CHEMISTRY LETTERS, pp. 831-832, 1974. Published by the Chemical Society of Japan

AN IMPROVED ROUTE TO NICKEL(0) CARBONYL DERIVATIVES WITH TERTIARY PHOSPHINE

Koji TANAKA, Yasuo KAWATA, and Toshio TANAKA
Department of Applied Chemistry, Faculty of Engineering, Osaka University,
Yamada-kami, Suita, Osaka 565

L_2NiCl_2 (L_2= $2Ph_3P$, $2MePh_2P$, $Ph_2PCH_2CH_2PPh_2$, and $Ph_2PCH{=}CHPPh_2$) reacts with carbon monoxide in the presence of MeSNa in ethanol to give $L_2Ni(CO)_2$ and dimethyldisulfide. $(Ph_3P)_2Ni(CO)_2$ is also synthesized by the reaction of $NiCl_2 \cdot 6H_2O$ with Ph_3P, MeSNa, and carbon monoxide. The pathway of these reactions is described.

Bis(tert-phosphine)nickel(0) dicarbonyls are usually prepared by reaction of nickel(0) tetracarbonyl with tertiary phosphine.[1-4] Recently, we have found that phosphine nickel(II) dichlorides react with carbon monoxide in the presence of ammonium N,N-diethylselenocarbamate in tetrahydrofuran at room temperature to give phosphine nickel(0) dicarbonyls.[5]

$$L_2NiCl_2 \quad + \quad 2Et_2NH_2 \cdot SeC(O)NEt_2 \xrightarrow{-2Et_2NH_2Cl} L_2Ni[SeC(O)NEt_2]_2$$

$$\xrightarrow{+2CO} L_2Ni(CO)_2 \quad + \quad Et_2NC(O)SeSeC(O)NEt_2$$

$$L_2 = 2Ph_3P,\ Ph_2PCH{=}CHPPh_2$$

This route to $L_2Ni(CO)_2$, however, requires a sophisticated starting material, the selenocarbamate. In this communication, we describe an improved route to the compounds of this type using sodium methylmercaptide instead of the selenocarbamate.

Two types of the reaction were carried out as follows.

Reaction I. Into a suspension of $(Ph_3P)_2NiCl_2$(1.53 mmol) in ethanol(20 ml) containing aqueous MeSNa(5ml of about 20%), carbon monoxide was passed with stirring for 3 hr at 35°C to force the reaction to completion, which was confirmed by color change from brown to colorless. The resulting precipitate was filtered and recrystallized from a benzene-ethanol mixture to give $(Ph_3P)_2Ni(CO)_2$. In the filtrate dimethyldisulfide was identified by gas chromatography. Other $L_2Ni(CO)_2$ (L_2= $2MePh_2P$, $Ph_2PCH_2CH_2PPh_2$, and $Ph_2PCH{=}CHPPh_2$) was similarly prepared by using the corresponding L_2NiCl_2. All the products were obtained in 60-70% yields.

Reaction II. Into a suspension of $NiCl_2 \cdot 6H_2O$(2.10 mmol) and Ph_3P(4.20 mmol) in ethanol(20 ml) containing aqueous MeSNa(5 ml), carbon monoxide was passed for 6-7 hr at 35°C. Precipitates which appeared were filtered and recrystallized from benzene-ethanol to give $(Ph_3P)_2Ni(CO)_2$.

Table 1 summarizes the properties and analysis of the products.

The reaction of L_2NiCl_2 with carbon monoxide in an ethanolic solution of KOH did not afford any nickel(0) carbonyl derivatives. In view of this result, the reaction I is not likely to proceed via a metal-hydride complex as the intermediate, which was suggested in the reaction of $(Ph_3P)_2PtCl_2$ with carbon monoxide and KOH, leading platinum(0) carbonyl derivatives.[7] By analogy with the reaction of

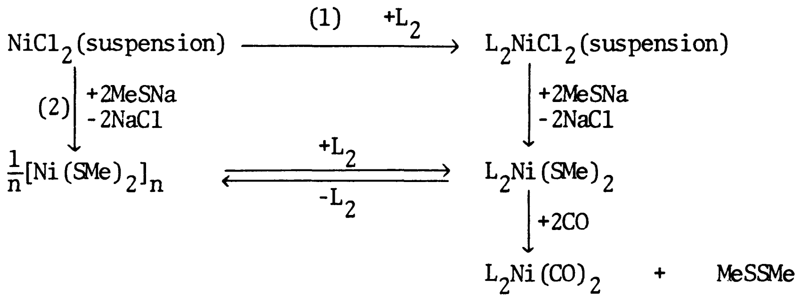
Table 1. Properties and Analysis[a)]

Compound	Mp(°C)	Color	%C %H	ν(CO)[b)]
$(Ph_3P)_2Ni(CO)_2$	205-206[c)]	Cream	71.44 4.62 (71.39) (4.73)	1999, 1936
$(MePh_2P)_2Ni(CO)_2$	105-107	Yellow	64.13 5.06 (65.28) (5.09)	1993, 1934
$Ph_2PCH_2CH_2PPh_2Ni(CO)_2$	137-139[d)]	White	65.53 4.60 (65.54) (4.71)	1998, 1936
$Ph_2PCH{=}CHPPh_2Ni(CO)_2$	158-160[e)]	Yellow	65.57 4.40 (65.79) (4.34)	2007, 1950

a) Calculated values in parenthesis. b) Nujol mulls. c) Lit. 206-209°C.[6)]
d) Lit. 138-140°C.[1)] e) Lit. 154-157°C.[3)]

L_2NiCl_2 with carbon monoxide in the presence of the selenocarbamate,[5)] the reaction I is assumed to involve a reductive elimination of the SMe group of $L_2Ni(SMe)_2$, which is considered to be formed as an intermediate.

There are two possible pathways, (1) and (2), in the reaction II as follows.



The path (1) would proceed by coordination of the phosphine ligand to $NiCl_2$ more or less dissolved in ethanol containing aqueous MeSNa, which is followed by the reaction I. It was previously reported that a nickel(II) salt reacted with carbon monoxide in ethanol containing EtSNa to form $Ni(SEt)_2$ as the intermediate, which resulted in $Ni(CO)_4$.[8)] Thus, the path (2) is also possible in the reaction II.

References

1) J. Chatt and F. A. Hart, J. Chem. Soc., 1378 (1960).
2) R. B. King, Organometallic Synthesis, 1, 181 (1965).
3) R. B. King and C. A. Eggers, Inorg. Chim. Acta, 2, 33 (1968).
4) Recently, triphenylphosphite nickel(0) carbonyls, $[(PhO)_3P]_3Ni(CO)$ and $[(PhO)_3P]_2Ni(CO)_2$, were prepared by reaction of nickel(II) acetylacetonate, $(PhO)_3P$, Et_3Al, and CO; J. R. Olechowski, J. Organometal. Chem., 32, 269 (1971).
5) K. Tanaka and T. Tanaka, Inorg. Nucl. Chem. Lett., 10, 605 (1974).
6) W. Reppe and W. J. Schweckendick, Ann. 560, 104 (1948).
7) J. Chatt and P. Chini, J. Chem. Soc., A, 1538 (1970).
8) W. Manchot and H. Gall, Ber., 62, 678 (1929).

(Received May 24, 1974)