# Preparation of Four- and Five-Membered Diruthenacycles and an Unusual Double Insertion of Carbon Monoxide. Crystal and Molecular Structures of $Ru_2(Me_2PCH_2PMe_2)_2(CO)_3[\mu\text{-}C_2(CO_2Me)_2][C(O)C(O)C_2(CO_2Me)_2]$ and $Ru_2(Me_2PCH_2PMe_2)_2(CO)_4[\mu\text{-}C(O)C_2(CO_2Me)_2]$

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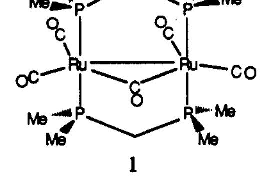
*Received December 23, 1991*

The reaction of $Ru_2(dmpm)_2(CO)_5$, where dmpm = bis(dimethylphosphino)methane, with dimethyl acetylenedicarboxylate (DMAD) resulted in the formation of three isolable products, each of which can be prepared in ~80% yield by varying the reaction conditions. In very concentrated solutions at room temperature, the presence of excess DMAD led to $Ru_2(dmpm)_2(CO)_3[\mu\text{-}C_2(CO_2Me)_2][C(O)C(O)C_2(CO_2Me)_2]$ in 81% yield. The X-ray crystal structure [$P2_12_12_1$ (No. 19) space group, $a$ = 13.932 (5) Å, $b$ = 14.360 (3) Å, $c$ = 17.854 (3) Å, $V$ = 3572 (3) Å$^3$, $Z$ = 4] established that one alkyne was bound as a *cis*-dimetalated alkene, while the other was incorporated into a five-membered metallacycle. This metallacycle appeared to have formed by the insertion of two carbon monoxide ligands into a metal–alkyne bond. When the reaction was conducted at room temperature in dilute solution, the product, $Ru_2(dmpm)_2(CO)_4[\mu\text{-}C(O)C_2(CO_2Me)_2]$ contained only 1 equiv of DMAD. X-ray crystallography [$P2_1/n$ (No. 14) space group, $a$ = 10.845 (5) Å, $b$ = 27.82 (1) Å, $c$ = 10.447 (5) Å, $\beta$ = 109.90 (4)°, $V$ = 2964 (5) Å$^3$, $Z$ = 4] showed the alkyne had again been incorporated into a five-membered metallacycle, in a 1,2-diruthenacyclopentenone arrangement. When the reaction of $Ru_2(dmpm)_2(CO)_5$ with DMAD was conducted at elevated temperatures or when $Ru_2(dmpm)_2(CO)_4[\mu\text{-}C(O)C_2(CO_2Me)_2]$ was heated, loss of one CO ligand to form a 1,2-diruthenacyclobutene resulted. Methyl propiolate was also found to react slowly (25–30 h at room temperature) with $Ru_2(dmpm)_2(CO)_5$ yielding a product that was analogous to the 1,2-diruthenacyclobutene described for DMAD.

## Introduction

The interaction of "A-frame" complexes with alkynes has been an area of intensive study.[1,2] While a variety of carbon–carbon bond forming reactions and alkyne oligomerizations have been observed with other binuclear complexes,[3,4] systems containing diphosphine ligands such as bis(diphenylphosphino)methane (dppm) or bis(dimethylphosphino)methane (dmpm) have been shown to simply add across the C–C triple bond of activated alkynes, such as dimethyl acetylenedicarboxylate (DMAD) or hexafluoro-2-butyne, to form cyclic structures, as shown in eq 1.[5,6] We recently reported that the reaction of the Ru(0) binuclear system $Ru_2(dmpm)_2(CO)_5$ (1) with a relatively nonactivated alkyne, diphenylacetylene, resulted in *cis*-dimetalation of the alkyne to form a diruthenacyclobutene.[7] As part of our continuing investigation of the reactivity of $Ru_2(dmpm)_2(CO)_5$, this report describes the formation of four- and five-membered dimetallacycles and an unusual double insertion of carbon monoxide in the reaction of $Ru_2(dmpm)_2(CO)_5$ with the electron-poor alkyne dimethyl acetylenedicarboxylate (DMAD). A preliminary communication of this work has appeared.[8]



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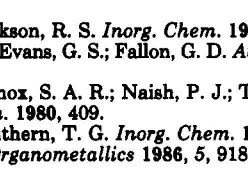

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## Experimental Section

**General Information.** $Ru_3(CO)_{12}$ (Strem), bis(dimethylphosphino)methane (dmpm, Strem), tetrafluoroboric acid–diethylether (Aldrich), methyl propiolate (Aldrich), dimethyl acetylenedicarboxylate (Aldrich), diethyl acetylenedicarboxylate (Aldrich), CO (CP grade, 99.3%, Air Products), and $^{13}$CO (99%, Aldrich) were used without further purification. $Ru_2(dmpm)_2(CO)_5$ and $Ru_2(dmpm)_2(CO)_4[\mu\text{-}C_2(CO_2Me)_2]$ were prepared as previously reported.[7] Toluene and diethyl ether ($Et_2O$) were dried by distillation from sodium benzophenone ketyl under nitrogen. Hexane was dried over sodium, and methylene chloride ($CH_2Cl_2$) was dried over calcium hydride. Both were distilled under $N_2$ prior to use. All reactions were conducted under a nitrogen atmosphere using standard Schlenk techniques. Infrared spectra were obtained on a Mattson Polaris FTIR spectrometer. $^1$H, $^{13}$C, and $^{31}$P NMR spectra were recorded on a Varian VXR-300 spectrometer. Mass spectra were collected on a VG 7070E-HF instrument. Elemental analyses were performed by M-H-W Laboratories. Table I contains a summary of the infrared and $^1$H and $^{13}$P NMR spectroscopic data.

**Preparation of $Ru_2(dmpm)_2(^{13}CO)_5$.** $Ru_2(dmpm)_2(CO)_5$ (1) (150 mg, 0.24 mmol) was charged to an 80-mL thick-walled reaction vessel equipped with a stirbar. Toluene (20 mL) was added, and the solution was freeze–pump–thaw degassed. $^{13}$CO (230 mL at 1 atm, 22 °C) was vacuum transferred from a storage bulb to

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(1) Hoffman, D. M.; Hoffmann, R.; Fisel, C. R. *J. Am. Chem. Soc.* 1982, *104*, 3858.

(2) Cowie, M.; Dickson, R. S. *Inorg. Chem.* 1981, *20*, 2682.

(3) Dickson, R. S.; Evans, G. S.; Fallon, G. D. *Aust. J. Chem.* 1985, *38*, 273.

(4) Dyke, A. F.; Knox, S. A. R.; Naish, P. J.; Taylor, G. E. *J. Chem. Soc., Chem. Commun.* 1980, 409.

(5) Cowie, M.; Southern, T. G. *Inorg. Chem.* 1982, *21*, 246.

(6) Mague, J. T. *Organometallics* 1986, *5*, 918.

(7) Johnson, K. A.; Gladfelter, W. L. *Organometallics* 1989, *8*, 2866.

(8) Johnson, K. A.; Gladfelter, W. L. *J. Am. Chem. Soc.* 1991, *113*, 5097.

0276-7333/92/2311-2534$03.00/0

**Table I. Spectroscopic Data**

| compd | $\nu_{CO}$ (cm$^{-1}$) | $^1$H NMR (ppm, CDCl$_3$) | $^{31}$P NMR (CDCl$_3$) (ppm rel to $H_3PO_4$) |
|---|---|---|---|
| 1 | 2033 (s), 1979 (s), 1933 (m), 1823 (w), 1700 (m), 1649 (w, toluene) | 0.905 (t, $J_{HP}$ = 2.8 Hz, 6 H, Me), 1.085 (t, $J_{HP}$ = 3.0 Hz, 6 H, Me), 1.186 (t, $J_{HP}$ = 2.5 Hz, 6 H, Me), 1.421 (t, $J_{HP}$ = 3.3 Hz, 6 H, Me), 1.8 (m, 4 H, CH$_2$), 3.54 (s, 3 H, OMe), 3.86 (s, 3 H, OMe) ($C_6D_6$) | AA′BB′ ($C_6D_6$), $\delta_a$ = 7.7, $\delta_b$ = 4.2 |
| 3 | 2042 (s), 1986 (s), 1835 (m), 1693 (m, br), 1642 (m), 1501 (w, $CH_2Cl_2$) | 1.22 (t, $J_{HP}$ = 3.5 Hz, 6 H, Me), 1.38 (t, $J_{HP}$ = 3.3 Hz, 6 H, Me), 1.66 (t, $J_{HP}$ = 3.45 Hz, 6 H, Me), 1.78 (t, $J_{HP}$ = 3.1 Hz, 6 H, Me), 1.87 (m, 2 H, CH$_2$), 2.85 (m, 2 H, CH$_2$), 3.64 (s, 3 H, OMe), 3.72 (s, 3 H, OMe), 3.79 (s, 3 H, OMe), 3.83 (s, 3 H, OMe) | 0.44 (t, $J_{PP}$ = 16 Hz), −2.98 (t, $J_{PP}$ = 16 Hz) |
| 4 | 1996 (m), 1968 (s), 1937 (m), 1912 (w), 1707 (w), 1674 (w), 1531 (w, $CH_2Cl_2$) | 1.12 (t, $J_{HP}$ = 2.7 Hz, 6 H, Me), 1.2 (t, $J_{HP}$ = 2.6 Hz, 6 H, Me), 1.46 (t, $J_{HP}$ = 2.8 Hz, 6 H, Me), 1.57 (t, $J_{HP}$ = 2.8 Hz, 6 H, Me), 1.86 (m, 2 H, CH$_2$), 3.2 (m, 2 H, CH$_2$), 3.5 (s, 3 H, OCH$_3$), 3.63 (s, 3 H, OCH$_3$) | AA′BB′ (toluene-$d_8$), $\delta_a$ = −0.87, $\delta_b$ = −2.03, $J_{AA'} = J_{BB'} \geq 175$ Hz, $J_{AB} = J_{A'B'}$ = 51 Hz, $J_{AB'} = J_{A'B}$ = 33 Hz |
| 5 | 1982 (m), 1951 (s), 1923 (m), 1900 (w), 1685 (w, toluene) | 1.09 (s, 12 H, Me), 1.18 (m, 2 H, CH$_2$), 1.45 (s, 12 H, Me), 2.75 (m, 2 H, CH$_2$), 3.65 (s, 6 H, OMe) ($C_6D_6$) | −4.1 (s) |
| 6 | 2041 (s), 1985 (s), 1832 (m), 1716 (m), 1686 (m), 1643 (m), 1504 (w, $CH_2Cl_2$) | 1.25 (m, 12 H, Me), 1.38 (t, $J_{HP}$ = 3 Hz, 6 H, Me), 1.65 (t, $J_{HP}$ = 3 Hz, 6 H, Me), 1.75 (t, $J_{HP}$ = 3 Hz, 6 H, Me), 1.82 (m, 2 H, CH$_2$), 2.91 (m, 2 H, CH$_2$), 4.08 (quart, $J_{HH}$ = 7 Hz, 2 H, OEt), 4.16 (quart, $J_{HH}$ = 7 Hz, 2 H, OEt), 4.22 (quart, $J_{HH}$ = 7 Hz, 2 H, OEt), 4.31 (quart, $J_{HH}$ = 7 Hz, 2 H, OEt) | 0.6 (t, $J_{PP}$ = 16 Hz), −3.1 (t, $J_{PP}$ = 16 Hz) |
| 7, 8 | 2041 (s), 1985 (s), 1833 (m), 1713 (m), 1688 (m), 1642 (m), 1503 (w, $CH_2Cl_2$) | 1.25 (m, 18 H, Me), 1.4 (m, 12 H, Me), 1.65 (m, 18 H, Me), 1.76 (m, 12 H, Me), 1.83 (m, 4 H, CH$_2$), 2.92 (m, 4 H, CH$_2$), 3.64 (s, 3 H, OMe), 3.74 (s, 3 H, OMe), 3.79 (s, 3 H, OMe), 3.84 (s, 3 H, OMe), 4.10 (quart, $J_{HH}$ = 7 Hz, 2 H, OEt), 4.19 (quart, $J_{HH}$ = 7 Hz, 2 H, OEt), 4.25 (quart, $J_{HH}$ = 7 Hz, 2 H, OEt), 4.35 (quart, $J_{HH}$ = 7 Hz, 2 H, OEt) | 0.5 (m, br), −3.0 (m, br) |
| 9 | 1976 (m), 1943 (s), 1914 (s), 1890 (m), 1673 (w) | 1.52 (t, 12 H, Me), 1.58 (t, 12 H, Me), 2.40 (m, 2 H, CH$_2$), 2.83 (m, 2 H, CH$_2$), 3.54 (s, 3 H, OMe), 8.76 (s, 1 H) | AA′BB′, $\delta_a$ = −1.98, $\delta_b$ = −2.51, $J_{AA'} = J_{BB'} \geq$ 150 Hz, $J_{AB} = J_{A'B'}$ = 42 Hz, $J_{AB'} = J_{A'B}$ = 20 Hz |

