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The Reaction of *o*-Lithio-*N*,*N*-dimethylbenzylamine with Metal Carbonyls

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We have previously reported that lithium aroyl or acylmetal carbonylates, $Li[RCOM(CO)_n]$ (M= Ni, Fe), are formed as intermediates in the reaction of organolithium compounds with mononuclear metal carbonyls at low temperature (−50—−70°C). Fischer and Maasböl[1] have also described the formation of lithium benzoylmetal pentacarbonylate by the reaction of phenyllithium with metal hexacarbonyl (metal=Cr, Mo and W); they also revealed that these carbonylates are stable mononuclear-transition metal carbene complexes.

Although an attempt to isolate the pure complexes of the corresponding nickel or iron carbonylate was unsuccessful, their synthetic applications were investigated since lithium aroyl or acylmetal carbonylates showed useful reactivities in organic reactions. However, the nickel complexes showed different reaction behavior from the iron or the Group VI transition metal complexes. For example, lithium aroylnickel carbonylate gave acyloins by hydrolysis,[2] 1,4-diketones by reaction with acetylenes,[3] and α-diketones by thermal decomposition[4] (Eq. 1), while lithium aroyl or acylmetal carbonylates (metal=Fe,[5a)] Cr, Mo and W[5b)]) gave alde-

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[1] E. O. Fischer and A. Maasböl, *Angew. Chem.*, **76**, 645 (1964); *Chem. Ber.*, **100**, 2445 (1967).

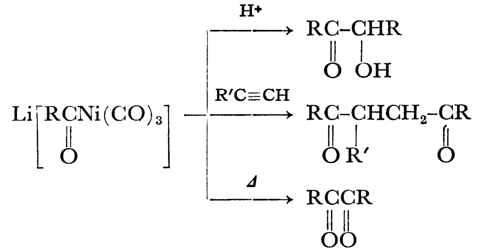
[2] M. Ryang, K-M. Song, Y. Sawa and S. Tsutsumi, *J. Organometal. Chem.*, **5**, 305 (1966).

[3] Y. Sawa, I. Hashimoto, M. Ryang and S. Tsutsumi, *J. Org. Chem.*, **33**, 2159 (1968).

[4] K-M. Song, Y. Sawa, M. Ryang and S. Tsutsumi, This Bulletin, **38**, 330 (1965).

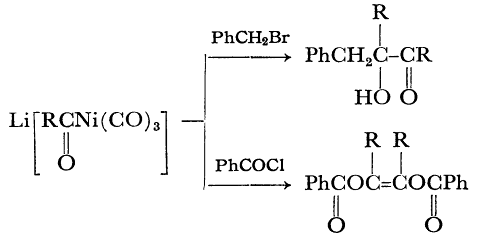
[5] a) M. Ryang, I. Rhee and S. Tsutsumi, *ibid.*, **37**, 341 (1964). b) E. O. Fischer and A. Massböl, German Pat. 1214233 (1966).

hydes in good yields by hydrolysis, but did not give 1,4-diketones from the reaction with acetylenes.[3]



(1)

Furthermore, lithium aroylnickel carbonylates gave acyloins by a reaction with benzyl bromide and en-diol-diesters by a reaction with benzoyl chloride (Eq. 2), whereas lithium aroyliron carbonylates yielded ketones[6] (Eq. 3).



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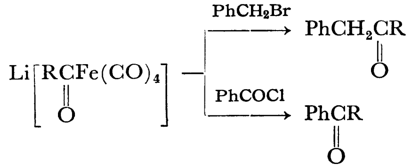


(3)

The above results suggest that lithium aroylnickel and -iron carbonylates behave toward various reagents as if the former is a dinuclear, and the latter, a mononuclear complex, for two aroyl or acyl groups are introduced into the products in the case of the nickel complex and one aroyl or acyl group in the case of the iron complex, although the relationship between the structure of the intermediate and the products has not yet been established. Furthermore, it has been reported that the mononuclear iron carbonylate anion exists, but no mononuclear nickel carbonylate anion exists.[7] These results provide one suggestion regarding the structure of the present nickel complexes.

Hereupon, it was considered to be probable that when a nitrogen-containing substituent which has a coordinating ability with the transition metal is present at the *ortho* position of phenyllithium, the nickel carbonylate would also behave as a mononuclear intermediate complex similar to iron carbonylate. In this paper, we wish to report on our study of the reactions of lithium-*o*-*N*,*N*-dimethylaminomethyl phenylmetal (iron or nickel) carbonylates with such organic halides as benzyl bromide or benzoyl chloride and the decomposition of the carbonylates with an iodine-methanol solution.

Results and Discussion

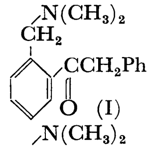
In general, alkyl or aryllithium is very reactive toward nickel carbonyl and the reaction proceeds exothermically even at −70°C, but the reaction of *o*-lithio-*N*,*N*-dimethylbenzylamine[8] with nickel carbonyl took place at −20°C. After stirring had been continued for 10 hr, organic halide was added and the mixture was stirred at 12°C for 2 hr. The resulting reaction mixture was treated and the products were isolated by ordinary methods; the results are summarized in Table 1.

