axis of the ellipsoid (3.5 Å), n^2 is the refractive index,[30] and D is the static dielectric constant of the medium.[31] The value of $\Delta V_{calc}^{\ddagger}$ employing this expression was found to be -8.4 cm^3 mol^{-1}. Thus, the value of $\Delta V_{obs}^{\ddagger}$ can be accounted for almost exclusively by solvent electrostriction, and this dramatically illustrates the enormous role of the medium in this redox process.

We have previously shown[13] that the dielectric continuum model is not appropriate for analyzing IT bands for the dinuclear, I, since the energies of the IT bands are dependent upon the ionic strength of the medium. Therefore, the values we quote in this work are valid, strictly speaking, only for an ionic strength of 0.081 M. An estimate of the value of $\Delta V_{obs}^{\ddagger}$ at zero ionic strength was made assuming that the effect of ionic strength was not markedly pressure dependent. This gave $\Delta V_{obs}^{\ddagger} = -7.1$ cm^3 mol^{-1}. Thus, the value of $\Delta V^{\ddagger}$ is not very sensitive to this parameter, and the quoted value can be considered to be a reasonable estimate of this quantity.

This work confirms the hypothesis that for very weakly coupled binuclears such as I, in which electron tunnelling is the major mechanism for electron transfer between the metal centers, moderate increases in pressure may cause large changes in the rate of electron exchange, especially when significant van der Waals interactions are possible. Whether this will always result in an enhancement of electron transfer remains to be seen. We are presently examining pressure effects of other weakly coupled binuclears in a variety of media to determine the generality of these results.

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Lanthanide-Promoted and Nickel Cyanide Catalyzed Carbonylation Reactions under Phase-Transfer Conditions

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Abstract: The nickel cyanide and phase transfer [NaOH, $PhCH_3$, $R_4N^+X^-$] catalyzed carbonylation of benzyl chlorides is promoted by lanthanide salts [$CeCl_3$, $LaCl_3$]. This simple reaction is sensitive to the concentration of the lanthanide compound, sodium hydroxide, quaternary ammonium salt, and nickel catalyst. The nature of the organic phase and phase transfer agent also influences the reaction rate. The acceleration of the reaction may be a consequence of coordination of a nickel cyanide nitrogen lone pair to the lanthanide salt.

The transition metal complex catalyzed carbonylation of halides is a useful method for the synthesis of carboxylic acids. Elevated temperatures and/or pressures are often required for the homogeneous hydroxycarbonylation reaction catalyzed by nickel, palladium, or platinum complexes.[2]

Phase-transfer catalysis has been utilized recently for metal complex catalyzed oxidation, reduction, and carbonylation reactions.[3] These processes occur under mild conditions, and workup of the organic products if usually simple. For instance, cobalt carbonyl[4,5] or palladium(0) complexes,[6] are capable of catalyzing the carbonylation of benzylic halides to carboxylic acids under phase-transfer conditions.

$$ArCH_2X + CO \xrightarrow[\text{NaOH, } C_6H_6\text{, } R_4N^+X^- \text{, room temp., 1 atm}]{Co_2(CO)_8 \text{ or } Pd(PPh_3)_4} ArCH_2COOH \quad (1)$$

Lanthanides have attracted considerable interest in recent years as reagents and catalysts in organic synthesis.[7-9] It was envisaged that lanthanide compounds could assist the carbonylation of benzyl halides possibly by interaction with the catalytic species. We now report that certain lanthanides successfully promote the carbonylation reaction, this being the first example of the use of lanthanide complexes as catalysts in a phase-transfer process.