the liquid nitrogen cooled reaction vessel. The reaction vessel was sealed while cold and then allowed to warm to room temperature (internal pressure approximately 3.5 atm at 22 °C). The vessel was heated to 70 °C, with stirring, for 24 h. An infrared spectrum of the solution showed 60% enrichment (based on the relative intensities of bridging CO stretch). The product was isolated as a yellow powder after solvent removal.

**Preparation of $Ru_2(dmpm)_2(CO)_3[\mu\text{-}C_2(CO_2Me)_2][C(O)C(O)C_2(CO_2Me)_2]$ (3).** Compound 1 (100 mg, 0.16 mmol) was charged to a 50-mL three-neck flask equipped with a stirbar and gas adapter then dissolved in toluene (5 mL). DMAD (50 $\mu$L, 0.40 mmol) was added via syringe through a septum. The solution turned red immediately upon addition, and after stirring 5–10 min a dark orange solid precipitated. The solid was allowed to settle, and the supernatant was removed through a cannula. The orange powder was washed with hexane (3 × 5 mL) and then dried under vacuum (yield = 118 mg, 81%). Red crystalline material was obtained by recrystallizing from saturated CHCl$_3$ solutions layered with Et$_2$O. $^{13}$C NMR (CDCl$_3$): $\delta$ 15.4 (t, $J_{CP}$ = 15 Hz, 2 Me), 17.4 (mult, 4 Me), 20.0 (t, $J_{CP}$ = 15 Hz, 2 Me), 34.7 (t, $J_{CP}$ = 12 Hz, CH$_2$), 50.95 (s, OCH$_3$), 51.38 (s, OCH$_3$), 51.43 (s, OCH$_3$), 51.63 (s, OCH$_3$), 127.5 (m), 136 (s), 151.3 (m), 163.7 (s), 172.1 (s), 178.27 (s), 178.34 (s), 189.5 (t, $J_{CP}$ = 8.3 Hz), 196.2 (t, $J_{CP}$ = 12 Hz), 198.8 (s), 218.7 (m), 222 (t, $J_{CP}$ = 8.2 Hz), 254.6 (t, $J_{CP}$ = 11 Hz). Anal. Calcd for $Ru_2(dmpm)_2(CO)_5[C_2(CO_2Me)_2]_2$: C, 36.00; H, 4.44; P, 13.76. Found: C, 36.13; H, 4.53; P, 13.59. Mass spectrum ($^{101}$Ru): *m/e* 901, int 17%, [P]$^+$; fragments observed: [P − *n*CO]$^+$ where *n* = 1–4.

**$^{13}$CO-Enriched $Ru_2(dmpm)_2(CO)_3[\mu\text{-}C_2(CO_2Me)_2][C(O)C(O)C_2(CO_2Me)_2]$.** The $^{13}$CO-enriched material was prepared using the same procedure described above, starting with $^{13}$CO-enriched 1. IR ($\nu_{CO}$, CH$_2$Cl$_2$): 2042 (s), 2022 (s), 1987 (s), 1963 (s), 1835 (w), 1799 (w), 1696 (s, br), 1642 (m), 1609 (m), 1503 (m), 1432 (m). $^{13}$C NMR (CDCl$_3$, enriched peaks only): $\delta$ 189.5 (t, *J* = 7 Hz), 196.3 (t, *J* = 11.5 Hz), 198.8 (t, *J* = 11.5 Hz), 218.8 (m), 254.5 (m) (This spectrum was *not* $^{31}$P decoupled).

**Preparation of $Ru_2(dmpm)_2(CO)_3[\mu\text{-}C_2(CO_2Et)_2][C(O)C(O)C_2(CO_2Et)_2]$ (6).** 1 (100 mg, 0.16 mmol) was charged to a 50-mL three-neck flask equipped with a stirbar and gas adapter and then dissolved in toluene (5 mL). Diethyl acetylenedicarboxylate (64 $\mu$L, 0.40 mmol) was added via syringe through a septum. The solution turned red immediately upon addition but was allowed to stir for 30 min at room temperature. The solvent was stripped under vacuum, and the residue was redissolved in CH$_2$Cl$_2$ (1 mL). The dark red solution was cooled to 0 °C and then layered with Et$_2$O (10 mL). After 2 h at 0 °C, red crystals had formed. The supernatant was removed through a cannula, and the crystals were washed with Et$_2$O (2 × 5 mL) and dried (yield = 35%). $^{13}$C NMR (CDCl$_3$): $\delta$ 14.08 (s, 2 Me), 14.16 (s, Me), 14.36 (s, Me), 15.5 (t, $J_{CP}$ = 15 Hz, 2 Me), 17.5 (mult, 4 Me), 20.2 (t, $J_{CP}$ = 15 Hz, 2 Me), 34.75 (t, $J_{CP}$ = 12 Hz, CH$_2$), 59.61 (s, OCH$_2$CH$_3$), 59.87 (s, OCH$_2$CH$_3$), 60.04 (s, OCH$_2$CH$_3$), 60.24 (s, OCH$_2$CH$_3$),127.0 (m), 136.6 (s), 149.8 (m), 163.9 (s), 172.1 (s), 177.70 (s), 177.76 (s), 189.7 (t, $J_{CP}$ = 8.5 Hz), 196.5 (t, $J_{CP}$ = 12 Hz), 199.1 (s), 218.9 (m), 219.2 (t, $J_{CP}$ = 9 Hz), 254.7 (t, $J_{CP}$ = 12 Hz).

**Preparation of Solutions of $Ru_2(dmpm)_2(CO)_5[C_2(CO_2R)_2]$ (2).** 1 (25 mg, 0.04 mmol) was charged to a 25-mL three-neck flask equipped with a gas adapter and magnetic stirbar and then dissolved in toluene (5 mL), and the solution was cooled to 0 °C. Dialkyl acetylenedicarboxylate (0.04 mmol) was added to the cold solution directly via syringe and the reaction was stirred at 0 °C for 1 h. During this time the color of the solution changed from yellow to red-orange. All attempts to crystallize this material were unsuccessful; however, the species is stable in solution for several hours (6–8 h) at room temperature. $^{13}$C NMR ($C_2H_4Cl_2$) of $Ru_2(dmpm)_2(CO)_5[C_2(CO_2Me)_2]$: $\delta$ 15.66 (m, Me), 17.33 (m, Me), 19.83 (m, Me), 40.35 (q, $J_{CP}$ = 10.5 Hz, CH$_2$), 50.32 (s, OCH$_3$), 50.83 (s, OCH$_3$), 144 (m), 155.9 (s), 176.88 (s), 177.37 (s), 200.0 (t, $J_{CP}$ = 12.8 Hz, CO), 214.0 (t, $J_{CP}$= 12 Hz, CO), 215.2 (m, CO), 221.3 (m, CO), 247.3 (m, CO).

**Reaction of 2 (R = Et) with DMAD.** A toluene solution (5 mL) of $Ru_2(dmpm)_2(CO)_5[C_2(CO_2Et)_2]$ (0.04 mmol) was prepared as described above. DMAD (5 $\mu$L, 0.04 mmol) was added to the cold solution via syringe. The reactants were mixed by stirring at 0 °C for 5 min, and then the solution was allowed to warm to room temperature. As the solution warmed, the color darkened from red-orange to red. Approximately 20 min after removal of the ice bath, the reaction was stopped by precipitation of the products with hexane (10 mL).

