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Preliminary communication

Reactions of benzoyl(carbonyl)transition metal complexes with $LiNMe_2$: on the feasibility of a reaction route to α-keto amide through an acyl(carbamoyl)cobalt intermediate

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Abstract

CO-coordinated benzoyltransition metal complexes, $PhCOCo(CO)_3L$ ($L = PPh_3$, PCy_3, and PMe_3), $PhCOMn(CO)_5$, and $PhCORe(CO)_5$, have been prepared and their reactions with $LiNMe_2$ examined. The reactions give α-keto amide ($PhCOCONMe_2$) after treating the systems with Br_2 or organic halides.

Conversion of organic halides into α-keto acid derivatives with introduction of two CO molecules can be promoted by palladium and cobalt complexes. Detailed studies on the mechanism of the palladium-catalyzed double carbonylation have revealed that the key step in the catalytic cycle involves nucleophilic attack of amine or alcohol (in conjunction with Et_3N) on a CO-coordinated acylpalladium complex to give an acyl(carbamoyl)- or acyl(alkoxycarbonyl)-palladium complex that reductively eliminates α-keto amide or α-keto ester, respectively [1–3].

$$[RCOPd(CO)L_2]X + HNu \xrightarrow[-Base\cdot HX]{+Base} [RCOPd(CONu)L_2] \xrightarrow{-PdL_2} RCOCONu \quad (1)$$

(HNu = amines and alcohols)

On the other hand, for the cobalt-catalyzed double carbonylation of benzyl halides, a specific double CO insertion has been assumed [4]. However, the possibility of α-keto acid derivative formation by a route similar to that in the palladium case has not been examined with cobalt and other transition metal complexes *. In this study we present evidence indicating that the route involving nucleophilic

* An α-keto acid formation process by reductive elimination of benzoyl and hydroxycarbonyl groups from a cobalt complex has been assumed for the cobalt-catalyzed double carbonylation of phenyl bromide without unequivocal experimental evidence [5].

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Table 1

Reactions of the benzoylcarbonyl complexes with $LiNMe_2$ and Br_2 [a]

Run	Complex	$LiNMe_2$ (equiv/complex)	Atmosphere	Reaction temperature (°C)	Products (yield, %)		
					$PhCOCONMe_2$	$PhCONMe_2$	Other
1	**1a**	1.5	CO	−78	70	22	–
2	**1a**	1.5	Ar	−78	69	24	–
3 [b]	**1a**	1.5	CO	r.t.	0	55	Ph_2CO (22)
4	**1b**	1.5	Ar	−78	83	17	–
5	**1b**	1.5	Ar	r.t.	74	26	–
6 [b]	**1b**	1.5	Ar	r.t.	0	14	Ph_2CO (14)
7	**1c**	5	Ar	−78	22	78	–
8	**1c**	5	Ar	r.t.	87	13	–
9	**1c**	5	CO	r.t.	84	2	–
10 [b]	**1c**	5	Ar	r.t.	0	28	–
11	**2**	5	Ar	−78	24	34	–
12	**3**	5	Ar	−78	72	28	–

[a] The reaction of the complex (0.05 mmol) with $LiNMe_2$ was carried out in THF (1 ml) for 1 h at the temperature indicated above. Two equivalents of Br_2 relative to $LiNMe_2$ was then added, and the resulting solution was analyzed by GLC. [b] The reaction was performed for 24 h without treatment with Br_2.

attack on CO-coordinated acyl-transition metal complexes can also be operative in the cobalt systems.

$PhCOCo(CO)_3(PPh_3)$ (**1a**) was prepared by published procedures [6]. New benzoylcobalt complexes, $PhCOCo(CO)_3L$ ($L = PCy_3$ *, **1b**; PMe_3, **1c**), were prepared by reactions of $Na[Co(CO)_3L]$ with PhCOCl, and were identified by elemental analysis and IR and NMR spectroscopy **. Reactions of **1a–1c** with $LiNMe_2$ in THF followed by treatment with a CH_2Cl_2 solution of Br_2 afford $PhCOCONMe_2$ together with $PhCONMe_2$ (Table 1, runs 1–10).

$$PhCOCo(CO)_3L \xrightarrow[THF,\ CO\ or\ Ar]{+LiNMe_2} \xrightarrow{+Br_2} PhCOCONMe_2 + PhCONMe_2 \qquad (2)$$

($L = PPh_3$, **1a**; PCy_3, **1b**; PMe_3, **1c**)

The reactions of **1a** and **1b** proceed readily even at −78°C to give the α-keto amide in > 70% yield, whereas the PMe_3-coordinated complex **1c** requires higher reaction temperatures to produce the α-keto amide in good yields. The presence of carbon monoxide in the system scarcely affects the yield of α-keto amide. Treatment of the reaction system with Br_2, after the reaction of the benzoylcobalt complexes and $LiNMe_2$, is essential to obtaining the α-keto amide; otherwise the system affords $PhCONMe_2$ and/or Ph_2CO. The latter compound may be produced by an intermolecular disproportionation between the benzoyl complex and a phenylcobalt species formed by decarbonylation of the benzoyl complex [7].

