CHEMISTRY LETTERS, pp. 1217-1220, 1976. Published by the Chemical Society of Japan

SELECTIVE FORMATION OF KETONE, DIKETONE AND ALDEHYDE BY THE CO INSERTION INTO NICKEL-ALKYL BONDS OF DIALKYLNICKEL COMPLEXES. A NOVEL NICKEL-CATALYZED SYNTHESES OF KETONES AND TERTIARY ALCOHOLS FROM GRIGNARD REAGENTS, ARYL HALIDES, AND CARBON MONOXIDE

Takakazu YAMAMOTO, Teiji KOHARA, and Akio YAMAMOTO
Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Ookayama, Meguro, Tokyo 152

Reaction of dialkylnickel complexes, NiR_2L_2 (R = CH_3, C_2H_5, C_3H_7; L = 1/2(2,2′-bipyridine), 1/2[1,2-bis(diphenylphosphino)ethane], triethylphosphine) with carbon monoxide give ketones, diketones, and aldehydes depending on the reactivity of the dialkylnickel complexes and the reaction temperature. Nickel complexes NiY_2L_2 (Y = halogen or alkyl; L = ligand) catalyze formation of ketones and tertiary alcohols from Grignard reagents, aryl halides, and carbon monoxide.

Insertion of carbon monoxide into a transition metal-carbon σ-bond constitutes a crucial elementary step in industrially important processes such as carbonylation of olefins1) and methanol2) and in syntheses of ketones and diketones by reactions of transition metal carbonyls with alkyl(aryl) halides3) or with non-transition metal alkyls.4) However, fundamental studies on insertion of carbon monoxide into transition metal-alkyl bonds of isolated transition metal alkyls and on the reactivities of the transition metal acyls formed by the insertion of carbon monoxide are relatively limited.5,6) In this paper we report the insertion of carbon monoxide into the nickel-alkyl bonds of isolated dialkylnickel complexes to produce ketones, diketones, and aldehydes depending on the nature of the nickel-alkyl and -acyl bonds, and application of the results to a catalytic reaction.

Table 1 shows the products in the reactions of NiR_2(bpy) (bpy = 2,2'-bipyridine), NiR_2(dpe) (dpe = 1,2-bis(diphenylphosphino)ethane), and $Ni(CH_3)_2(PEt_3)_2$ (PEt_3 = triethylphosphine) with CO. When dehydrated CO was bubbled into a tetrahydrofuran (5 ml) solution of $Ni(C_2H_5)_2$(bpy) (0.42 g, 1.5 mmol) at -78°C, the color of the solution immediately changed from deep green ($Ni(C_2H_5)_2$(bpy)) to deep red ($Ni(CO)_2$(bpy)) and one mole of diethyl ketone per one mole of $Ni(C_2H_5)_2$(bpy) was formed as determined by NMR spectroscopy and gas chromatography. Similar results were obtained by employing acetone or diethyl ether as the solvent and at room temperature. The red residue which remained after evaporation of the solvent was crystallized from acetone and idenfitied as $Ni(CO)_2$(bpy) from IR spectrum7) and elemental analysis. The reactions of $Ni(C_3H_7)_2$(bpy) with CO also proceeded smoothly at -78°C and room temperature to give dipropyl ketone.

In contrast to the reactions of $Ni(C_2H_5)_2$(bpy) and $Ni(n\text{-}C_3H_7)_2$(bpy) with CO, it took long time to complete the reactions of $Ni(CH_3)_2$(bpy) with CO and products varied depending on the reaction temperature. At -45°C or below 2,3-butanedione was produced exclusively, whereas at 13°C or above acetone was the main product. At around 0°C