**Table II. Summary of Crystallographic Data**

| | Crystal Parameters | |
|---|---|---|
| compd | $Ru_2(dmpm)_2(CO)_3[\mu\text{-}C_2(CO_2Me)_2][C(O)C(O)C_2(CO_2Me)_2]$ (3) | $Ru_2(dmpm)_2(CO)_4[\mu\text{-}C(O)C_2(CO_2Me)_2]$ (4) |
| cryst syst | orthorhombic | monoclinic |
| space group | $P2_12_12_1$ (No. 19) | $P2_1/n$ (No. 14) |
| formula | $Ru_2C_{27}H_{40}O_{13}P_4$ | $Ru_2C_{21}H_{34}O_9P_4$ |
| fw, g mol$^{-1}$ | 898.64 | 756.53 |
| *a*, Å | 13.932 (5) | 10.845 (5) |
| *b*, Å | 14.360 (3) | 27.82 (1) |
| *c*, Å | 17.854 (3) | 10.447 (5) |
| $\beta$, deg | | 109.90 (4) |
| *V*, Å$^3$ | 3572 (3) | 2964 (5) |
| *Z* | 4 | 4 |
| $\rho$(calcd), g cm$^{-3}$ | 1.671 | 1.695 |
| temp, °C | −101 | −101 |
| abs coeff, cm$^{-1}$ | 10.62 | 12.55 |
| cryst dimens, mm | 0.400 × 0.100 × 0.100 | 0.450 × 0.250 × 0.200 |
| trans factors (max to min), % | 114–91 | 105–90 |
| abs corr applied | empirical (DIFABS) | empirical (DIFABS) |
| | Measurement of Intensity Data | |
| diffractometer | Enraf-Nonius CAD-4 | |
| radiation | Mo K$\alpha$ ($\lambda$ = 0.710 73 Å) | |
| monochromator | graphite crystal | |
| programs used | Enraf-Nonius CAD-4-SDP programs | |
| method of structure solution | Patterson method | Patterson method |
| scan type | $\omega$–$2\theta$ | $\omega$–$2\theta$ |
| scan range, deg | 0–50 | 0–56 |
| no. of reflns measd | $\pm h,k,l$ | $h,k,\pm l$ |
| no. of unique reflns | 6299 | 7311 |
| no. of reflns used | 5179 | 5816 |
| cutoff | $2\sigma$ | $2\sigma$ |
| *p* | 0.05 | 0.05 |
| *R* | 0.050 | 0.033 |
| $R_w$ | 0.055 | 0.040 |
| error in observ of unit weight | 1.03 | 1.04 |

**Preparation of $Ru_2(dmpm)_2(CO)_4[\mu\text{-}C(O)C_2(CO_2Me)_2]$ (4).** 1 (50 mg, 0.08 mmol) was charged to a 100-mL three-neck flask equipped with a stirbar, a gas adapter, and a pressure-equalizing addition funnel and then dissolved in toluene (10 mL). DMAD (10 $\mu$L, 0.08 mmol) was dissolved in toluene (10 mL), and the solution was added dropwise over 10 min, causing the color to change from yellow to red. The solution was allowed to stir at room temperature overnight (~16 h), and the color faded to orange. The toluene was removed under vacuum, and the residue was redissolved in $CH_2Cl_2$ (5 mL). Diethyl ether was added to this solution until it became cloudy (~5 mL), and air-stable orange crystals (yield = 46 mg, 78%) were obtained by cooling this saturated solution. $^{13}C$ NMR ($CDCl_3$): $\delta$ 19.0 (m, 4 Me), 21.5 (m, 4 Me), 46.6 (m, $CH_2$), 50.3 (s, $OCH_3$), 51.1 (s, $OCH_3$), 162.5 (s), 166.9 (s), 178.6 (t, $J_{CP}$ = 14 Hz), 181.4 (s), 192 (m, 2 C), 208 (m), 209 (m), 262.6 (m). Anal. Calcd for $Ru_2(dmpm)_2(CO)_5[C_2(CO_2Me)_2]$: C, 32.88; H, 4.66; P, 16.97. Found: C, 33.16; H, 4.63; P, 16.76. Mass spectrum ($^{101}Ru$): *m/e* 758, int 30%, $[P]^+$; fragments observed: $[P - nCO]^+$ where *n* = 1–4.

**$Ru_2(dmpm)_2(CO)_4[\mu\text{-}C_2(CO_2Me)_2]$ (5).** Prepared as previously reported.[7] $^{13}C$ NMR ($CDCl_3$): $\delta$ 19.7 (m, Me), 21.6 (m, Me), 39.0 (q, $J_{CP}$ = 11.3 Hz, $CH_2$), 50.7 (s, $OCH_3$), 142.8 (t, $J_{CP}$ = 4.5 Hz, vinyl), 175.4 (s, ester CO), 197.1 (t, $J_{CP}$ = 8.5 Hz, CO), 211.1 (t, $J_{CP}$ = 5.3 Hz, CO).

**Attempted Carbonylation of 5.** A toluene solution (20 mL) of 5 (25 mg) was charged to a 50-mL high-pressure Parr reactor equipped with an overhead stirrer, and the reactor was pressurized to 68 atm of CO. The reactor was placed in an aluminum heating block, equipped with a digital temperature controller, and heated to 100 °C. An IR spectrum of a sample of the solution after 1 h at 100 °C showed no reaction had occurred. The temperature was raised to 120 °C. An infrared spectrum of a sample of the solution after 20 h under these conditions showed no reaction had occurred.

**Reaction of $Ru_2(dmpm)_2(CO)_5$ with $HCCCO_2Me$ (9).** 1 (0.05 g, 0.081 mmol) was charged to a 50-mL, three-neck flask equipped with a stirbar, a gas adapter, and a pressure-equalizing addition funnel and then dissolved in toluene (10 mL). A toluene solution (5 mL) of $HCCCO_2Me$ (8 mL, 0.08 mmol) was added dropwise over 10 min. No color change was observed. After 2 h at room temperature, however, IR spectroscopy established the reaction was complete. The solvent was removed under vacuum, and the residue was redissolved in $CH_2Cl_2$ (5 mL). Small portions of $Et_2O$ (12 × $^1/_2$ mL) were added to precipitate the pale yellow powder (yield = 36 mg, 63%). $^{13}C$ NMR ($CDCl_3$): $\delta$ 19.9 (m, Me), 21.5 (m, Me), 40.4 (q, $J_{CP}$ = 13 Hz, $CH_2$), 50.8 (s, $OCH_3$), 152.3 (m, vinyl CH), 171.8 (m, vinyl $CCO_2Me$), 186 (s, ester CO), 198.2 (m, 2 CO), 211.7 (m, 2 CO). Mass spectrum ($^{101}Ru$): *m/e* 673, int 100%, $[P]^+$; fragments observed: $[P - nCO]^+$ where *n* = 1–4.

**X-ray Crystallographic Studies of 3 and 4.** Red needle-shaped crystals of 3 and orange block-shaped crystals of 4 were grown as described. A suitable crystal of each was removed directly from the supernatant, coated with a high-viscosity hydrocarbon, mounted on a fiber, and cooled to −101 °C. A preliminary peak search of 25 centered reflections indicated that the crystal was orthorhombic for 3 and monoclinic for 4. The space group $P2_12_12_1$ (No. 19) was chosen for 3, based on the systematic absences ($h00$ ($h = 2n + 1$), $0k0$ ($k = 2n + 1$), $00l$ ($l = 2n + 1$)). The space group $P2_1/n$ (No. 14) was chosen for 4 based on the systematic absences ($h0l$ ($h + l = 2n + 1$), $0k0$ ($k = 2n + 1$)). The intensities of three representative reflections (measured after every 75 min of X-ray exposure time) declined by 7% for 3 (no decay was observed for 4). A linear correction factor was applied to the data to account for the decay. Table II includes the details of the structural analyses. All non-hydrogen atoms of the dimers were refined anisotropically. Hydrogen atoms were included in the structure factor calculation in idealized positions using $d_{C-H}$ = 0.95 Å and an isotropic temperature factor 20% greater than the $B_{eq}$ value of the carbon to which they were bonded. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.85 and −0.79 e Å$^{-3}$ for 3 and 0.58 and −0.76 e Å$^{-3}$ for 4. One full quadrant of data was collected for 3 and used in the refinement without averaging the Friedel pairs. Refinement of the opposite enantiomer gave $R$ = 0.052, $R_w$ = 0.057, and GOF = 1.06. The values of the atomic scattering factors used in the calculations were taken from the usual tabulations,[9-11] and the

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(9) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp Table 2.2A.

(10) Cromer, D. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp Table 2.3.1.