* PCy_3 = tricyclohexylphosphine.

** **1b** IR (KBr): 2036, 1960, 1930, and 1617 cm^{-1}; $^{13}C\{^1H\}$ NMR (THF-d_8, −78°C): δ 201.4 (d, J(CP) 18 Hz, $CO_{terminal}$), 236.3 (d, J(CP) 31 Hz, $CO_{benzoyl}$). **1c** IR (KBr): 2044, 1978, 1939, and 1617 cm^{-1}; $^{13}C\{^1H\}$ NMR (THF-d_8, −78°C): δ 200.2 (d, J(CP) 22 Hz, $CO_{terminal}$), 237.2 (d, J(CP) 35 Hz, $CO_{benzoyl}$).

Table 2

Effects of the various compounds on the α-keto amide formation from **1c** and $LiNMe_2$ [a]

Run	Additive	Yield (%/1c)	
		$PhCOCONMe_2$	$PhCONMe_2$
1	MeI	65	1
2	$(MeO)_2SO_2$	73	1
3	$PhCH_2Cl$	55	0
4	PhBr	17	1
5	PhCl	15	2

[a] The reaction of **1c** (0.05 mmol) with $LiNMe_2$ (0.075 mmol) was performed in THF (1 ml) at room temperature for 2 h under Ar. The additive (0.15 mmol) was then added. The resulting solution was stirred for 30 min at room temperature and analyzed by GLC.

Table 2 demonstrates that the α-keto amide can be obtained with organic halides and dimethyl sulfate instead of Br_2. Methyl iodide and dimethyl sulfate are particularly effective, whereas phenyl halides show modest reactivities.

Reactions of **1a** with nucleophiles other than $LiNMe_2$ were also examined. Reaction with *sec*-BuONa (5 equiv./**1a**) at room temperature in THF followed by treatment with Br_2 gave PhCOCOO-*sec*-Bu (18%/**1a**) and PhCOO-*sec*-Bu (26%). Similar treatment of **1a** with MeONa gave the corresponding ester, but no α-keto ester formation was observed even in the presence of crown ether. Reaction of **1a** with Et_2NH afforded only amide.

The formation of α-keto acid derivatives from CO-coordinated acyltransition metal complexes is not limited to cobalt. Benzoylcarbonyl complexes of manganese and rhenium, $PhCOM(CO)_5$ (M = Mn (**2**) and Re (**3**)) [8], showed similar reactivities to the cobalt analogs and gave α-keto amide upon their treatment with $LiNMe_2$ and Br_2 (Table 1, runs 11 and 12).

The first step in the α-keto amide formation from the benzoylcarbonyl complexes is nucleophilic attack of $LiNMe_2$ on the terminal CO ligand to give anionic benzoylcarbamoyl complexes (A) *,**. The benzoylcarbamoyl complexes thus formed may be resistant to a direct reductive elimination because of their anionic character. Interaction of **A** with Br_2 or organic halides (RX) results in "oxidatively-induced reductive elimination" of the benzoyl and carbamoyl groups to give α-keto amide [11].

$$PhCOM(CO)_nL + LiNMe_2 \rightleftarrows \underset{(A)}{[PhCOM(CONMe_2)(CO)_{n-1}L]Li} \xrightarrow{Br_2 \text{ or } RX} PhCOCONMe_2 \qquad (3)$$

(M = CO, $n = 3$, L = tertiary phosphine; M = Mn and Re, $n = 4$, L = CO)

* IR spectrum of the reaction solution of **1c** and $LiNMe_2$ (1.2 equiv) in THF at room temperature revealed absence of **1c** and formation of a new cobalt species in the system: 1912s, 1850vs, and 1582m cm^{-1}. These absorptions are assignable to ν(CO) bands of $Li[PhCOCo(CONMe_2)(CO)_2(PMe_3)]$ as compared with the IR data for $Al[MeCOMn(CONMe_2)(CO)_4]_3$ [9].

** Cobalt(I) carbonyl complexes ($YCo(CO)_4$; Y = alkyl and halide ligands), are known to react with sodium alkoxide (NaOR) to form anionic $Na[YCo(COOR)(CO)_3]$ type complexes which are analogous to complex **A** in eq. 3 [10].

The recent study on the cobalt-catalyzed double carbonylation of phenyl bromide and calcium hydroxide to give PhCOCOOH showed that the double carbonylation reaction proceeds only when the catalytic system contains methyl iodide or dimethyl sulfate [5]. The results in Table 2 suggests that the methyl compounds added to the system may accelerate the reductive elimination of benzoylformic acid from an anionic benzoyl(hydroxycarbonyl)cobalt intermediate.

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