Lewis acid promoted, cobalt-catalyzed, and phase-transfer-catalyzed carbonylation of iodo arenes and iodo alkanes

Jong Tae Lee, and Howard Alper

Organometallics, **1990**, 9 (12), 3064-3066• DOI: 10.1021/om00162a017 • Publication Date (Web): 01 May 2002

Organometallics is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

5 H), 2.60–1.91 (m, 6 H), 1.79–1.43 (m, 4 H), 1.33–1.12 (m, 4 H), 1.12–0.97 (m, 2 H), 0.80 (t, 3 H, $J = 7.3$ Hz); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 211.8, 143.1, 128.5, 128.2, 126.3, 51.44, 46.93, 44.38, 41.36, 32.25, 29.82, 28.83, 25.20, 22.65, 15.22; MS (EI) 41 (25), 55 (11), 69 (11), 91 (100), 97 (17), 105 (9), 115 (4), 147 (25), 244 (3); exact mass calcd for $C_{17}H_{24}O$ 244.1827, obsd 244.1824.

1-Cyclohexyl-2-phenylhexanone (34). The (α-butylbenzyl)copper reagent (6.3 mmol) was prepared as indicated in the synthesis of **33**. Cyclohexanecarbonyl chloride (0.66 g, 4.5 mmol) was then added at −70 °C. The reaction mixture was then warmed to −20 °C, stirred overnight, and worked up as usual. Purification of the residue by flash chromatography (ether:hexane = 1:19) afforded 1.07 g (92% yield) of **34**: IR (neat) 2934 (s), 2854 (s), 1710 (s), 1493 (m), 1485 (m), 1452 (s), 1370 (m), 1144 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.33–7.19 (m, 5 H), 3.76 (t, 1 H, $J = 7.5$ Hz), 2.32–2.42 (m, 1 H), 2.07–1.58 (m, 6 H), 1.49–1.07 (m, 10 H), 0.84 (t, 3 H, $J = 6.9$ Hz); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 213.5, 139.5, 128.7, 128.4, 127.0, 57.31, 50.28, 32.74, 29.93, 29.15, 28.27, 25.93, 25.83, 25.34, 22.66, 13.90; MS (EI) 41 (12), 55 (19), 83 (100), 91 (37), 104 (4), 111 (34), 146 (5), 202 (3), 258 (2); exact mass calcd for $C_{18}H_{26}O$ 258.1984, obsd 258.1977.

3,4-Diphenyl-4-oxobutyronitrile (35). (α-(2-Cyanoethyl)-benzyl)zinc chloride was prepared from α-(2-cyanoethyl)benzyl chloride (**11**, 1.08 g, 6 mmol) according to procedure C. GLC analysis showed complete conversion in 22 h with 5% Wurtz coupling. After the transmetalation to the corresponding copper reagent by the addition of $CuCN\cdot 2LiCl$ (as indicated above), benzoyl chloride (0.61 g, 4.3 mmol) was added at −60 °C. The reaction mixture was then warmed to −20 °C, stirred for 8 h, and worked up as usual. Purification of the residue by flash chromatography (hexane:ethyl acetate = 9:1) afforded 0.89 g (83% yield) of **35**: IR (Nujol) 2954 (s), 2926 (s), 2855 (s), 2235 (m), 1677 (s), 1452 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.95 (d, 2 H, $J = 8.4$ Hz), 7.47–7.25 (m, 8 H), 4.73 (t, 1 H, $J = 7.0$ Hz), 2.42–2.36 (m, 2 H), 2.26–2.16 (m, 2 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 198.2, 137.6, 136.1, 133.3, 129.4, 128.8, 128.6, 128.2, 127.8, 119.3, 51.95, 29.02, 15.14; MS (EI) 41 (8), 49 (17), 65 (4), 77 (8), 84 (12), 91 (28), 104 (19), 117 (20), 122 (4), 128 (7), 144 (100), 157 (5), 171 (11), 183 (8), 211 (6), 257 (2); exact mass calcd for $C_{16}H_{19}NO_2$ 257.1416, obsd 257.1405.

