhydrous diethyl ether; carbon monoxide was then introduced into the solution at 12°C for 4 hr. The organic layer, separated after the hydrolysis of the reaction mixture, was divided into a neutral part, an acidic part and a phenolic part by means of the ordinary method. The neutral part was distilled under reduced pressure to give the following fractions: (1) b. p. 90—140°C/20 mmHg 2.6 g., (2) b. p. 105—150°C/1 mmHg 4.9 g., (3) b. p. 150—160°C/1 mmHg 1.0 g. and (4) b. p. 190—200°C/1 mmHg 0.4 g. Fraction 1 was identified as biphenyl by its mixed melting point measurement (m. p. 70°C, recrystallized from ethanol). Fraction 2 was recrystallized from ligroin to give white crystals, m. p. 133—134°C, and was identified as benzoin from the results of a mixed melting point measurement, infrared-spectra measurements and an elemental analysis.

Found: C, 79.43; H, 5.56. Calcd. for $C_{14}H_{12}O_2$: C, 79.22; H, 5.70%.

Fraction 3 solidified on standing and was recrystallized from benzene-ligroin to give white crystals, m. p. 161—162°C, which were identified as triphenylcarbinol by a mixed melting point measurement with an authentic sample.

When tetrahydrofuran was used as a solvent, benzophenone (11.5%) was isolated in addition to the above products, and its structure was determined by the results of infrared spectra measurements and a mixed melting point measurement of its oxime (m. p. 140—141°C, recrystallized from ligroin). Furthermore, benzoic acid was obtained from the acidic part and phenol from the phenolic part.

*The Reaction of Carbon Monoxide with Triphenylchromium.*5)—4.5 g. of chromium trichloride was added at −30°C to a tetrahydrofuran solution of phenylmagnesium bromide which had been prepared by using 15.1 g. of bromobenzene, 2.3 g. of magnesium and 133 ml. of anhydrous tetrahydrofuran, and then the stirring was continued for a further 8 hr. at −25°C. Then dry, pure carbon monoxide was bubbled into the solution at −25°C for 5 hr. The reaction mixture was hydrolized by ethanol-2 N hydrochloric acid and divided into a neutral part, an acidic part and a phenolic part. The neutral part was distilled under reduced pressure to give the following fractions: (1) b. p. ~90°C/12 mmHg 1.1 g., (2) b. p. 105—130°C/1 mmHg 3.3 g. and (3) b. p. 130—190°C/1 mmHg 0.9 g. Fraction 1 was identified as biphenyl by mixed melting point measurements. The infrared spectrum of fraction 2 showed the presence of a carbonyl group (1655 cm⁻¹), and fraction 2 was confirmed to be benzophenone from the results of a mixed melting point measurement of its 2,4-dinitrophenylhydrazone (m. p. 236—237°C, recrystallized from ethyl acetate).

Found: C, 62.98; H, 3.96. Calcd. for $C_{19}H_{14}O_4N_4$: C, 62.98; H, 3.89%.

Fraction 3 was recrystallized from ligroin to give white crystals (m. p. 136—138°C); the infrared spectrum of these crystals showed the presence of a carbonyl group (1675 cm⁻¹).

Found: C, 87.77; H, 6.16. Calcd. for $C_{20}H_{16}O$: C, 88.20; H, 5.92%.

These crystals were identified as diphenylbenzoylmethane by a mixed melting point measurement with an authentic sample. Small amounts of benzoic acid and phenol were isolated from the acidic part and the phenolic part respectively. When the reaction in diethyl ether was carried out under similar conditions, the products in Table I were isolated.

*The Reaction of Carbon Monoxide with Phenylcopper.*10)—Phenylcopper was prepared by the reaction of cuprous iodide (19 g., 0.1 mol.) with phenylmagnesium bromide in a diethyl ether solution (0.1 mol.) or with phenyllithium in diethyl ether (0.1 mol.) at −15—−5°C. The reaction with carbon monoxide was carried out under several conditions (Table I). As a reaction product, biphenyl was obtained in a good yield, but no carbonyl compounds were obtained in isolable amounts.

*The Reaction of Carbon Monoxide with Diphenylcadmium.*11) — To a tetrahydrofuran solution of phenylmagnesium bromide (0.1 mol.), 9.2 g. (0.05 mol.) of anhydrous cadmium chloride was added at −30°C; the reaction mixture was then kept at

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8) Re: acetone formation from methylcobalt tetracarbonyl, cf. W. Hieber, O. Vohler and G. Braun, *Z. Naturforsch.*, **13b**, 192 (1958), and Re: the synthesis of tetraphenylcyclopentadienone, cf. G. N. Schrauzer, *J. Am. Chem. Soc.*, **81**, 5307 (1959).

9) E. G. Rochow, D. T. Hurd and R. N. Lewis, "The Chemistry of Organometallic Compounds," John Wiley & Sons, New York (1957), p. 251; M. Tsutsui and H. Zeiss, *J. Am. Chem. Soc.*, **81**, 6090 (1959).

10) H. Gilman, R. G. Jones and L. A. Woods, *J. Org. Chem.*, **17**, 1630 (1952).

11) C. G. Stuckwisch and J. V. Balley, ibid., **28**, 2362 (1963).

15°C for 1 hr. while it was being stirred. The introduction of carbon monoxide was carried out at 15°C or 30°C for 3 hr. After hydrolysis, benzene was obtained in a good yield, but no carbonyl compounds were isolated.

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