

A METAL-METAL BONDED DINUCLEAR RUTHENIUM KETENE COMPLEX

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We report the synthesis of metal-metal bonded dinuclear ruthenium ketene complex $[\text{CpRu}(\text{CO})_2]_2(\mu\text{-CH}_2\text{CO})(\mu\text{-CO})$, **3**, ($\text{Cp}=\eta^5\text{-C}_5\text{H}_5$) which contains the unique structural feature, of a $\mu\text{-}\eta^2(\text{C},\text{C})$ ketene group bridging two metal centers. Complex **3** is prepared by a rare intramolecular CO insertion to the methylene group of a Ru complex $[\text{CpRu}(\text{CO})_2]_2(\mu\text{-CH}_2)$, **1**, in the absence of CO or any donor ligand. The *cis* and *trans* isomers of **3** originating from the arrangement of the Cp groups and the unsymmetrically bridging ketene group, are observed in the NMR spectra. Unlike a ketene complex without a metal-metal bond $[\text{CpRu}(\text{CO})_2]_2(\mu\text{-CH}_2\text{CO})$, **2**, complex **3** exhibits the chemistry of a ketene molecule and might be used as a stoichiometric ketene precursor in organic reactions.

Organometallic methylene and Ketene complexes have been under investigation due to their role in the Fischer-Tropsch and related reactions. Special attention has been given to the character of the C-C bond and its formation in a number of such complexes¹⁻³. Recently we reported the isolation of the first methylene complex without a metal-metal bond $[\text{CpRu}(\text{CO})_2]_2(\mu\text{-CH}_2)$, **1**, ($\text{Cp}=\eta^5\text{-C}_5\text{H}_5$) by the reaction of $[\text{CpRu}(\text{CO})_2]\text{Na}$ with CH_2Cl_2 at -40°C . Under 1 atm CO pressure, **1** undergoes a CO insertion reaction to yield a no metal-metal bonded ketene complex $[\text{CpRu}(\text{CO})_2]_2(\mu\text{-CH}_2\text{CO})$, **2**. However, in order to rationalize many other C_2 products observed in the reactions of **1**, a metal-metal bonded ketene complex $[\text{CpRu}(\text{CO})_2]_2(\mu\text{-CH}_2\text{CO})(\mu\text{-CO})$, **3**, was proposed in that report. In this paper, we describe the isolation of this structurally and chemically novel ketene complex **3**.