TABLE 1. THE REACTIONS OF *o*-LITHIO-*N*,*N*-DIMETHYLBENZYLAMINE WITH ORGANIC HALIDE AND IODINE–METHANOL

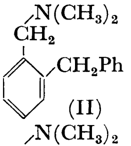
	Li[RCOFe(CO)$_n$]		Li[RCONi(CO)$_m$]*	
$PhCH_2Br$	I 26.7%**	II trace	I 5.0%	II 11.1%
PhCOCl	III 12.6%		III 27.2%	
I_2/CH_3OH	IV 18.1%		IV 5.2%	

* R=*o*-*N*,*N*-dimethylaminomethylphenyl.

** All the yields in this paper are based on the *N*,*N*-dimethylbenzylamine used. Unreacted *N*,*N*-dimethylbenzylamine was recovered, while the high-boiling residue formed in these reactions was not examined.



(I)



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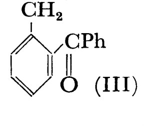

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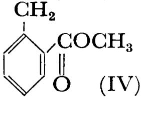

(IV)

As may be seen in Table 1, the same products are formed in the cases of both nickel and iron, although the yields of the products are low, while such results have not yet been observed from the reaction of nickel carbonyl with aryllithium which does not contain an amino group at the *ortho* position. Consequently, it may be considered that the structure of the nickel complex becomes similar to that of the iron complex by an intramolecular

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[6] Y. Sawa, M. Ryang and S. Tsutsumi, unpublished work.

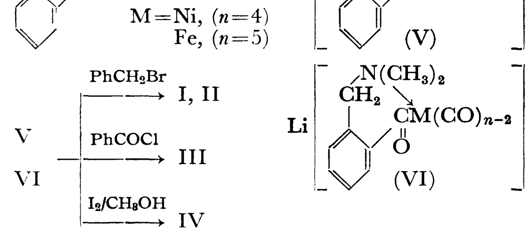
[7] H. Wakamatsu, "Organometallic Chemistry," Kagaku Dojin, Japan (1966), p. 107.

[8] A. C. Cope, *J. Organometal. Chem.*, **8**, 531 (1967).

coordination of the nitrogen to the nickel atom; that is, a mononuclear nickel carbonylate complex will be formed.

Cope[8] has reported that the stable carbon-cobalt σ-bonding complex was isolated from the reaction of cobalt dichloride with *o*-lithio-*N*,*N*-dimethylbenzylamine. However, cobalt dichloride reacts with phenyllithium or phenylmagnesium bromide to give an unstable diphenylcobalt, which then decomposes to form biphenyl above -20°C.[9]

In an attempt to isolate the intermediate nickel complex which would be stabilized by the coordination of nitrogen, a white solid was obtained after the solvent had been removed under nitrogen, but the structure has not yet been determined. Although the structures of the intermediates are not clear, the present reaction may be considered to proceed according to the following paths;



Namely, in the reaction with benzyl bromide (V) and (VI) react to give ketone (I) and coupling product (II), and in the reaction with benzoyl chloride to give ketone (III) (α-diketone was not detected), although it is not evident whether the carbonyl group in ketone came from benzoyl chloride or from (VI). In the reaction with an iodine-methanol solution, (VI) reacts first with iodine; methanolysis then gives the ester (IV).

Fischer and Kiener[10] have recently reported that a dinuclear iron complex was isolated from the reaction of lithium aroyliron carbonylate with trityl chloride. However, the complex isolated does not necessarily reflect the precise structure of the proceeding anionic complex, since the possibility can not be completely neglected that the oxidation of the anionic mononuclear complex with trityl chloride results in the dimerization of the neutral complex thus produced.

The structures of the synthetically useful anionic complexes of iron and nickel are still open to question, and the relationship between the structure of a complex and its reactivity is one of the most interesting problems in organic synthesis using metal carbonyls.

Experimental

The *N*,*N*-dimethylbenzylamine, benzyl bromide, and benzoyl chloride used were obtained by the purification of commercial reagents by fractional distillation. A hexane solution of *n*-butyllithium was used without purification. The diethyl ether was dried over sodium wire, and all the reactions were carried out under a dry argon atomosphere.