Ethyl 6-Cyano-4-phenyl-2-methylenehexanoate (36). The (α-(2-cyanoethyl)benzyl)copper reagent (5.4 mmol) was prepared as indicated in the synthesis of **35**. Ethyl α-(bromomethyl)acrylate (0.83 g, 4.3 mmol) was then added at −70 °C. The reaction mixture was allowed to warm slowly to 0 °C and then worked up as usual. Purification of the residue by flash chromatography (CH_2Cl_2:hexane = 3:2) afforded 1.02 g (92% yield) of **36**: IR (neat) 2934 (m), 2249 (m), 1714 (s), 1453 (m), 1326 (m), 1304 (m), 1195 (s), 1140 (s), 1028 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.39–7.12 (m, 5 H), 6.09 (s, 1 H), 5.34 (s, 1 H), 4.18 (q, 2 H, $J = 7.1$ Hz), 3.0–2.87 (m, 1 H), 2.71–2.57 (m, 2 H), 2.23–1.84 (m, 4 H), 1.29 (t, 3 H, $J = 7.1$ Hz); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 166.8, 141.9, 138.1, 128.7, 127.6, 127.0, 126.8, 119.3, 60.64, 43.87, 38.97, 31.22, 15.25, 14.06; MS (EI) 40 (6), 51 (7), 77 (28), 105 (100), 115 (4), 143 (4), 181 (3), 249 (1); exact mass calcd for $C_{17}H_{15}NO$: 249.1154, obsd 249.1151.

Acknowledgment. We thank the National Institute of Health (GM 41908), the Horace H. Rackham School of Graduate Studies of the University of Michigan, and the Department of Chemistry of the University of Michigan for the generous support of this work.

Registry No. **1a**, 100-39-0; **1b**, 40400-13-3; **1c**, 28188-41-2; **1d**, 58305-56-9; **1e**, 117269-70-2; **1f**, 20443-98-5; **1g**, 62290-17-9; **1h**, 54589-54-7; **1i**, 127356-64-3; **1j**, 672-65-1; **1k**, 127356-65-4; **1l**, 72335-16-1; **5**, 705-73-7; **6**, 5195-20-0; **7**, 127356-50-7; **8**, 127356-51-8; **9**, 117269-58-6; **10**, 117269-59-7; **11**, 127356-52-9; **12**, 117269-57-5; **13**, 117269-60-0; **14**, 117269-61-1; **15**, 117269-62-2; **16**, 79159-71-0; **17**, 117269-63-3; **18**, 117269-64-4; **19**, 117269-65-5; **20**, 117269-66-6; **21**, 117269-67-7; **22**, 117269-68-8; **23**, 127356-53-0; **24**, 127356-54-1; **25**, 127356-55-2; **26**, 127356-56-3; **27**, 127356-57-4; **28**, 127356-58-5; (*E*)-**29**, 127356-59-6; (*Z*)-**29**, 127356-66-5; **30**, 127356-60-9; **31**, 28795-94-0; **32**, 117269-69-9; **33** (isomer 1), 127356-61-0; **33** (isomer 2), 127356-67-6; **34**, 127356-62-1; **35**, 19831-77-7; **36**, 127356-63-2; **37**, 1680-73-5; $CH_3CH_2CH_2CHO$, 123-72-8; (*E*)-$PhCH{=}CHC(O)CH_3$, 1896-62-4; $CH_2{=}C(CO_2\text{-}t\text{-}Bu)CH_2Br$, 53913-96-5; PhCHO, 100-52-7; Bu_3SnCl, 1461-22-9; PhCOCl, 98-88-4; $CH_2{=}CHCH_2Br$, 106-95-6; $CH_2{=}C(CH_3)CH_2Br$, 1458-98-6; $EtO_2CC{\equiv}CH$, 623-47-2; $CH_2{=}C(CO_2Et)CH_2Br$, 17435-72-2; ICH_2CH_2CN, 2517-76-2; $IZnCH_2CH_2CN$, 121236-17-7; $ClCH_2CH_2CN$, 542-76-7; 4-acetoxy-3-methoxybenzaldehyde, 881-68-5; 4-acetoxy-3-methoxybenzyl alcohol, 60835-68-9; 3-(cyclohexylcarbonyl)benzyl chloride, 127356-49-4; α-butylbenzyl alcohol, 583-03-9; perillaldehyde, 2111-75-3; 2-cyclohexen-1-one, 930-68-7; 3-iodo-2-cyclohexen-1-one, 56671-82-0; cyclohexylcarbonyl chloride, 2719-27-9; 4-hydroxy-4-phenylbutyronitrile, 24241-74-5; vanillin, 121-33-5; iodocyclohexane, 626-62-0; 3-(chloromethyl)benzoyl chloride, 63024-77-1; 2-methyl-1,4-naphthoquinone, 58-27-5; 2-methyl-1,4-naphthohydroquinone, 481-85-6; 2-methyl-1,4-naphthohydroquinone diacetate, 573-20-6; 1,4-diacetoxy-2-(bromomethyl)naphthalene, 100915-42-2; 2-iodobenzyl chloride, 59473-45-9; cyclohexanone, 108-94-1.

