Surface species arising from the decomposition of 1 might also be considered as precursors for the observed gas-phase cyclic hydrocarbons. These include $(PhC\equiv CPh)Co_2(CO)_6$, a known intermediate in the thermal decomposition of 1 in solution,[19] and free diphenylacetylene. Hydrogenated diphenylacetylenes were seen on the surface of the dry mixed material after H_2 treatment at quantitative conversion of the capping group. However, they were present in small quantities and could have been produced during dry mixing as was noted.

The $(PhC\equiv CPh)Co_2(CO)_6$ complex is stable under CO/H_2 in solution at room temperature for 3 months.[23] At moderate temperatures under CO pressure, $(RC\equiv CR)Co_2(CO)_6$ complexes give cyclopentadienones, R_4C_5O.[24] These high molecular weight species would be expected to reside on the surface.

At present, it is difficult to explain the cyclic C_6/C_7 ring ratios in terms of surface precursors other than 2. Further studies are in progress and include H_2, CO, and CO/H_2 treatments of materials prepared by wet impregnation of $(PhC\equiv CPh)Co_2(CO)_6$, solutions containing both $Co_2(CO)_8$ and diphenylacetylene and diphenylacetylene itself.

Acknowledgment. We gratefully acknowledge the Center for Energy and Mineral Resources at Texas A&M University for support of this work. We also thank Ms. LeaAnn Smith for preparing most of the $PhCCo_3(CO)_9$ used in this study and Dr. James Brooks and Mr. Tom McDonald for the GC–MS results.

Registry No. 1, 13682-03-6; SiO_2, 7631-86-9; Al_2O_3, 1344-28-1; H_2, 1333-74-0; CO, 630-08-0; C_6H_6, 71-43-2; $C_6H_5CH_3$, 108-88-3; c-C_6H_{12}, 110-82-7; c-$C_6H_{11}CH_3$, 108-87-2; c-$C_6H_{11}CH_2CH_2C_6H_{11}$-c, 3321-50-4; c-$C_6H_{11}CH_2CH_2CH_2C_6H_{11}$-c, 3178-24-3; $PhCH_2CH_2C_6H_{11}$-c, 1603-61-8; $PhCH_2CH_2CH_2Ph$, 1081-75-0; $PhCH{=}CHPh$, 103-29-7; c-$C_6H_{11}CH(CH_3)Ph$, 4413-16-5; c-$C_6H_{11}CH_2CH(CH_3)Ph$, 78811-31-1.

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Cyanonickel(II) Complexes as Catalysts for the Phase-Transfer-Catalyzed Carbonylation of Allyl Halides. The Isolation of the Catalytically Active Species $[Ni(CO)_3CN^-]$

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Allyl chlorides and bromides can be carbonylated to acids by cyanonickel(II) catalysts under phase-transfer-catalysis conditions. The most useful catalyst precursor is nickel cyanide, and the key catalytic species is believed to be the cyanotricarbonylnickel anion. The latter was isolated and characterized as the bis(triphenylphosphine)nitrogen(1+) salt.

Although the chemistry of transition-metal cyano complexes has been extensively investigated, few reactions are known in which such complexes function as catalysts.[1] Carbonylation reactions are especially intriguing in this regard, due to the similarity in the properties of low valent transition metal complexes containing the isoelectronic cyano and carbonyl ligands. The mechanism of the *stoichiometric* carbonylation of benzylic bromides by hexacyanodinickelate(I)[2] has been studied and is believed to proceed via the intermediacy of $[Ni(CN)_2(CO)_2]^{2-}$.[3] Carbonylation can be accompanied by reduction, coupling, or displacement of X^- by cyanide ion. The stoichiometric carbonylation $[Ni(CN)(Ph)(P)_2]$ (P = tertiary phosphine) complexes affording benzoyl cyanide has also been examined.[4]

Phase-transfer catalysis is an important technique in organic chemistry[5,6] and has in recent years been applied to metal-catalyzed reactions.[7] In carbonylation reactions catalyzed by cobalt, rhodium, iron, and ruthenium carbonyls, one can take advantage of the fact that the reactivity of hydroxide ion, under phase-transfer conditions, far exceeds that in dilute aqueous solution,[8] thus promoting the generation (and regeneration) of carbonylmetalate anions (the real catalytic species) from the neutral carbonyls or higher valent metal compounds and carbon monoxide.

