

Organometallics, Communications

Supporting Information

**Preparation, Reaction, and Catalysis of a New Ruthenium Carbamate Complex
 $\text{Et}_2\text{NCO}_2\text{RuH}(\text{CO})(\text{PCy}_3)_2$**

Tetsuo Tsuda*⁺ and Moto-o Shiro*⁺⁺

⁺ Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University,
Yoshida, Kyoto 606-8501, Japan

⁺⁺ X-Ray Research Institute, Rigaku Corporation, Matsubara, Akishima, Tokyo 196-8666,
Japan

1) Experimental Procedures and Spectroscopic Data of 1,4-Diphenylbuten-3-yne (3), $\text{Et}_2\text{NCO}_2\text{RuH}(\text{CO})(\text{PCy}_3)_2$ (4), and $(\text{PhC}\equiv\text{C})_2\text{Ru}(\text{CO})(\text{PCy}_3)_2$ (5), and Poly(phenylacetylene) (6).

General Procedures. IR spectra were determined on a Perkin-Elmer 1600 spectrophotometer. ^1H NMR (270 MHz) and ^{13}C NMR (67.5 MHz) spectra were taken in CD_2Cl_2 unless otherwise stated on a JEOL JNM-EX-270 instrument. Their chemical shifts are reported in ppm on the δ scale relative to tetramethylsilane and were calibrated against the solvent resonance. Coupling constants (J) are in hertz. A MASS spectrum was obtained on a JEOL JMS-DX-300 instrument. Gas chromatographic (GC) analyses of organic products were made on a Shimadzu GC-12A instrument employing a 20% silicone DC 550/Celite 545 column (1 m) or a 20% polyethylene glycol (PEG) 20M/Celite 545 column (1 m), He carrier gas, and bibenzyl as an internal standard. GC analysis of CO_2 gas was made on a Shimadzu GC-12A instrument employing an activated charcoal column (4 m), H_2 carrier gas, and methane gas as an internal standard. Gel permeation chromatography (GPC) was performed in chloroform using a SHODEX K-802 column with polystyrene standards. Preparative layer chromatography (PLC) was carried out using 20/20/0.2 cm plates prepared with Merck silica gel 60 PF-254. Melting point of the ruthenium complex was measured in a glass capillary under nitrogen and

was uncorrected. THF, toluene, and Et_2NH were distilled over CaH_2 under nitrogen. Phenylacetylene (**2**) was distilled under nitrogen. $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ was a commercial reagent and was used as purchased. PBu_3 , PCy_3 (tricyclohexylphosphine), and PPh_3 were commercial reagents and were used as purchased. Carbon dioxide was a commercial reagent (assay: minimum 99.99 vol %) supplied by Kyoto Teisan, Co., Ltd. and was used without further purification.

Dimerization of Phenylacetylene (2**) Catalyzed by $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$.** The reaction was carried out under nitrogen. The experimental procedure of the $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}/\text{PBu}_3/\text{Et}_2\text{NH}/\text{CO}_2/\text{2}$ reaction as a representative is as follows. A stirred mixture containing $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ (0.013 g, 0.050 mmol), toluene (2.0 mL), PBu_3 (0.025 mL, 0.10 mmol), Et_2NH (0.21 mL, 2.0 mmol), and **2** (0.11 mL, 1.0 mmol) in a 50 mL stainless steel autoclave was heated at 100 °C for 20 h under CO_2 pressure (50 kg/cm²: initial pressure at room temperature). CO_2 gas was purged off cooling the autoclave by ice water. The resulting reaction mixture was analyzed by GC employing the silicone column after the addition of dibenzyl (0.0456 g, 0.250 mmol) as an internal standard. 1,4-Diphenylbuten-3-yne (**3**) was formed in 56% yield ((*Z*)-**3**/*E*-**3** = 3.2) together with the formation of β -[(*N,N*-diethylcarbamoyl)oxy]styrene (**1**) in 2.0% yield ((*Z*)-**1**/*E*-**1** = 4.3). GC analysis of the reaction product indicated that the formation of 1,3,5-triphenylbenzene is negligible. Compound (*Z*)-**3** (Murahashi, S.; Yamamura, M.; Yanagisawa, K.; Mita, N.; Kondo, K. *J. Org. Chem.* **1979**, *44*, 2408) was isolated by PLC (hexane) followed by GC from the reaction mixture obtained by a large-scale reaction. (*Z*)-**3**: IR (neat, cm⁻¹) 3057, 3022, 1997, 1596, 1489, 1411, 1028, 915, 782, 755, 689; ¹H NMR 5.95 (d, *J* = 11.9, 1 H), 6.74 (d, *J* = 11.9, 1 H), 7.30-7.55 (m, 8 H), 7.95 (diffused d, *J* = 7.3, 2 H); ¹³C NMR 87.9, 95.5, 106.9, 123.1, 128.0, 128.2, 128.3, 128.4, 131.1, 136.3, 138.4; MS *m/z* 204 (*MH*⁺). Authentic (*E*)-**3** was prepared according to the literature (Okuro, K.; Furuune, M.; Enna, M.; Miura, M.; Nomura, M. *J. Org. Chem.* **1993**, *58*, 4716). (*E*)-**3**: ¹H NMR 6.41 (d, *J* = 16.2, 1 H), 7.05 (d, *J* = 16.2, 1 H), 7.30-7.49 (m, 10 H). A mixture of (*Z*)-**1** and (*E*)-**1** (Mahe, R.; Sasaki, Y.; Bruneau, C.; Dixneuf, P. H. *J. Org. Chem.* **1989**, *54*, 1518) was isolated by PLC (CH_2Cl_2 /petroleum ether = 1/1 (v/v)) from the reaction product obtained by a large-scale $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}/\text{Et}_2\text{NH}/\text{CO}_2/\text{2}$