Lewis Acid Promoted, Cobalt-Catalyzed, and Phase-Transfer-Catalyzed Carbonylation of Iodoarenes and Iodoalkanes[†]

Jong-Tae Lee and Howard Alper*

Department of Chemistry, Ottawa–Carleton Chemistry Institute, University of Ottawa,
Ottawa, Ontario, Canada K1N 6N5

Received February 7, 1990

Iodoarenes and iodoalkanes can be carbonylation to carboxylic acids under mild conditions using cobalt chloride or acetate, potassium cyanide, base, and PEG-400 as the phase-transfer agent. The reaction is promoted by Lewis acids such as boron trifluoride etherate, with ferrous chloride as a copromoter.

The carbonylation of iodoarenes to carboxylic acids has attracted considerable attention in recent years. Examples include the palladium(II)-catalyzed carbonylation of iodoarenes using K_2CO_3 and *N*,*N*-dimethylformamide,[1] the ruthenium trichloride catalyzed reaction at elevated temperatures and pressures using lithium carbonate as a base and lithium iodide as a promoter,[2] and the nickel cyanide,

---

[†] Dedicated to the memory of John Stille, who made outstanding contributions to organometallic and polymer chemistry, including the area of carbonylation reactions.

(1) Bumagin, N. A.; Nikitin, K. V.; Beletskaya, I. P. *J. Organomet. Chem.* **1988**, *358*, 563.

0276-7333/90/2309-3064$02.50/0

Table I. Carbonylation of Iodobenzene[a]

entry	cat.[b] (mol %)	PTC (mol %)	promoter (mol %)	yield,[c] %	
				benzoic acid	benzophenone
1	A (10)	CTAB (2)		16	7
2	A (10)	CTAB (2)	$CeCl_3 \cdot 7H_2O$ (10)	34	3
3		CTAB (2)	$CeCl_3 \cdot 7H_2O$ (10)	0	0
4	A (10)		$CeCl_3 \cdot 7H_2O$ (10)	6	0
5	B (10)	CTAB (2)	$CeCl_3 \cdot 7H_2O$ (10)	33	3
6	A (10)	CTAB (2)	$AlCl_3$ (10)	32	4
7	A (10)	CTAB (2)	$ZnCl_2$ (10)	34	4
8	A (10)	CTAB (2)	$TiCl_4$ (10)	27	9
9	A (10)	CTAB (2)	$Ti(Oi\text{-}Pr)_4$ (10)	30	6
10	A (10)	CTAB (2)	$BF_3 \cdot Et_2O$	40	4
11	A (10)	CTAB (2)	$Zn(OAc)_2 \cdot 2H_2O$ (10)	39	6
12	A (20)	CTAB (2)	$BF_3 \cdot Et_2O$ (20)	16	tr
13	A (20)	CTAB (8)	$BF_3 \cdot Et_2O$ (20)	16	7
14	A (20)	CTAB (4)	$BF_3 \cdot Et_2O$ (40)	2	tr
15	A (20)	CTAB (4)	$BF_3 \cdot Et_2O$ (20)	46	6
16	A (20)	TBAHS (4)	$BF_3 \cdot Et_2O$ (20)	31	13
17	A (20)	PEG-400 (5)		31	4
18	A (20)	PEG-400 (5)	$BF_3 \cdot Et_2O$ (20)	39	9
19	A (20)	PEG-400 (10)	$BF_3 \cdot Et_2O$ (20)	31	15
20	C (20)[d]	PEG-400 (5)	$BF_3 \cdot Et_2O$ (20)	48	5
21	C (20)[e]	PEG-400 (5)	$BF_3 \cdot Et_2O$ (20)	44	7
22	C (20)[f]	PEG-400 (5)	$BF_3 \cdot Et_2O$ (20)	44	3
23	C (20)[g]	PEG-400 (5)	$BF_3 \cdot Et_2O$ (20)	23	4
24	D (20)	PEG-400 (5)	$BF_3 \cdot Et_2O$ (20)	tr	tr
25	C (20)[f]	CTAB (4)	$BF_3 \cdot Et_2O$ (20)	5	0
26	C (20)[d]	CTAB (4)	$BF_3 \cdot Et_2O$ (20)	21	7

