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Linking Two Alkyne-Bridged Dicobalt Complexes via a Urea-Based Ligand: Synthesis and Spectroscopic and Structural Characterization of $\{[Co_2(CO)_6(\mu\text{-}HC{\equiv}C\text{-})]\text{-}CH_2NH\}_2C{=}O$

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Transition metal-mediated carbonylation of organic molecules has attracted much attention over the past few decades.[1] Examples of carbonylation of amines are rare, and reactions always require the severe conditions of high temperature and pressure.[2] We report herein an unusual carbonylation of a primary amine at room-temperature, employing $Co_2(CO)_8$ as a catalyst.

Treatment of $Co_2(CO)_8$ with $HC{\equiv}CCH_2NH_2$ in THF at 25 °C for 3 h yielded an unusual complex, $\{[Co_2(CO)_6(\mu\text{-}HC{\equiv}C\text{-})]\text{-}CH_2NH\}_2C{=}O$ (**1**; 40%) (Scheme 1).[3] The structure of **1** was established by an X-ray diffraction analysis. The ORTEP drawing, and selected bond distances and angles are displayed in Figure 1.[4] The compound **1** can be regarded as a deprotonated urea linked by two alkyne-bridged dicobalt moieties on both sides. Alternatively, it can be viewed as two propargylamine-bridged dicobalt complexes coupled by a carbonyl group. Evidently, carbonylation took place, linking two propargylamine-bridged dicobalt complexes during the reaction. To the best of our knowledge, complex **1** is the first example of its kind produced in one-pot reaction.[5]

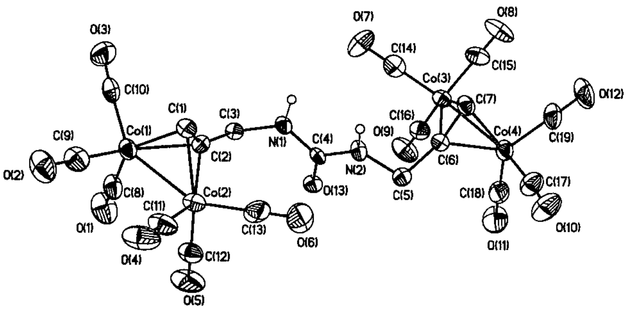
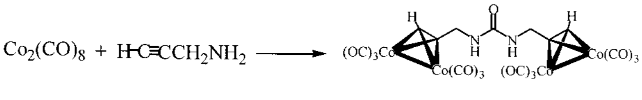


Figure 1. The molecular structure of $\{[Co_2(CO)_6(\mu\text{-}HC{\equiv}C\text{-})]\text{-}CH_2NH\}_2C{=}O$ **1**. Some hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (deg) for **1**: Co(1)−C(1) 1.940(8), Co(1)−C(2) 1.950(8), Co(1)−Co(2) 2.474(16), Co(2)−C(1) 1.940(8), Co(2)−C(2) 1.951(7), C(1)−C(2) 1.309(9), O(13)−C(4) 1.226(6), C(6)−C(7) 1.304(10), N(1)−C(4) 1.326(8), N(1)−C(3) 1.468(8), N(2)−C(4) 1.328(8), N(2)−C(5) 1.467(8); Co(1)−C(1)−Co(2) 79.2(3), Co(1)−C(2)−Co(2) 78.7(3), Co(4)−C(7)−Co(3) 79.0(3), Co(3)−C(6)−Co(4) 79.4(3), C(4)−N(1)−C(3) 122.2(6), C(4)−N(2)−C(5) 123.7(6), N(1)−C(3)−C(2) 110.6(5), N(2)−C(5)−C(6) 111.0(6).

