New Electron-Deficient Alkene and Alkyne Derivatives of Ru₅(μ₅-C)(CO)₁₅: The Syntheses and Crystal Structure Analyses of Ru₅(μ₅-C)(CO)₁₃ [C₂H₂(CO₂Me)₂] and Ru₅(μ₅-C)(CO)₁₅ [C₂(CO₂Me)₂]

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Treatment of carbido cluster Ru₅(μ₅-C)(CO)₁₅ with Me₃NO in acetonitrile solution followed by addition of dimethyl maleate or dimethyl acetylene dicarboxylate affords new clusters Ru₅(μ₅-C)(CO)₁₃[C₂H₂(CO₂Me)₂] (1) and Ru₅(μ₅-C)(CO)₁₅[C₂(CO₂Me)₂] (2), respectively. Single crystal X-ray structural studies reveal that both complexes contain a wingtip-bridged butterfly pentametallic skeleton. In complex 1 the maleate fragment is coordinated to one wingtip Ru atom through its carbon-carbon double bond and to the adjacent Ru atom by the formation of two O → Ru dative bonding interactions, while the acetylene dicarboxylate fragment in 2 is best considered as a cis-dimetallated alkene, linking one hinge Ru atom and the nearby Ru atom at the bridged position. Crystal data for 1: space group P 42/n; a = 20.199(6), c = 13.841(3) Å, Z = 8; final R₁ = 0.025, R_m = 0.026 for 3963 reflections with I > 2σ(I). Crystal data for 2: space group P2₁/n; a = 9.634(3), b = 20.062(6), c = 17.372(5) Å, β = 90.62(2)°, Z = 4; final R₁ = 0.033, R_m = 0.036 for 4683 reflections with I > 3σ(I).

KEY WORDS: Ruthenium carbide; carbonyl; alkyne; alkene; dimethyl maleate; dimethyl acetylene dicarboxylate.

INTRODUCTION

The ruthenium carbido cluster Ru₅(μ₅-C)(CO)₁₅ was first prepared in trace amount from the reaction of Ru₄(μ-H)₄(CO)₁₂ with ethylene [1].

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Subsequently, an indirect procedure involving the high pressure carbonylation of Ru₅(μ₅-C)(CO)₁₇ was selected to produce this medium-nuclearity carbido cluster compound in large quantity [2]. Much chemistry of Ru₅(μ₅-C)(CO)₁₇ has been reported since then. Thus, the further addition of carbon monoxide or weakly coordinated acetonitrile under mild conditions afforded the wingtip-bridged butterfly clusters Ru₅(μ₅-C)(CO)₁₆ and Ru₅(μ₅-C)(CO)₁₇(NCMe), respectively [3]. The addition of Au(PPh₃)Cl to Ru₅(μ₅-C)(CO)₁₅ formed Ru₅(μ₅-C)(CO)₁₆(μ-Cl)(μ-AuPPh₃) which then eliminated one mole of CO to form Ru₅(μ₅-C)(CO)₁₅(μ-Cl)(μ-AuPPh₃) where bridging chlorine ligand functions as a three-electron donor [4]. Coordination of H₂S, H₂Se and HSR, R = Me or Et, led to the formation of the clusters Ru₅(μ₅-C)(CO)₁₄(μ-H)(μ-SH), Ru₅(μ₅-C)(CO)₁₄(μ-H)(μ-SeH), and Ru₅(μ₅-C)(CO)₁₄(μ-H)(μ-S), respectively [5]. In these molecules, the Ru₅ frameworks resemble that of the bridged-butterfly geometry in Ru₅(μ₅-C)(CO)₁₅(NCMe) with the hydride associated with the hinge Ru-Ru bond and the thiolate group bridging across the hinge and the bridged ruthenium atoms. The nucleophiles, such as with LiMe, Na₅C₅H₅ and [PPN][NO₂], reacted with Ru₅(μ₅-C)(CO)₁₅ to afford anionic cluster complexes, while upon addition of the aurated cation [AuPR₃]⁺, R = Ph or Et, giving the acyl cluster Ru₅(μ₅-C)(CO)₁₄(μ-MeCO)(μ-AuPPh₃), the cyclopentadienyl cluster CpRu₅(μ₅-C)(CO)₁₄(μ-AuPPh₃) and the nitrosyl cluster Ru₅(μ₅-C)(CO)₁₃(NO)(μ-AuPEt₃) [6]. In most cases, the reactions are clean and produce only one major product. This novel reactivity pattern has encouraged us to investigate the subsequent reactions of Ru₅(μ₅-C)(CO)₁₅ with unsaturated hydrocarbons except for the diene molecules, as the latter are known to produce a wide variety of structurally characterized arené clusters [7]. In this paper we describe the reactions of Ru₅(μ₅-C)(CO)₁₅ with electron-deficient dimethyl maleate and dimethyl acetylene dicarboxylate, and will emphasize on the X-ray structure of the alkene and alkyne derivatives Ru₅(μ₅-C)(CO)₁₃[C₂H₂(CO₂Me)₂] (1) and Ru₅(μ₅-C)(CO)₁₃[C₂(CO₂Me)₂] (2) obtained.
EXPERIMENTAL PROCEDURE

General Information and Materials. Infrared spectra were recorded on a Perkin Elmer 2000 FT-IR spectrometer. 1H and 13C NMR spectra were recorded on a Bruker AM-400 (400.13 MHz) or a AMX-300 (300.6 MHz) instrument. Chemical shifts are quoted with respect to internal standard tetramethylsilane. Mass spectra were obtained on a JEOL-HXII0 spectrometer operating in fast atom bombardment (FAB) mode. All reactions were performed under a nitrogen atmosphere using deoxygenated solvents dried with an appropriate reagent. Reactions were monitored by analytical thin-layer chromatography (5735 Kieselgel 60 F254, E. Merck) and the products were separated on commercially available preparative thin-layer chromatographic plates (Kieselgel 60 F254, E. Merck). The elemental analyses were performed at the NSC Regional Instrument Center at National Cheng Kung University, Tainan, Taiwan.