[a] Reaction conditions. (i) Runs 1–11: iodobenzene (10 mmol), 5 N NaOH (20 mL), $CoCl_2 \cdot 6H_2O$ or $Co(OAc)_2 \cdot 4H_2O$ (1.0 mmol), KCN (2.0 mmol), CTAB (0.1 mmol), promoter (1.0 mmol), 90–95 °C, 1 atm of CO, 17 h. (ii) Runs 12–26: iodobenzene (5 mmol), 5 N NaOH or KOH (20 mL of KOH used in conjunction with PEG-400), $CoCl_2 \cdot 6H_2O$ (1.0 mmol), KCN (2.0 mmol), $FeCl_2$ (if used), $BF_3 \cdot Et_2O$ (if used), phase-transfer catalyst, 90–95 °C, 1 atm of CO, 17 h. [b] A = $CoCl_2 \cdot 6H_2O$/KCN. B = $Co(OAc)_2 \cdot 4H_2O$/KCN. C = $CoCl_2 \cdot 6H_2O$ + $FeCl_2$/KCN. D = $FeCl_2$/KCN. [c] Yield of *pure* isolated products. [d] $CoCl_2 \cdot FeCl_2$ = 1/1. [e] $CoCl_2 \cdot 6H_2O/FeCl_2$ = 3/1. [f] $CoCl_2 \cdot 6H_2O/FeCl_2$ = 9/1. [g] $CoCl_2 \cdot 6H_2O/FeCl_2$ = 1/3.

phase-transfer-catalyzed reaction at 1 atm.[3] In addition, it has been shown that bis(triphenylphosphine)platinum dichloride can catalyze the related methoxycarbonylation of iodoarenes using potassium carbonate and methanol in dioxane.[4]

$$\mathrm{RI + CO + CH_3OH \xrightarrow[K_2CO_3,\ 70\ kg/cm^2]{PtCl_2(PPh_3)_2,\ 120\ ^\circ C} RCOOCH_3 + HI}$$

The latter system can also be applied to the more challenging carbonylation of iodoalkanes to the corresponding esters.

Several useful phase-transfer-catalyzed hydrogenation reactions have been described where an anionic cobalt cyanide, generated from cobalt chloride and potassium cyanide, is the active catalytic species (e.g., conversion of dienes to monoolefins).[5] To our knowledge, there have been no publications on the use of in situ generated cobalt cyanides as catalysts for carbonylation reactions. Such a catalytic system would be appreciably less expensive than that involving platinum complexes for the carbonylation of iodoarenes and iodoalkanes. This paper describes the use of cobalt chloride, potassium cyanide, and a Lewis acid promoter for the carbonylation of iodo compounds. These are also the first examples of the phase-transfer-catalyzed carbonylation of iodoalkanes.