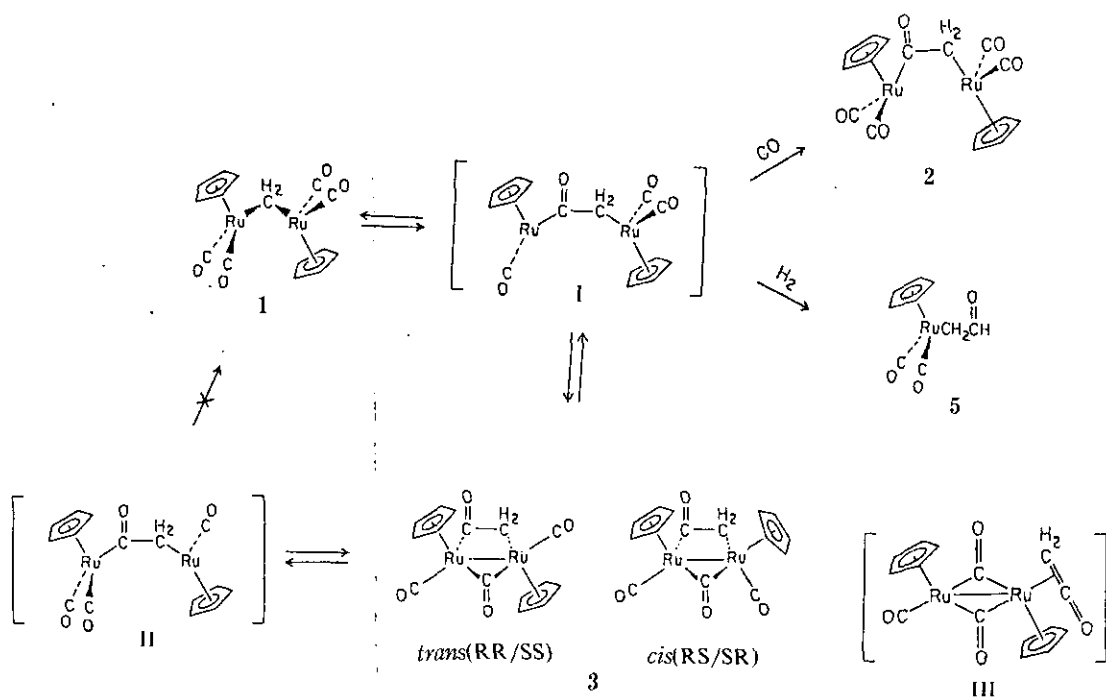
RESULTS AND DISCUSSION

Since complexes **1** and **3** are structural isomers and **1** shows remarkably facile carbonylation chemistry, it seems plausible to design the synthesis of **3** by a simple

isomerization of **1**. Indeed, an orange solid was precipitated out of a yellow toluene solution of **1** upon standing at room temperature for 2 days. The yield was moderate, 45%. From the analysis described below, this orange solid was determined to have the structure **3**. In addition to the interesting structural feature, that is the $\mu\text{-}\eta^2(\text{C},\text{C})$ bridging ketene group in **3**, the transformation from **1** to **3** involves a rare intramolecular CO insertion in the absence of a CO atmosphere or any donor ligands. Surprisingly, such a process takes place even in the solid state, but with lower yield.

The elemental analysis of **3** is consistent with the proposed formula. The IR spectrum in tetrachloroethylene gives three characteristic CO stretching peaks: 1970, 1803, and 1643 cm^{-1} which can be attributed to the CO stretching of the terminal, bridging and ketene CO respectively. The structure of complex **3**, shown in Scheme I, is consistent with these data. Since the ketene group in **3** is unsymmetrically bridged between two metal centers, one would expect four different isomers: *trans* and *cis* with the corresponding (RR, SS) and (RS, SR) pairs.

* The author, an associate professor at the National Taiwan University, wishes to dedicate this paper to Dr. Chien.



Scheme I

This is supported by the nmr results. At -30° , two sets of absorption peaks at (5.34(s), 5.19(s), isomer A) and (5.34(s), 5.26(s), isomer B) with the ratio of about 10:1 in CD_2Cl_2 are observed in a nmr spectrum, see Fig. 1. Each set is assigned to the two different Cp groups of one isomer pair (*cis* or *trans* pair). The assignment of the overlapped peak at 5.34 ppm is determined by the integration. Similarly, there are two AX coupling pairs at (2.62(d), 1.52(d), $J_{\text{H-H}}=5.3 \text{ Hz}$, A) and (2.10(d), 0.94(d), $J_{\text{H-H}}=5.5 \text{ Hz}$, B) with the same ratio. These can be assigned to the corresponding non-equivalent geminal hydrogen atoms in the ketene groups of the *cis/trans* isomers. The non-equivalence is due to the different environments of the two geminal hydrogen atoms in both isomers where one H is close to the Cp group and the other to the CO group. From the integration, we can assign peaks at 5.34, 5.19, 2.65, 2.10 ppm to the major isomer pair (A, *cis* or *trans*) and the rest to the minor ones (B). However, at this stage we can not tell which is which. The

ratio A:B is both temperature and solvent dependent. At room temperature, the ratio is about 5:1 and 3:1 in CD_2Cl_2 and d^6 -acetone respectively and the concentration of B is negligible in d^6 -benzene and CDCl_3 .

Not surprisingly, at room temperature all the peaks are broadened and show a tendency to collapse. Unfortunately, complex 3 decomposed above 50° and the coalescence was not observed in a 200 MHz NMR spectrometer. The broadening of the NMR peaks can be explained by the dynamic equilibrium between the different isomers of 3. This transformation could be achieved by rotating one Ru-ketene bond of transient species I and/or II each containing a 16 electron metal center (see Scheme I). The species differs from that in the $[\text{CpRu}(\text{CO})_2]_2$ system⁷⁻⁹ where the metal-metal bond is preserved in rotation. Indirect evidence for the existence of I is provided from the following observations. First when 3 is heated to 50° in an nmr tube, complex 1 along with several other products (Ca 50%) is observed as in the