Foâ and Cassar reported the carbonylation of allyl chlorides under phase-transfer conditions, using nickel tetracarbonyl as the catalyst.[9] Mixtures of unsaturated acids of *undefined* stereochemistry were obtained in 67–85% yield, after 6–10 h at 25–45 °C and 1 atm, using Aliquat 336 or benzyltriethylammonium chloride as the phase-transfer agent. It was shown that under these reaction conditions nickel tetracarbonyl is reduced by carbon monoxide and hydroxide ion to the known[10] cluster anions

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Table I. Carbonylation of Allyl Bromide by CO/$R_4N^+X^-$/Ni(II)/5 M NaOH at Room Temperature[a]

cat. precursor	$R_4N^+X^-$	organic phase[b]	yield,[c] %	(*E*)-2-butenoic acid	3-butenoic acid
$K_2Ni(CN)_4$	$(C_4H_9)_4N^+HSO_4^-$	A	39	87	13
	$(C_4H_9)_4N^+HSO_4^-$	A	25[d]	20	80
$Ni(CN)_2$		A	82	79	21
	$(C_4H_9)_4N^+HSO_4^-$	A	98	79	21
	$(C_4H_9)_4N^+HSO_4^-$	A	25[d]		100
	$(C_4H_9)_4N^+HSO_4^-$	A	59[e]		100
	$(C_4H_9)_4N^+HSO_4^-$	A	86[f]	7	93
	$(C_4H_9)_4N^+HSO_4^-$	B	90	93	7
	$(C_4H_9)_4N^+HSO_4^-$	C	87	87	13
	$C_{12}H_{25}N(CH_3)_3Cl^-$	A	94	75	25
	$C_{16}H_{33}N(CH_3)_3{}^+Br^-$	A	90	77	23
	Aliquat 336	A	87	79	21
	$PhCH_2N(C_2H_5)_3{}^+Cl^-$	A	87	78	22
$NiSO_4$/KI	$(C_4H_9)_4N^+HSO_4^-$	A	17[g]	100	
$NiSO_4$	$(C_4H_9)_4N^+HSO_4^-$	A			

[a] See Experimental Section for general procedure. [b] A = 4-methyl-2-pentanone; B = $PhCH_3$; C = *tert*-amyl alcohol. [c] Isolated yields. [d] 0.5 M NaOH. [e] 1.0 M NaOH. [f] 1.5 M NaOH. [g] Reaction at 50 °C.

$Ni_5(CO)_{15}{}^{2-}$ and $Ni_6(CO)_{16}{}^{2-}$ and that the latter are able to catalyze the carbonylation of allylic halides. This method has the disadvantage of requiring the use of the extremely toxic nickel tetracarbonyl. Various nickel(II) complexes, including nickel cyanide [$Ni(CN)_2$], have been used in homogeneous catalysis instead of $Ni(CO)_4$;[11] however, a reducing agent (e.g., iron/manganese alloy) is usually needed to generate the catalytically active species and catalyst promoters such as thiourea or halide ion are often added as well.[12] One role of halide ion may be to generate $[Ni(CO)_3X]^-$ where X^- = Cl^-, Br^-, and I^-.[13,14]

It was anticipated that cyanonickel(II) complexes could effectively catalyze carbonylation reactions under phase-transfer conditions and that such reactions may proceed via the mononuclear complex $Ni(CO)_3CN^-$. To our knowledge, no publications have appeared on the isolation of pure $Ni(CO)_3CN^-$.[15] We now wish to report that cyanonickel(II) complexes indeed are useful catalysts in biphasic and phase-transfer-catalyzed reactions and that $Ni(CO)_3CN^-$ probably plays a key role in these processes.

