Nickel-Complex-Promoted Carboxylation of Haloarenes Involving Insertion of CO2 into NiII-C Bonds

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Nickel-Complex-Promoted Carboxylation of Haloarenes Involving Insertion of CO_2 into Ni^{II}—C Bonds

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Summary: NiBr(Ph)(bpy) reacts with CO_2 (1 atm) in DMF to cause carboxylation of the phenyl ligand. Acidolysis of the reaction mixture gives a mixture of benzoic acid (55%/Ni) and biphenyl (21%/Ni). Reaction of bromobenzene with CO_2 in the presence of a stoichiometric amount of $Ni(cod)_2$ (cod = 1,5-cyclooctadiene) and 2,2′-bipyridine in DMF also gives a mixture of benzoic acid and biphenyl whose yields depend on the reaction conditions, such as the solvent, concentration of the Ni complex, and the presence or absence of bpy ligand. Carboxylation reactions of bromobenzene and of p-bromotoluene in DMF give benzoic acid and p-methylbenzoic acid in 54% and 79% yields, respectively, while reactions in less polar solvents such as THF and benzene give biaryl exclusively.

Table 1. Reaction of Haloarenes with CO_2 in the Presence of $Ni(cod)_2$

	conditions					yield of the product (%)[a]	
run no.	Ar—X	$[Ni(cod)_2]$ (M)	[Ar—X]/ $[Ni(cod)_2]$	solvent	L[b]	ArC-OOH	Ar—Ar
1	PhBr	0.030	1.0	DMF	bpy	54	9
2	PhBr	0.120	1.0	DMF	bpy	35	26
3	PhBr	0.030	1.0	DMF		3	9
4	PhCl	0.030	1.0	DMF	bpy	51	0
5	PhI	0.030	1.0	DMF	bpy	25	10
6	PhBr	0.120	2.0	DMF	bpy	17	50
7	PhBr	0.120	2.0	DMF	PPh_3	5	69
8	PhBr	0.120	2.0	DMF		4	81
9	PhBr	0.180	2.0	THF	bpy	0	81
10	PhBr	0.180	2.0	benzene	bpy	0	83
11	*p*-MeC_6H_4Br	0.030	1.0	DMF	bpy	79	5
12	*p*-$MeOC_6H_4Br$	0.030	1.0	DMF	bpy	54	*c*
13	*p*-FC_6H_4Br	0.030	1.0	DMF	bpy	33	*c*

[a] Yields based on the amount of $Ni(cod)_2$ used. [b] $[bpy]/[Ni(cod)_2] = 1.0$, $[PPh_3]/[Ni(cod)_2] = 2.0$. [c] Not measured.

Introduction

Insertion of CO_2 into a transition-metal−carbon bond is a crucial step in the carboxylation of organic compounds promoted by transition-metal complexes.[1] Organonickel(0) complexes are effective in cooligomerization of CO_2 with alkyne, alkene, and diene to give the corresponding carboxylic acid or lactone[2−6] through coupling of π-coordinated unsaturated molecules with CO_2 in a concerted manner.[7,8] However, there are fewer reports on Ni-complex-promoted carboxylation of organic molecules involving CO_2 insertion into a Ni—C bond. (η^3-Allyl)nickel(II) complexes and highly strained nickelacyclopentane undergo facile insertion of CO_2 into the Ni—C bond to give the corresponding lactone.[9−11] The nickelacyclopentane $(Me_3P)_2\overline{Ni{-}C_6H_4{-}C(Me)_2{-}CH_2}$ also undergoes insertion of CO_2 into the Ni—aryl bond preferentially to give the corresponding seven-membered oxanickelacycle.[12] $NiEt_2(bpy)$ reacts with CO_2 to give diethyl ketone and a nickel propionate complex, possibly through initial insertion of CO_2 into the Ni—ethyl bond.[13] Recently, electrocarboxylation of bromobenzene catalyzed by $NiCl_2(dppp)$ (dppp = 1,3-bis(diphenylphosphino)propane) was reported to give benzoic acid. This reaction is believed to involve insertion of CO_2 into the Ni—C bond of an arylnickel(I) intermediate to give the corresponding nickel(I) benzoate complex rather than insertion into a Ni^{II}—phenyl bond.[14] Reaction of monoarylnickel(II) complexes, Ni(Ph)L-(PPh_3) (L = $acac^-$, $Ph_2P{-}CH{-}CPh{-}O^-$, $Ph_2As{-}CH{-}C{-}Ph{-}O^-$), with CO_2 in toluene was reported by Behr et al. to give CO_2 insertion products only in small amounts (<3.3%).[15] They also observed that $NiCl(Ph)(PPh_3)_2$ does not undergo the carboxylation at all. Here we report that the monoarylnickel(II) complex Ni(Br)Ph-(bpy) reacts easily with CO_2 in DMF to give benzoic acid. The related $Ni(cod)_2$-promoted carboxylation of haloare-

