pyridine were added and this suspension was slowly added to a solution of **2** (0.05 mol) in 50 ml of ether at 0°. The reaction mixture was stirred at 0° for 1 hr and then at room temperature for 5–6 hr. The reaction mixture was cooled in an ice bath and 100 ml of saturated aqueous ammonium chloride solution was slowly added. The phases were separated and the aqueous layer was extracted twice with 50-ml portions of ether. The combined ethr extract was dried ($MgSO_4$), filtered, and evaporated. The resultant oil was distilled at reduced pressure to yield the alkynyl-1-thiophosphonates **3**.

In the preparation of **3k** ($R = C_6H_5$, $R' = CH_3$) only ether was used as a solvent.

Registry No.—**3a**, 20553-76-8; **3b**, 30238-04-1; **3c**, 30238-05-2; **3d**, 30238-06-3; **3e**, 30238-07-4; **3f**, 30238-08-5; **3g**, 30238-09-6; **3h**, 30238-10-9; **3i**, 30238-11-0; **3j**, 30238-12-1; **3k**, 30238-13-2.

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Reactions of Lithium Dimethylcarbamoylnickel Carbonylate

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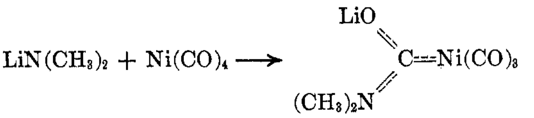
In a previous paper[1] we have reported the formation of an air-sensitive anionic carbamoylnickel complex, $Li[(CH_3)_2NCONi(CO)_3]$ (**1**), by the addition of lithium dimethylamide to nickel carbonyl and the reaction of **1** with phenylacetylene to yield 2-phenyl-*N*,*N*,*N'*,*N'*-tetramethylsuccinamide and *N*,*N*-dimethylcinnamamide under mild conditions. More recently, anionic organometal carbonylates have been shown to be effective nucleophilic reagents in organic syntheses and several types of new reactions have been established: *e.g.*, nucleophilic acylation of organic halides[2,3] and conjugated enones[4] using lithium acyl metal carbonylates derived from organolithium compounds and mononuclear metal carbonyls, and alkoxycarbonylation of organic halides[5] using nickel carbonyl and potassium alkoxide.

In this paper, we wish to report the reaction of lithium dimethylcarbamoylnickel carbonylate (**1**) as a nucleophilic carbamoylation reagent. The reaction of alkyl carbamoyl chloride with carbanion has been well known as a method for electrophilic carbamoylation accompanying a carbon–carbon bond formation.[6] The anionic carbamoyl group may show different behavior than the cationic one and give rise to a new type of organic reaction. Because of the difficulty in forming such a group, there are few reports on nucleophilic carbamoylation except the reaction system of biscarbamoylmercury compounds and *n*-butyllithium at very low temperature.[7]

Results and Discussion

Assumed Structure of Lithium Dimethylcarbamoylnickel Carbonylate (1).—Addition of nickel carbonyl to the white ether suspension of lithium dimethylamide yields a clear red solution without carbon monoxide evolution. The infrared spectrum of this solution shows peaks at 1973 (vs), 1954 (s) ($\nu_{C=O}$ of terminal carbonyl of the anionic complex), and 1560 cm^{-1} (m, broad) ($\nu_{C=O}$ and $\nu_{C=N}$ of the carbamoyl group bonded to nickel[8]). These data suggest that the $Ni(CO)_3$ group in **1** has C_{3v} symmetry (two infrared active terminal carbonyl vibrations) and that the carbamoyl group is bonded to nickel as a carbene type ligand (eq 1). (Recently, lithium oxydiethylaminocarbenechromium pentacarbonylate has been isolated by the analogous reaction using lithium diethylamide and chromium hexacarbonyl in ether.[9])



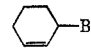
$$LiN(CH_3)_2 + Ni(CO)_4 \longrightarrow \overset{LiO}{\underset{(CH_3)_2N}{\rangle}}C{=\!=}Ni(CO)_3 \qquad (1)$$

Reaction of 1 with Organic Halides.—Treatment of **1** with several organic halides, RX or RCOX, in ether results in formation of the acid amides $RCON(CH_3)_2$. The examples cited in Table I illustrate the synthesis of *N*,*N*-dimethyl acid amides using the indicated reactants and reaction conditions.

