Tetrahedron Letters,Vol.23,No.39,pp 3999-4002,1982 0040-4039/82/393999-04$03.00/0
Printed in Great Britain

CONCERNING THE MECHANISM OF A CYANOMETALLATE MEDIATED CARBONYLATION REACTION

by

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Abstract: The $[Ni(CN)_2(CO)_2]^{2-}$ anion (I) reacts with either one or two equivalents of benzyl bromide in either water/acetone or anhydrous acetonitrile to produce mainly 1,3-diphenyl-2-propanone. Excess carbon monoxide inhibits the reaction. These results are interpreted as indicating that I is an intermediate in the reaction of $K_4[Ni_2(CN)_6]$ with CO and $PhCH_2Br$ to form 1,3-diphenyl-2-propanone.

Although the mechanisms through which organic halides undergo carbonylation by transition metal carbonyl complexes have been the subject of intensive investigations,[1] the reaction of benzyl bromide with potassium hexacyanodinickelate[I], $K_4[Ni_2(CN)_6]$, "Belluci's salt", in the presence of CO to yield 1,3-diphenyl-2-propanone is, to date, the only example of transition metal mediated carbonylation involving a cyanide complex[2] (eq. 1).

$$K_4[Ni_2(CN)_6] + PhCH_2Br \xrightarrow[H_2O\text{-acetone}]{CO} \underset{90.4\%}{PhCH_2C(O)CH_2Ph} \qquad (1)$$

Since it has been established[3] that Belluci's salt disproportionates quantitatively in liquid NH_3 in the presence of CO according to equation (2),

$$K_4[Ni_2(CN)_6] + 2CO \xrightarrow[\text{l. }NH_3]{} K_2[Ni(CN)_2(CO)_2] + K_2[Ni(CN)_4] \qquad (2)$$

and that potassium tetracyanonickelate is unreactive with benzyl bromide,[2b] the intermediacy of the dicyanodicarbonylnickel [0] anion, $[Ni(CN)_2(CO)_2]^{2-}$, 1, is plausible. This possibility was noted by Hashimoto et al.[2b], who, however, seem to prefer a mechanism in which an initially formed benzylnickel species reacts with additional CO to form a benzoylnickel complex by insertion. A complicating consideration is the claim that aqueous solution of 1 are pH sensitive and form $Ni(CO)_4$ in neutral aqueous media in the presence or CO.[4] Nickel tetracarbonyl has been shown to react with benzyl bromide in dimethylformamide to give 1,3-diphenyl-2-propanone in high yield.[5]

As part of a more general study of the reactivity of low-valent transition metal cyanide complexes, we have examined the relationship of compound 1 to reaction (1). We find that reaction of either the mixture $K_2[Ni(CN)_2(CO)_2]$ + $K_2[Ni(CN)_4]$ or of $[P(C_6H_5)_4]_2$ $[Ni(CN)_2(CO)_2]$, 1a,[3] with benzyl bromide produces 1,3-diphenyl-2-propanone. Reactions of the mixture of potassium salts or 1a with either one or two equivalents of benzyl bromide, with and without CO present, were carried out. The results of these experiments are summarized in Table I.[6]

Table 1.

	$K_2[Ni(CN)_2(CO)_2]$+$K_2[Ni(CN)_4]$: $PhCH_2Br$	% Yield		
Expt.	Molar Ratio	1,3-diphenyl-2-propanone	bibenzyl	benzyl cyanide
1	1:2	89%	~6%	<1%
2	1:2 (CO present)	52%	~3%	not detected
Lit.[10]	$K_4[Ni_2(CN)_6]$: halide			
	1:2	90.4%	3.1%	not detected
	$[(C_6H_5)_4P]_2[Ni(CN)_2(CO)_2]$: $PhCH_2Br$			
3	1:1	75%	~9%	not detected
4	1:2	46%	~6%	not detected
5	1:1 (CO present)	38%	--	not detected
6	1:2 (CO present)	21%	<1%	not detected