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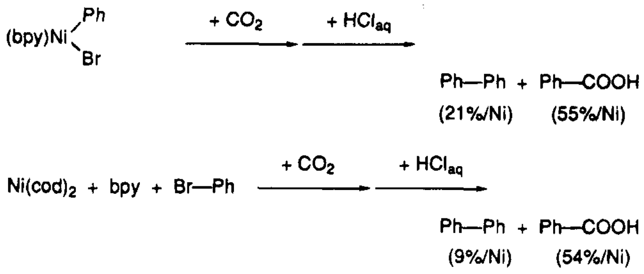
Scheme 1



nes to give the corresponding carboxylic acids in moderate or good yields is also described.

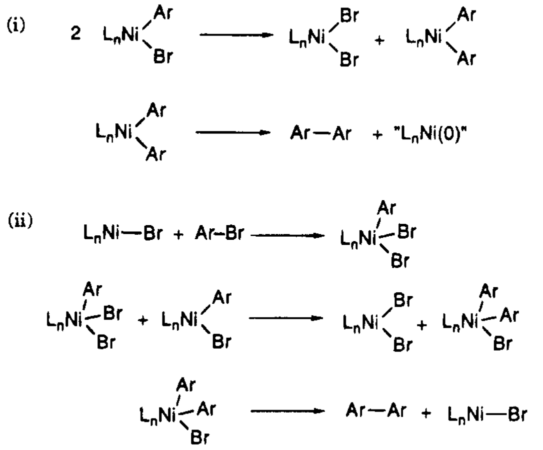
Results and Discussion

NiBr(Ph)(bpy) reacts with CO_2 in DMF to give a mixture of biphenyl (21%/Ni) and benzoic acid (55%/Ni), the latter of which is formed by acidolysis of the reaction mixture. The IR spectrum of the product before acidolysis shows peaks at 1690 and 1400 cm^{-1}, which are assigned to ν_{as}(COO) and ν_s(COO) vibrations of the benzoate group coordinated to the Ni center. The results indicate that CO_2 insertion into the Ni—phenyl bond occurs during the reaction, although neither isolation nor more detailed characterization of the nickel benzoate product was feasible.

Since NiBr(Ph)(bpy) is obtained by oxidative addition of bromobenzene to $Ni(cod)_2$ in the presence of bpy, the above results suggest that direct carboxylation of bromobenzene could be achieved by using the $Ni(cod)_2$—bpy system. Reaction of $Ni(cod)_2$—bpy with bromobenzene under CO_2 in DMF actually gives a mixture of biphenyl and benzoic acid. Table 1 summarizes results of the carboxylation reaction under various conditions. Reactions of equimolar amounts of bromobenzene and of chlorobenzene with $Ni(cod)_2$ in the presence of bpy under CO_2 give benzoic acid in 54% and 51% yields, respectively, while reaction of iodobenzene gives the product in lower yield (25%) (runs 1, 4, and 5). *p*-Bromotoluene reacts similarly with CO_2 to give *p*-methylbenzoic acid in 79% yield (run 11). Carboxylation of *p*-bromoanisole and of *p*-bromofluorobenzene gives the corresponding carboxylic acids in 54% and 33% yields, respectively (runs 12 and 13). Yields of the carboxylation products are not directly related to the electron-releasing or -withdrawing nature of the para substituent of the substrates. It seems to be partly due to the fact that the reaction rate of concomitant biaryl formation from aryl bromides under similar conditions is seriously influenced by substituents of the aryl groups.[16] The reactions without bpy and with PPh_3 ligand give almost negligible amounts of the carboxylation product (runs 3, 7, and 8).