TABLE I

DIMETHYLCARBAMOYLATION OF ORGANIC HALIDES

$$\underset{\mathbf{1}}{Li[(CH_3)_2NCONi(CO)_3]} + RX \text{ (or RCOX)} \longrightarrow RCON(CH_3)_2{}^{a}$$

Organic halides (RX or RCOX)	Reaction time, hr (temp, °C)	$RCON(CH_3)_2$, % yield[b]
trans-PhCH=CHBr	7 (10)	96.0
PhI	5 (37)	98.2
$PhCH_2Br$	12 (33)	64.8[c]
CH_2=$CHCH_2Br$	0.5 (15)	35.9[d]
	10 (20)	99.3
CH_3COCl	0.5 (22)	75.9[e]
n-C_4H_9COCl	0.5 (22)	97.1[e]
PhCOCl	5 (30)	95.6[e]

[a] Reactants ratio, $LiN(CH_3)_2$:$Ni(CO)_4$:halide = 1:2:2. [b] Yields were calculated based on $LiN(CH_3)_2$ used. [c] Other product, $PhCH_2N(CH_3)_2$ (33.2%). [d] Product, CH_3CH=$CHCON(CH_3)_2$. [e] None of $RCOCON(CH_3)_2$ was detected.

In general, the reactivity sequence of alkyl halides

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(1) S. Fukuoka, M. Ryang, and S. Tsutsumi, *J. Org. Chem.*, **33**, 2973 (1968).

(2) Y. Sawa, M. Ryang, and S. Tsutsumi, *Tetrahedron Lett.*, 5189 (1969).

(3) Y. Sawa, M. Ryang, and S. Tsutsumi, *J. Org. Chem.*, **35**, 4185 (1970).

(4) E. J. Corey and L. S. Hegedus, *J. Amer. Chem. Soc.*, **91**, 4926 (1969).

(5) E. J. Corey and L. S. Hegedus, *ibid.*, **91**, 1233 (1969).

(6) R. B. Wagner and H. D. Zook, "Synthetic Organic Chemistry," Wiley, New York, N. Y., 1953, p 576.

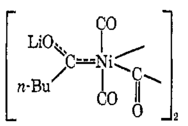
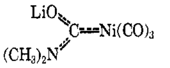
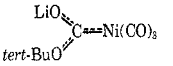
(7) U. Schöllkopf and F. Gerhart, *Angew. Chem., Int. Ed. Engl.*, **6**, 805 (1967).

(8) It has been reported that the neutral carbamoyl transition metal complex shows a $\nu_{C=O}$ peak (m or w) at 1535 ± 10 cm^{-1} in π-$C_5H_5Fe(CO)_2(CONR_2)$ [R. B. King, *J. Amer. Chem. Soc.*, **85**, 1918 (1963)], 1625 cm^{-1} in π-$C_5H_5Fe(CO)_2(CONHCH_3)$ [L. Busetto and R. J. Angelici, *Inorg. Chim. Acta*, **2**, 391 (1968)], 1512 cm^{-1} in *cis*-$Re(CO)_4(NH_2CH_3)(CONHCH_3)$ [H. Behrens, E. Linder, and P. Pässler, *Z. Anorg. Allg. Chem.*, **365**, 137 (1969)], and 1598 cm^{-1} in (n-$C_3H_7)_2NCOCo(CO)_3(PPh_3)$ [J. Palágyi and L. Markó, *J. Organometal. Chem.*, **17**, 453 (1969)].

(9) E. O. Fischer and H. J. Kollmeier, *Angew. Chem., Int. Ed. Engl.*, **9**, 309 (1970).