Table I. Carbonylation of Benzylic Chlorides Catalyzed by $Ni(CN)_2{\cdot}4H_2O$, $CeCl_3{\cdot}7H_2O$, and $C_{16}H_{33}N(CH_3)_3^+Br^-$ [a]

substrate	reaction time, h	% conversion	% isolated yield[b]
$PhCH_2Cl$	4.5	97	89
p-$ClC_6H_4CH_2Cl$	6.5	88	82
o-$ClC_6H_4CH_2Cl$	6.5	80	76
p-$CH_3C_6H_4CH_2Cl$	7.0	48	42
o-$CH_3C_6H_4CH_2Cl$	7.25	67	55
1-chloromethylnaphthalene	7.0	71	60
2-chloromethylnaphthalene	6.0	90	70

[a] Conditions: $Ni(CN)_2{\cdot}4H_2O$ [1.0 mmol], $C_{16}H_{33}N(CH_3)_3^+Br^-$ [0.177 mmol], $CeCl_3{\cdot}7H_2O$ [0.8 mmol], $PhCH_3$ (25 mL), 5 N NaOH [25 mL], $ArCH_2Cl$ [10.0 mmol], CO (1 atm, 90 ± 5 °C). [b] Yields are of *pure* materials. Products were identified by comparison of physical data [mp, IR, NMR, MS] with those for authentic materials. Carboxylic acids are the only products formed in these reactions.

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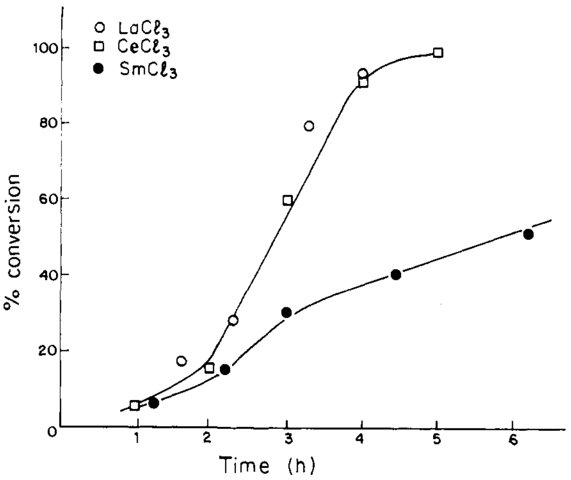

Figure 1. Plot of the percent conversion of benzyl chloride with time for different lanthanide salts ($PhCH_2Cl$, 10.0 mmol; $C_{16}H_{33}N(CH_3)_3^+Br^-$, 0.177 mmol; $Ni(CN)_2 \cdot 4H_2O$, 1.0 mmol; $LnCl_3$, 0.8 mmol; 5 N NaOH, 25 mL; $PhCH_3$, 25 mL; CO, 1 atm, 90 °C).

Results and Discussion

In 1985, one of us[10] described the use of cyanonickel(II) complexes as catalysts for the phase transfer catalyzed carbonylation of allylic halides to acids. The catalytically active species is believed to be the cyanotricarbonylnickelate ion. Slow conversion to phenylacetic acid occurred when the nickel cyanide system was used with benzyl chloride as the reagent. Specifically, exposure of benzyl chloride to carbon monoxide in 5 N sodium hydroxide and toluene, in the presence of catalytic quantities of tetrabutylammonium bromide and hydrated nickel cyanide, at 90 °C and 1 atm for 4.5 h, resulted in only 35% conversion to phenylacetic acid.

When benzyl chloride was treated with catalytic amounts of hydrated nickel cyanide, hydrated cerium chloride, and a quaternary ammonium salt in a mixture of sodium hydroxide (5 N) and toluene for 4.5 h at 90 °C and 1 atm of carbon monoxide, phenylacetic acid was isolated in 89% yield (97% conversion). The ratio of $PhCH_2Cl/Ni(CN)_2 \cdot 4H_2O/CeCl_3 \cdot 7H_2O$ used was 10/1.0/0.8. Good conversions were realized when these conditions were applied to a variety of benzylic chlorides for reaction times of 4.5–7.25 h, with isolated yields ranging from 42–89%. The results presented in Table I indicate that the presence of an electron-withdrawing substituent (i.e., *p*-Cl) is beneficial relative to an electron-donating group (i.e., *p*-CH_3, *o*-CH_3). Hydrolysis of the chloride to the alcohol takes place when a methoxy group is located at the para position of the benzylic halide.