Scheme 1



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The molecular structure of **1** reveals that two $Co_2(CO)_6$ fragments point away from each other to avoid the steric hindrance. The averaged bond distance of Co(1)−Co(2) and Co(3)−Co(4) is 2.476 Å, which is within the usual Co−Co bond length region.[6] The averaged bond angle of C(3)−N(1)−C(4) and C(4)−N(2)−C(5) is 123.0°, which indicates that the two nitrogen atoms exist nearly in sp^2 hybridization. The existence of a carbonyl group is confirmed by the distinct, strong absorption of a 1686 cm^{-1} signal in infrared region, which is a characteristic of an imide carbonyl group.

The reactions of $Co_2(CO)_8$ with propargylamine at various reaction conditions were carried out, and results are listed in Table 1. There are several observations worthy of noting. First, the yield of **1** was improved to 48% under 1 atm of carbon monoxide. Second, the amount of **1** improved when the molar ratio of $Co_2(CO)_8$ to propargylamine was increased; the opposite result was obtained when the molar ratio of $Co_2(CO)_8$ to propargylamine was decreased. Third, the yield of **1** decreased in the presence of NEt_3.

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(3) Synthesis of **1**. A solution of $Co_2(CO)_8$ (0.60 g, 0.175 mmol) and propargylamine (0.12 mL, 0.175 mmol) in 20 cm^3 of THF was frozen and degassed. The solution was then allowed to warm to room temperature and stirred for 3 h. Subsequently, the resulting red solution was filtered through silica gel, and purification with centrifugal thin-layer chromatography (CTLC) was carried out. The first red color band of the title compound $\{[Co_2(CO)_6(\mu\text{-}HC{\equiv}C\text{-})]\text{-}CH_2NH\}_2C{=}O$, **1**, was eluted with CH_2Cl_2, and the solvent was removed in vacuo to yield **1** (40%) (0.50 g, 0.706 mmol). FAB mass spectrum of **1**: m/z 708 [M^+]. Elemental analysis; calc. for $C_{19}H_8Co_4N_2O_{13}$: C, 32.00; H, 1.10; N, 4.00. Found: C, 32.22; H, 1.84; N, 4.40. Selected spectroscopic data for **1**. IR (CH_2Cl_2) ν (CO)/cm^{-1}: 2093s, 2058s, 1686s (C=O). ^{1}H NMR-($CDCl_3$): δ 6.07(s, 1H, ≡CH), 4.68(t, J_{H-H} = 5.6 Hz, 1H, NH), 4.57(d, J_{H-H} = 6.0 Hz, 2H, CH_2). ^{13}CNMR($CDCl_3$): δ 199.4(s, CO), 156.7(s, C=O), 93.9, 72.2(s, C≡CH), 43.0(s, CH_2).

(4) Crystal data for **1**: $C_{19}H_8Co_4N_2O_{13}$, M = 707.99, tetragonal, space group $P4_32_12$, a = 16.808(16), b = 16.808(16), c = 19.121(3) Å, α = 90, β = 90, γ = 90°, V = 5402.0(10) Å^3, Z = 8, D_c = 1.741 Mg/m^3, μ = 2.477 mm^{-1}, F(000) = 2784, T = 293(2) K, R_1 = 0.0480, wR_2 = 0.0971. A suitable crystal of **1** was sealed in thin-walled glass capillaries under a nitrogen atmosphere and mounted on a Siemens Smart CCD diffractometer. The crystallographic data were collected using a $\theta - 2\theta$ scan mode with Mo Kα radiation. The space group determination was based on a check of the Laue symmetry and systematic absences and confirmed by the structure solution. The structure was solved by direct methods using Siemens SHELXTL PLUS package.[i] All non-H atoms were located from successive Fourier maps. Anisotropic thermal parameters were used for all non-H atoms, and fixed isotropic parameters were used for H atoms that were refined using a riding model.[ii] (i) G. M. Sheldrick, *SHELXTL PLUS User's Manual*, Revision 4.1; Nicolet XRD Corporation: Madison, Wisconsin, 1991. (ii) The hydrogen atoms were maintained on carbons or oxygens in their idealized positions and held fixed with the C−H distances of 0.96 Å.

