Double Addition of CO_2 and CH_3OH to Ruthenium Carbonyl Complex with Novel Monodentate Dithiolene

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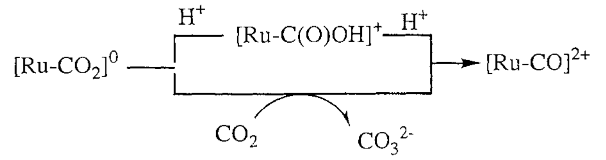
A ruthenium carbonyl complex with unique monodentate $SSC_2(CN)_2^{2-}$ was prepared, while analogous $SSC_2Ph_2^{2-}$ derivative underwent electrophilic and nucleophilic attacks of CO_2 and CH_3OH to the thiolato and the CO ligands to produce the Ru complex with thio-carboxylic acid and methoxy carbonyl units.

Much attention has been paid to activation of CO_2 on metal complexes directed toward reduction of CO_2 to useful chemicals.[1] We have been investigating electro- and photochemical reduction of CO_2 catalyzed by ruthenium-polypyridyl carbonyl complexes.[2] The catalytic activity of those metal complexes is ascribed to strong affinity of CO_2 and to the smooth conversion from CO_2 to CO on Ru irrespective of the presence and the absence of proton sources (Scheme 1).



Scheme 1. Conversion from CO_2 to CO on Ru in the presence and absence of proton.

Polypyridyl ligands in the metal complexes also play the key role as the electron reservoirs in the reduction of CO_2 by the ligand localized redox reactions. Introduction of dithiolene ligands to Ru as another redox active site is expected to expand the dynamic potential ranges, where ruthenium-polypyridyl carbonyl complexes work as the redox catalysts, since redox potentials of dithiolenes are generally more positive than those of polypyridyls. Here, we report the characterization of two ruthenium-terpyridyl carbonyl complexes with novel monodentate dithiolene ligands, $[Ru(CO)_2(mnt\text{-}\kappa^1 S)(terpy\text{-}\kappa^3\text{-}N,N',N'')]$ (mnt = $SSC_2(CN)_2$) (**1**) and $[Ru(CO)(C(O)OCH_3)\text{-}(S(CPh)SCPh)(C(O)OH))(terpy\text{-}\kappa^3\text{-}N,N',N'')]$ (**2**), and their crystal structures.

The reaction of an equimolar amount of $[Ru(CO)_2Cl(terpy)]PF_6$ (114 mg, 0.2 mmol) with Na_2mnt (37 mg, 0.2 mmol) in CH_3OH (100 cm^3) gave a clear red solution in 2 hours at room temperature under air, and yellow crystals of **1** deposited out of the solution in an 80% yield. Molecular structure of **1** is shown in Figure 1. The ruthenium center is in the octahedral geometry with two carbon atoms of carbonyl groups, three nitrogen atoms of terpyridine, and one sulfur atom of the mnt. In most of metal-mnt complexes, the ligand coordinates to metals with the κ^2-chelating fashion. The unusual monodentate mnt in **1** indicates low nucleophilicity of S21. The bond distance of Ru - C2 (1.85(2) Å) *trans* to S1 atom of mnt is slightly shorter than that of Ru - C1 (1.94(2) Å) *trans* to center of terpyridine. The relatively short distance of Ru - C2 indicates strong interaction between Ru and S1.