Concomitant formation of biaryl is observed in almost all the carboxylation reactions. $Ni(cod)_2$-promoted dehalogenative coupling of bromoarene in the absence of CO_2 was reported to give the corresponding biaryl in high yields[17] and has been recently extended to polycondensation of dibromoarenes to give polyarenes.[18] A mechanistic study on the reaction using the $Ni(cod)_2$—bpy system in DMF has revealed that the C—C coupling reaction proceeds through disproportionation of the initially formed NiBr(Ar)(bpy) to give $NiBr_2$(bpy) and $NiAr_2$(bpy), the latter of which is responsible for reductive elimination of biaryl (path i in Scheme 2).[16] Another C—C bond-forming reaction involving Ni(I) and Ni(III) intermediates (path ii in Scheme 2) is operative in the reactions in less polar solvents such as THF and toluene[19] but does not occur in DMF because it is much slower than the reaction through path i in the polar solvent.[1b] Formation of biaryl in the reaction under CO_2 in DMF is also attributed to coupling of bromobenzene through the disproportionation pathway because biphenyl is formed in 26% yield in the reaction using $Ni(cod)_2$ at 0.120 M (run 2) and in 9% yield in the reaction using the complex at 0.030 M (run 1).[20]

Scheme 2. Plausible Reaction Pathways for Ni(0)-Complex-Promoted Coupling of Bromoarene (i) in DMF and (ii) in Toluene



The reactions of bromobenzene with CO_2 in THF and in benzene give biphenyl exclusively (runs 9 and 10). Carboxylation is inhibited under the conditions because coupling of bromobenzene in these solvents is slower than that in DMF. Thus, DMF used as solvent enhances both dehalogenative coupling and carboxylation of bromobenzene promoted by the Ni(0) complex. The significant acceleration of the carboxylation by DMF suggests a reaction pathway involving a cationic intermediate such as $[Ni(Ar)(bpy)(DMF)]^+Br^-$ that undergoes insertion of a CO_2 molecule into the Ni—C bond. The cationic intermediate seems to be formed in considerable amounts in the reaction mixture, since $NiBr_2$(bpy) in DMF is reported to be completely dissociated into $[NiBr(bpy)(sol)]^+$ and Br^-, as revealed by calorimetric measurement of ternary complex formation among Ni^{2+}, Br^-, and bpy in DMF.[21] Scheme 3 summarizes a

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[20] The difference in the results of runs 1 and 2 in Table 1 seems to be closely related to the rate of disproportionation under the conditions. The concentration of $Ni(cod)_2$ may influence the rate of the carboxylation under 1 atm of CO_2 to some extent because the molar ratio of CO_2 and the Ni complex in the solution changes depending on the conditions. However, carboxylation using $Ni(cod)_2$ at 0.030 M under 10 atm of CO_2 gives the same results as the reaction under 1 atm of CO_2.

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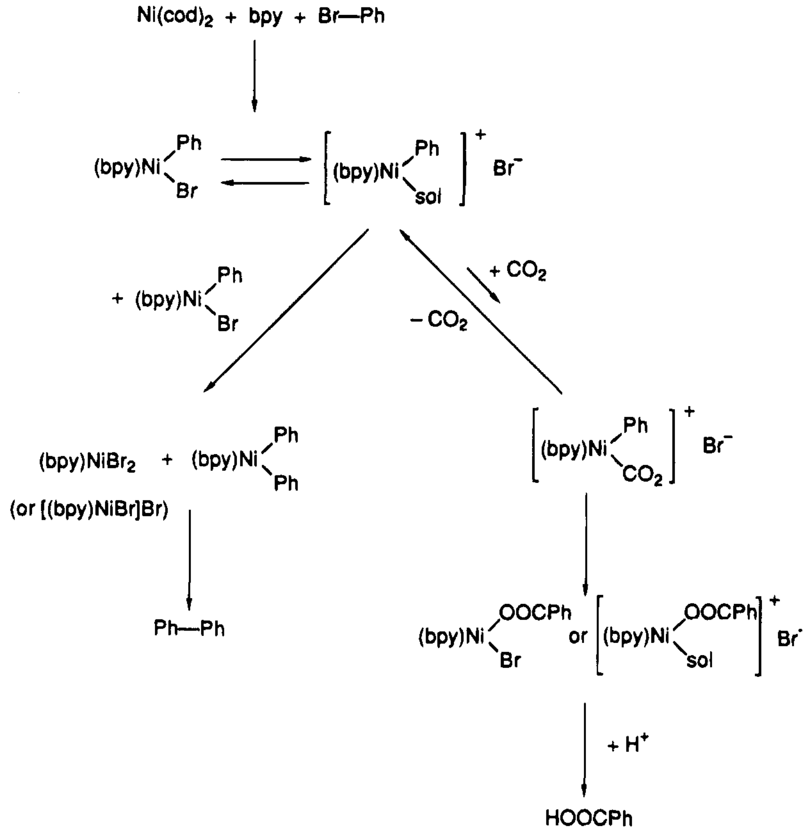
Scheme 3. Proposed Mechanism for Ni(cod)$_2$-Promoted Coupling and Carboxylation of Bromobenzene in DMF