(5) A related coupling reaction between one CO, one ethylamine, and one alkyne-bridged multi-cobalt complex $\{Co_2(CO)_6(\mu\text{-}HC{\equiv}C\text{-})CCo_3(CO)_9\}$ in the presence of CuCl was reported: Worth, G. H.; Robinson, B. H.; Simpson, J. *J. Organomet. Chem.* **1993**, *450*, 219.

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Table 1. The Reaction of $Co_2(CO)_8$ with Propargylamine[a]

entry	[M]:[PA]:$[NEt_3]$[b]	CO	**1**, yield (%)
1	1.0:1.0:0	−	40
2	1.0:1.0:0	1 atm	48
3	1.5:1.0:0	−	54
4	1.0:3.0:0	−	32
5	1.0:1.0:2.0	−	22

[a] All of the above reactions were carried out at room temperature for 3 h. [b] [M] is $Co_2(CO)_8$; [PA] is propargylamine.

The mechanism of this catalytic process is not clear; nevertheless, it is believed that the propargylamine must play a dual role here. A reaction mechanism for the formation **1** was proposed as follows (Figure 2). First, the triple bond of the propargylamine ligand bridges with the dicobalt carbonyl and forms $[Co_2(CO)_6(\mu\text{-}HC{\equiv}C{-}CH_2NH_2)]$, **2**. The acidity of the amine protons of **2** is enhanced through the coordination of dicobalt fragment to the propargylamine ligand.[7] It is, then, followed by the coordination of another equivalent of $Co_2(CO)_8$ by **2** through its amine site; at the same time, this causes the cleavage of the cobalt−cobalt bond. Presumably, an activated complex $[Co_2(CO)_6(\mu\text{-}HC{\equiv}C{-}CH_2\text{-}NH)\text{-}Co(CO)_4]$, with a direct Co−N covalent bond, and $HCo(CO)_4$ were formed. Most probably, a CO insertion process takes place between the Co−N bond and forms the Co−amido bond while another equivalent of **2** coordinates to this activated complex. Finally, the product, **1**, results from the reductive elimination of two dicobalt-bridged organic moieties from the cobalt metal center.

The alkylidynetricobalt nonacarbonyl complex, $[Co_3(CO)_9(\mu_3{-}CCH_2CH_3)]$, **3**, along with **1** were obtained from the above reaction; the same reactants were used, but the reaction temperature was raised from 25 to 45 °C for 5 h.[8] Alternatively, the compound $[Co_3(CO)_9(\mu_3{-}CCH_2CH_3)]$, **3**, alone was obtained from the reaction of $Co_2(CO)_8$ with $HC{\equiv}CCH_2SPh$ instead of $HC{\equiv}CCH_2NH_2$ at 65 °C for 5 h, whereas the alkyne-bridged dicobalt complex, $Co_2(CO)_6\{\mu\text{-}HC{\equiv}CCH_2SPh\}$ **4**, was obtained when the reaction temperature was maintained below 25 °C. It is observed that temperature of the reaction plays an important role in determining its product formation.

Preliminary results show that only the alkyne-bridged dicobalt complex $Co_2(CO)_6(\mu\text{-}HC{\equiv}CCH_2NHCH_3)$, **5**, was obtained when a secondary amine, $HC{\equiv}CCH_2NHCH_3$, was employed.[9] The failure of carbonylation of the secondary amine might account for the decreased accessibility of the initially formed secondary amine complex of **5** toward the center of the activated cobalt catalyst for further reaction. A similar result was obtained when $HC{\equiv}CCH_2NH_2$ was reacted with the DPPM-bridged dicobalt compound $\{\mu\text{-}P,P{-}PPh_2CH_2PPh_2\}Co_2(CO)_6$, and the alkyne-bridged dicobalt complex $[\{\mu\text{-}P,P{-}PPh_2CH_2PPh_2\}Co_2(CO)_4\{\mu\text{-}HC{\equiv}CCH_2NH_2\}]$, **6**, was obtained as the only isolable product. The steric effect due to the bulkiness of the DPPM ligand might have played a predominant role here again in determining the product formation. More thoughtful investigations of these reactions are currently being undertaken.

