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Preparation, Reaction, and Catalysis of the New Ruthenium Carbamato Complex $Et_2NCO_2RuH(CO)(PCy_3)_2$

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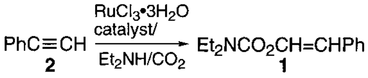
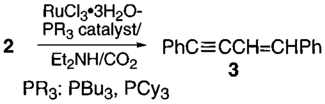
*Summary: CO_2 promoted the $RuCl_3{\cdot}3H_2O$-catalyzed dimerization of phenylacetylene (**2**) in the presence of PR_3 (R = Bu, Cy) and Et_2NH to afford 1,4-diphenyl-1-buten-3-yne (**3**). $Et_2NCO_2RuH(CO)(PCy_3)_2$ (**4**) and $(PhC{\equiv}C)_2Ru(CO)(PCy_3)_2$ (**5**) were isolated by the $RuCl_3{\cdot}3H_2O/PCy_3/Et_2NH/CO_2$ and **4**/**2** reactions, respectively, and catalyzed the dimerization of **2** to afford **3** with the concomitant formation of a poly(phenylacetylene).*

One of us developed recently transition-metal-catalyzed alkyne cycloaddition polymerization[1] as a new and useful method of polymer synthesis using the transition-metal-catalyzed monoyne cycloaddition as a polymer-forming elementary reaction. We are therefore interested in the monoyne reaction effected by an easily accessible transition-metal catalyst. Synthesis of enol carbamate **1** by the $RuCl_3{\cdot}3H_2O$-catalyzed phenylacetylene (**2**)/Et_2NH/CO_2 reaction was previously reported (eq 1).[2] On the basis of a finding that addition of a PBu_3 ligand to the reaction mixture suppressed almost completely the formation of **1** and, instead, effected the dimerization of **2** to afford 1,4-diphenyl-1-buten-3-yne (**3**), the $RuCl_3{\cdot}3H_2O/PBu_3$ system was suggested to be an efficient catalyst for the alkyne dimerization.[2]

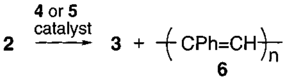


$$\underset{\mathbf{2}}{PhC{\equiv}CH} \xrightarrow[Et_2NH/CO_2]{RuCl_3{\cdot}3H_2O\ catalyst/} \underset{\mathbf{1}}{Et_2NCO_2CH{=}CHPh} \quad (1)$$

We examined the dimerization of **2** by the $RuCl_3{\cdot}3H_2O/PR_3$ catalytic system together with related reactions involving Et_2NH and/or CO_2. The $RuCl_3{\cdot}3H_2O/PBu_3$ system was ineffective, but the $RuCl_3{\cdot}3H_2O/PCy_3$ system (PCy_3 = tricyclohexylphosphine) formed **3**. CO_2 promoted the $RuCl_3{\cdot}3H_2O$-catalyzed formation of **3** in the presence of PR_3 and Et_2NH (eq 2). On the basis of these findings, the new ruthenium carbamato complex $Et_2NCO_2RuH(CO)(PCy_3)_2$ (**4**) was isolated by the one-pot $RuCl_3{\cdot}3H_2O/PCy_3/Et_2NH/CO_2$ reaction, along with the ruthenium bis(alkynyl) complex $(PhC{\equiv}C)_2Ru(CO)(PCy_3)_2$ (**5**) by the **4**/**2** reaction with CO_2 evolution (Scheme 1). The complexes **4** and **5** exhibited a dual catalytic activity to effect the dimerization and polymerization of **2** concomitantly to afford **3** and poly(phenylacetylene) (**6**) (eq 3). These findings indicate that the role of CO_2 in the CO_2-promoted $RuCl_3{\cdot}3H_2O$-catalyzed formation of **3** is the facile generation of the catalytically active ruthenium bis(alkynyl) complex **5** via the ruthenium carbamato complex **4**.



$$\mathbf{2} \xrightarrow[Et_2NH/CO_2]{RuCl_3{\cdot}3H_2O\text{-}PR_3\ catalyst/} \underset{\mathbf{3}}{PhC{\equiv}CCH{=}CHPh} \quad (2)$$
$$PR_3:\ PBu_3,\ PCy_3$$



$$\mathbf{2} \xrightarrow{\mathbf{4}\text{ or }\mathbf{5}\ catalyst} \mathbf{3} + \underset{\mathbf{6}}{\left(CPh{=}CH \right)_n} \quad (3)$$