Table 1. Products in the Reaction of Dialkylnickel Complexes with CO

Compound[a]	Solvent[b]	Temp.(°C)	Time	Products (yield, %)
$Ni(C_2H_5)_2(bpy)$	THF	-78	A few min	$C_2H_5COC_2H_5$(100), $Ni(CO)_2(bpy)$
"	"	r.t.	A few min	$C_2H_5COC_2H_5$(90), $Ni(CO)_2(bpy)$(50)[c]
$Ni(C_3H_7)_2(bpy)$	Ether	-78	A few min	$C_3H_7COC_3H_7$(90), $Ni(CO)_2(bpy)$
"	Acetone	r.t.	A few min	$C_3H_7COC_3H_7$(80), $Ni(CO)_2(bpy)$
$Ni(CH_3)_2(bpy)$	Ether	-78	1 day	$CH_3COCOCH_3$(90)
"	"	-45	5 hr	$CH_3COCOCH_3$(90)
"	"	-17	1 day	CH_3COCH_3(10), $CH_3COCOCH_3$(70)
"	"	1	7 hr	CH_3COCH_3(40), $CH_3COCOCH_3$(40)
"	"	13	3 hr	CH_3COCH_3(90)
$Ni(CH_3)_2(dpe)$	"	-78	12 hr	CH_3COCH_3(8), $CH_3COCOCH_3$(61), $Ni(CO)_2(dpe)$
"	"	r.t.	48 hr	CH_3COCH_3(73), $Ni(CO)_2(dpe)$(100)
$Ni(CH_3)_2(PEt_3)_2$	"	-78	10 min	CH_3COCH_3(98), $Ni(CO)_2(PEt_3)_2$(89)
"	"	r.t.	90 min	CH_3COCH_3(93), $Ni(CO)_2(PEt_3)_2$
$Ni(C_2H_5)_2(dpe)$	THF	-78	48 min	C_2H_5CHO(37), C_2H_4, $Ni(CO)_2(dpe)$
"	"	r.t.	3 hr	C_2H_5CHO(52), C_2H_4(64)

a. bpy = 2,2'-bipyridine, dpe = 1,2-bis(diphenylphosphino)ethane.

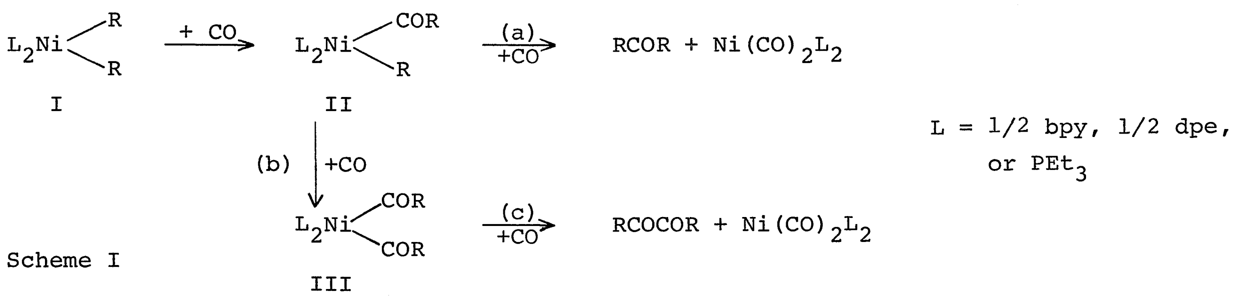
b. THF = tetrahydrofuran, ether = diethyl ether.

c. The yield after recrystallization. The NMR spectrum showed the formation of equimolar amounts of $Ni(CO)_2(bpy)$ and $C_2H_5COC_2H_5$.

both acetone and 2,3-butanedione were obtained. $Ni(CO)_2(bpy)$ was isolated from the reaction mixture after the completion of the reaction at higher temperatures, but at lower temperatures initially formed $Ni(CO)_2(bpy)$ was converted to $Ni(CO)_4$ and bpy on prolonged contact with CO.

Reactions of $Ni(CH_3)_2(dpe)$ with CO gave analogous results to those of the reactions of $Ni(CH_3)_2(bpy)$ with CO, although formation of a small amount of acetone at -78°C was observed. However, reactions of $Ni(CH_3)_2(PEt_3)_2$ with CO gave somewhat different results. The reaction proceeded smoothly even at -78°C and the product was acetone even at the temperature.