proposed mechanism of the carboxylation and coupling of bromobenzene involving [Ni(Ph)(bpy)(DMF)]$^+$Br$^-$ as the intermediate common to both reactions. [Ni(Ph)(bpy)(DMF)]$^+$Br$^-$ undergoes CO$_2$ insertion into the Ni—C bond or intermolecular aryl ligand transfer to give NiAr$_2$(bpy), depending on the concentrations of the Ni complex in the reaction mixture. The reactions will lead to formation of benzoic acid and of biphenyl, respectively. Facile CO$_2$ insertion into the Ni—Ph bond of the cationic intermediate can be attributed to a coordinated solvent molecule which is easily replaced by a CO$_2$ molecule and a nickel center with Lewis acidity higher than that of neutral Ni(II) complexes.

In summary, Ni(cod)$_2$—bpy-promoted carboxylation of bromoarene is achieved by using DMF as the solvent. The reaction proceeds through smooth insertion of CO$_2$ into Ni^{II}—Ph bond, while the insertion was considered to be almost negligible in previous studies.

Experimental Section

Materials and Measurement. All the manipulations of the nickel complexes were carried out under a nitrogen or CO$_2$ atmosphere using standard Schlenk techniques. The solvents were dried by the usual method, distilled, and stored under nitrogen. Ni(cod)$_2$ and NiBr(Ph)(bpy) were prepared according to the literature.[22,23] IR spectra were recorded on a JASCO-IR810 spectrophotometer. Gas chromatograms were recorded on a Shimadzu GC-8A equipped with a 2 m column packed with Unisole 10T-H$_3$PO$_4$. Yields of the products were determined by GC using 4,4′-dimethylbiphenyl or biphenyl as the internal standard.

Reaction of NiBr(Ph)(bpy) with CO$_2$. To a Schlenk flask containing NiBr(Ph)(bpy) (77 mg, 0.21 mmol) was added CO$_2$-saturated DMF (7 mL) under a CO$_2$ stream. Heating the resulting mixture resulted in a change of the color from dark red to dark brown in the first 15 min and then into pale green. After 15 h of reaction GC analysis of the solution showed formation of biphenyl (6.7 mg, 21%/Ni). DMF was then evaporated to give a green residue which was decomposed by aqueous HCl. THF (0.5 mL) was added to extract the organic products, from which benzoic acid was detected by GC (14 mg, 55%).

Reaction of Haloarenes with CO$_2$ in the Presence of Ni(cod)$_2$. To a Schlenk flask containing Ni(cod)$_2$ (170 mg, 0.62 mmol) and 2,2′-bipyridine (97 mg, 0.62 mmol) under a CO$_2$ stream was added DMF (21 mL) and then bromobenzene (97 mg, 0.62 mmol). Heating the reaction mixture at 60 °C caused an immediate color change of the reaction mixture to black. After further heating for 10 h, GC analysis of the solution showed formation of biphenyl (8.6 mg, 9%/Ni). DMF was then evaporated to give a green residue, which was decomposed by aqueous HCl. THF (0.5 mL) was added to extract the organic products, from which benzoic acid was detected by GC (53 mg, 54%).

Reactions under other conditions and the reactions of *p*-bromotoluene, *p*-bromoanisole, and *p*-bromofluorobenzene were carried out analogously.

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