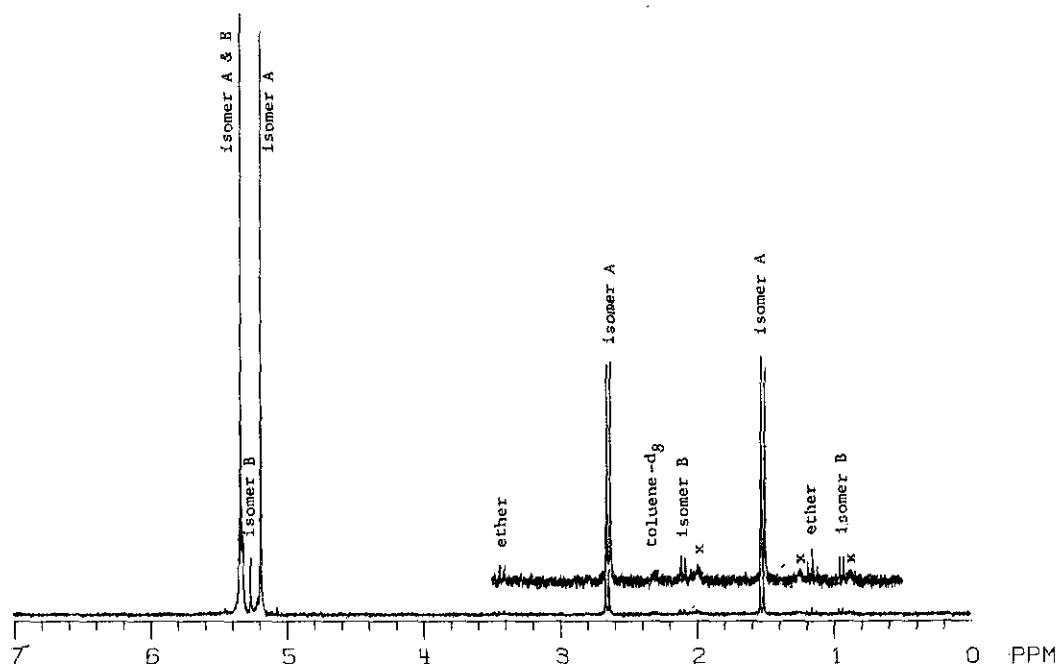


Fig. 1. ^1H NMR spectrum of **3** in CD_2Cl_2 at -30° .

nmr spectrum. The formation of **1** could be explained by two reversible pathways between **1**, **I** and **3** (see Scheme I). The byproducts, not yet completely identified, could come from **II** with the 16 electron center located at the CH_2 -bonded Ru atom where the deinsertion to **1** is not possible. The reversible transformation between **1** and **3** also rules out the possibility that **3** might have structure III^{10-12} . Secondly, we isolate a formylmethyl complex $\text{CpRu}(\text{CO})_2(\text{CH}_2\text{CHO})$, **5**¹³, from a reaction of **1** with H_2 at 55° which presumably goes through intermediate **I**.

Formation of the C_2 unit was further confirmed by ^{13}C labling studies. We prepared ^{13}C labeled complex **3** which is 99% labeled on the methylene carbon and about 30% labeled on the carbonyl carbon. In the ^{13}C NMR spectra of this complex, the C-C bond formation was clearly indicated by the C-C coupling constants ($J_{\text{C-C}}$) of 32 Hz and 31 Hz for isomer A and B. The $J_{\text{C-C}}$ falls within the range of several other ruthenium C_2 compounds: 42 Hz for $\text{CpRu}(\text{CO})_2(\text{CH}_2\text{CHO})$, **5**, 27 Hz for

$[\text{CpRu}(\text{CO})_2]_2(\mu\text{-CH}_2\text{CO})$ and 22 Hz for $[\text{Cp}_2\text{Ru}_2(\text{CO})_3\text{PMe}_3](\mu\text{-CH}_2\text{CO})$.

Reactions of **3** with small molecules follow the same pattern as that of **1**. Namely, acetic acid and methyl acetate are observed in the reaction of **3** with H_2O and MeOH respectively. The rate of these reactions is however, faster for **3** compared with that of **1**. Interestingly, quantitative NN-dimethylacetamide and an amine complex $[\text{Cp}_2\text{Ru}_2(\text{CO})_3(\text{Me}_2\text{NH})]$ were observed instantaneously upon the mixing of **3** with 2 equivalents of dimethylamine. On the contrary, the ketene complex without metal-metal bond **2** was inert toward these small molecules. Complex **3** is therefore a potential ketene precursor for stoichiometric organic reactions.