The results of the $RuCl_3{\cdot}3H_2O$-catalyzed head-to-head dimerization of **2** to form **3** under various conditions are summarized in Table 1. The $RuCl_3{\cdot}3H_2O/PBu_3$ system was ineffective (entry 4), but addition of Et_2NH produced **3** (entry 5). In contrast, the $RuCl_3{\cdot}3H_2O/PCy_3$ system exhibited a considerable activity (entry 10), but addition of Et_2NH had no effect (entry 11). It is noteworthy that further addition of CO_2 increased the catalytic activity of the $RuCl_3{\cdot}3H_2O/PBu_3$ and PCy_3/Et_2NH systems (entries 7, 12) without significant formation of the carboxylated product **1**. Various ruthenium catalysts are reported for the alkyne head-to-head dimerization.[3] All these ruthenium catalysts are the preformed ruthenium hydrido complexes or their derivatives. Thus, the composite $RuCl_3{\cdot}3H_2O/PR_3/Et_2NH/CO_2$ system (R = Bu, Cy) is a new and unique catalyst, although its efficiency is not high.

The $RuCl_3{\cdot}3H_2O$-catalyzed dimerization of **2** promoted by Et_2NH/CO_2 suggests intermediacy of a ruthenium carbamato complex. The new ruthenium carbamato complex $Et_2NCO_2RuH(CO)(PCy_3)_2$ (**4**)[4] was isolated in

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(4) Characteristic spectral data of **4**: IR (cm^{-1}; Nujol) 2061 (RuH), 1897 (CO), 1521, 1497 (NCO_2); ^1H NMR (δ, ppm; C_6D_6) −17.1 (t, $^2J(HP)$ = 19.3 Hz, RuH); ^{13}C NMR (δ, ppm; C_6D_6) 163.9 (NCO_2), 208.0 (t, $^2J(CP)$ = 14.1 Hz, CO). Anal. Calcd for $C_{42}H_{77}NO_3P_2Ru$: C, 62.50; H, 9.62; N, 1.74. Found: C, 62.25; H, 9.54; N, 1.62. The PCy_3 ligand plays an important role in the formation of **4**: preparation of the ruthenium carbamato complex without PCy_3 by the $RuCl_3{\cdot}3H_2O/Et_2NH/CO_2$ reaction was unsuccessful.

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Scheme 1

$$\begin{array}{c} RuCl_3{\cdot}3H_2O/PCy_3/Et_2NH \\ \downarrow \; CO_2 \\ Et_2NCO_2RuH(CO)(PCy_3)_2 \;\; \mathbf{4} \\ \mathbf{2} \downarrow \; -CO_2 \\ (PhC{\equiv}C)_2Ru(CO)(PCy_3)_2 \;\; \mathbf{5} \end{array}$$

Table 1. $RuCl_3{\cdot}3H_2O$-Catalyzed Dimerization of Phenylacetylene (2) To Afford 1,4-Diphenyl-1-buten-3-yne (3) (Eq 2)[a]

entry	amt of **2**, mmol	amt of $RuCl_3{\cdot}3H_2O$, mmol	PR_3, PR_3/Ru[b]	amt of Et_2NH, mmol	amt of CO_2, kg/cm^2	yield of (*Z*)-**3**, %[c]
1	1	0.05	0	0	0	1.2
2	1	0.05	0	2	0	5.2
3	1	0.05	0	2	50	4.3[d]
4	1	0.05	PBu_3, 2	0	0	2.6
5	1	0.05	PBu_3, 2	2	0	33
6	2	0.1	PBu_3, 1	4	50	15[e]
7	1	0.05	PBu_3, 2	2	50	43[f]
8	1	0.05	PBu_3, 4	2	50	22
9	2	0.1	PBu_3, 2	4	50	53
10	1	0.05	PCy_3, 2	0	0	36
11	1	0.05	PCy_3, 2	2	0	34
12	1	0.05	PCy_3, 2	2	50	48[g]
13	1	0.05	PPh_3, 2	2	50	37