**Table III. Positional Parameters for $Ru_2(dmpm)_2(CO)_3[\mu\text{-}C_2(CO_2Me)_2][C(O)C(O)C_2(CO_2Me)_2]$ (3)**

| atom | *x* | *y* | *z* |
|---|---|---|---|
| Ru1 | 0.65964 (5) | 0.56450 (5) | 0.51596 (4) |
| Ru2 | 0.51122 (5) | 0.45001 (4) | 0.41953 (3) |
| P11 | 0.6768 (2) | 0.4308 (2) | 0.5925 (1) |
| P12 | 0.6568 (2) | 0.6812 (1) | 0.4224 (1) |
| P21 | 0.5374 (2) | 0.3168 (2) | 0.4929 (1) |
| P22 | 0.5021 (2) | 0.5761 (1) | 0.3360 (1) |
| C1 | 0.6540 (9) | 0.3238 (7) | 0.5444 (5) |
| C2 | 0.6124 (6) | 0.6432 (6) | 0.3324 (5) |
| C3 | 0.8007 (9) | 0.4110 (8) | 0.6248 (7) |
| C4 | 0.614 (1) | 0.4295 (9) | 0.6781 (6) |
| C5 | 0.5612 (9) | 0.2076 (8) | 0.4472 (6) |
| C6 | 0.4529 (9) | 0.2838 (8) | 0.5613 (7) |
| C7 | 0.7745 (7) | 0.7290 (7) | 0.3981 (6) |
| C8 | 0.5910 (7) | 0.7876 (7) | 0.4447 (6) |
| C9 | 0.4811 (7) | 0.5518 (6) | 0.2378 (4) |
| C10 | 0.4085 (6) | 0.6619 (7) | 0.3553 (6) |
| C11 | 0.7767 (7) | 0.6099 (6) | 0.5524 (5) |
| C12 | 0.5953 (7) | 0.6432 (7) | 0.5891 (5) |
| C13 | 0.3133 (6) | 0.4107 (5) | 0.3542 (5) |
| C14 | 0.2077 (6) | 0.4119 (6) | 0.3408 (4) |
| C15 | 0.088 (1) | 0.450 (2) | 0.2534 (8) |
| C16 | 0.3569 (6) | 0.4437 (6) | 0.4165 (5) |
| C17 | 0.2903 (6) | 0.4863 (6) | 0.4741 (5) |
| C18 | 0.2279 (7) | 0.4725 (7) | 0.5944 (6) |
| C19 | 0.3750 (6) | 0.3687 (5) | 0.2992 (5) |
| C20 | 0.4800 (6) | 0.3597 (6) | 0.3305 (4) |
| C22 | 0.4851 (6) | 0.5219 (7) | 0.5070 (5) |
| C23 | 0.7236 (6) | 0.4854 (6) | 0.4294 (5) |
| C24 | 0.8266 (6) | 0.4887 (6) | 0.4101 (5) |
| C25 | 0.9827 (7) | 0.5153 (8) | 0.4547 (6) |
| C26 | 0.6592 (6) | 0.4394 (6) | 0.3890 (4) |
| C27 | 0.6939 (6) | 0.3911 (6) | 0.3195 (5) |
| C28 | 0.7879 (8) | 0.2666 (8) | 0.2745 (6) |
| O1 | 0.1479 (5) | 0.3848 (5) | 0.3818 (4) |
| O2 | 0.1879 (5) | 0.449 (1) | 0.2746 (4) |
| O3 | 0.2525 (5) | 0.5600 (5) | 0.4662 (3) |
| O4 | 0.2813 (4) | 0.4330 (5) | 0.5339 (3) |
| O5 | 0.3542 (5) | 0.3410 (4) | 0.2372 (3) |
| O6 | 0.5278 (5) | 0.3005 (4) | 0.3016 (3) |
| O7 | 0.8595 (5) | 0.4849 (5) | 0.3473 (4) |
| O8 | 0.8841 (4) | 0.4986 (5) | 0.4694 (4) |
| O9 | 0.6845 (5) | 0.4184 (4) | 0.2568 (3) |
| O10 | 0.7422 (4) | 0.3105 (4) | 0.3369 (3) |
| O11 | 0.8444 (5) | 0.6415 (5) | 0.5776 (4) |
| O12 | 0.5629 (5) | 0.6948 (5) | 0.6300 (4) |
| O22 | 0.4348 (5) | 0.5510 (7) | 0.5542 (4) |

**Table IV. Bond Distances (Å) in $Ru_2(dmpm)_2(CO)_3[\mu\text{-}C_2(CO_2Me)_2][C(O)C(O)C_2(CO_2Me)_2]$ (3)**

| | | | |
|---|---|---|---|
| A. Metal–Metal and Metal–Ligand | | | |
| Ru1–Ru2 | 3.153 (1) | Ru2–P21 | 2.347 (2) |
| Ru1–P11 | 2.369 (3) | Ru2–P22 | 2.349 (2) |
| Ru1–P12 | 2.366 (2) | Ru2–C16 | 2.153 (8) |
| Ru1–C11 | 1.87 (1) | Ru2–C20 | 2.097 (8) |
| Ru1–C12 | 1.95 (1) | Ru2–C22 | 1.907 (8) |
| Ru1–C22 | 2.51 (2) | Ru2–C26 | 2.138 (8) |
| Ru1–C23 | 2.115 (9) | | |
| B. Intraligand | | | |
| P11–C1 | 1.79 (1) | P21–C1 | 1.87 (1) |
| P12–C2 | 1.813 (9) | P22–C2 | 1.814 (8) |
| C11–O11 | 1.14 (1) | C22–O22 | 1.14 (1) |
| C12–O12 | 1.13 (1) | C23–C26 | 1.33 (1) |
| C23–C24 | 1.48 (1) | C26–C27 | 1.50 (1) |
| C16–C13 | 1.35 (1) | C13–C19 | 1.44 (1) |
| C16–C17 | 1.51 (1) | C13–C14 | 1.49 (1) |
| C19–C20 | 1.57 (1) | C20–O6 | 1.197 (9) |
| C19–O5 | 1.21 (1) | | |

effects for anomalous dispersion were included for the non-hydrogen atoms. The positional parameters, bond distances, and

**Table V. Bond Angles (deg) for $Ru_2(dmpm)_2(CO)_3[\mu\text{-}C_2(CO_2Me)_2][C(O)C(O)C_2(CO_2Me)_2]$ (3)**

| | | | |
|---|---|---|---|
| A. Ligand–Metal–Ligand | | | |
| C11–Ru1–C12 | 88.0 (4) | C22–Ru2–C26 | 115.5 (3) |
| C11–Ru1–C23 | 94.2 (4) | C22–Ru2–C20 | 156.3 (3) |
| C11–Ru1–P12 | 90.4 (3) | C22–Ru2–C16 | 81.5 (3) |
| C11–Ru1–P11 | 89.7 (3) | C22–Ru2–P21 | 90.8 (3) |
| C12–Ru1–C23 | 175.2 (4) | C22–Ru2–P22 | 95.3 (3) |
| C12–Ru1–P12 | 93.3 (3) | C26–Ru2–C20 | 87.9 (3) |
| C12–Ru1–P11 | 97.5 (3) | C26–Ru2–C16 | 162.5 (3) |
| C23–Ru1–P12 | 82.5 (2) | C26–Ru2–P21 | 86.2 (2) |
| C23–Ru1–P11 | 86.7 (2) | C26–Ru2–P22 | 86.8 (2) |
| P12–Ru1–P11 | 169.18 (8) | P22–Ru2–P21 | 172.29 (9) |
| B. Intraligand | | | |
| Ru1–P11–C1 | 113.7 (3) | Ru2–P21–C1 | 111.5 (3) |
| Ru1–P12–C2 | 114.6 (3) | Ru2–P22–C2 | 112.7 (3) |
| Ru1–C11–O11 | 175.4 (8) | Ru2–C22–O22 | 155.4 (7) |
| Ru1–C12–O12 | 174.3 (9) | Ru2–C14–C17 | 119 (2) |
| Ru1–C23–C26 | 112.3 (6) | Ru2–C16–C13 | 118.9 (6) |
| P11–C1–P21 | 115.9 (6) | Ru2–C20–C19 | 114.3 (5) |
| P12–C2–P22 | 115.2 (4) | C20–C19–C13 | 110.4 (7) |
| C19–C13–C16 | 116.1 (8) | | |

**Table VI. Positional Parameters for $Ru_2(dmpm)_2(CO)_4[\mu\text{-}C(O)C_2(CO_2Me)_2]$ (4)**

| atom | *x* | *y* | *z* |
|---|---|---|---|
| Ru1 | 0.19225 (2) | 0.108106 (9) | 0.15549 (3) |
| Ru2 | 0.17174 (2) | 0.13421 (1) | 0.41977 (3) |
| P11 | 0.21416 (8) | 0.02857 (3) | 0.23141 (9) |
| P12 | 0.18223 (8) | 0.18949 (3) | 0.09048 (9) |
| P21 | 0.27443 (8) | 0.06193 (3) | 0.51622 (9) |
| P22 | 0.08902 (8) | 0.20868 (3) | 0.32608 (9) |
| C1 | 0.3248 (3) | 0.0210 (1) | 0.4066 (3) |
| C2 | 0.1682 (3) | 0.2340 (1) | 0.2134 (3) |
| C3 | 0.2808 (4) | −0.0126 (1) | 0.1364 (4) |
| C4 | 0.0646 (4) | −0.0035 (1) | 0.2225 (4) |
| C5 | 0.3192 (4) | 0.2122 (1) | 0.0457 (4) |
| C6 | 0.0433 (4) | 0.2036 (1) | −0.0615 (4) |
| C7 | 0.1765 (4) | 0.0228 (1) | 0.5840 (4) |
| C8 | 0.4208 (3) | 0.0684 (1) | 0.6651 (4) |
| C9 | 0.1092 (4) | 0.2581 (1) | 0.4456 (4) |
| C10 | −0.0859 (3) | 0.2117 (1) | 0.2325 (4) |
| C11 | 0.2186 (4) | 0.0909 (1) | −0.0080 (4) |
| C12 | 0.0073 (3) | 0.1046 (1) | 0.0856 (4) |
| C13 | 0.4486 (3) | 0.1420 (1) | 0.3868 (3) |
| C14 | 0.5932 (3) | 0.1524 (1) | 0.4482 (4) |
| C15 | 0.7867 (4) | 0.1386 (2) | 0.6356 (5) |
| C16 | 0.3977 (3) | 0.1178 (1) | 0.2696 (3) |
| C17 | 0.4929 (3) | 0.0953 (1) | 0.2142 (4) |
| C18 | 0.5948 (5) | 0.0967 (2) | 0.0497 (5) |
| C19 | 0.3628 (3) | 0.1633 (1) | 0.4579 (3) |
| C21 | 0.1805 (4) | 0.1553 (1) | 0.5935 (4) |
| C22 | −0.0014 (3) | 0.1064 (1) | 0.3702 (4) |
| O1 | 0.6548 (3) | 0.1769 (1) | 0.3984 (3) |
| O2 | 0.6477 (3) | 0.1303 (1) | 0.5685 (3) |
| O3 | 0.5505 (3) | 0.0583 (1) | 0.2590 (3) |
| O4 | 0.5047 (3) | 0.1180 (1) | 0.1067 (3) |
| O5 | 0.4111 (3) | 0.1960 (1) | 0.5397 (3) |
| O11 | 0.2265 (4) | 0.0791 (1) | −0.1098 (3) |
| O12 | −0.1052 (3) | 0.1023 (1) | 0.0377 (3) |
| O21 | 0.1866 (4) | 0.1696 (1) | 0.6978 (3) |
| O22 | −0.1044 (3) | 0.0906 (1) | 0.3436 (3) |

bond angles for 3 are listed in Tables III–V and in Tables VI–VIII for 4.