reaction without PBU_3 . (Z)-1: IR (neat, cm^{-1}) 3085, 3056, 3025, 2976, 1717, 1660, 1426, 1270, 1158, 1071, 965, 784, 757; ^1H NMR 0.84 (t, $J = 7.1$, 3 H), 0.91 (t, $J = 7.1$, 3 H), 2.93 (q, $J = 6.9$, 2 H), 3.07 (q, $J = 7.3$, 2 H), 5.46 (d, $J = 7.3$, 1 H), 7.08-7.58 (m, 5 H), 7.66 (d, $J = 7.6$, 1 H). (E)-1: ^1H NMR 6.34 (d, $J = 12.5$), 8.27 (d, $J = 12.2$).

Preparation and Isolation of Ruthenium Carbamate Complex $\text{Et}_2\text{NCO}_2\text{RuH}(\text{CO})(\text{PCy}_3)_2$ (4). Preparation and isolation of **4** were carried out under nitrogen. A mixture containing $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ (0.26 g, 1.0 mmol), PCy_3 (0.42 g, 1.5 mmol), Et_2NH (4.1 mL, 40 mmol), and THF (40 mL) in a 100 mL stainless steel autoclave was heated at 100 °C for 20 h under CO_2 pressure (50 kg/cm^2 : initial pressure at room temperature). CO_2 gas was purged off cooling the autoclave by ice water. After removal of a THF-insoluble ammonium salt by filtration, the THF solvent was evaporated *in vacuo*. Addition of hexane (15 mL) to the residue gave a hexane-insoluble precipitate, which was filtered off. The resulting hexane solution was evaporated *in vacuo* to give the residue, to which anhydrous ethanol (7.5 mL) was added to precipitate a white solid. This ethanol-insoluble solid was collected, washed with anhydrous ethanol, and dried *in vacuo*. Its hot and saturated hexane solution over a small amount of insoluble solid was taken and allowed to stand overnight at room temperature to generate colorless prismatic crystals of **4**. Optimization of the yield of **4** was not done except for the PCy_3/Ru ratio. In separate experiments, the yields of **4** were determined by ^1H NMR spectroscopy of the resulting reaction mixtures using benzyl ether as an internal standard. Relative peak area of two methylene signals of ethyl group of **4** at δ 3.34 and 3.45 to a methylene signal of benzyl ether δ 4.47 gave the following yields of **4**: 27% ($\text{PCy}_3/\text{Ru} = 2$), 31% ($\text{PCy}_3/\text{Ru} = 1.5$), and 23% ($\text{PCy}_3/\text{Ru} = 1$). The crystals of **4** were stable in air at least for 2 h while their solution was slowly darkened in air. **4**: mp. 216 °C; IR (nujol, cm^{-1}) 2061, 1897, 1521, 1497, 1315, 1004, 846, 733; ^1H NMR (C_6D_6) -17.1 (t, $J = 19.3$, 1 H), 1.16 (t, $J = 6.9$, 3 H), 1.18 (t, $J = 7.3$, 3 H), 1.33 (br s), 1.55-1.96 (m), 2.06-2.40 (m), 3.34 (q, $J = 6.9$, 2 H), 3.45 (q, $J = 7.1$, 2 H); ^{13}C NMR (C_6D_6) 14.6, 14.9, 27.1, 28.25, 28.34, 28.41, 28.45, 28.52, 28.59, 29.6, 30.9, 35.1, 35.2, 35.4, 39.6, 39.8, 163.9, 207.81, 208.03, 208.23. Anal. Calcd for $\text{C}_{42}\text{H}_{77}\text{NO}_3\text{P}_2\text{Ru}$: C, 62.50; H, 9.62; N, 1.74. Found: C, 62.25; H, 9.54; N, 1.62. In the other separate experiment, the formation of tricyclohexylphosphine oxide