[a] Conditions: solvent, toluene 2 mL; reaction temperature, 100 °C; reaction time, 20 h; CO_2, initial pressure at room temperature in a 50 mL stainless steel autoclave. [b] Molar ratio. [c] Based on **2** and determined by GC using bibenzyl as an internal standard. [d] $Et_2NCO_2CH{=}CHPh$ (**1**) ((*Z*)-**1**/(*E*)-**1** = 4.3) was concomitantly formed in 37% yield. [e] Conditions: solvent, toluene 4 mL. **1** was formed in 11% yield. [f] (*Z*)-**3**/(*E*)-**3** = 3.2. **1** was formed in 2.0% yield. [g] (*Z*)-**3**/(*E*)-**3** = 3.5. **1** was formed in 3.4% yield.

moderate yield as colorless prismatic crystals from an ethanol-insoluble part of the reaction mixture formed by the one-pot $RuCl_3{\cdot}3H_2O/PCy_3/Et_2NH/CO_2$ reaction without **2**. The transition-metal carbamato complexes represent a class of compounds of considerable interest.[5] Transition-metal amide/CO_2[5a,d−f] and transition-metal halide/R_2NH/CO_2[5g,i] reactions are the two common preparative methods of transition-metal carbamato complexes $(R_2NCO_2)_nM$. Thus, the formation of **4** containing the CO and hydrido ligands generated concomitantly by the one-pot $RuCl_3{\cdot}3H_2O/PCy_3/Et_2NH/CO_2$ reaction is unique.[6]

The molecular structure of **4** determined by X-ray diffraction analysis is shown in Figure 1.[7] The ruthenium atom has a distorted-octahedral geometry. The bond lengths relevant to the bidentate carbamato ligand along with the small O1−Ru1−O2 bond angle were similar to those of the Me_2NCO_2 ligand of $[Me_2NCO_2Ru(PMe_2Ph)_4]PF_6$.[8]

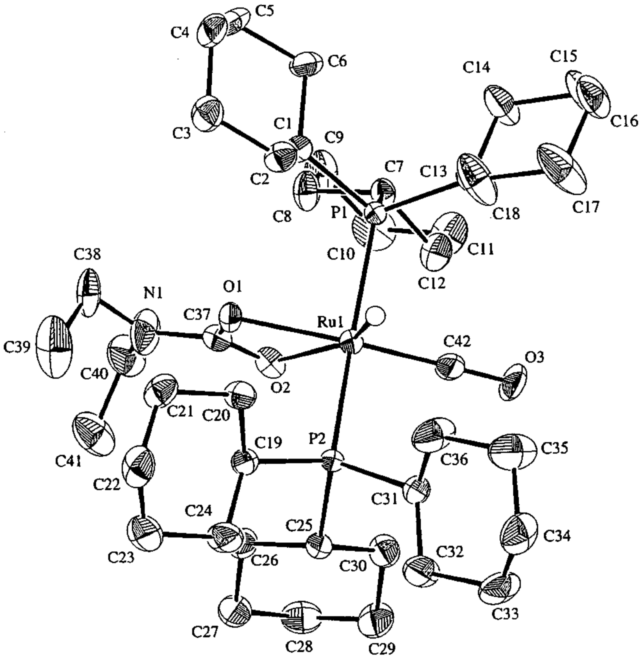

Figure 1. ORTEP structure (50% thermal ellipsoid probability) of $Et_2NCO_2RuH(CO)(PCy_3)_2$ (**4**). H atoms are omitted for clarity, except for Ru1−H.

Interestingly, it was found that addition of **2** to **4** in toluene at 50 °C evolved CO_2 gas in 44 and 50% yields after 0.5 and 4 h, respectively. The ruthenium bis(alkynyl) complex $(PhC{\equiv}C)_2Ru(CO)(PCy_3)_2$ (**5**)[9] was isolated in good yield as prismatic crystals containing one THF solvent molecule per two ruthenium atoms by the reaction of **4** with **2** (**2**/**4** = 6, PCy_3/**4** = 2, toluene, reflux) and subsequent recrystallization from a THF/hexane solution (Scheme 1). The formation of a $PhC{\equiv}C{-}Ru$ bond by the reaction of a $R_2NCO_2{-}Ru$ bond with **2** is unprecedented.