When iodobenzene was treated with carbon monoxide, 5 N sodium hydroxide, using hydrated cobalt chloride and potassium cyanide (10/1/2 ratio of $PhI/CoCl_2/CN^-$) as the catalytic system, and cetyltrimethylammonium bromide (CTAB) as the phase-transfer agent, for 17 h at 90–95 °C and 1 atm, benzoic acid was isolated in 16% yield and benzophenone in 7% yield (Table I, entry 1). No reaction occurs in the absence of potassium cyanide or without the metal catalyst.

It was previously shown that lanthanide reagents could promote the carbonylation of benzyl chlorides using in situ generated cyanotricarbonylnickelate as the catalyst.[6] When ceric chloride was employed as the lanthanide reagent (1/1 ratio of $CoCl_2/CeCl_3$), the yield of benzoic acid essentially doubled (to 34%) with benzophenone formed in 3% yield (entry 2). No reaction occurs when using the lanthanide alone (entry 3), while the yield of acid is only 6% when the carbonylation reaction was effected without CTAB (entry 4). Comparable results were obtained using cobalt acetate instead of cobalt chloride (entries 2 and 5). A series of other Lewis acids were used as promoters, the best results being attained with boron trifluoride or zinc acetate (entries 6–11). Increasing the proportion of cobalt chloride and either CTAB or $BF_3 \cdot Et_2O$ is detrimental to the reaction, while benzoic acid was isolated in 46% yield by increasing the amount of cobalt chloride (5/1 ratio of $PhI/CoCl_2$) but not CTAB or $BF_3 \cdot Et_2O$ (entries 13–15). While tetrabutylammonium hydrogen sulfate was less useful as a phase-transfer agent, poly(ethylene glycol) (PEG-400, with 5 N KOH as the base) with added boron trifluoride etherate, was competitive with CTAB (entries 16–18). The proportion of benzophenone increases by using more PEG-400 (entry 19). The yield of benzoic acid was raised by using ferrous chloride as a second promoter, provided the proportion of $CoCl_2/FeCl_2$ is no less than 1/1 (entries 20–24—mmol of PhI/total mmol of $CoCl_2$ and $FeCl_2$ is the same).

$$\mathrm{RI + CO \xrightarrow[KCN,\ FeCl_2,\ BF_3 \cdot Et_2O]{PEG\text{-}400,\ 90\text{–}95\ ^\circ C,\ CoCl_2 \cdot 6H_2O,\ 5\ N\ KOH,\ 1\ atm} RCOOH}$$

---

(2) Steinmetz, G. R.; Rule, M. U.S. Patent 4, 705, 890, Nov. 10, 1987.

(3) Amer. I.; Alper, H. *J. Org. Chem.* **1988**, *53*, 5147.

(4) Takeuchi, R.; Tsuji, Y.; Fujita, M.; Kondo, T.; Watanabe, Y. *J. Org. Chem.* **1989**, *54*, 1831.

(5) Lee, J. T.; Alper, H. *J. Org. Chem.* in press.

(6) Amer. I.; Alper, H. *J. Am. Chem. Soc.* **1989**, *111*, 927.

Table II. Carbonylation of Iodoarenes and Iodoalkanes[a]

substrate	reaction time, h	product, %[b]
PhI	17	PhCOOH, 44
$3\text{-}CH_3C_6H_4I$	15	$3\text{-}CH_3C_6H_4COOH$, 37
$3\text{-}CH_3C_6H_4I$[c]	17	$3\text{-}CH_3C_6H_4COOH$, 7
$4\text{-}CH_3C_6H_4I$	15	$4\text{-}CH_3C_6H_4COOH$, 54
$2\text{-}CH_3C_6H_4I$	24	$2\text{-}CH_3C_6H_4COOH$, 6
$3\text{-}CH_3OC_6H_4I$	15	$3\text{-}CH_3OC_6H_4COOH$, 37
$3\text{-}ClC_6H_4I$	24	$3\text{-}ClC_6H_4COOH$, 41
$1\text{-}C_{10}H_7I$[d]	27	$1\text{-}C_{10}H_7COOH$, 24 $C_{10}H_8$, 70
$2\text{-}C_4H_3SI$[e]	24	$2\text{-}C_4H_3COOH$, 3
$CH_3(CH_2)_{10}CH_2I$	24	$CH_3(CH_2)_{11}COOH$, 45; $C_{12}H_{26}$, 33 $C_{10}H_{21}CH{=}CH_2$, 18
$CH_3(CH_2)_6CH_2I$	24	$CH_3(CH_2)_7COOH$, 29[f]
$CH_3(CH_2)_2CH_2I$	24	$CH_3(CH_2)_3COOH$, 33[f]
$(CH_3)_2CHCH_2CH\text{-}(CH_3)I$	17	$(CH_3)_2CHCH_2CH(CH_3)COOH$, 46[f]
iodocyclohexane	17	cyclohexanecarboxylic acid, 35[f]