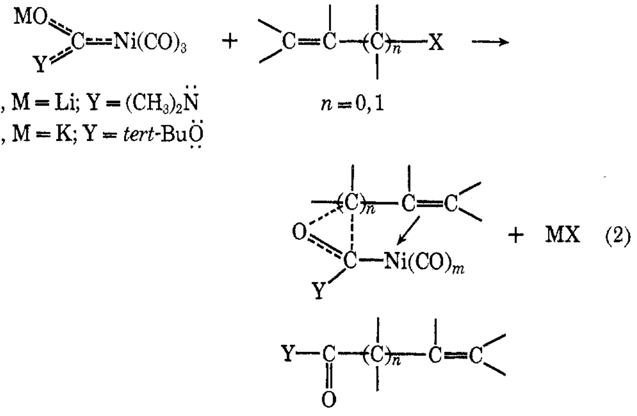
Table II

Carbonyl Stretching Frequencies of the Anionic Organonickel Carbonylate in Ether at 20°[a]

Formation reaction	Assumed structure		Terminal CO, cm^{-1}	Bridging CO, cm^{-1}
n-BuLi + $Ni(CO)_4$		(3)	1985, 1962	1845, 1819, 1795
$(CH_3)_2NLi$ + $Ni(CO)_4$		(1)	1973, 1954	
$tert$-BuOK + $Ni(CO)_4$		(2)	1963, 1920	

[a] *Cf.* $Ni(CO)_4$ which absorbs at 2053 cm^{-1} in ether.

in the nucleophilic substitution reaction is RI > RBr > RCl, but neither alkyl iodides such as methyl iodide and *n*-butyl iodide nor *tert*-butyl bromide undergo dimethylcarbamoylation under these conditions. Alkenyl halides, which are less susceptible to nucleophilic substitution than alkyl halides, undergo dimethylcarbamoylation easily. Hence it appears that halogen attached to saturated carbon (except allyl halides) is much less reactive than that on trigonal carbon. This is probably owing to acceleration of the reactivity of the halides by the coordination of the double bond to the nickel atom. The reactivity of **1** toward organic halides resembles that observed in alkoxycarbonylations[5] using nickel carbonyl and potassium alkoxide. Further, the infrared spectra of **1** and of the reaction mixture of potassium *tert*-butoxide and nickel carbonyl both have two terminal carbonyl absorptions at lower frequencies than that of nickel carbonyl (Table II). These observations suggest that the active species in the two systems have closely related structures. Analogous to **1**, the complex **2** is assumed to be an anionic organonickel carbonylate with a carbene type ligand, and both dimethylcarbamoylation and alkoxycarbonylation of organic halides may be described schematically by the following (eq 2).



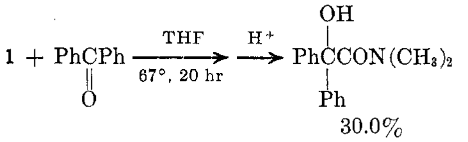
1, M = Li; Y = $(CH_3)_2\ddot{N}$

2, M = K; Y = *tert*-Bu$\ddot{O}$

Table II shows the carbonyl stretching frequencies of the anionic organonickel carbonylates, lithium pentanoylnickel carbonylate **3**, **1**, and potassium *tert*-butoxycarbonylnickel carbonylate **2**, derived from the reactions indicated in the first column.

In the reaction of **1** with acyl chlorides, *N*,*N*-dimethyl acid amides were obtained but no *N*,*N*-dimethyl α-keto acid amides were found. This may show that the cationic acyl group attaches itself to the nitrogen atom as the proton in acid hydrolysis[1] of **1**.

