CHEMISTRY LETTERS, pp. 1983-1986, 1989.

$Co_2(CH_2{=}C{=}O)(CO)_7$ as an Active Intermediate for Cobalt-catalyzed Alkoxycarbonylation of CH_2Br_2

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The dicobalt ketene complex, $Co_2(CH_2{=}C{=}O)(CO)_7$, in which the $CH_2{=}C{=}O$ ligand coordinated to one of the cobalt atoms by η^2-(C,C) manner, was cleanly isolated by the treatment of $Co_2(CO)_8$ with CH_2Br_2 in the presence of Zn, and promoted catalytic alkoxycarbonylation of CH_2Br_2.

Transition metal ketene complexes have drawn considerable attention as model compounds or virtually as C_2-template for carbon monoxide reduction leading to highly value-added oxygenates.[1,2] On relevance of CO activation by transition metal complexes, we previously reported transition metal-catalyzed alkoxycarbonylation of geminal dihaloalkanes leading to the corresponding carboxylates, and discussed potential importance of transition metal ketene intermediates as active species in these catalyses.[3] Basic to the understanding of these reactions is investigation on the structure and chemical properties of active intermediates formed from the complicated reaction mixture involving transition metal catalyst. In this papers, we report the isolation and chemical properties of dicobalt ketene complex, $Co_2(CH_2{=}C{=}O)(CO)_7$, as a reaction intermediate for $Co_2(CO)_8$-catalyzed alkoxycarbonylation of CH_2Br_2, and describe its possible reaction mechanism.

$$R^1R^2CX_2 + CO + CH_3OH \xrightarrow[\text{[M]}]{Zn} R^1R^2CHCO_2CH_3 + ZnX_2$$

$$R^1,\ R^2 = H,\ CH_3 \qquad X = Cl,\ Br$$

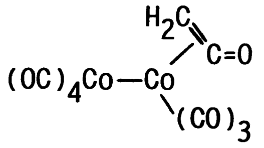
Treatment of $Co_2(CO)_8$ (1.00 g, 2.93 mmol) with CH_2Br_2 (10.2 g, 58.6 mmol) in THF in the presence of Zn (3.83 g, 59.0 mmol) at 20 °C for 2 days gave a dark brown suspension generating CH_4 [90% per $Co_2(CO)_8$], C_2H_4 (260%) and C_2H_6 (70%). After passing the solution through a celite pad under N_2, the dark brown solution was evaporated to dryness. By cooling the ether solution extracted from the residual brown solids, $Co_2(CH_2{=}C{=}O)(CO)_7$ (**1**) was isolated as very air sensitive yellow orange crystals with 32% yield.[4]

The structure of **1** was determined mainly by its spectral analysis using IR, NMR, and MS spectroscopies. The IR spectrum(KBr) of **1** reveals a typical signal

$$Co_2(CO)_8 \quad + \quad CH_2Br_2 \quad + \quad Zn \longrightarrow Co_2(CH_2{=}C{=}O)(CO)_7$$