Results and Discussion

Treatment of allyl bromide with carbon monoxide, catalytic quantities of potassium tetracyanonickelate, and Aliquat 336, 5 M NaOH, and *tert*-amyl alcohol as the organic phase, at 60 °C for 7 h and then 14 h at room temperature, afforded (*E*)-2-butenoic acid in only 2.5% yield. However, when the solution of the nickel complex was pretreated with carbon monoxide at 50–70 °C for 1–3 h (i.e., without the organic substrate), the yield of the acid increased to 28%. A somewhat higher yield (37%) was attained by using tetrabutylammonium hydrogen sulfate as the phase-transfer agent. The yield of (*E*)-2-butanoic acid was 39% by using 4-methyl-2-pentanone as the organic phase (Table I).

Superior to $K_2Ni(CN)_4$ was $Ni(CN)_2$ which converted allyl bromide to (*E*)-2-butenoic acid in 69% yield when the entire process was carried out at 50 °C. But the optimum method for effecting the carbonylation reaction consists of generation of the catalytically active species (i.e., pretreatment at 60 °C for 2–3 h), followed by slow addition of the substrate to the phase-transfer system which was cooled to room temperature. In that event, nearly quantitative yields of (*E*)-2-butenoic and 3-butenoic acids are produced.

The results in Table I indicate that, while a quaternary ammonium salt is beneficial for the carbonylation reaction, the latter can occur in the absence of the phase-transfer agent (i.e., a biphasic process). The best phase-transfer catalyst is tetrabutylammonium hydrogen sulfate, but dodecyltrimethylammonium chloride and cetyltrimethylammonium bromide are also useful. *tert*-Amyl alcohol, toluene, and 4-methyl-2-pentanone were used as the organic phase, with 4-methyl-2-pentanone being the solvent of choice. The base concentration significantly influences the yield and product distribution. As the base concentration is reduced from 5 M to 1.5, 1.0, and 0.5 M, the yield of butenoic acids obtained from allyl bromide decreases from 98% to 25% (0.5 M). Furthermore, while the ratio of (*E*)-2-butenoic/3-butenoic acid is 3.65/1.00 at 5 M NaOH, only the unconjugated acid results at 0.5 M or 1 M NaOH. At 1.5 M NaOH, a small amount of base-catalyzed isomerization is observed, giving the thermodynamically more stable (*E*)-2-butenoic acid. Use of potassium tetracyanonickelate as the catalyst, and 0.5 M NaOH, also gave lower yields of butenoic acids, with the unconjugated isomer as the major one.

Other non-cyanonickel(II) catalysts such as nickel iodide and nickel sulfate are completely ineffective. (*E*)-2-Butenoic acid is formed, albeit in 17% yield, when allyl bromide is carbonylated in the presence of both $NiSO_4$ and KI (1.6:1.0:1.0 mole ratio of allyl bromide/KI/$NiSO_4$) at 50 °C. Several other findings are worth noting. First, the optimum ratio of nickel complex to quaternary ammonium salt is 5:1, with modest reductions in product yields occurring with increased phase-transfer catalyst concentration. Second, the yields of acids decrease with an increase in temperature. Third, the use of synthesis gas (i.e., 1:1 CO/H_2) instead of carbon monoxide results in lower product yields, as witnessed by the formation of butenoic acids from allyl bromide in 71% yield [71.4 28.6 (*E*)-2-butenoic/3-butenoic acid] compared with 98% yield in the case of carbon monoxide.

The $Ni(CN)_2$ phase-transfer-catalyzed carbonylation reaction is applicable to both allylic chlorides and bromides (see Table II for results). Fine yields of acids were obtained by using allyl halides with an allyl substituent at the 1- or 3- but not the 2-position of the allyl unit. Only the *E* isomer of 2-butenoic acid is obtained from allyl chloride or bromide, the byproduct being the unconjugated

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Table II. Carbonylation of Allyl Halides by $CO/Ni(CN)_2/(C_4H_9)_4N^+HSO_4^-$/5 M NaOH/4-Methyl-2-pentanone