## Results

**Structure of $Ru_2(dmpm)_2(CO)_3[\mu\text{-}C_2(CO_2Me)_2][C(O)C(O)C_2(CO_2Me)_2]$ (3).** Single-crystal X-ray crystallography of 3 showed the structure consisted of well-separated molecular units. As shown in Figure 1, the axial $Ru_2P_4$ framework of this molecule was found to be nearly planar (twist angle = 4.16°, defined as the angle between planes Ru1–P11–P12–Ru2 and Ru2–P21–P22–Ru1). The equatorial plane of 3 was shown to contain three carbon monoxide ligands, one bridging alkyne, and a five-mem-

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(11) Cromer, D. T.; Ibers, J. A. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp Table 2.2C.

**Table VII. Bond Distances (Å) in $Ru_2(dmpm)_2(CO)_4[\mu\text{-}C(O)C_2(CO_2Me)_2]$ (4)**

| | | | |
|---|---|---|---|
| **A. Metal–Metal and Metal–Ligand** | | | |
| Ru1–Ru2 | 2.936 (1) | Ru2–P21 | 2.353 (1) |
| Ru1–P11 | 2.335 (1) | Ru2–P22 | 2.336 (1) |
| Ru1–P12 | 2.356 (1) | Ru2–C21 | 1.880 (4) |
| Ru1–C11 | 1.888 (4) | Ru2–C22 | 1.931 (4) |
| Ru1–C12 | 1.890 (4) | Ru2–C19 | 2.132 (3) |
| Ru1–C16 | 2.156 (3) | | |
| **B. Intraligand** | | | |
| P11–C1 | 1.827 (4) | P21–C1 | 1.825 (4) |
| P12–C2 | 1.827 (4) | P22–C2 | 1.818 (4) |
| C11–O11 | 1.142 (5) | C21–O21 | 1.140 (5) |
| C12–O12 | 1.151 (4) | C22–O22 | 1.144 (5) |
| C16–C13 | 1.340 (4) | C13–C14 | 1.506 (4) |
| C13–19 | 1.496 (4) | C16–C17 | 1.485 (5) |
| C19–O5 | 1.23 (3) | C17–O3 | 1.210 (4) |
| C14–O1 | 1.192 (5) | | |

**Table VIII. Bond Angles (deg) for $Ru_2(dmpm)_2(CO)_4[\mu\text{-}C(O)C_2(CO_2Me)_2]$ (4)**

| | | | |
|---|---|---|---|
| **A. Ligand–Metal–Ligand** | | | |
| C11–Ru1–C12 | 96.0 (2) | C21–Ru2–C22 | 96.3 (2) |
| C11–Ru1–C16 | 94.9 (1) | C21–Ru2–C19 | 88.5 (2) |
| C11–Ru1–P12 | 89.4 (1) | C21–Ru2–P22 | 90.8 (1) |
| C11–Ru1–P11 | 92.1 (1) | C21–Ru2–P21 | 89.6 (1) |
| C11–Ru1–Ru2 | 175.9 (1) | C21–Ru2–Ru1 | 172.2 (1) |
| C12–Ru1–C16 | 168.9 (1) | C22–Ru2–C19 | 175.2 (1) |
| C12–Ru1–P12 | 90.0 (1) | C22–Ru2–P22 | 92.5 (1) |
| C12–Ru1–P11 | 93.1 (1) | C22–Ru2–P21 | 92.7 (1) |
| C12–Ru1–Ru2 | 88.0 (1) | C22–Ru2–Ru1 | 91.5 (1) |
| C16–Ru1–P12 | 88.64 (9) | C19–Ru2–P22 | 87.26 (9) |
| C16–Ru1–P11 | 87.97 (9) | C19–Ru2–P21 | 87.47 (9) |
| C16–Ru1–Ru2 | 81.0 (1) | C19–Ru2–Ru1 | 83.7 (1) |
| P12–Ru1–P11 | 176.39 (3) | P22–Ru2–P21 | 174.70 (3) |
| P12–Ru1–Ru2 | 91.29 (3) | P22–Ru2–Ru1 | 88.08 (3) |
| P11–Ru1–Ru2 | 86.93 (3) | P21–Ru2–Ru1 | 90.86 (4) |
| **B. Intraligand** | | | |
| Ru1–P11–C1 | 113.9 (1) | Ru2–P21–C1 | 117.6 (7) |
| Ru1–P12–C2 | 117.1 (1) | Ru2–P22–C2 | 114.6 (1) |
| Ru1–C11–O11 | 175.5 (3) | Ru2–C21–O21 | 177.8 (4) |
| Ru1–C12–O12 | 177.2 (4) | Ru2–C22–C22 | 178.1 (3) |
| Ru1–C16–C13 | 126.5 (2) | Ru2–C19–C13 | 119.1 (2) |
| P11–C1–P21 | 108.8 (2) | P12–C2–P22 | 111.3 (2) |
| C16–C13–C19 | 121.3 (3) | | |

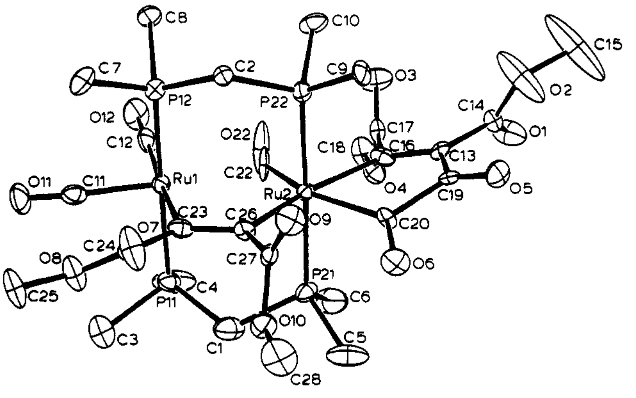

**Figure 1.** ORTEP drawing of $Ru_2(dmpm)_2(CO)_3[\mu\text{-}C_2(CO_2Me)_2][C(O)C(O)C_2(CO_2Me)_2]$ (3) showing the atom labels. Thermal ellipsoids are drawn at the 50% probability level.

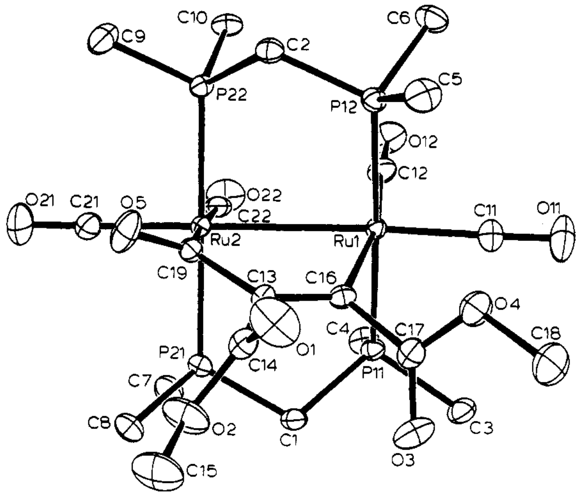

**Figure 2.** ORTEP drawing of $Ru_2(dmpm)_2(CO)_4[\mu\text{-}C(O)C_2(CO_2Me)_2]$ (4) showing the atom labels. Thermal ellipsoids are drawn at the 50% probability level.

bered metallacycle. The long Ru1–Ru2 distance of 3.153 (1) Å indicated the absence of any direct metal–metal bond. The metal–carbon distances for the bridging alkyne [Ru1–C23 = 2.115 (9) and Ru2–C26 = 2.138 (8) Å] were typical of Ru–C single bonds and in combination with the C23–C26 distance of 1.33 (1) Å indicated a *cis*-dimetalated alkene bonding mode. The Ru2–C22–O22 angle of 155.4 (7)° and the Ru1–C22 bond distance of 2.51 (2) Å suggest a semibridging carbonyl interaction for C22–O22. The infrared spectrum of 3 in solution exhibited an absorption at 1835 cm$^{-1}$ that could be assigned to a semibridging CO.

The most unusual feature of this molecule is the five-membered metallacycle involving Ru2 which appears to have resulted from the insertion of two CO ligands into a metal–alkyne bond. The Ru2–C16 distance of 2.153 (8) Å is typical of a Ru–C single bond, and the C16–C13 distance of 1.35 (1) Å is characteristic of a C–C double bond. The C13–C19 distance of 1.44 (1) Å shows a reasonable shortening compared to a C–C single bond as would be expected for an $\alpha,\beta$-unsaturated ketone. The metallacycle was found to be distinctly nonplanar, having a dihedral angle (defined as the angle between planes composed of Ru2–C20–C16 and C16–C13–C19–C20) of 18°.

**Structure of $Ru_2(dmpm)_2(CO)_4[\mu\text{-}C(O)C_2(CO_2Me)_2]$ (4).** Single-crystal X-ray crystallography of 4 established that the structure consisted of well-separated molecular units. The Ru1–Ru2 distance of 2.936 (1) Å was the same as that observed for $Ru_2(dmpm)_2(CO)_4(PhCCPh)$ (Ru1–Ru2 = 2.938 (2) Å)[7] indicative of a single Ru–Ru bond. As shown in Figure 2, the axial positions were occupied by the bridging dmpm ligands. The $Ru_2P_4$ framework of this molecule was twisted (twist angle = 19.82°, defined as the angle between planes containing Ru1–P11–P12–Ru2 and Ru2–P21–P22–Ru1) in comparison to $Ru_2(dmpm)_2(CO)_4(PhCCPh)$ (twist angle = 10.02°).[7] Kubiak and coworkers have suggested that the degree of twisting observed in these diphosphine molecules reflects the ability of the bridging ligands to accommodate an ideally staggered conformation (twist = 45°).[12] Such a conformation would minimize both electronic repulsions and steric interactions between adjacent metal centers.

The equatorial plane of 4 was shown to contain four terminal carbon monoxide ligands and a three-carbon bridge between Ru1 and Ru2. The bridging group was composed of the two alkyne carbons of the DMAD and one CO group forming an ester-substituted diruthenacyclopentenone. The Ru1–C16 and Ru2–C19 distances of 2.156 (3) and 2.132 (3) Å are typical for Ru–C single bonds. The C19–C13 distance of 1.496 (4) Å and the C19–O5 distance of 1.23 (3) Å are consistent with an $\alpha,\beta$-unsaturated ketone.