The molecular structure of **5** determined by X-ray diffraction analysis is shown in Figure 2.[10] The geometry around the ruthenium center is a distorted square pyramid: the ruthenium atom deviates from the P1−C37−P2−C45 plane by 0.237(1) Å toward the CO ligand. Change of the bidentate carbamato ligand of **4** into the monodentate alkynyl ligand of **5** with concomitant generation of one vacant coordination site in the presence of an excess amount of PCy_3 is noteworthy in

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(6) Some routes are possible for the ruthenium-mediated conversion of CO_2 into CO; see: Fu, P-f.; Khan, M. A.; Nicholas, K. M. *J. Organomet. Chem.* **1996**, *506*, 49, and references therein. Gas chromatographic analysis of the reaction mixture formed by the $RuCl_3{\cdot}3H_2O/PCy_3/Et_2NH/CO_2$ reaction indicated the insignificant formation of $O{=}PCy_3$, which excludes the deoxygenation of CO_2 by PCy_3.

(7) Crystal structure data for **4**: $C_{42}H_{77}NO_3P_2Ru$, colorless, monoclinic, $P2_1/c$ (No. 14), $a = 20.398(6)$ Å, $b = 9.588(3)$ Å, $c = 24.566(5)$ Å, $\beta = 113.75(2)°$, $Z = 4$, $R = 0.041$, GOF = 1.30. One of the *N*-ethyl groups, C38 and C39 in Figure 1, is disordered at the two locations close to each other with an occupancy ratio of 4:6 (the location shown in Figure 1).

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(9) Characteristic spectral data of **5**·0.5THF: IR (cm^{-1}; Nujol) 2074 (C≡C), 1920 (CO), 1594 (Ph); ^{1}H NMR (δ, ppm; C_6D_6) 7.04 (t, $J = 7.4$ Hz, 1 H, Ph), 7.27 (t, $J = 7.6$ Hz, 2 H, Ph), 7.76 (d, $J = 8.3$ Hz, 2 H, Ph); ^{13}C NMR (δ, ppm; THF-d_8): 122.8, 125.1, 128.6, 129.9, 130.0 (t, ^2J(CP) = 14.1 Hz), 130.2, 130.4, 130.8, 207.1 (t, ^2J(CP) = 12.6 Hz). Anal. Calcd for $C_{55}H_{80}O_{1.5}P_2Ru$: C, 71.17; H, 8.69. Found: C, 70.90; H, 8.69.

(10) Crystal structure data for **5**·0.5THF: $C_{55}H_{80}O_{1.5}P_2Ru$, yellow, monoclinic, $P2_1/n$ (No. 14), $a = 20.907(3)$ Å, $b = 22.683(4)$ Å, $c = 10.522(1)$ Å, $\beta = 90.32(1)°$, $Z = 4$, $R = 0.050$, GOF = 1.35. One of the cyclohexyl rings, C31−C36 in Figure 2, is disordered at the two locations close to each other with an equal probability.

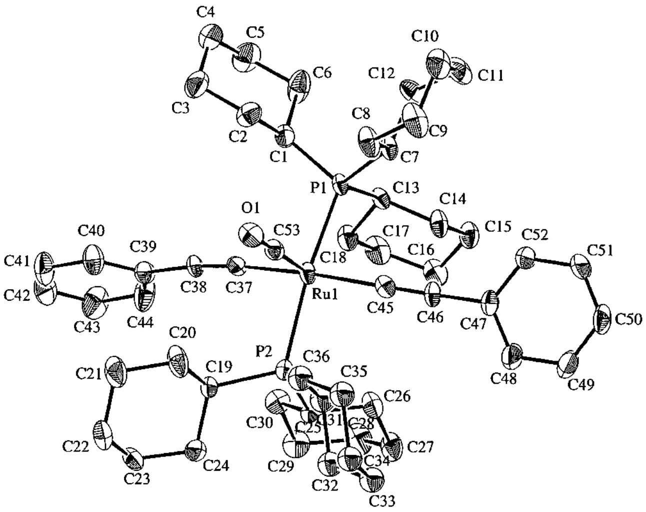

Figure 2. ORTEP structure (50% thermal ellipsoid probability) of $(PhC{\equiv}C)_2Ru(CO)(PCy_3)_2{\cdot}0.5THF$ ($\mathbf{5}{\cdot}0.5THF$). H atoms and free solvent are omitted for clarity.