halide	yield of acids,[a] %	product distribution
$CH_2{=}CHCH_2Br$	98[b,c]	(*E*)-2-butenoic acid, 79 3-butenoic acid, 21
$CH_2{=}CHCH_2Cl$	88	(*E*)-2-butenoic acid, 86 3-butenoic acid, 14
$PhCH{=}CHCH_2Br$	67	(*E*)-4-phenyl-3-butenoic acid, 100
$PhCH{=}CHCH_2Cl$	84[d]	(*E*)-4-phenyl-3-butenoic acid, 100
$CH_3CH{=}CHCH_2$-Br	91	3-pentenoic acid, 44 2-methyl-3-butenoic acid, 4 (*Z*)-2-methyl-2-butenoic acid, 52
$(CH_3)_2C{=}CHCH_2$-Br	87	4-methyl-3-pentenoic acid, 83 2,2-dimethyl-3-butenoic acid, 17
$CH_2{=}CHCH$-$(CH_3)Cl$	93	3-pentenoic acid, 68 2-methyl-3-butenoic acid, 14 (*Z*)-2-methyl-2-butenoic acid, 18
$CH_2{=}C(CH_3)CH_2$-Br		

[a] Isolated yields. [b] 81% yield after 135 min. [c] 71% yield using CO/H_2 instead of CO [71/29 ratio of (*E*)-2-butenoic acid/3-butenoic acids]. [d] 71% yield using $CO:/H_2$.

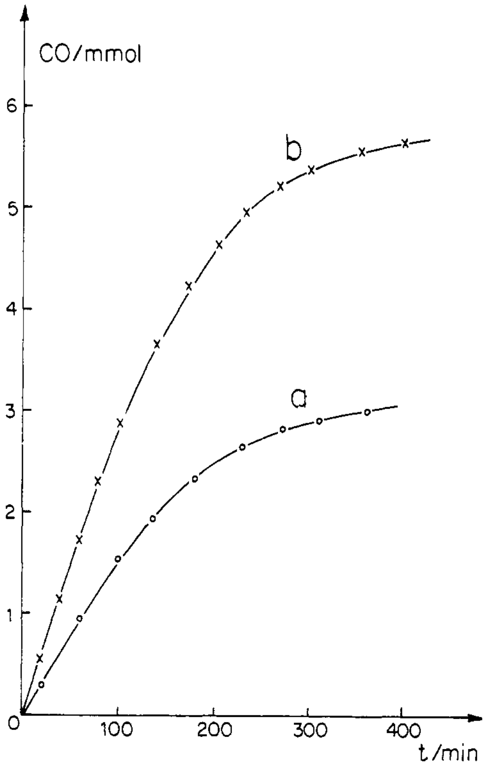
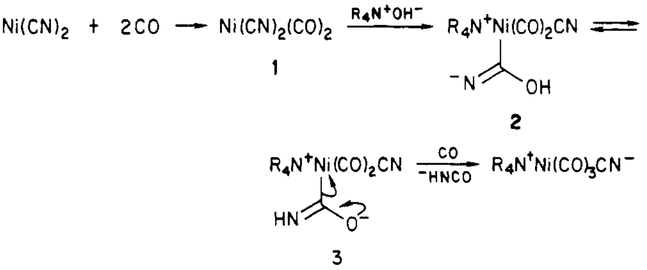


Figure 1. Gas uptake during reduction of $Ni(CN)_2$ by CO/NaOH. Conditions: $Ni(CN)_2$, 1 mmol (a), 2 mmol (b); 25 mL of 1 M NaOH; 25 mL of 4-methyl-2-pentanone; $(C_4H_9)_4HSO_4^-$, 0.2 mmol (a), 0.4 mmol (b).

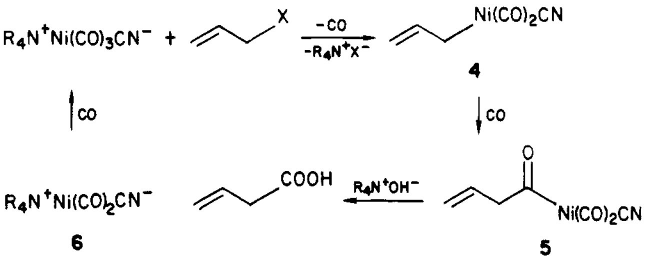
acid. The presence of a phenyl substituent on the double bond affords only the acid with the retained double bond in an *E* configuration. Different proportions of acids are obtained from 1-bromo-2-butene and 3-chloro-1-butene, but the only 2-methyl-2-butenoic acid formed is of *Z* stereochemistry. Interestingly, 2-pentenoic acid was not detected by using either substrate. It should be noted that, although all of these reactions were allowed to stir overnight at room temperature, they were essentially complete in 3–5 h.