(Issleib, K.; Brack, A. Z. *Anorg. Allg. Chem.* **1954**, 277, 258) was examined. Two reaction mixtures containing $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ (0.14 g, 0.50 mmol), PCy_3 (0.21 g, 0.75 mmol), Et_2NH (2.1 mL, 20 mmol), and THF (18 mL) with and without CO_2 (50 kg/cm²) were heated at 100 °C for 20 h in 50 mL stainless steel autoclaves. GC analysis of the reaction products using the silicone column and pentacosane as an internal standard indicated formations of tricyclohexylphosphine oxide in 6.0 and 4.5% yields on the basis of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$, respectively. Thus, the formation of tricyclohexylphosphine oxide was 1.5% and insignificant.

Dimerization of 2 Catalyzed by 4. The reaction was carried out in a glass ampul under nitrogen. A mixture of **4** (0.019 g, 0.024 mmol), **2** (0.055 mL, 0.5 mmol), and toluene (0.33 mL) was heated at 100 °C for 20 h. The resulting reaction mixture was analyzed by GC employing the PEG column after the addition of dibenzyl (0.0228 g, 0.125 mmol) as an internal standard. Compound **3** was formed in 34% yield ((*Z*)-**3**/*E*)-**3** = 19).

Isolation of Poly(phenylacetylene) (6) in the Dimerization Reaction of 2 Catalyzed by 4. The reaction was carried out in a glass ampul under nitrogen. A mixture of **4** (0.19 g, 0.24 mmol), PCy_3 (0.27 g, 0.96 mmol), **2** (0.55 mL, 5.0 mmol), and THF (3.3 mL) was heated at 100 °C for 20 h. The resulting reaction mixture was evaporated *in vacuo* to give the residue, which was dissolved in toluene (1 mL). Addition of ethanol (10 mL) precipitated a pale yellow powder, which was isolated by centrifugation, washed twice with ethanol (2 mL). The powder was dissolved in toluene (1 mL), which was added dropwise to stirred hexane (10 mL) to form a pale yellow powder. It was washed twice with ethanol (2 mL) and dried *in vacuo* to give poly(phenylacetylene) (**6**) (0.096 g, 19%). The molecular weight of **6** determined by GPC analysis was 6300. **6**: IR (film, cm⁻¹) 3060, 3027, 2924, 1944, 1600, 1492, 1451, 1344, 1272, 1185, 1165, 1132, 1075, 1030, 1013, 913, 834, 751, 696; ¹H NMR 3.4-4.1 (br m), 7.1 (br m); ¹³C NMR (100 MHz) 84.5, 85.2, 127.2, 128.2, 129.0, 131.9, 139.1, 139.9, 140.0. Anal. Calcd for $(\text{C}_8\text{H}_6)_n$: C, 94.08; H, 5.92. Found: C, 92.52; H, 6.18. The ¹H NMR signal of **6** at δ 3.4-4.1 was weak. Assignment of the ¹H NMR signal δ 3.4-4.1 together with ¹³C NMR signals at δ 84.5 and 85.2 is not clear at the present time.