The conditions for the carbonylation reaction were chosen following an examination of the influence of different parameters on the facility of the phase-transfer process. Let us now consider the following factors:

(i) **The Lanthanide Effect.** The nature of the lanthanide compound had an appreciable effect on the rate of the carbonylation reaction. The carbonylation of benzyl chloride in the absence of a lanthanide complex was very slow (35% conversion after 4 h; 43% after 16 h) when compared with reaction carried out in the presence of cerium(III) chloride (93% conversion after 4 h). Such lanthanide salt promotion was also found in the homogeneous nickel (II) acetate carbonylation of methanol.[11]

The catalytic activity of several other lanthanide complexes was examined. Lanthanium(III) chloride was as effective as cerium(III) chloride for the nickel cyanide catalyzed carbonylation of benzyl chloride with cetyltrimethylammonium bromide as the phase-transfer agent (93% conversion of reactant, in both cases, after 4 h). Samarium chloride is essentially inert (38% conversion after 4 h), particularly when one compares it with reaction in the absence of any lanthanide complex for the same period of time (35% conversion). However, approximately 50% conversion does take place after 6 h, using the samarium halide (Figure 1).

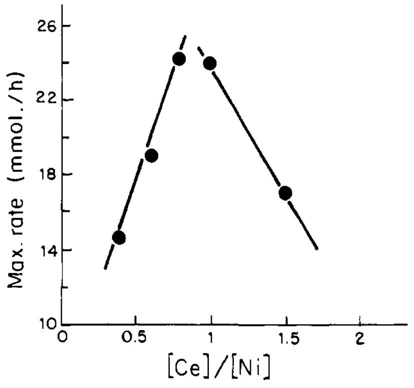

Figure 2. Dependence of the maximum rate, for the carbonylation of benzyl chloride, on the ratio of $CeCl_3/Ni(CN)_2$ (see caption for Figure 1 for reaction conditions).

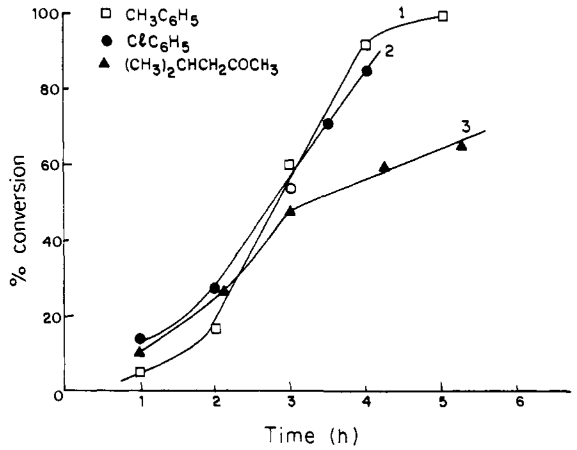

Figure 3. Plot of the percent conversion of benzyl chloride as a function of time with 25 mL of (1) $C_6H_5CH_3$, (2) C_6H_5Cl, and (3) $(CH_3)_2CHCH_2COCH_3$ as the organic phase (see caption for Figure 1 for reaction conditions).

(ii) **Cerium(III) Chloride Concentration.** The concentration of the lanthanide catalyst has a significant influence on the extent of conversion, with a maximum reached in the range of 0.8–1.0 $CeCl_3 \cdot 7H_2O/Ni(CN)_2 \cdot 4H_2O$ (Figure 2). The occurrence of a maximum in the lanthanide catalyst concentration–rate profile [analogous to the behavior found in the dependence of the rate on the phase transfer catalyst concentration (see v)] is not easy to rationalize. It is noteworthy that benzyl chloride does not undergo carbonylation in the absence of the nickel catalyst (i.e., with $CeCl_3$ alone).

(iii) **Organic Phase.** The degree of conversion of benzyl chloride was monitored with time using toluene, chlorobenzene, and 4-methyl-2-pentanone as the organic phase (conditions were otherwise the same as those described above). The results in Figure 3 indicate that more rapid reactions occur in nonpolar than in polar solvents. The maximum rate in toluene is 4.0 mmol/h compared to 2.9 mmol/h in chlorobenzene and 1.3 mmol/h in 4-methyl-2-pentanone. This trend contrasts with that reported for the rhodium trichloride–Aliquat 336 hydrogenation system under phase-transfer conditions.[12]

(iv) **Phase-Transfer Agent.** No carbonylation reaction occurs in the absence of the phase-transfer agent. A series of quaternary ammonium salts were employed as phase-transfer catalysts for the carbonylation of benzyl chloride. The results in Figure 4 indicate that the reaction is most favorable with quaternary ammonium salts containing one long chain alkyl group ($RN(CH_3)_3^+X^-$: R = $C_{10}H_{21}$, $C_{12}H_{25}$, $C_{14}H_{29}$, $C_{16}H_{33}$; X^- = Br^-, Cl^-).