The ketone and diketone formation most probably proceeds via CO insertion into the Ni-R bond(s) (Scheme 1). In fact in some alkylnickel complexes the CO inserted acylnickel complexes have been isolated,6) and formation of acetone from isolated platinum complexes having both methyl and acetyl groups have been reported.8)

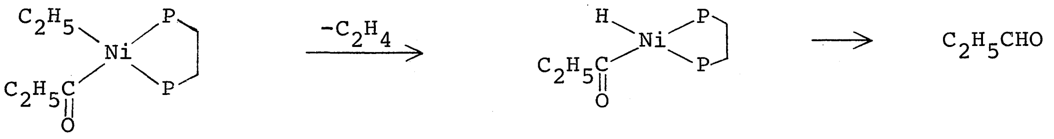


Scheme I

Formation of methyl ethyl ketone on addition of C_2H_5Br into the reaction system in the course of the reaction of $Ni(CH_3)_2(bpy)$ with CO supports the intermediacy of the acylnickel complexes. Furthermore, absence of 2,3-pentanedione in the products obtained on addition of C_2H_5Br into the reaction system excludes the intermediacy of a doubly CO inserted species $CH_3COCONi$ through which $CH_3COCOCH_3$ might be produced.

The product distribution between ketones and diketones may be accounted for in terms of the strengths of either or both of the alkyl-nickel and acyl-nickel bonds in the intermediate II. When they are weak, the reductive elimination of R and COR from II (reaction (a)) will take place even at -78°C. On the contrary, when they are strong, the reductive elimination will not occur at low temperatures and further insertion into another Ni-R bond (reaction (b)) will proceed slowly to give diketone through the reaction (c). If we compare the product distribution given in Table 1 with the order of the thermal stability in $NiR_2(bpy)$; $Ni(C_3H_7)_2(bpy)$ (decomposition point, 95°C) $<$ $Ni(C_2H_5)_2(bpy)$ (100°C) $<$ $Ni(CH_3)_2(bpy)$ (160°C),[9] and in the dimethylnickel complexes; $Ni(CH_3)_2(PEt_3)_2$ (40°C)[10] $<$ $Ni(CH_3)_2(dpe)$ (130°C)[11] $<$ $Ni(CH_3)_2(bpy)$ (160°C), we may conclude that the strength of the Ni-R bond rather than that of the Ni-COR bond predominantly determines the ease of the reductive elimination.

Reaction of $Ni(C_2H_5)_2(dpe)$ with CO takes a quite different course producing propionaldehyde and ethylene. β-Elimination from $C_2H_5Ni(COC_2H_5)(dpe)$ and reductive elimination of propionyl and hydrido ligands accounts for the results.



The difference in the reactivities between $C_2H_5Ni(COC_2H_5)(bpy)$ and $C_2H_5Ni(COC_2H_5)$(dpe) may be related to the difference in the course of thermolysis between $Ni(C_2H_5)_2$(bpy) and $Ni(C_2H_5)_2(dpe)$; the former gives mainly the coupling product C_4H_{10} on thermolysis,[9] whereas the latter affords the disproportionation products, C_2H_6 and C_2H_4,[10] suggesting that the β-elimination in $Ni(C_2H_5)_2(dpe)$ proceeds much more easily than that in $Ni(C_2H_5)_2(bpy)$. The results of the reaction of $Ni(C_2H_5)_2(dpe)$ with CO are consistent with the assumption that the reactivity of the Ni-R bond in the intermediate II determines the course of the reaction.

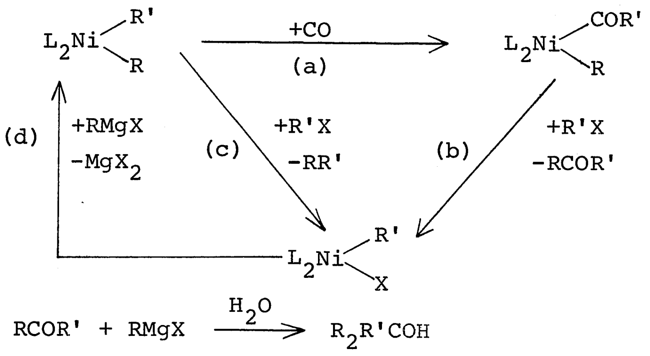
The ease of the formation of ketones by the reactions of dialkylnickel complexes with CO at room temperature prompted us to develop a new synthetic method of ketones and tertiary alcohols from Grignard reagent RMgX, alkyl(aryl) halide R'X and CO by using nickel complexes as the catalyst.

$$RMgX + R'X + CO \xrightarrow{NiY_2L_2} RCOR' + R_2R'COH \quad (Y = \text{halogen or alkyl})$$

When 260 mmol of C_6H_5MgBr and 190 mmol of C_6H_5Br were allowed to react in diethyl ether under reflux for 24 hr in the presence of 0.5 mmol of $Ni(C_2H_5)_2(bpy)$ with bubbling of CO, 58 mmol of diphenyl ketone, 39 mmol of triphenylmethyl alcohol, and 31 mmol of biphenyl were obtained after treatment of the reaction mixture with H_2O.