1

at 1705s assignable to $\nu_{C=O}$ of the $CH_2{=}C{=}O$ ligand and ν_{C-H}(saturated) at 2990m and 2950m in addition to the signals at 2070s, 1950vs, and 1935s cm^{-1} for $\nu_{C\equiv O}$(terminal). The ^1H-NMR spectrum in CD_2Cl_2 exhibits equivalent CH_2 proton resonance at δ 2.18, while the ^{13}C-NMR shows characteristic signals due to the ketene ligand at δ 30.4 [$\underline{C}H_2$, J_{C-H} 151 Hz] and 166.8 ($\underline{C}{=}O$) in addition to the terminal carbonyl signals at 195.6, 201.7, and 204.6, respectively. The fast atom bombardment mass spectrum of **1** gave the parent signal at 356. The cryoscopic molecular weight determination of **1** in benzene was most feasible for the cobalt-dimer structure (Found: 341, Calcd: 356). These spectral results are fully consistent with the η^2-(C,C) ketene structure.$^{1)}$ One of the interesting features of **1** is on the coordination mode of the η^2-(C,C) ketene ligand, that is, whether it coordinates to the both cobalt atoms through a bridging manner or not. Multinuclear metal ketene complexes are known mostly as μ_2- or μ_3-$CH_2{=}C{=}O$ structure.$^{1,5)}$ In IR spectra, $\nu_{C=O}$ of these bridging ketene ligands appears typically in the region of the frequencies between 1650 and 1550 cm^{-1} lower by 100 to 200 cm^{-1} compared with mononuclear metal η^2-(C,C) ketene complexes. Moreover, ^{13}C-NMR spectra reveal the carbonyl signal of μ_2- or μ_3-$CH_2{=}C{=}O$ in the range of 200 to 260 ppm. These spectral data are accounted for by their possible resonance structures involving oxycarbene and oxyvinyl species.$^{6)}$ Consequently, these observation may suggest that **1** has the η^2-(C,C) ketene structure **2** in which the $CH_2{=}C{=}O$ possibly coordinates to one of the cobalt atoms through its carbon-carbon double bond rather than the alternative μ_2-ketene structure **3**, although no crystallographical analysis is available so far.



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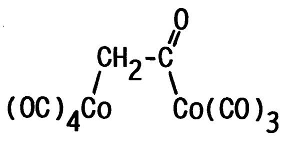

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The binuclear Co-ketene complex **1** was found to be remarkably reactive toward various nucleophiles under mild conditions as in the following equations. These findings are apparently in contrast to the reported chemical properties of multinuclear metal complexes of the bridging ketene.

Toluene solution of **1** readily reacted with excess CH_3OH to yield methylacetate (85%), while N,N-diethylacetamide (43%) was obtained by the reaction with diethylamine. Particular importance of **1** relevant to plausible intermediate for CO reduction is its high reactivity toward metal hydrides or molecular hydrogen under mild condition. Facile reduction of the ketene ligand converting into C_2H_5OH was quantitatively performed by the reaction with $LiAlH_4$

$$\begin{aligned} Co_2(CH_2{=}C{=}O)(CO)_7 &\xrightarrow{CH_3OH} CH_3CO_2CH_3 \\ &\xrightarrow{NH(C_2H_5)_2} CH_3CON(C_2H_5)_2 \\ &\xrightarrow{LiAlH_4} C_2H_5OH \\ &\xrightarrow{H_2} CH_4 + C_2H_6 + C_2H_5OH + CH_3CHO \end{aligned}$$

in THF at -20—0 °C. Hydrogenation of **1** in a pressure bottle (5 atm of H_2 in THF at 50 °C for 20 h) was carried out until the original orange color turned to deep brown. The resulting gas phase and solution were analyzed to contain CH_4 (32%/**1**), C_2H_6 (9%), C_2H_5OH (28%), and CH_3CHO (7%). Although most of the reported μ_2- and μ_3-ketene complexes were rather inert toward H_2, these observation on **1** indicates that multinuclear ketene complex in certain case can be substantially converted to C_2-oxygenates along with hydrocarbons under mild condition. We thought it most likely that this result should be ascribed virtually to high reactivity of non-bridging η^2-(C,C) ketene structure toward H_2 and a variety of nucleophiles.$^{6)}$ In particular, studies on the reactivity toward H_2 appears to be important because of the potential relevance of ketene intermediates on catalyst surfaces during CO reduction chemistry.

Interestingly, carbonylation of **1** in CH_3OH at 50 atm resulted in the formation of dimethylmalonate with 7% yield in addition to methylacetate (77%) as a main product.