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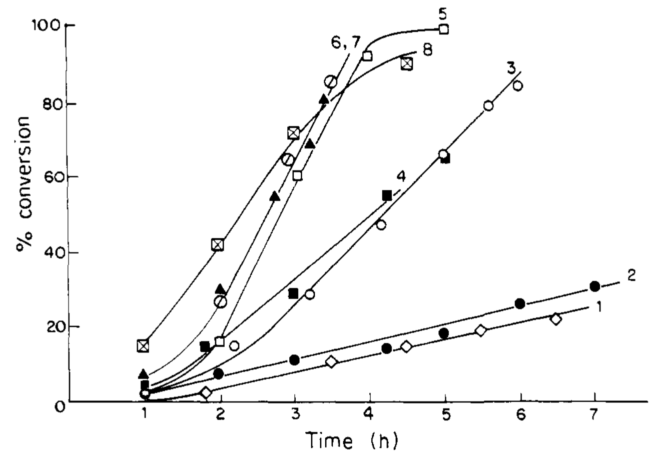

Figure 4. Plot of the percent conversion of benzyl chloride with time with different quaternary ammonium salts: (1) $(CH_3)_4N^+Br^-$ (◇); (2) $(C_8H_{17})_4N^+Br^-$ (●); (3) $(C_4H_9)_4N^+HSO_4^-$ (○); (4) $C_{12}H_{25}N(CH_3)_2C_2H_5{}^+Br^-$ (■); (5) $C_{16}H_{33}N(CH_3)_3{}^+Br^-$ (□); (6) $C_{12}H_{25}N(CH_3)_3{}^+Cl^-$ (▲); (7) $C_{14}H_{29}N(CH_3)_3{}^+Br^-$ (⊘); (8) $C_{10}H_{21}N(CH_3)_3{}^+Br^-$ (⊠). (See caption for Figure 1 for reaction conditions.)

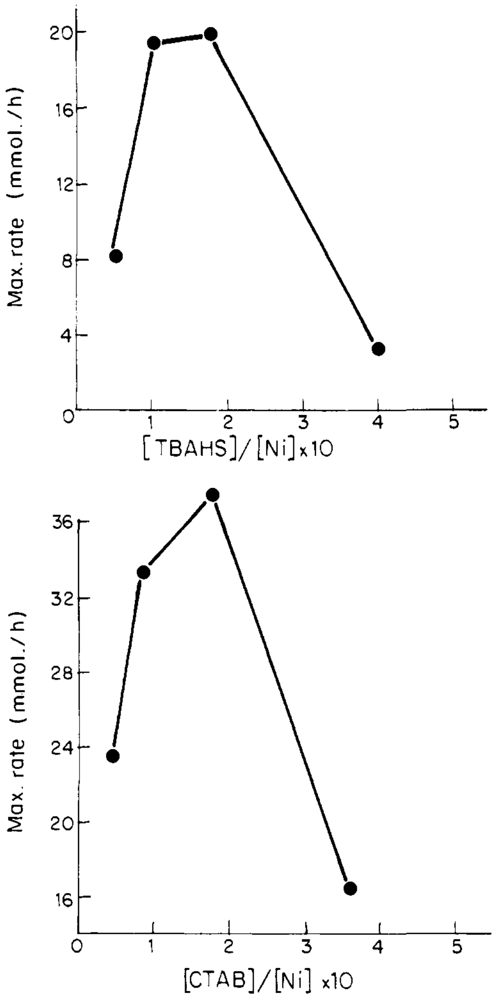

Figure 5. Dependence of the maximum rate for the carbonylation of benzyl chloride on the concentration of tetra-*n*-butylammonium hydrogen sulfate (TBAHS, upper plot) or cetyltrimethylammonium bromide (CTAB, lower plot) relative to the nickel catalyst. (See caption for Figure 1 for reaction conditions.)