Preparation and Isolation of Ruthenium Bis(alkynyl) Complex $[(\text{PhC}\equiv\text{C})_2\text{Ru}(\text{CO})(\text{PCy}_3)_2 \cdot (\text{THF})_{0.5}]$ (**5** $\cdot (\text{THF})_{0.5}$). Preparation and isolation of **5**

were carried out under nitrogen. A mixture containing **4** (0.17 g, 0.22 mmol), PCy₃ (0.12 g, 0.43 mmol), **2** (0.14 mL, 1.3 mmol), and toluene (4.0 mL) in a 50 mL flask was heated under a slow stream of nitrogen and reflux for 7 h. The solution was evaporated *in vacuo*. The residue was dissolved in THF (1 mL) and hexane (10 mL) under gentle heating. The solution was allowed to stand overnight at about 10 °C to generate prismatic yellow crystals of **5** (0.14g, 71%). **5**: mp. 105-110 °C; IR (nujol, cm⁻¹) 2074, 1920, 1594, 1482, 1445, 1205, 1068, 845; ¹H NMR (C₆D₆) 1.10-1.43 (m), 1.50-1.90 (m), 2.20-2.40 (m), 2.92-3.15 (m), 7.04 (t, *J* = 7.4), 7.27 (t, *J* = 7.6), 7.76 (d, *J* = 8.3); ¹³C NMR (THF-*d*₈) 27.4, 28.69, 28.74, 28.80, 30.9, 36.1, 36.2, 36.3, 122.8, 125.1, 128.6, 129.9, 130.0, 130.2, 130.4, 130.8, 207.0, 207.1, 207.2. Anal. Calcd for C₅₅H₈₀O_{1.5}P₂Ru: C, 71.17; H, 8.69. Found: C, 70.90; H, 8.69. In the ¹H NMR spectrum of **5**•(THF)_{0.5}, a triplet (*J* = 6.1) assignable to THF appeared at δ 3.61. In a separate experiment, CO₂ gas evolution was examined. To a stirred toluene (1.0 mL) solution of **4** (0.40 g, 0.050 mmol) in a 50 mL flask equipped with a rubber septum were added **2** (0.055 mL, 0.50 mmol) and methane gas (1.0 mL, 0.041 mmol) as a GC internal standard through the rubber septum using hypodermic syringes. The flask was heated to 50 °C. CO₂ gas evolution was monitored by GC analysis of a gaseous sample taken out through the rubber septum with a hypodermic syringe using the activated charcoal column. CO₂ gas was evolved in 44 and 50% yields after 0.5 and 4 h, respectively. No CO₂ gas evolved in the absence of **2**.

Dimerization of 2 Catalyzed by 5. The reaction was carried out in a glass ampul under nitrogen. A mixture of **5**•(THF)_{0.5} (0.028 g, 0.030 mmol), **2** (0.055 mL, 0.50 mmol), and THF (0.33 mL) was heated at 100 °C for 20 h. The resulting reaction mixture was analyzed by GC employing the PEG column after the addition of dibenzyl (0.0228 g, 0.125 mmol) as an internal standard. Compound **3** was formed in 35% yield ((*Z*)-**3**/*E*-**3** = 16). GC analysis employing the PEG column and dibenzyl as an internal standard of the separate reaction using **5**•(THF)_{0.5} (0.045 g, 0.048 mmol), PCy₃ (0.056 g, 0.20 mmol), **2** (0.11 mL, 1.0 mmol), and THF (0.66 mL) at 100 °C for 20 h showed the presence of unreacted **2** in 1.1% yield. The reaction in a THF-*d*₈ solvent was carried out in a glass ampul under nitrogen. A mixture of **5**•(THF)_{0.5} (0.023 g, 0.025 mmol), PCy₃ (0.014 g, 0.050 mmol), **2** (0.055 mL, 0.50 mmol),

benzyl ether (0.0228 g, 0.125 mmol) as an internal standard, and THF-*d*₈ (0.70 mL) was heated at 100 °C for 20 h. The ¹H NMR spectrum of the resulting reaction mixture showed the signals due to **3** and **5** together with a broad signal centered at δ 7.1. On the basis of the signal of benzyl ether at δ 4.47, the yield of (*Z*)-**3** was determined to be 40%.