A similar reaction using 58 mmol of 4-methylphenylmagnesium bromide, 47 mmol of 4-methylphenyl bromide and 0.7 mmol of $NiCl_2(bpy)$ gave 10 mmol of di(4-methylphenyl) ketone, 15 mmol of tri(4-methylphenyl)methyl alcohol, and 9 mmol of 4,4'-dimethylbiphenyl. $NiCl_2$(dpe) showed comparable catalytic activities for the syntheses of ketones and tertiary alcohols, whereas $NiBr_2$(triphenylphosphine)$_2$ had lower catalytic activities than these nickel complexes having bpy or dpe.

The following catalytic cycles account for the results.



Tamao, Kumada and coworkers, and Kochi et al. have already proposed the cycle comprising the steps (c) and (d) to explain the catalytic formation of RR' from RMgX and R'X in the presence of nickel complexes.[12)]

References

1) (a) R. F. Heck, "Organotransition Metal Chemistry, a Mechanistic Approach," Academic Press, New York, 1974.
2) J. F. Roth, J. H. Craddock, A. Hershman, and F. E. Paulik, Chem. Tech., 1971, 600.
3) (a) J. Schwartz, D. W. Hart, and J. L. Holden, J. Am. Chem. Soc., 94, 9269 (1972); (b) J. P. Collman, Acc. Chem. Res., 8, 342 (1975); (c) M. P. Cooke Jr. and R. M. Parlaman, J. Am. Chem. Soc., 97, 6863 (1975); (d) Y. Watanabe and Y. Takegami, Kagaku (Chemistry), 31, 678 (1976).
4) (a) J. D. Cotton, S. A. Knox, I. Paul, and F. G. A. Stone, J. Chem. Soc. A, 264 (1967); (b) D. Seyferth and R. J. Spohn, J. Am. Chem. Soc., 91, 3037 (1969); (c) Y. Hirota, M. Ryang, and S. Tsutsumi, Tetrahedron Lett., 19, 1531 (1971).
5) (a) H. Masai, K. Sonogashira, and K. Hagihara, Bull. Chem. Soc. Jpn., 41, 750 (1968); (b) G. Booth and J. Chatt, J. Chem. Soc. A, 1966, 634; (c) A. Yamamoto, A. Miyashita, T. Yamamoto, and S. Ikeda, Bull. Chem. Soc. Jpn., 45, 1583 (1972).
6) (a) H. F. Klein, Angew. Chem., 85, 403 (1973); (b) T. Saruyama, T. Yamamoto, and A. Yamamoto, Bull. Chem. Soc. Jpn., 49, 546 (1976).
7) R. S. Nyholm and L. N. Short, J. Chem. Soc., 1953, 2670.
8) (a) J. D. Ruddick, and B. L. Shaw, J. Chem. Soc. A, 2969 (1969); (b) M. P. Brown, R. J. Puddephatt, C. E. E. Upton, and S. W. Lavington, J. Chem. Soc. Dalton, 1613 (1974).
9) T. Yamamoto, A. Yamamoto, and S. Ikeda, J. Am. Chem. Soc., 93, 3350 (1971).
10) (a) M. Takamatsu, Ms. S. Thesis at Tokyo Institute of Technology; (b) A. Yamamoto et al., "Organotransition-Metal Chemistry," (Ed., Y. Ishii and M. Tsutsui) p,281, Plenum Press, New York (1975).
11) M. L. H. Green and M. H. Smith, J. Chem. Soc., (A), 1971, 639.
12) (a) K. Tamao, K. Sumitani, Y. Kiso, M. Zembayashi, A. Fujioka, S. Kodama, I. Nakajima, A. Minato, and M. Kumada, Bull. Chem. Soc. Jpn., 49, 1958 (1976); (b) D. G. Morrell and J. K. Kochi, J. Am. Chem. Soc., 97, 7262 (1975).

(Received September 11, 1976)