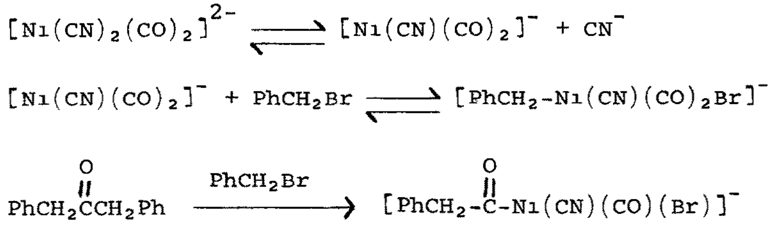
[a] A mixture of water and acetone was employed as solvent in entries 1 and 2; acetonitrile for entries 3 to 6. Reaction times and temperature were identical in every case.

1,3-Diphenyl-2-propanone was clearly the major organic product in each case. Product yields dropped significantly in the presence of CO or when two equivalents of halide per 1 were used. The effects of the two modifications are roughly additive. The reaction proceeds almost as well in a strictly anhydrous medium as in the mixed aqueous-organic solvent system used for reaction (1).

The effect of excess CO is consistent with a mechanism involving ligand loss prior to or as the rate determining step; carbonylation reactions retarded by CO are known.[8] Ligand loss has been shown to be kinetically important in related reactions of $Ni(CO)_4$ with allyl bromide[9] and iodobenzene.[10]

The effect of benzyl bromide on the ketone yield is most likely a manifestation of the presence of an alternate reaction path. Metal cyanide anions are potentially ambidentate nucleophiles, since the cyanide nitrogens as well as the metal center are sites of high electron density. In the presence of a higher concentration of benzyl bromide, reaction of an intermediate alkyl or acyl nickel cyanide species at a cyanide may become competitive with the reaction path leading to ketone. A competitive pathway leading to a metal-bound product is consistent with our inability to detect any additional organic products in the reactions with excess benzyl bromide.[11] Bands at 1629 and 1649 cm^{-1} in the infrared spectra of residues from these reactions are consistent with the presence of bridging isocyanides. A mechanism incorporating these features is outlined in Scheme I. The only nickel-containing product evident (by IR) in the 1:1 reaction residues is tetracyanonickelate(II), indicating that the real stoichiometry must be 2:1 halide to 1.

Scheme I



$$[Ni(CN)_2(CO)_2]^{2-} \rightleftharpoons [Ni(CN)(CO)_2]^- + CN^-$$

$$[Ni(CN)(CO)_2]^- + PhCH_2Br \rightleftharpoons [PhCH_2\text{-}Ni(CN)(CO)_2Br]^-$$

$$PhCH_2\overset{O}{\overset{\|}{C}}CH_2Ph \xleftarrow{PhCH_2Br} [PhCH_2\text{-}\overset{O}{\overset{\|}{C}}\text{-}Ni(CN)(CO)(Br)]^-$$

The above experiments offer the first evidence for the intermediacy of 1 in the carbonylation of benzyl bromide by $K_4[Ni_2(CN)_6]$ with carbon monoxide. Experiments are in progress to identify organonickel intermediates and to study the effect of halide structure and solvent on the reaction. That solvent may play an important role in these reactions is shown by the observation that while E-β-bromostyrene reacts with 1 in mixed water-methanol to give a mixture of E-cinnamaldehyde and E-methyl cinnamate,[2b] the major product of the reaction with 1a carried out in anhydrous acetonitrile is E-cinnamonitrile.[12]

Acknowledgements: Acknowledgement is made to the Donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the Research Corporation for the support of this research. The GC-Mass Spectrometer was purchased through a grant from the N.I.H. (GMO-7261). We thank Dr. Charles Coulson and Professor John Lowenstein for their assistance with the GC-MS.

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11. The recovered benzyl bromide in entries 4,5 and 6 was much less than expected based on the product yields observed.
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(Received in USA 12 July 1982)