It is conceivable that such catalysts are functioning in a surfactant-like manner. Replacement of one of the methyl groups of dodecyltrimethylammonium chloride by an ethyl group reduces the rate of carbonylation. Such behavior was observed in the phase-transfer Wacker oxidation $[PdCl_2/CuCl_2/C_6H_6/H_2O/R_4N^+X^-]$.[13] The results for tetraalkylammonium salts are unclear, as tetramethylammonium hydroxide (which remains in the aqueous phase) and tetra-*n*-octylammonium hydroxide (which is in the organic phase) are less effective than the tetra-*n*-butylammonium salt.

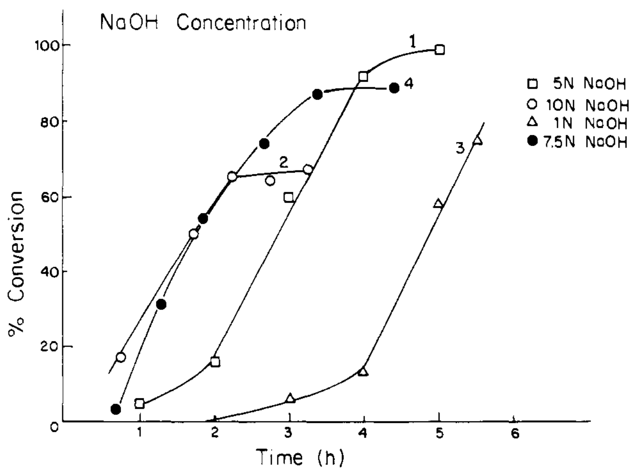

Figure 6. Time dependence of the extent of conversion of benzyl chloride, subject to the base concentration. (See caption for Figure 1 for reaction conditions.)

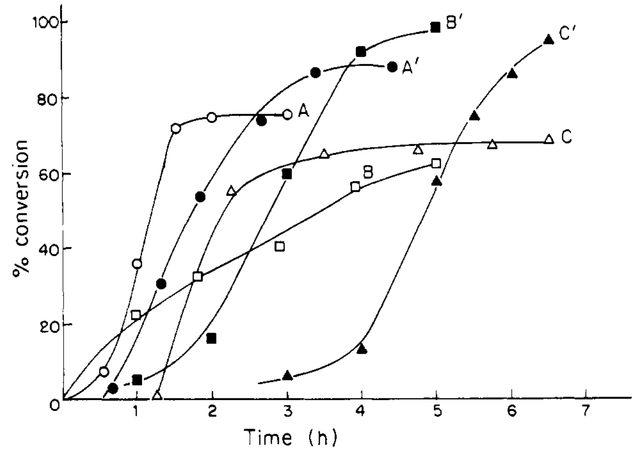

Figure 7. Comparison of the percent conversion of benzyl chloride with time, using $CeCl_3$ or $AlCl_3$ at different concentrations of NaOH: (A) 7.5 N NaOH, $AlCl_3$ (○); (A') 7.5 N NaOH, $CeCl_3$ (●); (B) 5 N NaOH, $AlCl_3$ (◇); (B') 5 N NaOH, $CeCl_3$ (◆); (C) 1 N NaOH, $AlCl_3$ (△); (C') 1 N NaOH, $CeCl_3$ (▲).

(v) **Phase-Transfer-Catalyst Concentration.** The maximum rate of the benzyl chloride carbonylation reaction is dependent on the concentration of the phase-transfer agent (e.g., tetrabutylammonium hydrogen sulfate or cetyltrimethylammonium bromide), with the most favorable $R_4N^+X^-/Ni(CN)_2{\cdot}4H_2O$ ratio being 0.177 (of the different ratios examined). Less conversion per hour occurred at lower or higher phase-transfer-catalyst concentrations (Figure 5).

(vi) **Base Concentration.** The concentration of the base in the aqueous phase has no influence on the reaction rate, but it appearently influences the induction time of the reaction. Also, high concentrations of sodium hydroxide (i.e., 7.5 N, 10 N) result in a leveling off of the carbonylation of benzyl chloride after 2–3 h (Figure 6: maximum conversion of 66%, 10 N NaOH; 88%, 7.5 N NaOH).