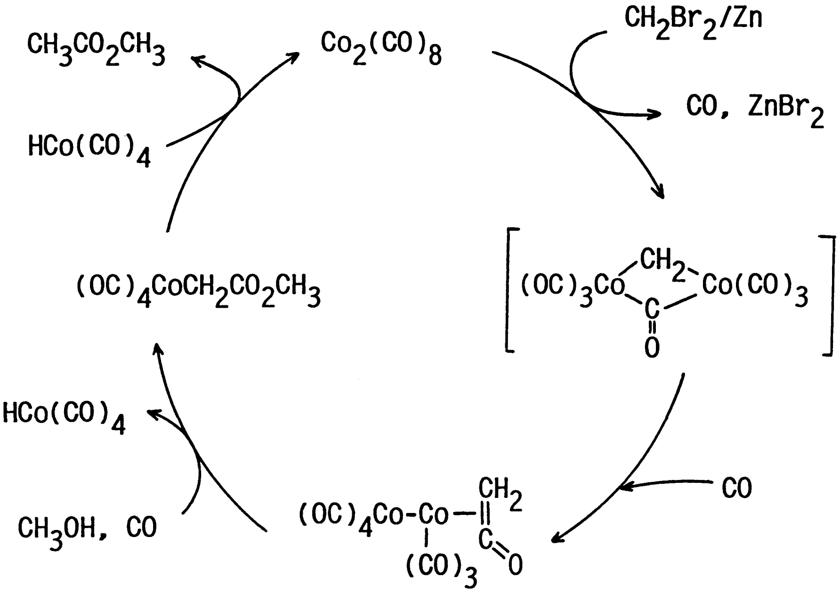
$$Co_2(CH_2{=}C{=}O)(CO)_7 + CO + CH_3OH \longrightarrow CH_2(CO_2CH_3)_2 + CH_3CO_2CH_3$$

The binuclear Co-ketene complex **1** was found to be capable for catalyzing methoxycarbonylation (5 atm CO in THF at -40—20 °C for 6 h) of CH_2Br_2 yielding methylacetate (385%/**1**) in the pesence of Zn, while aminocarbonylation took place also catalytically with rather slower process (184%/**1**).

On the basis of the above stoichiometric model reactions, cobalt-catalyzed alkoxycarbonylation of CH_2Br_2 may be accounted for by the combination of the elementary process, depicted in Scheme, of (a) initial formation of cobalt-carbene intermediate, which decomposed in part to give CH_4 and C_2H_4, (b) CO-coupling reaction with these carbene species resulting dicobalt ketene complex which was isolated, (c) nucleophilic attack of CH_3OH on the $CH_2{=}C{=}O$ ligand to form carbomethoxymethyl cobalt complex **4**$^{7)}$ as a transient and presumably $HCo(CO)_4$, (d) conceivable protonation of the alkyl cobalt species with $HCo(CO)_4$ to afford methylacetate and regenerate $Co_2(CO)_8$, of which formation was proved by MS analysis of the complex obtained by the reaction of **4** with $HCo(CO)_4$, as a carrier of the subsequent catalytic cycle.

Potential applicability of dicobalt ketene complex **1** as effective catalyst for the formation of dialkylmalonate is now actively investigated.

The authors are indebted to a Grant-in-Aid for Special Project Research by the Ministry of Education Science and Culture for financial support (No 61125003 and 62115002).



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4) When the reaction was performed under CO atmosphere (3 atm), yellow solids obtained were confirmed as $Co_2(CH_2=C=O)(CO)_8$ by MS spectral analysis although it could not be cleanly isolated.

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7) Treatment of **1** with 5 fold $NaOCH_3$ in THF led to light yellow solution, from which light yellow crystalline solids were isolated to be identified as carbomethoxymethyl cobalt complex, $Co(CH_2CO_2CH_3)(CO)_4$ **4** (27% yield) on the basis of its IR and NMR spectroscopies. IR(CH_2Cl_2) 2050w, 1947s($\nu_{C\equiv O}$), 1685s($\nu_{C=O}$); ^{1}H-NMR($CDCl_3$) δ 2.11(s, Co-$C\underline{H}_2$, 2H), 3.95(s, $OC\underline{H}_3$, 3H); ^{13}C-NMR($CDCl_3$) δ 4.6(Co-$\underline{C}H_2$), 59.3($O\underline{C}H_3$), 181.1(-$\underline{C}O_2$-), 198.4, 201.5(Co-$\underline{C}O$).

(Received August 11, 1989)