The formation of the catalytically active nickel complex during the pretreatment phase could be followed by measuring the uptake of carbon monoxide (Figure 1).[16] Three moles of carbon monoxide were absorbed by a solution of $Ni(CN)_2$ in NaOH/4-methyl-2-pentanone/$(C_4H_9)_4N^+HSO_4^-$, over a period of several hours at 60 °C. During this time the organic phase remained colorless, while the aqueous phase became bright yellow. Addition of bis(triphenylphosphine)nitrogen(1+) chloride [PPN^+Cl^-] to the aqueous phase gave a yellow solid which displayed three intense absorption bands in the infrared spectrum at 2108, 2045, and 1963 cm^{-1} (CH_2Cl_2). The analytical data, and the similarity of the IR results to those of $[Ni(CO)_3X]^-$ complexes [e.g., 2049.0, 1958.4 cm^{-1} for $(C_4H_4)_4N^+Ni(CO)_3I^-$ in acetone],[13] suggest that the anion can be formulated as $[Ni(CO)_3CN]^-$ having C_{3v} symmetry and ν_{CN} at 2108 cm^{-1}. Although the same anionic species was obtained by using $Ni(CN)_4^{2-}$ instead of $Ni(CN)_2$, the reduction of the dianion by CO/OH^- is nearly three times slower than that of $Ni(CN)_2$ and this may account for the higher acid product yields using $Ni(CN)_2$ as the catalyst.

Scheme I



Scheme II



A possible mechanism for the conversion of nickel cyanide to $Ni(CO)_3CN^-$ is outlined in Scheme I. Reaction of the nickel catalyst with carbon monoxide may give the dicyanodicarbonylnickel complex **1**. Attack by hydroxide ion at one of the cyanocarbon atoms of **1** would afford **2** which is convertible to **3** on hydrogen transfer. $R_4N^+Ni(CO)_3CN^-$ would then result on elimination of HCNO. Alternatively, it is conceivable that the initial step in this sequence is the attack of hydroxide ion at a cyanocarbon of $Ni(CN)_2$ followed by addition of two carbon monoxide ligands to give **2**.

The reaction of the pretreated catalyst mixture with the organic substrate was next examined. The organic phase becomes deep yellow on addition of the allyl halide, and in a fast reaction 1 mol of CO is evolved for 1 mol of substrate [using, for this purpose, an excess of $Ni(CO)_3CN^-$]. A relatively slow uptake of CO follows (see Figure 2) leading to the carbonylation product and to the regeneration of the catalyst (with the loss of the yellow color of the organic phase). These findings suggest the mechanism outlined in Scheme II. Reaction of the cyanotricarbonylnickel anion with allyl halide may give the

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[16] The reason that 1 M NaOH was used instead of 5 M NaOH for following the rate of uptake of carbon monoxide is that at the higher base concentration, there is some uptake of gas even in the absence of the nickel catalyst and the organic phase. At 1 M NaOH, consumption of carbon monoxide only occurs when $Ni(CN)_2$ is present.

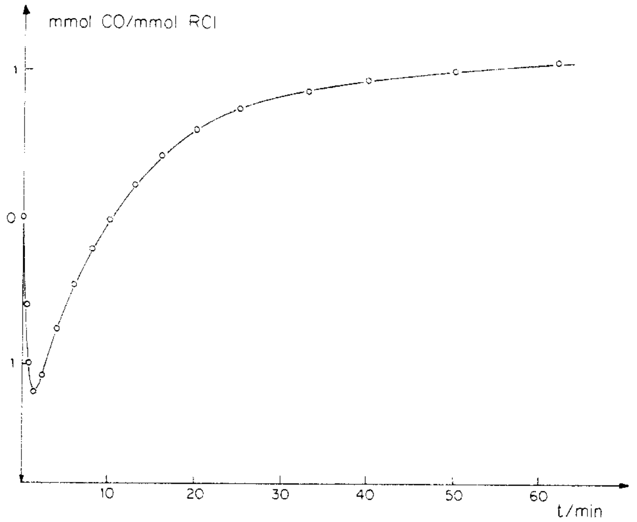

Figure 2. Evolution and subsequent uptake of carbon monoxide during the carbonylation of 1-chloro-3-phenyl-2-propene in the presence of $Ni(CO)_3CN^-$. Conditions: 25 mL of 1 M NaOH, 25 mL of 4-methyl-2-pentanone, 0.4 mmol of $(C_4H_9)_4N^+HSO_4^-$; 0.77 mmol of 1-chloro-3-phenyl-2-propene; 2.0 mmol of $Ni(CO)_3CN^-$.