Isolation of 6 in the Dimerization Reaction of 2 Catalyzed by 5. The reaction was carried out in a glass ampul under nitrogen. A mixture of **5**•(THF)_{0.5} (0.045 g, 0.048 mmol), PCy₃ (0.056 g, 0.20 mmol), **2** (0.11 mL, 1.0 mmol), and THF (0.66 mL) was heated at 100 °C for 20 h. The resulting reaction mixture was evaporated *in vacuo* to give the residue, which was dissolved in toluene (1 mL). Addition of ethanol (10 mL) precipitated a pale yellow powder, which was isolated by centrifugation, washed twice with ethanol (2 mL), and dried *in vacuo* to give **6** (0.014 g, 14%). The molecular weight of **6** determined by GPC analysis was 3000. The ¹H NMR spectrum of **6** showed the broad signal centered at δ 7.1 together with the weak and broad signal at δ 3.4-4.1.

Crystallography. Crystals in sealed glass capillaries were mounted on a Rigaku RAXIS-IV imaging plate area detector. The intensity data were collected using the oscillation technique and readout was performed in the 0.100 mm pixel mode. The data were corrected for Lorentz and polarization effects. An empirical absorption correction (RAXIS-IV, Data Processing Software, Rigaku Corporation, 1996) was also applied. The structures were solved by direct methods (Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, M.; Giacovazzo, C.; Guagliardi, A.; Polidori, G. SIR 92, A Program for Automatic Solution of Crystal Structures by Direct Methods, *J. Appl. Crystallogr.* **1994**, *27*, 435) and refined by full-matrix least squares techniques (teXsan, Single Crystal Structure Analysis Software, Version 1.9, Molecular Structure Corporation and Rigaku Corporation, 1998), $\Sigma w(|F_o| - |F_c|)^2$ being minimized. The crystal of **5** contains half mole of the THF solvent, which is disordered around an inversion center of the crystal. One of *N*-ethyl groups of **4** and one of cyclohexyl rings of **5** are disordered at two locations shown in the Tables of positional parameters using the corresponding unprimed and primed numbers, respectively.

2) Crystallographic Data of **4**

formula

C₄₂H₇₇NO₃P₂Ru

fw	807.09
cryst syst	monoclinic
space group	$P2_1/c$
cell constants	
a , Å	20.398(6)
b , Å	9.588(3)
c , Å	24.566(5)
β , deg	113.75(2)
V , Å ³	4397(2)
Z ,	4
T , K	203
D_{calcd} , g cm ⁻³	1.219
μ , mm ⁻¹	0.465
$F(000)$	1736
radiation (λ , Å)	graphite-monochromated Mo K α (0.71069)
cryst dims, mm	0.20 x 0.20 x 0.15
2θ range, deg	4 - 55
index ranges Å	$-26 \leq h \leq 0$, $0 \leq k \leq 12$, $-31 \leq l \leq 31$
transm coeff	1.0 - 0.88
no. of reflns collcd	8445
no. of reflns obsd with ($I > 3\sigma(I)$)	7326
no. of params refined	461
goodness-of-fit	1.30
R	0.041
R_w	0.059
$\Delta\rho_{\text{max}}$, e Å ⁻³	0.99

$\Delta\rho_{\min}$, e Å⁻³ -1.09

3) Crystallographic Data of 5

formula	C ₅₅ H ₈₀ NO _{1.5} P ₂ Ru
fw	928.25
cryst syst	monoclinic
space group	<i>P</i> 2 ₁ / <i>n</i>
cell constants	
<i>a</i> , Å	20.907(3)
<i>b</i> , Å	22.683(4)
<i>c</i> , Å	10.522(1)
β , deg	90.32(1)
<i>V</i> , Å ³	4989(1)
<i>Z</i> ,	4
<i>T</i> , K	173
<i>D</i> _{calcd} , g cm ⁻³	1.236
μ , mm ⁻¹	0.416
<i>F</i> (000)	1984
radiation (λ , Å)	graphite-monochromated Mo K α (0.71069)
cryst dims, mm	0.30 x 0.15 x 0.08
2 θ range, deg	4 - 50
index ranges	0 ≤ <i>h</i> ≤ 24, -26 ≤ <i>k</i> ≤ 0, -12 ≤ <i>l</i> ≤ 12
transm coeff	1.0 - 0.82
no. of reflns colld	7609
no. of reflns obsd with (<i>I</i> > 2 σ (<i>I</i>))	6276
no. of params refined	482
goodness-of-fit	1.35

R	0.050
R_w	0.072
$\Delta\rho_{\max}, e \text{ \AA}^{-3}$	0.85
$\Delta\rho_{\min}, e \text{ \AA}^{-3}$	-0.74