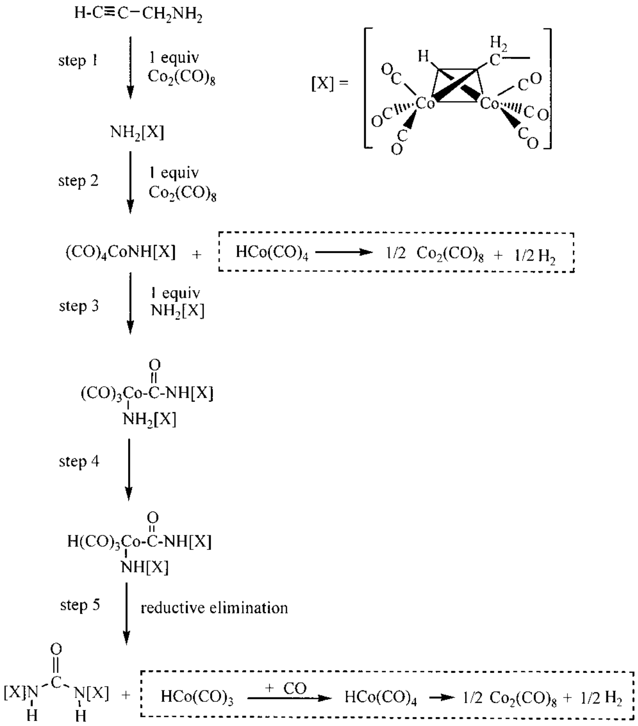

Figure 2. Proposed mechanism for the formation of **1**.

Acknowledgment. We are grateful to the National Science Council of the R.O.C. (Grant NSC 89-2113-M-005-026) for financially supporting this research. We are also grateful to the National Center for High-Performance Computing (NCHC) of the R.O.C. for providing computing time.

Supporting Information Available: Crystal data, atomic coordinates, bond lengths and angles, and anisotropic displacement prameters (CIF and PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(7) Computational means have also been employed in examining the change of acidity of propargylamine before and after the coordination of a dicobalt fragment. The equilibrium geometries, Mulliken charge population, and natural population analysis of $H{-}C{\equiv}C{-}CH_2{-}NH_2$ **(I)** and $Co_2(CO)_6[\mu\text{-}HC{\equiv}CCH_2NH_2]$ **(II)** were performed with Gaussian 98 Rev. A7 using the DFT-B3LYP/LanL2DZ method. The LanL2DZ basis set implemented in the Gaussian series of programs, which consists of Los Alamos effective core potentials[i] for Co atoms and D95 split valence basis functions[ii] for the C, O, and H atoms. The calculated Mulliken charge populations for two amine protons are both 0.2640 for (**I**) and they are 0.2718 and 0.2839 for (**II**). The calculated values from natural population analysis (NPA) for two amine protons are both 0.3706 for (**I**) and they are 0.3904 and 0.3925 for (**II**). The Mulliken charge population, and natural population analysis of **(I)** and **(II)** only reflect part of the whole story concerning the acidity of **(I)** and **(II)**. A more thoughtful treatment shall include the relative stabilities of their conjugate bases. i. (a) Wadt, W. R.; Hay, P. J. *J. Chem. Phys.* **1985**, *82*, 284−298. (b) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 270, 299−310. ii. Dunning, T. H., Jr.; Hay, P. J. In *Modern Theoretical Chemistry*; Schaefer, H. F., III, Ed.; Plenum: New York, 1976; Vol. 3, pp 1−29.

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(9) (a) Reaction of $Co_2(CO)_8$ with $HC{\equiv}CCH_2NHCH_3$ was carried out in THF at 25 °C for 3 h. (b) Gruselle, M.; Philomin, V.; Chaminant, F.; Jaouen, G. *J. Organomet. Chem.* **1990**, *399*, 317.