σ-allyl complex **4**. Ligand migration with addition of CO would convert **4** to **5** and the acid would then be formed by hydroxide ion cleavage of the nickel–acyl carbon bond. Carbonylation of the byproduct **6** would regenerate the catalytic species. Note that interconversion of the σ-allyl complex **4** with a π-allyl species is likely, as witnessed by the formation of isomeric acid products in some instances (e.g., 1-bromo-2-butene).

Experimental Section

General Data. Melting point determinations were made by using a Fisher-Johns apparatus. Infrared spectra were recorded on a Perkin-Elmer 783 spectrometer, while NMR spectra were run on a Varian EM360A or XL300 instrument. A VG Micromass 7070E spectrometer was used for mass spectral determinations.

Hydrated nickel cyanide [$Ni(CN)_2 \cdot 4H_2O$—purified], nickel iodide, nickel sulfate, bis(triphenylphosphine)nitrogen(1+) chloride, and the quaternary ammonium salts were commercial products. Potassium tetracyanonickelate was prepared according to a literature procedure.[17] The organic substrates were purified by distillation or by passing through a silica gel column prior to use. The uptake of carbon monoxide was followed using a thermostatted gas burette.

General Procedure for the Nickel(II) Phase-Transfer-Catalyzed Carbonylation of Allyl Halides. Carbon monoxide was rapidly bubbled for a few minutes through a stirred solution of 5 M NaOH (25 mL), 4-methyl-2-pentanone (25 mL), and tetrabutylammonium hydrogen sulfate (0.2 mmol). Nickel cyanide (1.0 mmol) was added, and the reaction mixture was heated at 60 °C for 3 h under a carbon monoxide atmosphere. After being cooled to room temperature, a solution of the allyl halide (11.6 mmol) in 4-methyl-2-pentanone (20 mL) was added drop-by-drop, over a 3-h period, and then stirring was continued overnight at room temperature. The phases were separated; the aqueous phase was washed with ether (2 × 25 mL) acidified (25 mL of 3 M H_2SO_4—*caution*! HCN may possibly be generated), and extracted with ether (4 × 25 mL). The combined ether extracts were washed with water (20 mL), dried ($MgSO_4$), and rotary evaporated to give the acid product(s).

The products were identified by comparison of physical data with authentic materials, and the isomer ratios were readily determined by NMR spectroscopy.

Bis(triphenylphosphine)nitrogen(1+) Cyanotricarbonylnickelate. A mixture of hydrated nickel cyanide (0.366 g, 2.0 mmol), 5 M NaOH (25 mL), and 4-methyl-2-pentanone (25 mL) was stirred under carbon monoxide at 60 °C for 2.5 h. The resulting mixture consisted of a light green-yellow aqueous phase and a colorless organic phase. After being cooled to room temperature, the aqueous phase was separated with a pipet and washed with methylene chloride (50 mL). To bis(triphenylphosphine)nitrogen(1+) chloride (0.76 g, 1.50 mmol) in methylene chloride (25 mL) in a Schlenk tube, under carbon monoxide, was added the washed aqueous phase, and the mixture was stirred for several minutes resulting in an intense yellow organic phase and a colorless aqueous phase. The former was carefully separated (by pipet) and concentrated to near dryness. Treatment of the residue with benzene (10 mL) followed by rotary evaporation gave 0.869 g (82%, based on PPN^+Cl^-) of yellow $(Ph_3P)_2N^+Ni(CO)_3CN^-$. Anal. Calcd for $C_{40}H_{30}N_2NiO_3P_2$: C, 67.92; H, 4.28; N, 3.96. Found: C, 67.56; H, 4.70; N, 3.79.

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