**Reaction of 1 with DMAD.** The addition of DMAD to 1 at room temperature resulted in a rapid color change from yellow to red. After stirring for several hours, the color slowly changed from red to orange. Upon heating,

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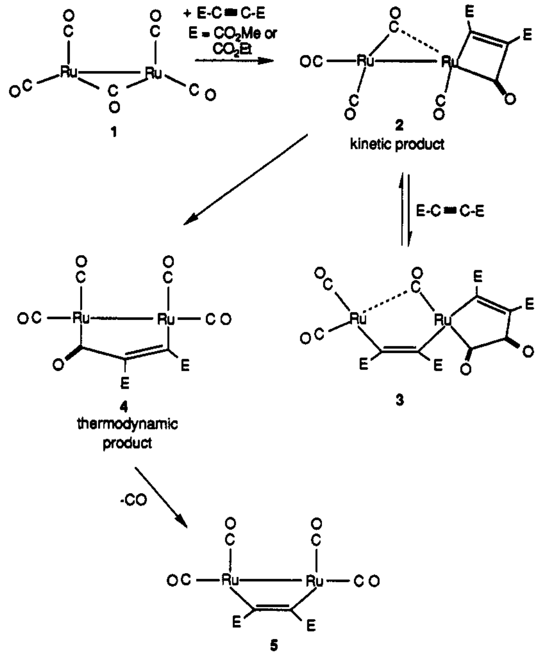
[12] Kullberg, M. L.; Lemke, F. R.; Powell, D. R.; Kubiak, C. P. *Inorg. Chem.* **1985**, *24*, 3589.

**Scheme I. Arrangement of Ligands around the Equatorial Plane of the Ru$_2$(dmpm)$_2$ Core**



the solution changed color from orange to yellow. The following sections describe the reaction conditions necessary to isolate each of these three products in high yield. Scheme I summarizes these transformations.

**(A) Isolation and Solution Spectroscopic Characterization of 3.** Addition of DMAD to concentrated solutions of 1 (15–20 mmol/L) at room temperature resulted in a gradual color change from yellow to red over a period of 5 min. When this solution was allowed to stir at room temperature an additional 5–10 min, a dark orange powder precipitated. The mass spectrum and elemental analysis were consistent with the molecular formula, Ru$_2$(dmpm)$_2$(CO)$_5$[C$_2$(CO$_2$Me)$_2$]$_2$. The infrared spectrum of a CH$_2$Cl$_2$ solution of 3 exhibited $\nu_{CO}$ absorptions at 2041 and 1986 cm$^{-1}$ and a semibridging CO absorption at 1836 cm$^{-1}$. The $^1$H NMR spectrum showed four singlets due to the methoxy groups and four resonances due to the methyls bound to phosphorus. In the solid-state structure of 3 the twist of the metallacyclic ring differentiates the phosphines above and below the equatorial plane. Because the NMR spectral data suggested a mirror plane lies in the equatorial plane of the molecule, either the structure of the metallacycle becomes planar in solution or rapid interconversion between the two conformers is occurring. The $^{13}$C{$^1$H} NMR spectrum contained signals due to the Me, CH$_2$, and OCH$_3$ groups between 15 and 52 ppm and 13 signals from 127 to 255 ppm representing the 13 remaining carbons of the molecule. The resonances that did not exhibit $^{31}$P coupling corresponded to those carbons not directly attached to a metal (see Figure 1). By virtue of the chemical shifts, the singlet at 136 ppm was assigned to the vinyl carbon, C13, and the singlet at 198.8 ppm was assigned to the carbonyl carbon, C19. Coupling of these resonances was observed in the $^{13}$C{$^1$H} NMR spectrum of the $^{13}$CO-enriched material, consistent with this assignment. The remaining singlets at 163.7, 172.1, 178.27, and 178.34 ppm were assigned to the ester carbonyl carbons. The $^{13}$C{$^1$H} NMR spectrum of the $^{13}$CO-enriched material allowed us to assign the multiplets at 189.5, 196.2, 198.8, and 254.6 ppm as originating from the metal carbonyls of 1. The chemical shift of the resonance at 254.6 ppm allowed its assignment to the semibridging carbonyl carbon, C22. The multiplets at 127.5, 151.3, and 222 ppm were assigned to the remaining vinyl carbons, C23, C26, and C16, but specific assignments were not possible.

**(B) Isolation and Solution Spectroscopic Characterization of 4.** Dropwise addition of toluene solutions of DMAD to less concentrated solutions of 1 (4–6 mmol/L) resulted in an initial color change from yellow to red. Over a period of 8–12 h at room temperature, the color changed from red to orange and the infrared spectrum showed complete conversion to a new product 4. This material could also be prepared by stirring a solution of 3 (CH$_2$Cl$_2$) at room temperature for 8–12 h. Recrystallization from CH$_2$Cl$_2$/Et$_2$O yielded an air-stable orange crystalline solid. The mass spectrum and elemental analysis indicated the molecular formula of the product was Ru$_2$(dmpm)$_2$(CO)$_5$[C$_2$(CO$_2$Me)$_2$]. The infrared spectrum included four terminal $\nu_{CO}$ bands between 1996 and 1912 cm$^{-1}$, the ester stretches at 1707 and 1674 cm$^{-1}$, and the $\nu_{C=C}$ band at 1531 cm$^{-1}$. The $^1$H NMR spectrum displayed two singlets at 3.50 and 3.63 ppm corresponding to the methoxy groups of the esters, thus establishing the inequivalence of the two ends of the alkyne. The AA′BB′ pattern observed in the $^{31}$P NMR spectrum also reflected the lack of symmetry in the molecule. The $^{13}$C{$^1$H} NMR showed signals for the CH$_3$ and CH$_2$ groups of the phosphine ligands between 19 and 47 ppm and two signals for the methoxy groups at 50.3 and 51.1 ppm. Two singlets at 162.5 and 166.9 ppm represented the ester carbonyl carbons and the three sets of multiplets at 208, 209, and 262.6 ppm corresponded to the metal carbonyls (assigned by $^{13}$CO enrichment). The multiplets at 208 and 209 ppm each represented two carbons (accidentally degenerate) and have been assigned to the terminal metal carbonyl ligands. The multiplet at 262.6 ppm has been assigned to the carbonyl of the diruthenacyclopentenone by virtue of its chemical shift. A similar shift (236.3 ppm) was reported by Takats and coworkers for a ruthenaosmacyclopentenone.[13] The phosphorus coupling exhibited by the resonance at 178.6 ppm allowed it to be assigned to the vinyl carbon attached to the metal, C16. The singlet at 181.4 ppm was assigned to the other vinyl carbon, C13. These spectroscopic data establish that the solution structure of 4 is the same as found in the solid state.

**(C) Isolation and Solution Spectroscopic Characterization of 5.** Addition of toluene solutions of DMAD to 1 (in dilute toluene solution) under the same conditions described for 4, followed by heating to reflux for 2–3 h, resulted in formation of a yellow product. Comparison of the spectroscopic data of this material to the structurally characterized Ru$_2$(dmpm)$_2$(CO)$_4$($\mu$-C$_2$Ph$_2$) allowed the unambiguous assignment of the structure of this molecule as the analogous 1,2-diruthenacyclobutene shown in Scheme I. The isolation and characterization of this product has been reported.[7]

**Reaction of 1 with HCCCO$_2$CH$_3$.** The reaction of 1 with methyl propiolate occurred in toluene at room temperature over a period of several hours. The molecular formula of the product was found to be Ru$_2$(dmpm)$_2$(CO)$_4$(HCCCO$_2$CH$_3$) (9) by the mass spectrum. The infrared spectrum of this species showed four terminal CO bands from 1976 to 1890 cm$^{-1}$ and an ester CO signal at 1673 cm$^{-1}$. The $^1$H NMR spectrum displayed a vinyl proton at 8.76 ppm (eliminating structures where the C–H bond had been cleaved) and the ester methoxy signal at 3.54 ppm. The $^{13}$C NMR spectrum contained signals for the methyl (19.9 and 21.5 ppm) and methylene (40.4 ppm) carbons of the phosphine and the methoxy (50.8 ppm) carbon of the ester. Resonances due to the vinyl carbons

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[13] Burn, M. J.; Kiel, G.-Y.; Seils, F.; Takats, J.; Washington, J. *J. Am. Chem. Soc.* **1989**, *111*, 6850.

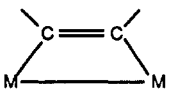
appeared as multiplets at 152.3 and 171.8 ppm. The gated decoupled $^{13}C\{^1H\}$ NMR spectrum allowed their assignment as the proton-substituted carbon at 152.3 ppm and the ester-substituted carbon at 171.8 ppm. The singlet at 186 ppm was assigned to the ester carbonyl carbon, and the multiplets at 198.2 and 211.7 ppm (each representing two carbons) were assigned to the metal carbonyls. There were no signals found downfield from the metal carbonyls. The spectroscopic data allowed assignment of the structure as a 1,2-diruthenacyclobutene.

**Characterization of $Ru_2(dmpm)_2(CO)_5[C_2(CO_2Me)_2]$ (2).** The addition of DMAD to 1 at low temperature (−40 to 0 °C) allowed observation of an intermediate species in the formation of compounds 3 and 4. Although it was necessary to prepare 2 at low temperatures, once formed, it was stable in solution at room temperature for several hours. The infrared spectrum of 2 showed three bands due to terminal metal carbonyls (2033, 1979, and 1933 cm$^{-1}$) and a band at 1823 cm$^{-1}$ (similar to the semibridging CO in the infrared spectrum of 3). The broad stretch at 1700 cm$^{-1}$ is due to the ester carbonyls, and a sharp stretch at 1649 cm$^{-1}$ is tentatively assigned to a metallacyclic CO. The $^1H$ and $^{31}P$ NMR spectra established that the only symmetry element remaining in the molecule was the equatorial mirror plane. The $^{13}C\{^1H\}$ NMR spectrum exhibited resonances between 15 and 55 ppm, which can be assigned to the methyl and methylene carbons of the phosphine ligands and the methoxy carbons of the esters. Between 140 and 250 ppm, nine signals appeared, three of which showed no phosphorus coupling. The resonance at 247.3 ppm was in a region similar to that for the semibridging CO in 3. We suggest that the two singlets at 176.9 and 177.4 ppm are due to the ester carbonyl carbons and that the third singlet could be due to a vinyl carbon which is not bound to a metal, perhaps as part of a metallacycle. On the basis of its chemical shift, the multiplet at 144 ppm is most likely the remaining vinyl carbon. $^{13}C$ enrichment studies indicated the signals at 200.0, 214.0, 215.2, 221.3, and 247.3 ppm are due to carbonyls. Although the spectroscopic data do not allow an unambiguous assignment of the structure of 2, the structure shown in Scheme I is consistent with our observations.