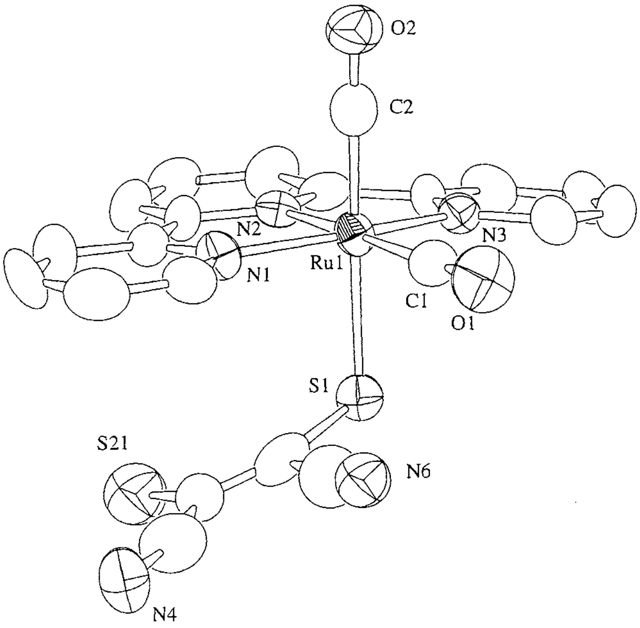
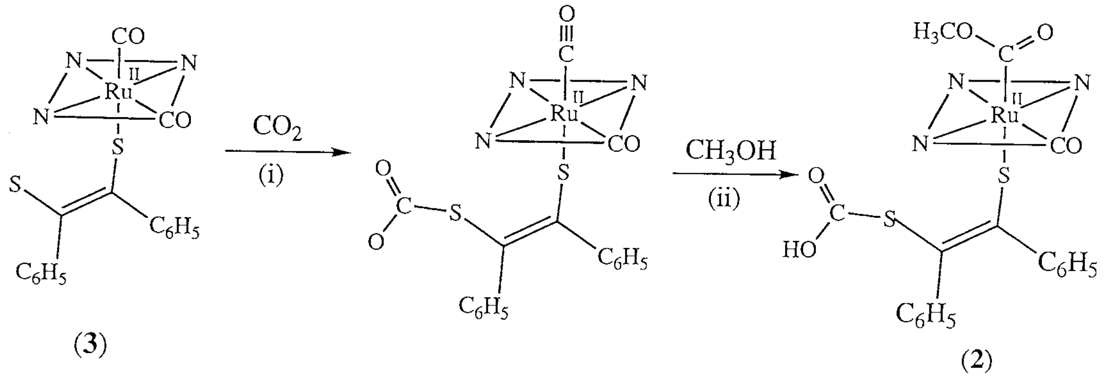


Figure 1. The molecular structure of **1**. Selected bond distances(Å): Ru1-S1 2.447(4), Ru1-N1 2.08(1), Ru1-N2 2.04(1), Ru1-N3 2.08(1), Ru1-C1 1.94(2), Ru1-C2 1.85(2).

The reaction between $[Ru(CO)_2Cl(terpy)]PF_6$ (114 mg, 0.2 mmol) and $Cs_2S_2C_2Ph_2$ (101 mg, 0.2 mmol) in CH_3OH (100 cm^3) at room temperature under air gave brown complex **2** in 60% yield after 1 day. The complex **2** is $[Ru(CO)(C(O)OCH_3)(S(CPh)SCPh)(C(O)OH))(terpy\text{-}\kappa^3\text{-}N,N',N'')]$ rather than the expected $[Ru(CO)_2(SSC_2Ph_2\text{-}\kappa^1 S)(terpy\text{-}\kappa^3 N,N',N'')]$ (**3**). Molecular structure of **2** is shown in Figure 2. Coordinating atoms to ruthenium and the overall feature are same as **1**. The most characteristic feature of **2** is that the carbonyl and the uncoordinated thiolate of **1** are changed to methoxy carbonyl and thio-carboxylic acid units, respectively. Although it is not clear that the thio-carboxylate unit of **2** exists as protonated or deprotonated form by X-ray analysis, the former is deduced from the elemental analysis and the charge balance of **2**. Bond distances and angles around the $Ru\text{-}C(O)OCH_3$ unit in **2** are very similar to those in $[Ru(CO)(C(O)OCH_3)(bpy)_2]PF_6$[5] as an analog of $[Ru(CO)(C(O)OH)(bpy)_2]CF_3SO_3$.[6] Unprecedented double addition of CO_2 and methanol to thiolate and carbonyl ligands located far from each other is apparently caused by the long-range π–π interaction between basic $Ph_2C_2SS^{2-}$ and acidic carbonyl units through d-orbitals of the ruthenium atom (Scheme 2).

In contrast to uncoordinated thiolato of **1**, that of **3** is



Scheme 2.

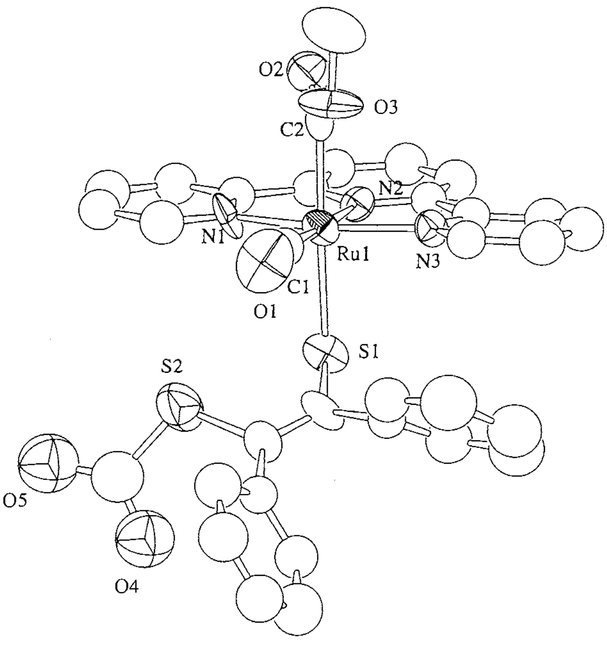


Figure 2. The molecular structure of **2**. Selected bond distances(Å): Ru1-S1 2.492(5), Ru1-N1 2.05(2), Ru1-N2 2.03(1), Ru1-N3 2.08(1), Ru1-C1 1.85(1), Ru1-C2 2.06(2). There are two independent molecules in one unit cell. The other molecule has the same ligand arrangement.