Reaction of 1 with Carbonyl Compounds.—Treatment of **1** with benzophenone in tetrahydrofuran results in formation of α-phenyl-*N*,*N*-dimethylmandelamide after hydrolysis (eq 3).



$$1 + PhC(=O)Ph \xrightarrow[67°,\ 20\ hr]{THF} \xrightarrow{H^+} PhC(OH)(Ph)CON(CH_3)_2 \quad 30.0\% \qquad (3)$$

Benzaldehyde reacts with **1** to give *N*,*N*-dimethylbenzamide (84.2%), and in the presence of **1**, acetophenone condenses to yield α-methylchalcone (77.2%) in ether and 1-methyl-1,3,5-triphenyl-2-benzoylcyclohexadiene-2,4 (83.8%) in tetrahydrofuran, although the mechanisms of those reactions are not clear.

Experimental Section

All reactions were carried out under nitrogen. Gas–liquid partition chromatographic analyses were performed on a Yanagimoto GCG-5DH instrument, using 2.5 m × 3 mm columns packed with 5% SE-30 or 20% PEG-20M, or on a Hitachi K53 instrument, using 1.5 m × 3 mm columns packed with SF-96 or 20% PEG-20M (carrier gas He). The infrared spectra of the ether solution of the complexes were taken on a Hitachi Perkin-Elmer 225 infrared recording spectrophotometer using a KBr cell and those of the other organic compounds were taken on a Shimazu IR 27 spectrophotometer.

Preparation of the Ether Solution of 1, 2, and 3.—To dimethylamine (25 mmol) dried with potassium hydroxide was added dropwise *n*-butyllithium (5 mmol) in *n*-hexane at 0°. The excess dimethylamine and *n*-hexane were then removed under reduced pressure at 40°. The ether (15 ml) solution of nickel carbonyl (10 mmol) was added to the ether (40 ml) suspension of lithium dimethylamide below 10° and the mixture was stirred for 1 hr. The resulting solution containing about 9 mol % of **1** was used for the infrared spectral measurement. The ether solution of **2** was prepared by adding nickel carbonyl (10 mmol) in ether (15 ml) to the *n*-hexane solution of *n*-butyllithium (5 mmol) below −40° and stirring for 1 hr. After being warmed to 20°, the infrared spectrum of the deep red solution of **2** was taken. A similar method was used for the preparation of **3** using potassium *tert*-butoxide (2.5 mmol) prepared from 0.1 g (2.5 mg-atoms) of potassium and *tert*-butyl alcohol in ether (40 ml) in place of lithium dimethylamide.

Reaction of 1 with Organic Halides.—The experimental execution of the dimethylcarbamoylation reaction is illustrated by the procedure for the synthesis of *trans*-*N*,*N*-dimethylcinnamamide from *trans*-β-bromostyrene. To the ether solution (60 ml) of **1** prepared from 25 mmol of lithium dimethylamide and 50 mmol of nickel carbonyl was added dropwise 9.15 g (50 mmol) of *trans*-β-bromostyrene in 10 ml of ether below 10° and the mixture was stirred for 7 hr at that temperature. After allowing to warm to room temperature, carbon monoxide was bubbled through the mixture for 1 hr to dispel any remaining nickel carbonyl. Anhydrous ethanol (30 ml) was added and the solution was distilled under reduced pressure to give 4.20 g of yellowish white crystals [bp 120–140° (0.7 mm)]. This was identified to be *trans-N,N*-dimethylcinnamamide by glpc and ir comparison with an authentic sample (yield 96.0%). *N,N*-Dimethyl-3-cyclohexene carboxylic acid amide [bp 98–99° (0.5 mm)] obtained from 3-bromocyclohexene was identified by the ir ($\nu_{C=O}$ 1645 cm^{-1}), the mass spectrum (*m/e* P = 153, 81, 72), and the nmr spectrum [τ 8.2–8.5 (m, 5 H), 7.3 (s, 6 H), 6.9 (m, 1 H), 4.5–4.7 (m, 2 H)]. *N,N*-Dimethylcrotonamide was isolated by preparative glpc and identified by the ir (conjugated $\nu_{C=O}$ and $\nu_{C=C}$ 1620 and 1665 cm^{-1}), the mass spectrum (*m/e* P = 113, 98, 69, 41), and the nmr spectrum [τ 8.3 (d, 3 H), 7.1 (s, 6 H), 3,9 (d, 1 H), 2.5 (m, 1 H)]. The other *N,N*-dimethyl acid amides cited in Table I were identified by glpc and ir comparison with authentic samples.

