

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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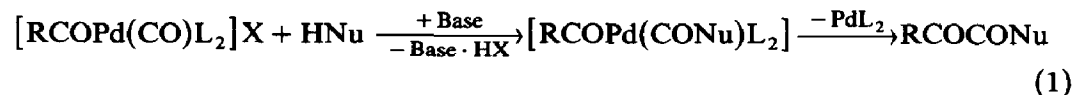
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Abstract

CO-coordinated benzoyltransition metal complexes, $\text{PhCOCo}(\text{CO})_3\text{L}$ ($\text{L} = \text{PPh}_3$, PCy_3 , and PMe_3), $\text{PhCOMn}(\text{CO})_5$, and $\text{PhCOTe}(\text{CO})_5$, 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].



(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].

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.

$\text{PhCOC}(\text{CO})_3(\text{PPh}_3)$ (**1a**) was prepared by published procedures [6]. New benzoylcobalt complexes, $\text{PhCOC}(\text{CO})_3\text{L}$ ($\text{L} = \text{PCy}_3$, **1b**; PMe_3 , **1c**), were prepared by reactions of $\text{Na}[\text{Co}(\text{CO})_3\text{L}]$ 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).



($\text{L} = \text{PPh}_3$, **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} ; $^{13}\text{C}\{^1\text{H}\}$ NMR ($\text{THF}-d_8$, -78°C): δ 201.4 (d, $J(\text{CP})$ 18 Hz, $\text{CO}_{\text{terminal}}$), 236.3 (d, $J(\text{CP})$ 31 Hz, $\text{CO}_{\text{benzoyl}}$). **1c** IR (KBr): 2044, 1978, 1939, and 1617 cm^{-1} ; $^{13}\text{C}\{^1\text{H}\}$ NMR ($\text{THF}-d_8$, -78°C): δ 200.2 (d, $J(\text{CP})$ 22 Hz, $\text{CO}_{\text{terminal}}$), 237.2 (d, $J(\text{CP})$ 35 Hz, $\text{CO}_{\text{benzoyl}}$).

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	$(\text{MeO})_2\text{SO}_2$	73	1
3	PhCH_2Cl	55	0
4	PhBr	17	1
5	PhCl	15	2

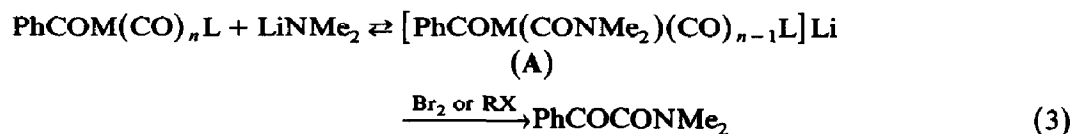
^a The reaction of **1c** (0.05 mmol) with LiNMe_2 (0.075 mmol) was performed in THF (1 ml) at room temperature for 2 h under Ar. The additive (0.15 mmol) was then added. The resulting solution was stirred for 30 min at room temperature and analyzed by GLC.

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, $\text{PhCOM}(\text{CO})_5$ ($\text{M} = \text{Mn}$ (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].



($\text{M} = \text{Co}$, $n = 3$, $\text{L} = \text{tertiary phosphine}$; $\text{M} = \text{Mn}$ and Re , $n = 4$, $\text{L} = \text{CO}$)

* 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 $\nu(\text{CO})$ bands of $\text{Li}[\text{PhCOCO}(\text{CONMe}_2)(\text{CO})_2(\text{PMe}_3)]$ as compared with the IR data for $\text{Al}[\text{MeCOMn}(\text{CONMe}_2)(\text{CO})_4]_3$ [9].

** Cobalt(I) carbonyl complexes ($\text{YCo}(\text{CO})_4$; $\text{Y} = \text{alkyl and halide ligands}$), are known to react with sodium alkoxide (NaOR) to form anionic $\text{Na}[\text{YCo}(\text{COOR})(\text{CO})_3]$ 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 PhCOCO_2H 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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