[a] Reaction conditions: 5 mmol of substrate, 5 N KOH (20 mL), $CoCl_2{\cdot}6H_2O$ (0.9 mmol), $FeCl_2$ (0.1 mmol), KCN (2.0 mmol), PEG-400 (0.25 mmol), $BF_3{\cdot}Et_2O$ (1.0 mmol), CO (1 atm), 90–95 °C. [b] Isolated yield. [c] 0.2 mmol of CTAB was used. [d] 1-Iodonaphthalene. [e] 1-Iodothiophene. [f] The yields of olefin and alkane were not determined.

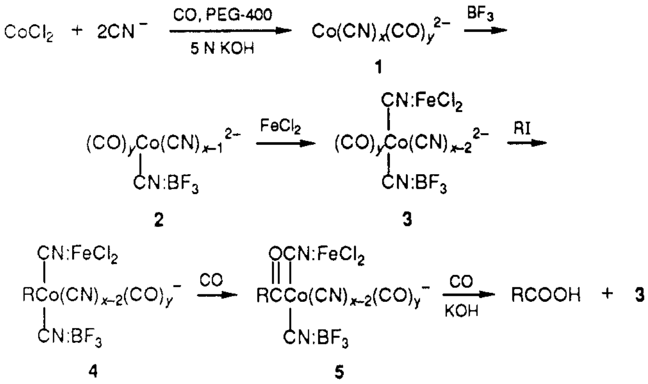
Interestingly, when CTAB is employed as the phase-transfer catalyst, the presence of $FeCl_2$ reduces the conversion of iodobenzene to products (entries 15, 25 and 26).

It is noteworthy that an increase in the proportion of $KCN/CoCl_2$ above 2/1 decreases the yield of benzoic acid. For example, if the conditions described in entry 18 of Table I were applied except for the use of 3/1 $KCN/CoCl_2$, benzoic acid was isolated in 24% yield (8% benzophenone). The yield of benzoic acid was only 12% (6% benzophenone) using a 5:1 ratio of $KCN/CoCl_2$.[7] Also, no benzoic acid is formed if $Co(CN)_5^{3-}$ is generated under nitrogen and then reacted with CO[7] followed by $FeCl_2$, $BF_3{\cdot}(C_2H_5)_2O$, and then iodobenzene.

The $CoCl_2/KCN$ ctalytic system, with $BF_3{\cdot}Et_2O$ and $FeCl_2$ as promoters and PEG-400 as the phase-transfer agent, was used to carbonylate a variety of iodoarenes (see Table II for data). Reasonable yields of pure acids (37–54%) were obtained from meta- and para-substituted iodobenzenes containing chloro, methyl, or methoxy substituents, while *o*-iodotoluene only reacted to a small extent. 1-Iodonaphthalene afforded 1-naphthalenecarboxylic acid in 24% yield and naphthalene in 70% yield, while thiophene-2-carboxylic acid was isolated in poor yield from 2-iodothiophene.