a) The Reaction of Benzyl Bromide with Lithium *o*-*N*,*N*-dimethylaminomethylphenylmetal Carbonylate. *N*,*N*-dimethylbenzylamine (0.04 mol) was added to *n*-butyllithium (0.048 mol) in *n*-hexane (60 m*l*), and then the mixture was refluxed for 16 hr. The reaction mixture thus changed from a colorless solution to a suspension of a white solid of *o*-lithio-*N*,*N*-dimethylbenzylamine. The ether solution (60 m*l*) of iron pentacarbonyl (0.04 mol) was added to the mixture at -50°C, and the reaction mixture was stirred for 10 hr at -20°C; the color of the mixture thus changed from orange-red to red-brown. After the addition of the ether solution (15 m*l*) of benzyl bromide (0.04 mol), the reaction was carried out at an elevated temperature (12°C) for 2 hr, after which the reaction mixture was separated into a benzene-soluble and a benzene-insoluble part. The benzene solution was distilled under reduced pressure to give the following fractions: (1) bp$\sim$120°C (1.0 mmHg), 1.3 g; (2) bp 140°C (1.0 mmHg), a trace, and (3) bp 150°C (1.0 mmHg), 2.7 g. Fraction (1) was found by vpc analysis to be a mixture of the following materials: bibenzyl (0.4 g, 11.0%) and dibenzyl ketone (0.8 g, 19.2%) [Column, S. E. 30, 2.25 m; column temperature, 230°C; flow rate of carrier gas (helium), 7 m*l*/min; flame ionization detecter; retention time, 4.8 and 9.7 min]. Fraction (2) was identified as *o*-benzyl-*N*,*N*-dimethylbenzylamine on the basis of the following data: Found: C, 85.28; H, 8.50%. Calcd for $C_{16}H_{19}N$: C, 85.04; H, 8.77%. NMR (τ): 7.90 (6H, singlet), 6.80 (2H, singlet), 5.91 (2H, singlet) and 2.95 (9H, multiplet). Mass (m^+/e): 225. IR: ν_{NCH} 2800 cm^{-1}. Fraction (3) was confirmed to be *o*-*N*,*N*-dimethylaminomethylphenyl benzyl ketone (26.7%); Found: C, 80.33; H, 7.73%. Calcd for $C_{17}H_{19}ON$: C, 80.57; H, 7.56%. NMR (τ): 7.83 (6H, singlet), 6.41 (2H, singlet), 5.86 (2H, singlet) and 2.73 (9H, multiplet). Mass (m^+/e): 253. IR ν_{CO} 1700, ν_{NCH} 2800 cm^{-1}.

In the case of nickel carbonyl, the reaction and treatment were carried out by a method similar to that described in the case of iron pentacarbonyl. The benzene solution was distilled under reduced pressure to give the following materials: *o*-*N*,*N*-dimethylaminomethylphenyl benzyl ketone (0.5 g, 5.0%), *o*-benzyl-*N*,*N*-dimethylbenzylamine (1.0 g, 11.1%), bibenzyl (1.1 g, 30.2%) and dibenzyl ketone (0.2 g, 4.8%).

b) The Reaction of Benzoyl Chloride with Lithium *o*-*N*,*N*-dimethylaminomethylphenylmetal Carbonylate. The reaction and treatment were similar to those described in (a). In the case of iron pentacarbonyl, the following fraction was given by distillation under reduced pressure: bp 113°C (1.0 mmHg), 1.2 g (12.6%). This material was confirmed to be *o*-*N*,*N*-dimethylaminomethyl benzophenone: Found: C, 80.13;

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9) M. Ryang, K. Yoshida, H. Yokoo and S. Tsutsumi, This Bulletin, **38**, 636 (1965).

10) E. O. Fischer and V. Kiener, *Chem. Commun.*, **1968**, 1378.

H, 7.25%. Calcd for $C_{16}H_{17}ON$: C, 80.30; H, 7.16%. NMR (τ): 8.08 (6H, singlet), 6.61 (2H, singlet), and 2.67 (9H, multiplet). Mass (m^+/e): 239. IR: ν_{CO} 1670, ν_{NCH} 2800 cm^{-1}.

In the case of nickel carbonyl, *o*-*N*,*N*-dimethylaminomethyl benzophenone was given in a yield of 27.2%. The reaction of benzoyl chloride with *N*,*N*-dimethylbenzylamine under these conditions as well as those described above did not give that ketone.

c) The Reaction of Iodine-methanol Solution with Lithium *o*-*N*,*N*-dimethylaminomethylphenylmetal Carbonylate. An iodine-methanol solution (11 g/50 m*l*) was added to lithium *o*-*N*,*N*-dimethylaminomethylphenyliron carbonylate, which had been prepared in the manner described in (a) at −20°C. Stirring was continued for 4 hr at room temperature, followed by refluxing for 3 hr. The benzene-soluble part obtained by the ordinary method was distilled under reduced pressure to give the following fraction: bp 105°C (13 mmHg), 1.4 g. The fraction was identified as methyl *o*-*N*,*N*-dimethylaminomethylbenzoate (18.1%): Found: C, 68.21; H, 7.80; N, 7.20%. Calcd for $C_{11}H_{15}NO_2$: C, 68.37; H, 7.82; N, 7.25%. NMR (τ): 7.81 (6H, singlet), 6.32 (2H, singlet), 6.17 (3H, singlet) and 2.56 (4H, multiplet). Mass (m^+/e): 193. IR: ν_{CO} 1740, ν_{COC} 1280, 1130 and ν_{NCH} 2800 cm^{-1}.

In the case of nickel carbonyl, methyl *o*-*N*,*N*-dimethylaminomethylbenzoate was obtained in a yield of 5.2%.