Table 2. Formation of 1,4-Diphenyl-1-buten-3-yne (3) by the Phenylacetylene (2) Dimerization Catalyzed by Ruthenium Carbamato Complex 4 and Bis(alkynyl) Complex 5[a]

$$\underset{\mathbf{2}}{2PhC{\equiv}CH} \xrightarrow[\text{catalyst}]{\mathbf{4}\text{ or }\mathbf{5}} \underset{\mathbf{3}}{PhC{\equiv}CCH{=}CHPh}$$

amt of **4** or **5**, mmol	amt of PCy_3, mmol	solvent	yield of **3**, %[b] Z	E	**3**, Z/E
4, 0.024	0	toluene	32	1.7	19
4, 0.024	0	THF	37	1.6	23
4, 0.024	0.1	toluene	52	5.6	9.3
4, 0.048	0.2	THF	57	4.9	12
5, 0.030[c]	0	THF	33	2.0	16
5, 0.024	0.1	toluene	49	5.2	9.2

[a] Conditions: **4** or **5**/**2** = 0.048; solvent, 0.33 mL; temperature, 100 °C; reaction time, 20 h. [b] Yields of (Z)- and (E)-**3** were determined by GC using bibenzyl as an internal standard. Another product is poly(phenylacetylene) (**6**). [c] **5**/**2** = 0.06.

comparison to the octahedral ruthenium bis(alkynyl) complexes such as *trans*-$(Et_3P)_2Ru(C{\equiv}CPh)_2(CO)_2$[11] and *cis*-$(i\text{-}Pr_3P)_2Ru(C{\equiv}CPh)_2(CO)_2$[12] and may be ascribed to steric congestion of the PCy_3 ligand on the basis of a face-to-face arrangement of its two C13−C18 and C25−C30 cyclohexyl rings. The bond lengths relevant to the phenylethynyl ligand were similar to those of *trans*-$(Et_3P)_2Ru(C{\equiv}CPh)_2(CO)_2$.

The complexes **4** and **5** catalyzed the dimerization of **2** to afford **3** (Table 2). It may be concluded, therefore, that **4** and **5** are important catalytic species in the dimerization of **2** by the $RuCl_3{\cdot}3H_2O/PCy_3/Et_2NH/CO_2$ system. The yield of **3** was not high, although almost complete consumption of the starting **2** was confirmed by ^1H NMR and gas chromatographic analyses of the **2**/**5** reaction mixture. The ^1H NMR spectrum of the resulting reaction mixture formed by the **5**/2 PCy_3/**2** reaction in THF-d_8 exhibited only the signals of **3** and **5**, except for a broad signal centered at δ 7.1. The latter signal was found to be due to a phenyl group of poly(phenylacetylene) (**6**):[13a] poly(phenylacetylene)s (**6**) with GPC molecular weights of 3000−6000 were isolated in 15−20% yield[14] in the **4**- and **5**-catalyzed reactions of **2** together with the formation of **3**, and their phenyl groups showed the ^1H NMR broad signal at δ 7.1. Thus, the dual catalysis of **4** and **5** with different natures, i.e., the dimerization and polymerization activities, is noteworthy and the ruthenium catalysis is not usual in the transition-metal-catalyzed acetylene polymerization.[13b,c] To the best of our knowledge, the alkyne dimerization and polymerization catalyzed by **4** is the first example of catalysis of a transition-metal carbamato complex, although stoichiometric reactions[15] of its carbamato group are well-known.

The isolation of **4** by the $RuCl_3{\cdot}3H_2O/PCy_3/Et_2NH/CO_2$ reaction, its conversion to **5** by **2** with CO_2 evolution, and the catalysis of **4** and **5** for the dimerization of **2** indicate that the role of CO_2 in the CO_2-promoted $RuCl_3{\cdot}3H_2O$-catalyzed formation of the noncarboxylated product **3** is the facile generation of the catalytically active ruthenium bis(alkynyl) complex **5**[3c] via the ruthenium carbamato complex **4**. CO_2 is previously reported to increase the efficiency and chemoselectivity of the platinum-catalyzed dimerization of butadiene[16a] and the palladium-catalyzed reaction of butadiene with water,[16b] in which the role of CO_2, however, is not clarified. Thus, the present CO_2-promoted ruthenium-catalyzed alkyne dimerization is a good example elucidating the function of CO_2 in a CO_2-promoted transition-metal-catalyzed organic reaction without CO_2 incorporation into a product by the isolation of participating transition-metal species.

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Supporting Information Available: Experimental procedures and spectroscopic data of **3**−**6** together with X-ray structural information on **4** and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[14] The low polymer yield may be due to the loss of oligomers and **6** with low molecular weights during the isolation of **6** with higher molecular weights by toluene/ethyl alcohol and toluene/hexane.

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