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

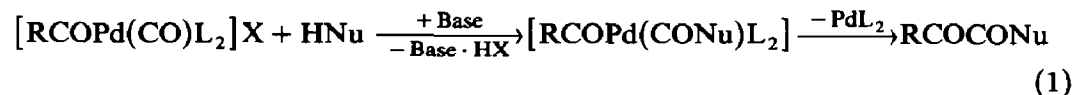**Nobuo Kawasaki, Kenji Masuzoe, Fumiyuki Ozawa, and Akio Yamamoto** *

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 227 (Japan)

(Received October 31st, 1988)

Abstract

CO-coordinated benzoyltransition metal complexes, PhCOCo(CO)$_3$L (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 (PhCO-CONMe$_2$) 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$_3$N) 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].

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

$$(1)$$

(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].

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$_2$CO (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$_2$CO (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)$_3$L (L = PCy$_3$ *, 1b; PMe$_3$, 1c), were prepared by reactions of Na[Co(CO)$_3$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$_2$Cl$_2$ solution of Br$_2$ afford PhCOCONMe$_2$ together with PhCONMe$_2$ (Table 1, runs 1–10).

$$\text{PhCOCo(CO)}_3\text{L} \xrightarrow[\text{THF, CO or Ar}]{+\text{LiNMe}_2} \xrightarrow{+\text{Br}_2} \text{PhCOCONMe}_2 + \text{PhCONMe}_2 \qquad (2)$$

(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$_2$CO. 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{^{1}H} 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{^{1}H} 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]

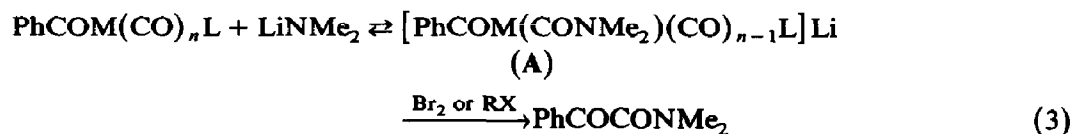| Run	Additive	Yield (%/1c)	
		PhCOCONMe$_2$	PhCONMe$_2$
1	MeI	65	1
2	(MeO)$_2$SO$_2$	73	1
3	PhCH$_2$Cl	55	0
4	PhBr	17	1
5	PhCl	15	2

[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$_2$NH 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].

$$PhCOM(CO)_nL + LiNMe_2 \rightleftarrows \left[PhCOM(CONMe_2)(CO)_{n-1}L\right]Li$$
$$(A)$$

$$\xrightarrow{Br_2 \text{ or } RX} PhCOCONMe_2 \qquad (3)$$

(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.

References

1 F. Ozawa, T. Sugimoto, Y. Yuasa, M. Santra, T. Yamamoto, and A. Yamamoto, Organometallics, 3 (1984) 683; F. Ozawa, T. Sugimoto, T. Yamamoto, and A. Yamamoto, ibid., 3 (1984) 692; F. Ozawa, H. Soyama, H. Yanagihara, I. Aoyama, H. Takino, K. Izawa, T. Yamamoto, and A. Yamamoto, J. Am. Chem. Soc., 107 (1985) 3235; F. Ozawa, N. Kawasaki, H. Okamoto, T. Yamamoto, and A. Yamamoto, Organometallics, 6 (1987) 1640. F. Ozawa, L. Huang, and A. Yamamoto, J. Organomet. Chem., 334 (1987) C9.

2 J. Chen and A. Sen, J. Am. Chem. Soc., 106 (1984) 1506; A. Sen, J. Chen, W.M. Vetter, and R.R. Whittle, ibid., 109 (1987) 148.

3 H. Yamashita, T. Kobayashi, T. Sakakura, and M. Tanaka, J. Mol. Catal., 40 (1987) 333; M. Tanaka, Yuki Gosei Kagaku Kyokaishi (J. Synth. Org. Chem. Jpn.), 45 (1987) 716, and ref. cited therein.

4 (a) H. Alper, Adv. Organomet. Chem., 19 (1981) 183. (b) M. Foa and F. Francalanci, J. Mol. Catal., 41 (1987) 89, and ref. cited therein.

5 F. Francalanci, E. Bencin, A. Gardano, M. Vincent, and M. Foa, J. Organomet. Chem., 301 (1986) C27; K. Itoh, M. Miura and M. Nomura, Bull. Chem. Soc. Japan, 61 (1988) 4151. See also: T. Kashimura, K. Kudo, S. Mori, and N. Sugita, Chem. Lett., (1986) 299, 483; J.Y. Lee and J.W. Wolfman (Ethyl Corp.), Japan Kokai Tokkyo Koho, (1984) JP 60-500445: Chem. Abstr., 102 (1985) 78371r; J.Y. Lee and T.J. Walter (Ethyl Corp.) U.S. Patent, (1984) 4473706; B. Fell and H. Chrobaczek, Chem. Ztg., 108 (1984) 291.

6 R.F. Heck and P.S. Breslow, J. Am. Chem. Soc., 84 (1964) 2499; W. Hieber and E. Lindner, Chem. Ber., 94 (1961) 1417.

7 R.G. Bergman, Acc. Chem. Res., 13 (1980) 113.

8 T.H. Coffield and J. Kozikowski, J. Org. Chem., 22 (1957) 598; W. Hieber, G. Braun, and W. Beck, Chem. Ber., 93 (1960) 901.

9 C.M. Lukehart, G.P. Torrence, and J.V. Zeile, Inorg. Chem., 15 (1976) 2393. For related studies see also: C.P. Casey and C.A. Bunnell, J. Am. Chem. Soc., 98 (1976) 436; C.P. Casey and D.M. Schenk, ibid., 102 (1980) 2723, 2728; C.M. Lukehart, Acc. Chem. Res., 14 (1981) 109, and ref. cited therein.

10 V. Galamb and G. Palyi, Organometallics, 6 (1987) 861; M. Tasi and G. Palyi, ibid., 4 (1985) 1523; F. Francalanci, A. Gardano, L. Abis, and M. Foa, J. Organomet. Chem., 251 (1983) C5.

11 J.P. Collman, L.S. Hegedus, J.R. Norton, and R.G. Fink, Principles and Applications of Organotransition Metal Chemistry, University Science Books, Mill Valley, CA, 1987.