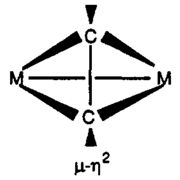
## Discussion

**Reaction of 1 with DMAD.** As shown in Scheme I, the reaction of 1 with DMAD resulted in the formation of three isolable products, each of which could be obtained in high yield by varying the reaction conditions. The product which resulted from heating dilute solutions containing a 1:1 ratio of 1 and DMAD was found to be analogous to the structurally characterized 1,2-diruthenacyclobutene $Ru_2(dmpm)_2(CO)_4(\mu\text{-}PhCCPh)$[7] in which one CO ligand has been displaced and the alkyne moiety is bound as a *cis*-dimetalated alkene. Heating solutions of any of the other products resulted in the formation of 5. The reaction of 1 with the terminal alkyne methyl propiolate was also found to result in loss of CO and formation of a *cis*-dimetalated alkene complex; however, no intermediates were observed.

Of the two common metal–alkyne interactions in dimetallic species, the *cis*-dimetalated bonding mode ($\mu$-$\eta^1$,$\eta^1$) prevails in A-frame complexes:



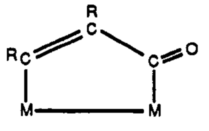
$\mu$-$\eta^1$,$\eta^1$
parallel



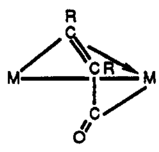
$\mu$-$\eta^2$
perpendicular

Hoffmann and co-workers[1] have used MO calculations to describe the parallel vs perpendicular interaction of alkynes with binuclear transition-metal molecules and determined that the preference for the parallel bonding mode among the A-frame systems is a result of the electronic structure of the metal.[1] In cases where the alkyne is bound perpendicular to the M–M bond, the metal fragments [e.g. $Co(CO)_3$] are isolobal to CH. In most A-frame systems, the metal fragments are isolobal to $CH_2$ and maximum overlap occurs with the parallel bonding mode of the acetylene. $RuP_2(CO)_2$ is a d$^8$ $ML_4$ fragment, isolobal to $CH_2$, so the parallel bonding mode of the acetylene is consistent with these theoretical studies.

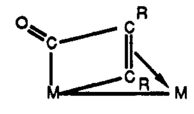
Stirring dilute solutions of a 1:1 mixture of 1:DMAD for several hours at room temperature resulted in initial formation of 2 (kinetic product) followed by its subsequent conversion to the 1,2-diruthenacyclopentenone 4. The dimetallacyclopentenone arrangement is not unique. A variety of bonding modes for this type of bridging unit have been reported; these are represented as 10,[13,14] 11,[15] and 12.[16,17] The molecular structure of 4 corresponded



**10**



**11**



**12**

to the bonding mode shown in structure **10** which has no $\pi$-coordination of the C–C double bond. The bond distances and angles were almost identical to those reported for the analogous structure $(\eta\text{-}C_5H_5)_2Rh_2(CO)_3(CF_3C_2CF_3)$ by Dickson and co-workers.[14] Heating solutions of 4 resulted in loss of CO and formation of 5. This conversion was found to be irreversible, even at high temperature and pressure (120 °C, 69 atm of CO).

When the reaction of 1 with DMAD was conducted in concentrated solutions of toluene (15–20 mmol/L) a red product was formed and subsequently crystallized from the solution 10–15 min after mixing. X-ray crystallography established the structure of this product, as shown in Figure 1. The unusual feature of this structure is the five-membered metallacycle about Ru2 which appears to have resulted from the insertion of two carbonyls into a metal–alkyne bond. Several $\alpha$-ketoacyl complexes have been reported, and the relationship of 3 to these will be discussed later.

Studies of the reaction of 1 with DMAD at low temperature have allowed us to observe an intermediate complex that precedes the formation of 3. While the structure of the intermediate could not be determined uniquely, structure 2 in Scheme I is isomeric with 4 and consistent with all available spectroscopic data. The slow addition of a toluene solution of DMAD to a dilute toluene solution of 1 was monitored by infrared spectroscopy to determine whether 3 would be observed under these conditions. The spectra showed conversion of 1 to 2 and 4; no 3 was detected. This suggests that 3 is not part of the reaction that

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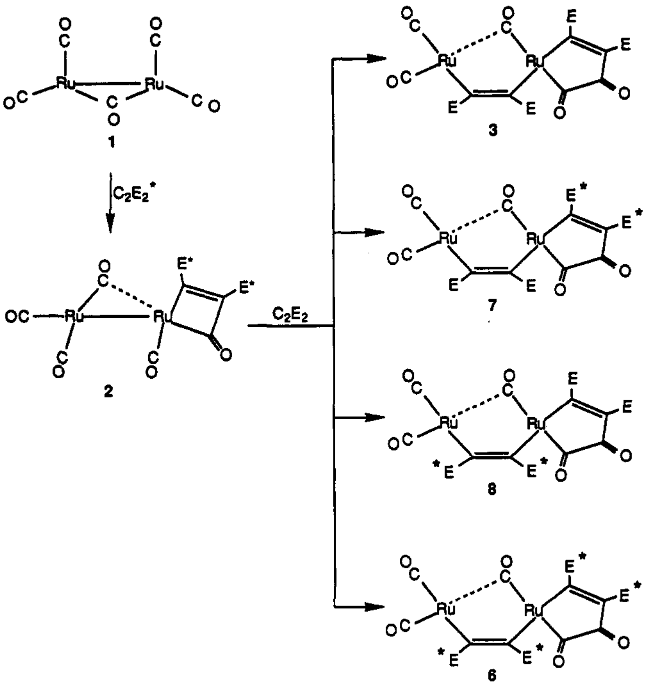
[14] Dickson, R. S.; Gatehouse, B. M.; Nesbit, M. C.; Pain, G. N. *J. Organomet. Chem.* **1981**, *215*, 97.

[15] Dyke, A. F.; Knox, S. A. R.; Naish, P. J.; Taylor, G. E. *J. Chem. Soc., Dalton Trans.* **1982**, 1297.

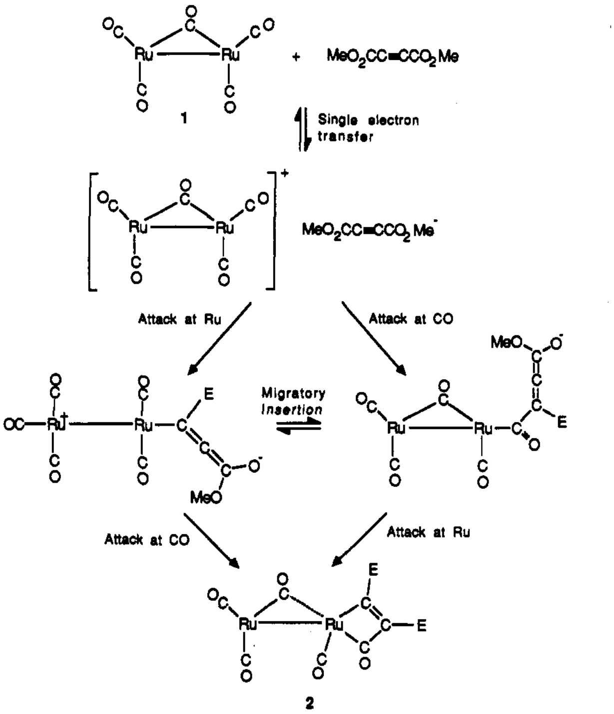
[16] Finnimore, S. R.; Knox, S. A. R.; Taylor, G. E. *J. Chem. Soc., Dalton Trans.* **1982**, 1783.

[17] Boag, N. M.; Goodfellow, R. J.; Green, M.; Hessner, B.; Howard, J. A. K.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1983**, 2585.

**Scheme II. Possible Products from the Trapping of Intermediate 2**



**Scheme III. Possible Mechanism of Initial Reaction of 1 with DMAD**



forms 4, but rather it forms by a competing reversible reaction that is favored at high concentrations by virtue of its rapid formation and limited solubility in toluene.

The fact that the two alkynes are in unique positions suggested that addition of a different alkyne to the intermediate, 2, could yield valuable insight into the reaction. Scheme II shows four possible products that could result by stirring solutions of 2 with a different alkyne. Observation of products 3 and 6 in addition to 7 and 8 would require dissociation of the alkyne in 2 followed by exchange. Formation of 7 or 8 or both would allow assignment of the sight of addition of the second alkyne. A toluene solution of 2 was prepared with diethyl acetylenedicarboxylate at 0 °C. To this cold solution, 1 equiv of DMAD was added with stirring. The solution was allowed to warm to room temperature and stirred an additional 15 min. At this point, all of the products were precipitated from the solution by the addition of hexane. The $^1H$ NMR spectrum exhibited resonances that corresponded to nearly equal amounts of four methylene and four methyl groups adjacent to the oxygen of the ester functional groups. This observation rules out the regiospecific formation of either 7 or 8. It does not allow us, however, to differentiate among various mixtures of 3 and 6–8.

Because 2 and 4 are isomers, we were interested in whether the conversion could be reversed. Infrared and $^1H$ and $^{31}P$ NMR spectra of solutions prepared from crystalline 4 have shown no signals due to 2. Furthermore, addition of excess DMAD to concentrated toluene solutions of 4 does not result in formation of 3. These observations suggest that rearrangement of 2 to 4 is an irreversible process.