EXPERIMENTAL

All manipulations of oxygen or water sensitive material were conducted in a nitrogen flushed Vacuum Atmospheres drybox or using the standard Schlenk and vacuum line techniques. Diethyl ether and

THF were dried over Na/benzophenone and were distilled under nitrogen before use. Hexane and pentane were dried by distillation under nitrogen over CaH_2 . NMR were recorded on the IBM NR-80, the Nicolet-200 or the Bruker WM-400 instruments. Elemental analyses were provided by Mikroanalytisches Labor Pascher, Germany. Infrared spectra were recorded on a Perkin-Elmer 983 spectrophotometer. Mass spectra were obtained using a VG Analytical 7070 High Resolution mass spectrometer. $\text{Na}[\text{CpRu}(\text{CO})_2]$ was prepared by Na/Hg reduction of $[\text{CpRu}(\text{CO})_2]_2$. The methylene dimer $[\text{CpRu}(\text{CO})_2]_2(\mu\text{-CH}_2)$, **1**, was prepared according to the method given in the previous paper².

(A) Preparation of the Ketene Complex **3**:

The preparation of $[\text{CpRu}(\text{CO})_2](\mu\text{-CH}_2\text{CO})(\mu\text{-CO})$, **3**, was carried out by slow room temperature pyrolysis of complex **1** in toluene solution. 200 mg of **1** was dissolved in 5 ml of toluene. The solution was protected from photolytic decomposition by wrapping with aluminium foil. The mixture turned to dark brown in 24 hours, then a bright orange precipitate formed. Toluene was first decanted, then the solid was washed three times with about 1 ml of cold toluene. Complex **3** was sparingly soluble in C_6H_6 , CH_2Cl_2 , toluene, and acetone and very soluble in THF. Analytical data: C, 39.25 (calcd. 39.30), H, 2.77 (calcd. 2.62). Mass spectrum: $[\text{M-CO}]^+$ ($m/e=431.8867$, calcd: 431.8860) and $[\text{M-2CO}]^+$ ($m/e=403.8922$, calcd: 403.8911) were observed. ^{13}C NMR data (CD_2Cl_2 , -30° , ppm): isomer A: 237.3 (bridging CO), 226.8 ($J_{\text{C-C}}=32\text{ Hz}$, ketene CD), 201.8, 200.3 (terminal CO), 93.6, 91.5 (Cps), -8.4 (CH_2 , $J_{\text{C-C}}=32\text{ Hz}$, $J_{\text{C-H}}=145.6\text{ Hz}$, $J_{\text{C-H}'}=154.6\text{ Hz}$); isomer B: 236.5 (bridging CO) 231.5 ($J_{\text{C-C}}=31\text{ Hz}$, ketene CO), 203.1, 201.1 (terminal CO), 94.5, 91.3 (Cps), -9.6 (CH_2 , $J_{\text{C-C}}=31\text{ Hz}$). IR (tetrachloroethylene, cm^{-1}): 1970 (terminal CO), 1803 (bridging CO), 1643 (ketene CO). ^1H NMR: see text.

(B) Reaction of **1** With H_2 :