Reaction of 1 with Benzophenone.—To the THF solution (60 ml) of 1 prepared from 25 mmol of lithium dimethylamide and 37 mmol of nickel carbonyl was added 4.55 g (25 mmol) of benzophenone in 20 ml of THF and the mixture was stirred for 20 hr at 67°. After hydrolysis with 30 ml of 3 *N* hydrochloric acid at room temperature, the solution was concentrated by removal of the THF under reduced pressure and was extracted with ether. The ethereal extract was washed with water saturated with sodium chloride until a neutral solution was obtained and dried with anhydrous magnesium sulfate. The extract was distilled under reduced pressure after removal of the ether to give fraction 1, bp 120–125° (0.7 mm), 3.32 g, and fraction 2, bp 140–145° (0.7 mm), 0.50 g. Fraction 1 consisted of the recovered benzophenone. By recrystallization of fraction 2 using petroleum ether–benzene, white crystals of α-phenyl-*N,N*-dimethylmandelamide (mp 103°) were obtained. This compound was identified by the ir (KBr ν_{OH} 3300 cm^{-1}, $\nu_{C=O}$ 1620 cm^{-1}), the mass spectrum (*m/e* P = 255, 183, 105), the nmr spectrum [τ 7.3 (broad, 6 H), 4.1 (s, 1 H, this peak disappeared on adding D_2O), 2.7 (s, 10H)], and the elemental analysis. The yield was 30% based on benzophenone converted.

Anal. Calcd for $C_{16}H_{17}NO_2$: C, 75.27; H, 6.71; N, 5.49. Found: C, 75.18; H, 6.66; N, 5.38.

Reaction of 1 with Benzaldehyde.—Treatment of 2.65 g (25 mmol) of benzaldehyde with 1 (25 mmol) by the method mentioned above resulted in formation of 1.68 g of *N,N*-dimethylbenzamide (84.2% based on benzaldehyde converted), which was identified by glpc, ir comparison with an authentic sample, the mass spectrum (*m/e* P = 149, 105), and the nmr spectrum [τ 7.0 (s, 6 H), 2.6 (s, 5 H)].

Reaction of 1 with Acetophenone.—To the ether solution of 1 (25 mmol) was added 6.00 g (50 mmol) of acetophenone and the solution was stirred for 24 hr at 18°. After hydrolysis with 30 ml of 3 *N* hydrochloric acid, the solution was extracted with ether. The extract was washed with water, saturated with sodium chloride, dried with anhydrous magnesium sulfate, and then was distilled under reduced pressure. The first fraction [bp 115° (80 mm), 2.50 g] was acetophenone recovered and the second fraction [bp 150–185° (2 mm), 2.61 g] was shown to contain 2.50 g of α-methylchalcone by a glpc analysis. This compound was isolated by preparative glpc and identified by the ir (conjugated $\nu_{C=O}$ and $\nu_{C=C}$, 1660 and 1600 cm^{-1}), the mass spectrum (*m/e* P = 222, 115, 105), and the nmr spectrum [τ 7.5 (s, 3 H), 2.9 (s, 1 H), 2.0–2.8 (m, 10 H)] (77.2% based on acetophenone converted). In the same reaction using THF as a solvent (67°, 10 hr), 3.00 g (25 mmol) of acetophenone was converted to 2.23 g of 1-methyl-1,3,5-triphenyl-2-benzoylcyclohexadiene-2,4 (mp 134–135° from petroleum ether–benzene). This was identified by the ir ($\nu_{C=O}$ 1670 cm^{-1}, $\nu_{C=C}$ 1640 and 1620 cm^{-1}), the mass spectrum (*m/e* P = 426, 411, 321, 105), the nmr spectrum [τ 8.4 (s, 3 H), 6.9 (s, 2 H), 3.9 (s, 1 H), 2.5–3.1 (m, 20 H)], and the elemental analysis.