While we have been able to identify uniquely three of the four species formed by the reaction of 1 with DMAD, questions remained regarding the mechanisms of these transformations. The initial reaction between 1 and DMAD occurs at an unusually low temperature for the reaction of a saturated metal carbonyl with an alkyne and it contrasts sharply with the higher temperature required (95 °C) to induce the reaction between 1 and diphenylacetylene to give $Ru_2(dmpm)_2(CO)_4(\mu\text{-}\eta^1,\eta^1\text{-}PhCCPh)$.[7] That the facile chemistry of the DMAD system required a strongly electron-deficient alkyne suggests that the pathway may involve an initial electron-transfer step. A similar mechanistic proposal has been made regarding the reaction of 1 with dimethyl fumarate and dimethyl maleate.[18] Haines and co-workers have studied[19] the electrochemistry of $Ru_2(dmpm)_2(CO)_5$ in benzonitrile and reported an irreversible oxidation at −0.23 V vs Ag/AgCl. The reduction potential for DMAD is −1.30 V vs SCE (−1.25 V vs Ag/AgCl) in dimethylformamide.[20] Unfortunately, the lack of reversibility of the $Ru_2(dmpm)_2(CO)_5$ oxidation precludes the calculation of an equilibrium constant for the reaction between it and DMAD. As suggested in Scheme III, following electron transfer, the radicals could recombine to form a Ru–C $\sigma$ bond. Migratory insertion of CO and subsequent ring closure of the zwitterionic intermediate would give 2. Methylation of 1 has been reported to give $[Ru_2(dmpm)_2(CO)_5(CH_3)]^+$ which rapidly absorbs CO to give $[Ru_2(dmpm)_2(CO)_5(C(O)CH_3)]^+$.[21] Alternatively, the radical recombination could involve direct C–C bond formation by nucleophilic attack of the anion on a coordinated CO.

Although the most unusual result in this chemistry is the observation of the double insertion of CO into the metal–alkyne bond, many examples of metal-catalyzed double-carbonylation reactions (eq 2) of organic halides

$$R\text{–}X + 2CO + Nu\text{–}H \rightarrow R\text{–}C(O)\text{–}C(O)\text{–}Nu + HX \qquad (2)$$

$$NuH = R'NH_2,\ R'OH,\ H_2O$$

have been reported.[22] Mechanistic studies of the most

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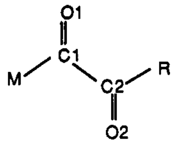
[18] Johnson, K. A.; Gladfelter, W. L. *Organometallics* **1991**, *10*, 376.

[19] Field, J. S.; Fransis, A. M. A.; Haines, R. J.; Woollam, S. F. *J. Organomet. Chem.* **1991**, *412*, 383.

[20] Le Guillanton, G.; Do, Q. T.; Simonet, J. *Tetrahedron Lett.* **1986**, *27*, 2261.

[21] Johnson, K. A.; Gladfelter, W. L. *Organometallics* **1990**, *9*, 2101.

**Table IX. Structural Comparison of α-Ketoacyls**[a]



| compd[b] | C1–O1 | C2–O2 | C1–C2 | M–C1–C2 | C1–C2–R |
|---|---|---|---|---|---|
| A | 1.19 (2) | 1.23 (2) | 1.41 (4) | 113 (2) | 121 (3) |
| B | 1.230 (8) | 1.367 (9) | 1.667 (1) | 114.50 (1) | 119.0 (1) |
| C | 1.214 (5) | 1.186 (5) | 1.552 (6) | 120.8 (3) | 116.6 (5) |
| D | 1.203 (6) | 1.212 (5) | 1.527 (7) | 112.6 (3) | 118.6 (4) |
| E | 1.197 (9) | 1.21 (1) | 1.57 (1) | 114.3 (5) | 110.4 (7) |

[a] Distances in angstroms, angles in degrees. [b] Key: A = Pd$(PPh_3)_2$(Cl)[C(O)C(O)$OCH_3$],[33] B = Pt$(PPh_3)_2$(Cl)[C(O)C(O)Ph],[27] C = Mn$(CO)_5$[C(O)C(O)$CH_3$],[34] D = Cp′Mn(CO)(NO)[C(O)C(O)tol],[32] E = $Ru_2(dmpm)_2(CO)_3[\mu\text{-}C_2(CO_2Me)_2][C(O)C(O)C_2(CO_2Me)_2]$, this work.

common palladium-catalyzed system have shown that the critical C–C bond forming step occurs via reductive elimination from a bis(acyl) complex.[23–29] Except for alkyls of lutetium[30] and thorium,[31] the alternative C–C coupling pathway involving the consecutive insertion of two carbon monoxides into a metal–carbon bond has not been observed. Only one example of a migratory insertion of CO into a d-block metal–acyl bond has been reported.[32]

Compound **3** represents the first example of a d-block molecule containing an α-ketoacyl moiety that has been formed by the double insertion of carbon monoxide. Table IX shows a comparison of the bond distances and angles within the α-ketoacyl portion of **3** and those of other examples of this structural moiety. Although the α-ketoacyl in **3** is bound as a chelating rather than terminal ligand, the bond distances and angles within this portion of the molecule are very similar to those previously reported.

Rationalizing the structure of **3** using electron-counting rules is difficult. Overall the diruthenium group must carry a formal oxidation state of +4. Assigning a +2 oxidation state to each metal would imply that Ru1 would be a 16-electron center with a formal charge of +1, while Ru2 would be considered an 18-electron center having a formal charge of −1. The presence of the semibridging carbonyl would serve to shift some electron density from the electron-rich Ru2 to the unsaturated Ru1. The metal–phosphorus bond distances in **3** differ significantly about Ru1 and Ru2, with Ru1–P11 and Ru1–P12 being elongated in comparison to Ru2–P21 and Ru2–P22, a trend which is opposite that expected. An alternative would involve assigning Ru1 and Ru2 oxidation states of 0 and +4, respectively. This would be consistent with the trend in Ru–P distances and would place a formal charge of −1 on Ru1 and +1 on Ru2. The semibridging CO could exist to help delocalize the buildup of negative charge on Ru1. The intermediate situation where Ru1 is +1 and Ru2 is +3 can be ruled out by the observation that the complex is diamagnetic (based on the unperturbed $^{31}P$ NMR spectral signals). While ample superexchange pathways are available, it is unlikely that the coupling would be strong enough to make the dimer diamagnetic at room temperature.

As a final comment, we find remarkable the facility of the transformations that occur around the equatorial plane of this binuclear complex. While our data do not allow specific cause-and-effect relationships to be established, we can point to four factors which may contribute to the ease of these reactions. The ability of the dmpm ligand to stabilize the ruthenium in a variety of oxidation states combined with the ease of Ru–Ru bond breakage and formation allows the $Ru_2(dmpm)_2$ unit to act as an "electron reservoir". Perhaps the most significant ramification of this is that CO dissociation is no longer a prerequisite for activating the incoming ligand. In addition, the small size of the diphosphine undoubtedly contributes to the overall reactivity of the complex. Finally, the mobility of the ligands around the equatorial plane allows ligands to be "parked" temporarily while reactions which require more than one coordination site take place elsewhere on the complex. This is another feature which may facilitate chemistry by bypassing ligand dissociation.

## Summary

We have described the reaction of an electron-rich Ru(0) binuclear system with the electron-poor alkyne dimethyl acetylenedicarboxylate and have found it to result in three isolable products, each of which can be prepared in high yield by varying the reaction conditions. The ultimate product obtained at elevated temperature was the diruthenacyclobutene, in which the alkyne was bound as a *cis*-dimetalated alkene. The room-temperature product, under dilute conditions, was shown by the spectroscopic data and X-ray crystallography to be a diruthenacyclopentenone, in which a new carbon–carbon had been formed. The most unusual product was formed under conditions of high concentration and was shown by X-ray crystallography to contain a five-membered metallacycle consisting of one ruthenium center, two vinyl carbons from the alkyne, and two carbonyl carbons, attached to each other. Two new carbon–carbon bonds were formed by an apparent double insertion of carbon monoxide. Further investigations of the reactivity of $Ru_2(dmpm)_2(CO)_5$ are underway.

**Acknowledgment.** The research was supported by a grant (CHE-9021923) from the National Science Foundation. K.A.J. gratefully acknowledges fellowship support from the University of Minnesota, Department of Chemistry. We thank Prof. Doyle Britton for determining the crystal structures and Prof. Martin Cowie for a copy of J. Jenkins' thesis.

**Supplementary Material Available:** Tables of positional parameters, thermal parameters, bond distances, and bond angles for **3** and **4** (25 pages). Ordering information is given on any current masthead page.

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(22) Collin, J. *Bull. Soc. Chim. Fr.* **1988**, 976.

(23) Chen, J.-T.; Sen, A. *J. Am. Chem. Soc.* **1984**, *106*, 1506.

(24) Ozawa, F.; Sugimoto, T.; Yuasa, Y.; Santra, M.; Yamamoto, T.; Yamamoto, A. *Organometallics* **1984**, *3*, 683.

(25) Ozawa, F.; Sugimoto, T.; Yamamoto, T.; Yamamoto, A. *Organometallics* **1984**, *3*, 692.

(26) Ozawa, F.; Soyama, H.; Yanagihara, H.; Aoyama, I.; Takino, H.; Izawa, K.; Yamamoto, T.; Yamamoto, A. *J. Am. Chem. Soc.* **1985**, *107*, 3235.

(27) Sen, A.; Chen, J.-T.; Vetter, W. M.; Whittle, R. R. *J. Am. Chem. Soc.* **1987**, *109*, 148.

(28) Ozawa, F.; Huang, L.; Yamamoto, A. *J. Organomet. Chem.* **1987**, *334*, C9.

(29) Sakakura, T.; Yamashita, H.; Kobayashi, T.; Hayashi, T.; Tanaka, M. *J. Org. Chem.* **1987**, *52*, 5733.

(30) Evans, W. J.; Wayda, A. L.; Hunter, W. E.; Atwood, J. L. *J. Chem. Soc., Chem. Commun.* **1981**, 706.

(31) Moloy, K. G.; Fagan, P. J.; Manriquez, J. M.; Marks, T. J. *J. Am. Chem. Soc.* **1986**, *108*, 56.

(32) Sheridan, J. B.; Johnson, J. R.; Handwerker, B. M.; Geoffroy, G. L.; Rheingold, A. L. *Organometallics* **1988**, *7*, 2404.

(33) Fayos, J.; Dobrzynski, E.; Angelici, R. J.; Clardy, J. *J. Organomet. Chem.* **1973**, *59*, C33.

(34) Casey, C. P.; Bunnell, C. A.; Calabrese, J. C. *J. Am. Chem. Soc.* **1976**, *98*, 1166.