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REACTION OF LITHIUM PHENYLACETYLIDE WITH METAL CARBONYL

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We have previously reported that alkyl- or aryllithiums react smoothly with nickel carbonyl [$Ni(CO)_4$] or iron pentacarbonyl [$Fe(CO)_5$] at low temperature ($-70^\circ \sim -50^\circ$) to form the synthetically useful intermediate complexes; lithium acyl- or aroylmetal carbonylates (1). In general, organotransition metal σ-complexes play important roles in organic synthesis but the reaction of transition metal acetylides which contain σ-bond between transition metal and sp carbon has not yet been studied in detail.

We now wish to report the formation of lithium phenylethynylmetal carbonylates by the reaction between lithium phenylacetylide and mononuclear metal carbonyls and to show a novel reaction behavior of the above intermediate complexes.

Into the suspension of lithium phenylacetylide prepared from phenylacetylene (0.025 mole) and n-butyllithium (0.025 mole) in 30 ml of n-hexane at 0° was added 4.3 g (0.025 mole) of $Ni(CO)_4$ in 50 ml of tetrahydrofuran (THF) at -30°. The reaction mixture was kept at -30° for 15 hrs. under stirring and gradually colored to red-brown. After addition of iodine-methanol solution at -30°, organic reaction products were extracted with diethyl ether.

In the case of $Fe(CO)_5$, the reaction took place at -15° and the decomposition with iodine-methanol was carried out at reflux temperature of the solvents (ca. 55°) (2). The structure of products were determined on the basis of the results of ir, nmr, mass, glc and elemental analysis. The products and yields are summarized in Table I.

Table I

$M(CO)_n$	$M(CO)_n/RLi$	solvent	temp (°C)	products (%)[a]		
				I	II	III
$Ni(CO)_4$	1	THF	-30	10.0	-	trace
	2	THF	-30	8.0	48.0[b]	trace
	1	pyridine	-30	7.5	20.0	trace
$Fe(CO)_5$	1	THF[c]	-15	33.0	-	7.0
	1	pyridine	-15	7.5	-	2.0

I, $C_6H_5C{\equiv}CCO_2CH_3$ II, $C_6H_5C{\equiv}CC{\equiv}CC_6H_5$ III, $C_6H_5CH{=}CHCO_2CH_3$

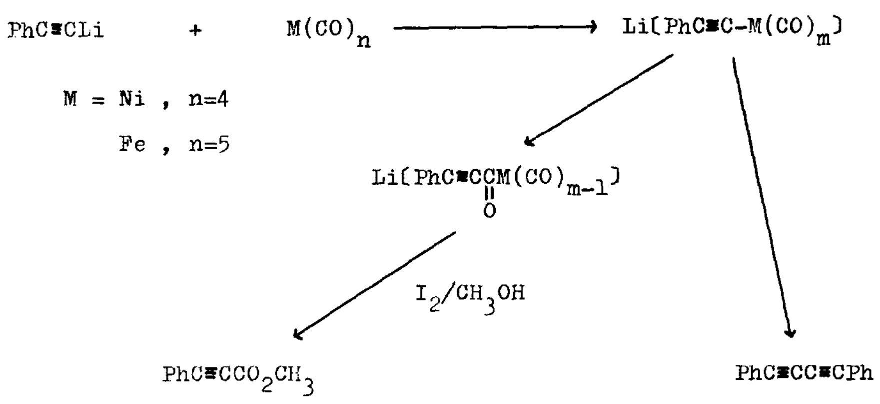
a) Theoretical yield, based on phenylacetylene used, and unreacted lithium phenylacetylide was recovered as phenylacetylene.

b) The reaction of lithium phenylacetylide with iodine-methanol gave only small amount of II.

c) Dimethyl phenylfumalate was also obtained in a yield of 11%.

The results in Table I show a remakable difference in the reaction behavior between the intermediate nickel and iron complex, especially in the formation of diphenylbutadiyne (II); that is, II was produced from nickel complex in moderate yields but in the case of iron complex, esters such as methyl phenylpropiolate, methyl cinnamate and dimethyl phenylfumalate were obtained and the dimer II was no detected. Furthermore, the treatment of the reaction mixture from $Ni(CO)_4$ with bromine, followed by adding methanol, gave II in a yield of 80%, but the same treatment of the reaction mixture from $Fe(CO)_5$ gave unidentified esters instead of II. Hydrolysis of the reaction mixture from $Ni(CO)_4$ gave also the dimeric product II i a yield of 20% and α-phenylacrylic acid (27%). Thus, the treatment of the reaction mixture from $Ni(CO)_4$ with iodine-methanol or bromine was found to favor the formation of the dimeric product II, although the reason has not yet been obvious.

A simple scheme for the formation of ester and dimer is depicted as follows.



It is interesting to note that carbon monoxide was inserted into the bond between transition metal and *sp* carbon to yield methyl phenylpropiolate in despite of the increased π-bonding character of the bond*. During the course of our study, it has been reported that the addition of triphenylphosphine into phenylethynyl-π-cyclopentadienyliron dicarbonyl gave phenylethynyl-π-cyclopentadienyliron carbonyl triphenylphosphine but none of the carbon monoxide inserted products was isolated, while the same treatment of alkyl-π-cyclopentadienyliron dicarbonyl yielded the carbon monoxide inserted product, acyl-π-cyclopentadienyliron carbonyl triphenylphosphine (3). This result shows the difficulty of carbon monoxide insertion into the bond between transition metal and *sp* carbon, so the formation of methyl phenylpropiolate seems to be the first case of carbon monoxide insertion into the bond of transition metal and *sp* carbon. However, the yield of carbon monoxide inserted product decreases considerably compared to the results of the reaction of $Ni(CO)_4$ or $Fe(CO)_5$ with alkyl- or aryllithium compound (1). The following result is especially intriguing; that is, although lithium *p*-toluoylnickel carbonylate which had been prepared by using *p*-tolyllithium and $Ni(CO)_4$ in diethyl ether was reacted with bromine to yield *p*-tolil (73%) (1-b), the reaction

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* It has been found that the distance between nickel and *sp* carbon in $(Et_3P)_2Ni$-$(C\equiv CPh)_2$ is considerably shorter (1.87 Å) than the value calculated as a single bond (2.08 Å) (4).

mixture from lithium phenylacetylide and $Ni(CO)_4$ was decomposed with bromine to give the hydrocarbon dimer II in a yield of 80% instead of α-diketone.

A detailed description of the mechanism and further application will be reported in due course.

References

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2. When the reaction with $Ni(CO)_4$ was carried out above -20°, vigorous evolution of carbon monoxide was observed and, after the treatment of the reaction mixture with iodine-methanol, phenylacetylene was recovered quantitatively. Furthermore, the reaction with $Fe(CO)_5$ above -15° gave unidentified iron complex.
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