(vii) **Transition-Metal-Complex Concentration.** The carbonylation of benzyl chloride is useful on a preparative scale. Use of an increased substrate to nickel cyanide concentration slows down the reaction. Nevertheless, carbonylation does proceed as witnessed by the isolation of phenylacetic acid in 68% yield from benzyl chloride after 6.5 h, by use of a 20:1 ratio of substrate/Ni

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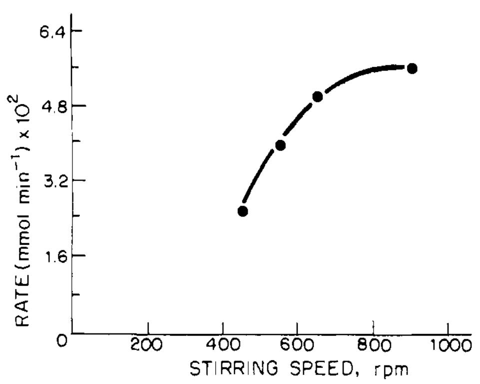
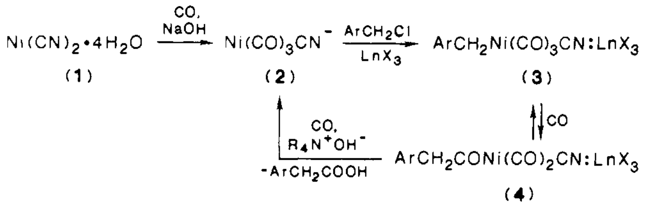


Figure 8. Dependence of the rate on stirring speed for the carbonylation of benzyl chloride—100-mL flask, Teflon-coated magnetic stirring bar (2.54 cm. × 0.95 o.d.), 1KAMAG-RET-G stirrer. (Conditions as noted in the caption to Figure 1.)

Scheme I



complex. The system also works at higher concentrations (i.e., 50/1 and 100/1 ratio of substrate to nickel complex gives 87% (84.5% yield) and 72% (59% yield) conversion, respectively, after 16 h).

(viii) **Comparison of Cerium with Aluminum Trichlorides.** One possible role that the lanthanide reagent may play in these reactions is that of a Lewis acid.[14] The percent conversion of benzyl chloride was determined as a function of time, using cerium chloride or aluminum chloride at different base concentrations (Figure 7). With 5 or 7.5 N NaOH, aluminum chloride is more effective in the early stages of the reaction (i.e., time to generate active species), but eventually the maximum conversion is at a lower level than that of cerium(III) chloride. Similar results were obtained at 1 N NaOH. In summary, although there are some similarities in the reactivity patterns of cerium and aluminum chlorides, cerium chloride is a more active promoter overall (using 10/1 substrate/catalyst ratio).

Mechanistic Considerations

A possible mechanism for the carbonylation reaction is outlined in Scheme I. The first step involves generation of the cyanotricarbonylnickelate anion (**2**) from nickel cyanide (**1**) via the pathway that was previously proposed.[10] The generation of **2** in the aqueous phase can be accelerated by the base and this is in accord with the influence of the base concentration on the reaction. The organic substrate may then react with **2** to give neutral nickel complex **3** which then undergoes ligand migration affording acyl complex **4**. It is conceivable that the conversion of **2** to **3** and of **3** to **4** occurs at the interface since it is unlikely that the alkyl and acylnickel complexes are soluble in aqueous base. Consistent with an interfacial mechanism[15] is the fact that phase-transfer agents containing one long chain alkyl group are the most useful for the carbonylation process, as well as the observation that among the quaternary ammonium salts with shorter chain alkyl groups (i.e., $<C_{10}$), tetrabutylammonium hydrogen sulfate is the most effective. Furthermore, the reaction rate does depend on the stirring speed as the results in Figure 8 clearly indicate.

The role of the quaternary ammonium salt may be to transfer $R_4N^+OH^-$ to the organic phase where it participates in the conversion of **4** to the acid, with regeneration of nickel catalyst **2**. This step may be facile, and it is dependent on the nucleophilicity of the hydroxide ion, which in turn is subject to the properties of the phase-transfer agent.[15] Note that the fact one can use a $R_4N^+X^-/Ni(CN)_2 \cdot 4H_2O$ ratio far removed from unity (i.e., 0.177, in contrast to cobalt[4,5] and rhodium[12] catalysis under phase-transfer conditions) suggests that **2** remains in the aqueous phase.