It was gratifying to learn that iodoalkanes could undergo carbonylation to the corresponding acids using cobalt chloride as the catalyst. Byproducts of the iodoalkane carbonylation reaction include the saturated alkane and the terminal olefin. The latter is not involved in the formation of acids from iodoalkanes since 1-dodecene was recovered unchanged on attempted carbonylation under identical conditions to those used for 1-iododecane. Although the noted byproducts are formed in the carbonylation of iodoalkanes to acids, the process is, nevertheless, attractive when compared with the catalytic reactions. For example, although bis(triphenylphosphine)platinum dichloride catalyzes the synthesis of esters from iodoalkanes, carbon monoxide, and methanol, high pressures (70 kg/cm^2) and elevated temperatures are requried.[4]

Scheme I



A possible mechanism for the carbonylation reaction is illustrated in Scheme I. Treatment of cobalt chloride with potassium cyanide, base, and PEG-400 may afford a cyanocarbonylcobaltate, **1**. Binding of one of the cyano ligands to boron trifluoride can give **2** (note that the Lewis acid may bind to a carbonyl ligand instead), which may use another such ligand to form an adduct, **3**, with $FeCl_2$. Reaction of **3** with the organic substrate may, at least in the case of iodoarenes, proceed by an electron-transfer pathway to form **4**. Ligand migration of **4** to **5**, followed by base-induced acyl carbon–cobalt bond cleavage may afford the acid and regenerate **3**. Note that anionic cobalt complexes of structural type $[XYCo(CO)_3]^-$ (where X = alkyl, aryl; Y = halide; COOR), related in some sense to **4** and **5**, have been isolated and characterized.[8-10]

In conclusion, the $CoCl_2/KCN/BF_3{\cdot}Et_2O/FeCl_2$/PEG-400 catalytic system is a useful one for the carbonylation of iodoarenes and iodoalkanes to carboxylic acids. The reaction proceeds under mild conditions, and product isolation is simple.

Experimental Section

General Considerations. Melting points were determined by using a Fisher-Johns apparatus. The following instrumentation was used for accumulating spectra data: Perkin-Elmer 783 spectrometer (infrared), Varian EM360, Gemini 200, or 300-MHz spectrometers (nuclear magnetic resonance), and VG 7070 spectrometer (mass).

The iodo compounds weer purchased from commercial sources and were distilled, if necessary, prior to use. All of the catalysts were obtained from commercial sources and were used as received.

General Procedure for the Carbonylation of Iodo Compounds. Carbon monoxide was bubbled through a stirred solution of 5 N KOH (10 mL) containing 0.10 g (0.25 mmol) of PEG-400, $CoCl_2{\cdot}6H_2O$ (0.215 g, 0.90 mmol), $BF_3{\cdot}(C_2H_5)_2O$ (0.142 g, 1.0 mmol), and $FeCl_2$ (0.013 g, 0.10 mmol). After 10 min, potassium cyanide (0.130 g, 2.0 mmol) in 5 N KOH (10 mL) was added, the mixture was stirred for 3 h at 90–95 °C under CO, the substrate (5.0 mmol) was then added, and stirring was continued for 15–24 h (see Table II for reaction times). After cooling to room temperature, the mixture was extracted with ether (20 mL) to remove benzophenone or any alkane or alkene byproducts.

The aqueous solution was acidified (10% HCl) and extracted with ether or ethyl acetate (3 × 30 mL), and the ether extract was washed with H_2O (30 mL), dried ($MgSO_4$), and then concentrated by rotary evaporation, affordng the acid. Further purification, if necessary, was effected by distillation or recrystallization. The products were identified by comparison of spectral data (IR, NMR, MS) with those for authentic materials.

Acknowledgment. We are grateful to British Petroleum and to the National Sciences and Engineering Research Council of Canada for support of this research.

---

(7) Guastalla, G.; Halpern, J.; Pribanic, M. *J. Am. Chem. Soc.* **1973**, *95*, 1575. Halpern, J.; Guastalla, G.; Bercaw, J. E. *Coord. Chem. Rev.* **1972**, *8*, 167.

(8) Francalanci, F.; Gardano, A.; Abis, L.; Foa, M. *J. Organomet. Chem.* **1983**, *251*, C5.

(9) Tasi, M.; Palyi, G. *Organometallics* **1985**, *4*, 1523.

(10) Roper, M.; Kruger, C. *J. Organomet. Chem.* **1988**, *339*, 159.