Anal. Calcd for $C_{32}H_{26}O$: C, 90.10; H, 6.14. Found: C, 90.06; H, 6.01.

Registry No.—1, 30304-90-6; *trans-N,N*-dimethylcinnamamide, 17431-39-9; *N,N*-dimethyl-3-cyclohexenecarboxylic acid amide, 30318-35-5; α-phenyl-*N,N*-dimethylmandelamide, 30318-36-6; α-methylchalcone, 4258-37-1; 1-methyl-1,3,5-triphenyl-2-benzoylcyclohexadiene-2,4, 24233-07-6.

The Question of Ring Inversion in 2,3,6,7-Tetramethoxy-9,10-dihydroanthracene[1,2]

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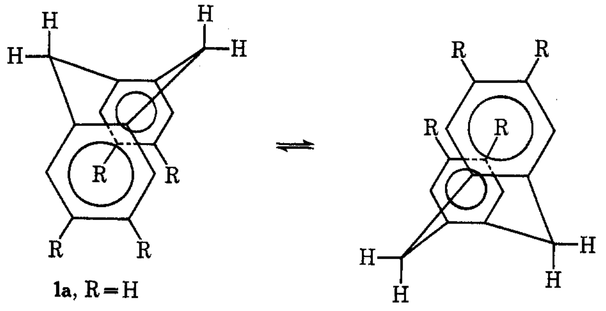
9,10-Dihydroanthracene (1a) undergoes a rapid boat-to-boat ring inversion at a rate which exceeds the limits of nmr time scale observability, even at low temperatures.[3,4] However, it was recently reported[5] that 2,3,6,7-tetramethoxy-9,10-dihydroanthracene (1b), together with the 2,7-dimethoxy and 1,2,3,5,6,7-hexamethoxy analogs, does not undergo this rapid ring-inversion process[6] and shows distinct axial and equatorial methylene protons characteristic of a rigid boat conformation. We felt that it would be highly unusual, and, if true, extremely important that substituents so far from the center ring could exert such a strong influence on the inversion process and that a reinvestigation was in order.



1a, R = H
b, R = OCH_3

The methoxy derivatives originally studied by nmr were prepared by a modified method of Robinson.[7] It has subsequently been suggested, however, that Robinson's procedure involving the condensation of veratrole with formaldehyde does not produce any dihydroanthracenes.[8] In fact, the related reaction of veratryl alcohol with acid[9] leads to the trimer "cyclotriveratrylene."[10]

For our purposes, we wanted to prepare an appropriate system by the simplest route available, free from possible side reactions. We began with the

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[1] This investigation was supported, in part, by a grant from the Eli Lilly Co., Indianapolis, Ind.

[2] Some preliminary experiments were carried out at the Ben May Laboratory for Cancer Research, University of Chicago.

[3] W. B. Smith and B. A. Shoulders, *J. Phys. Chem.*, **69**, 2022 (1965). See also D. Y. Curtin, C. G. Carlson, and C. G. McCarty, *Can. J. Chem.*, **42**, 565 (1964).

[4] A planar conformation seems to be a less likely explanation. See, in addition to ref 1, A. W. Brinkman, M. Gordon, R. G. Harvey, P. W. Rabideau, J. B. Stothers, and A. L. Ternay, *J. Amer. Chem. Soc.*, **92**, 5912 (1970).

[5] F. G. Jimenez, M. C. Perezamador, and J. R. Alcayde, *Can. J. Chem.*, **47**, 4489 (1969).

[6] Studied from −20 to +55°.

[7] G. M. Robinson, *J. Chem. Soc.*, **107**, 267 (1915).

[8] C. Casinovi and A. Oliverio, *Ann. Chim.* (*Rome*), **46**, 929 (1956), and references therein.

[9] Conditions very similar to ref 3: A. S. Lindsey, *J. Chem. Soc.*, 1685 (1965).

[10] This system shows distinct methylene protons even at high temperatures.[9]