In this reaction sequence, the nitrogen lone pair of **2** and/or **3** (one cannot rule out coordination by a carbonyl oxygen) may coordinate to the lanthanide salt. Such coordination may accelerate the carbonyl insertion process (i.e., **3** to **4**), taking advantage of the Lewis acid character of the lanthanide salt. Interactions between organolanthanides and transition-metal complexes have been the subject of a number of studies.[16] Since the ratio of $Ni(CN)_2 \cdot 4H_2O/CeCl_3$ has a significant influence on the rate of the carbonylation reaction with a maximum reached at a ratio of approximately 1, an alternate function of the lanthanide salt, i.e., in reacting with $ArCH_2X$ to give $ArCH_2{}^+LnX_4{}^-$, is probably not operative here (a linear relation between the rate of the carbonylation and the LnX_3 concentration would then be anticipated).

In conclusion, lanthanide compounds can effectively promote the nickel cyanide and phase-transfer-catalyzed carbonylation of benzyl chlorides. This is the first example of the use of lanthanides in a transition-metal-catalyzed phase-transfer process, and it shows the interesting effects of various factors on the reaction.

Experimental Section

General Data. Infrared spectra were recorded on a Perkin-Elmer 783 spectrometer, NMR spectral determinations were made with a Varian EM360A and/or XL300 spectrometer, and a VG5050 micromass spectrometer was used for mass spectral determinations. Gas chromatographic determinations, used for following the progress of reactions, were made on a Varian 3400 instrument equipped with a 10% OV-101 on Chromosorb W column. The lanthanide halides were purchased from Aldrich Chemical Co. and were used as received.

General Procedure for the Lanthanide-Promoted and Nickel Cyanide Catalyzed Carbonylation of Benzyl Chlorides. A solution of hydrated nickel cyanide (1.0 mmol) and cerium(III) chloride (0.8 mmol) in 5 N NaOH (25 mL) was added to a toluene (25 mL) solution containing the quaternary ammonium salt (0.177 mmol) and the benzylic chloride (10–100 mmol) (*p*-xylene or cyclooctane was added as an internal standard). The mixture was stirred under carbon monoxide (1 atm) at 90 ± 5 °C (the aqueous phase became red after about 1 h). The reaction was followed by gas chromatography and after completion, the mixture was cooled to room temperature, the phases were separated, and ice was added to the aqueous phase. The latter was carefully acidified with 10% HCl and then extracted with ether (4 × 25 mL). The combined ether extracts were washed with water (20 mL), dried ($MgSO_4$), and concentrated to give the carboxylic acid.

Acknowledgment. We are indebted to British Petroleum and to the Natural Sciences and Engineering Research Council for support of this research.

Registry No. $Ni(CN)_2 \cdot 4H_2O$, 13477-95-7; $CeCl_3 \cdot 7H_2O$, 18618-55-8; $C_{16}H_{33}N(CH_3)_3{}^+Br^-$, 57-09-0; $PhCH_2Cl$, 100-44-7; $PhCH_2CO_2H$, 103-82-2; *p*-$ClC_6H_4CH_2Cl$, 104-83-6; *p*-$ClC_6H_4CH_2CO_2H$, 1878-66-6; *o*-$ClC_6H_4CH_2Cl$, 611-19-8; *o*-$ClC_6H_4CH_2CO_2H$, 2444-36-2; *p*-$H_3CC_6H_4CH_2Cl$, 104-82-5; *p*-$H_3CC_6H_4CH_2CO_2H$, 622-47-9; *o*-$H_3CC_6H_4CH_2Cl$, 552-45-4; *o*-$H_3CC_6H_4CH_2CO_2H$, 644-36-0; 1-chloromethylnaphthalene, 86-52-2; 1-naphthylacetic acid, 86-87-3; 2-chloromethylnaphthalene, 2506-41-4; 2-naphthylacetic acid, 581-96-4.

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