A C_6D_6 solution of **1** (50 mg) was placed

in a Fischer-Porter reaction vessel. The atmosphere of the reaction vessel was replaced with H_2 gas by two freeze-thaw cycles. The vessel was then pressurized to 40 psig and heated to 55° for 3 hours. The resulting solution turned purple NMR analysis of this solution indicated the formation of $\text{CpRu}(\text{CO})_2(\text{CH}_2\text{C}(\text{O})\text{H})$, **5**. A column packed with Florosil was employed to separate the formylmethyl complex from the mixture. The mixture was first eluted with ether/hexane solution. The formylmethyl complex was then eluted with THF, yielding a brown oil after the THF was removed. Spectra data for **5**: Mass spectra: parent peak at $m/e=265.9524$ (calcd. 265.9510), IR (hexane, cm^{-1}): 2031, 1976, 1674; ^1H NMR (C_6D_6 , ppm): 9.46 (t, $J_{\text{H-H}}=5.1\text{ Hz}$, 1H, CHO), 4.39 (s, 5H, Cp), 2.13 (d, $J_{\text{H-H}}=5.1\text{ Hz}$, 2H, CH_2); ^{13}C NMR (CD_2Cl_2 , ppm): 200.4 (terminal CO), 200.1 (CHO, $J_{\text{C-H}}=164.6\text{ Hz}$, $J_{\text{C-H}'}=3.6\text{ Hz}$), 88.9 (Cp), 7.7 (CH_2 , $J_{\text{C-H}}=139.7\text{ Hz}$, $J_{\text{C-H}'}=28.6\text{ Hz}$).

(C) Alternate Route to **5**: Hydrolysis of an Acetal Complex

A ruthenium acetal complex was prepared by the reaction of $\text{Na}[\text{CpRu}(\text{CO})_2]$ with $\text{ClCH}_2\text{CH}(\text{OMe})_2$ in THF. The solvent was removed after the reaction was completed as indicated by IR monitoring. The product was extracted into hexane. Removal of hexane under vacuum yielded an oily product which was identified to be $\text{CpRu}(\text{CO})_2\text{CH}_2\text{CH}(\text{OMe})_2$ by spectroscopic methods. ^1H NMR (C_6D_6 , ppm): 4.69 (s, 5H, Cp), 4.54 (t, $J_{\text{H-H}}=5.6\text{ Hz}$, 1H, CH), 3.28 (s, 6H, OMe), 1.88 (d, $J_{\text{H-H}}=5.6\text{ Hz}$, 2H, CH_2). IR (hexane, cm^{-1}): 2025, 1967 (ν_{CO}), 1110, 1077, 1046 (ν_{OMe}). A THF solution of the acetal complex was then hydrolyzed by the adsorbed water in Florosil as it was passed through a column packed with Florosil. After the yellow band, eluted by THF, was collected, the solvent was removed under vacuum. The NMR of the product in C_6D_6 indicated the formation of **5**.

(D) Reaction of **1** with Acetaldehyde

Complex **1**, (ca. 50 mg) was dissolved in C_6D_6 and a stoichiometric amount of

$\text{CH}_3\text{C}(\text{O})\text{H}$ was added. The reaction was monitored by NMR spectroscopy. An intermediate having two broad Cp peaks at 4.72 and 4.60 ppm and two broad CH_3 peaks at 2.57 and 1.33 ppm was observed first to increase then slowly decrease in concentration. The two final products which formed slowly were identified as $\text{CpRu}(\text{CO})_2\text{CH}_3$ and **5**. The intermediate was later identified to be **3**. The methyl and formylmethyl ruthenium complexes were separated by column chromatography. Yields are about 45% based on NMR data. NMR data for $\text{CpRu}(\text{CO})_2\text{CH}_3$ (in C_6D_6 , ppm): 4.51 (s, 5H, Cp), 0.51 (s, 3H, Me).

(E) Reaction of **3** with Nucleophile

Reactions of **3** with nucleophiles such as H_2O , Me_2NH , MeOH were carried out in NMR tubes. Since **3** is only sparingly soluble in benzene, a saturated solution of **3** in C_6D_6 was employed. The nucleophile in the appropriate solvent was added into the NMR tube containing the solution of **3**. For Me_2NH , reaction takes place instantaneously upon mixing two components. NMR spectra of the mixture indicated the formation of $\text{CH}_3\text{C}(\text{O})\text{NMe}_2$ and $\text{Cp}_2\text{Ru}_2(\text{CO})_2(\text{Me}_2\text{NH})$; ^1H NMR (C_6D_6 , ppm): 4.94 (s, 5H, Cp), 4.47 (s, 5H, Cp), 1.86 (d, $J_{\text{H-H}}=6.2\text{ Hz}$, 6H, NMe_2), -0.09 (br, 1H, NH). Reactions with the other nucleophiles are slower and thus the product formation could be observed to increase in a matter of hours. Organic products from these reaction were identified by adding authentic

chemicals into the NMR tube and then watching the increase in the intensity of the peaks. CH_3COOH and CH_3COOMe were identified in this way.

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