basic enough to undergo an electrophilic attack of CO_2 in air (path (i)). The addition of CO_2 to uncoordinated thiolato inevitably enhances the acidity of the carbonyl group located *trans* to the coordinated sulfur atom, which induces the subsequent nucleophilic attack of methanol to the carbonyl group. The proton transfer from the methanol molecule attached to the CO ligand to the basic SCO_2 moiety will also serve the stabilization of both carboxylic and methoxy carbonyl groups of **2** (path (ii)). It is worthy to note that ruthenium methoxy carbonyl complexes such as $[Ru(CO)(C(O)OCH_3)(bpy)_2]PF_6$ [5] and $[Ru(CO)_2Cl(C(O)OCH_3)(bpy)]$ [7] are prepared by the reaction of CH_3ONa with the corresponding Ru-CO complexes, but easily undergo hydrolysis reactions. On the other hand, **2** is spontaneously formed in CH_3OH without strong bases in air.[8] The unusual double addition of CO_2 and CH_3OH to monodentate Ph_2C_2SS and the CO groups of **3**, therefore, is ascribed to the synergistic effect of nucleophilicity of the former and electrophilicity of the latter.

References and Notes

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3 Crystal data for $C_{22}H_{15}O_3N_5S_2Ru$ ([**1**]•CH_3OH): FW = 562.6, Triclinic, a = 9.389(4), b = 14.122(4), c = 8.817(3) Å, α = 90.98(3), β = 103.42(3), γ = 96.32(3)°, V = 1129.2(8)Å^3, T = 300K, space group $P\bar{1}$(No. 2), Z = 2, ρ = 1.65 g cm^{-3}, μ(Mo Kα) = 9.14 cm^{-1}, 3174 reflections measured, 2954 unique (R_{int} = 0.048) which were used in all calculations. The final R (Rw) were 0.060 (0.054) for [$I > 2.0\sigma(I_o)$]. The structure was solved by direct methods and all the non-hydrogen atoms were refined anisotropically. The mnt was largely disordered, thus detailed bond distances and angles for mnt could not be described. Hydrogen atoms were located by calculation and not refined.

4 Crystal data for $C_{33}H_{27}O_6N_3S_2Ru$ ([**2**]•H_2O): FW = 726.8, Triclinic, a = 14.579(3), b = 19.743(4), c = 12.948(3) Å, α = 108.34(2), β = 94.30(2), γ = 98.16(2)°, V = 3473(1) Å^3, T = 300K, space group $P\bar{1}$(No. 2), Z = 4, ρ = 1.38 g cm^{-3} μ(Mo Kα) = 6.16 cm^{-1}, 13678 reflections measured, 12946 unique (R_{int} = 0.138) which were used in all calculations. The final R (Rw) were 0.083 (0.076) for [$I > 3.0\sigma(I_o)$]. The crystal contains two independent molecules in the asymmetric unit. The structures were solved by direct methods, and the ruthenium, sulfur and nitrogen atoms, the atoms in carbonyl and methoxy carbonyl ligands, and ethylene carbon atoms of $Ph_2C_2S_2$-COOH were refined anisotropically.
Characterization data of [**2**]. Anal. Found: C, 55.91%; H, 3.77%; N, 5.86%. Calcd for $C_{33}H_{25}O_5N_3S_2Ru$ (MW 708.8): C, 55.92%; H, 3.56%; N, 5.93%. Because the sample was dried in vacuo for elemental analysis, the calculated formula of **2** does not include solvent H_2O. ESI MS (DMF): *m/z* 692 ([M-OH]$^+$), 664 ([M-COOH]$^+$), 636 ([M-COOH-CO]$^+$), 605 ([M-COOH-CO-OCH_3]$^+$), 577 ([M-COOH-$(CO)_2$-OCH_3]$^+$). IR (KBr): ν(CO) 1966, 1711, 1684 cm^{-1}.

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8 When this reaction was treated in ethanol, ethoxy carbonyl complex $[Ru(CO)(C(O)OC_2H_5)(SS(COOH)C_2Ph_2)(terpy)]$ formed, which was characterized by ESI-mass.