Reaction of Ru$_5$(µ$_3$-C)(CO)$_5$ with Dimethyl Maleate. An acetonitrile solution (10 ml) of freshly sublimed Me$_3$NO (8.8 mg, 0.12 mmol) was added dropwise into a CH$_2$Cl$_2$ solution (25 ml) of Ru$_5$(µ$_3$-C)(CO)$_5$ (50 mg, 0.053 mmol) within 30 min. After the addition of Me$_3$NO solution was completed, the color of solution faded from red to light red. Dimethyl maleate (60 µl, 0.504 mmol) was added into the flask using a microsyringe. The solvents were removed under vacuum and the oily residue was redissolved into a mixture of CH$_2$Cl$_2$ (10 ml) and heptane (30 ml). The heating was continued for 10 min until the color changed to dark red. Then the solvent was removed and the residue was redissolved in the minimum of CH$_2$Cl$_2$ and separated by thin-layer chromatography. Development with a 1:2 mixture of dichloromethane and hexane produced an orange band, which was extracted from silica gel to yield 28 mg of Ru$_5$(µ$_3$-C)(CO)$_5$[C$_2$H$_2$(CO$_2$Me)$_2$] (1, 0.027 mmol, 51%) after recrystallization.

Spectral data for 1: MS spectrum (FAB, $^{102}$Ru), m/z 1029(M$^+$). IR(CH$_2$Cl$_2$): v(CO), 2082 (m), 2046 (vs), 2036 (s), 2023 (s), 1998 (br, m), 1969 (br, m) cm$^{-1}$; v(esther-CO), 1610 (br, m) cm$^{-1}$; 1H NMR (CD$_2$Cl$_2$, 294 K): δ 4.12 (d, 1H, J$_{H-H}$ = 9.4 Hz), 3.96 (s, 3H), 3.68 (d, 1H, J$_{H-H}$ = 9.4 Hz), 3.62 (s, 3H). 13C NMR (CD$_2$Cl$_2$, 294 K): δ 463.6 (µ$_3$-C), 200.1 (CO), 199.1 (CO), 197.0 (2CO), 196.2 (br, 2CO), 193.1 (CO), 190.9 (CO), 189.0 (CO$_2$Me), 182.5 (CO$_2$Me), 55.4 (OCH$_3$), 55.1 (OCH$_3$), 40.9 (CH), 37.8 (CH). Elemental analysis for C$_{20}$H$_8$O$_{17}$Ru$_5$: Calcd.: C, 23.42; H, 0.79. Found: C, 23.25; H, 0.85.

Reaction of Ru$_5$(µ$_3$-C)(CO)$_5$[C$_2$H$_2$(CO$_2$Me)$_2$] with CO. To a 50 ml reaction flask, 18 mg of Ru$_5$(µ$_3$-C)(CO)$_5$[C$_2$H$_2$(CO$_2$Me)$_2$] (0.017 mmol), 10 ml of CH$_2$Cl$_2$ and 15 ml of heptane were added. The resulting
solution was stirred at reflux temperature under a CO atmosphere for 40 min during which time the color changed from orange to dark red slowly. The solvent was removed and the residue was separated by thin-layer chromatography (dichloromethane:hexane = 1:2), affording 8 mg of Ru₅(μ₅-C)(CO)₁₅ (0.008 mmol, 49 %) as the only isolable product.

**Reaction of Ru₅(μ₅-C)(CO)₁₅ with Dimethyl Acetylene Dicarboxylate.** An acetonitrile solution (15 ml) of freshly sublimed Me₃NO (17.6 mg, 0.23 mmol) was added dropwise into a CH₂Cl₂ solution (50 ml) of Ru₅(μ₅-C)(CO)₁₅ (200 mg, 0.212 mmol) within 30 min. After the addition of Me₃NO solution was completed, the color faded from red to light red. Dimethyl acetylene dicarboxylate (151 μl, 1.23 mmol) was then added into the reaction flask. The mixture was then stirred at room temperature for 20 min. and the color changed to dark red. The solvent was removed under vacuum and the residue was separated by thin-layer chromatography using

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*Features common to all determinations: λ(Mo-Kα) = 0.7107 Å; minimize function: Σ[w||F₀ − Fᵣ||²], weighting scheme: w⁻¹ = σ²(F₀) + |g| F₀²; G.O.F. = [Σ w ||F₀ − Fᵣ||²] / (Nₑ − Nᵣ)₁/² (Nₑ = number of observations; Nᵣ = number of variables).
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*B (eq) is the mean of the principal axes of the thermal ellipsoid.
Table III. Atomic Coordinates and Equivalent Isotropic Displacement Coefficients for 2

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<tr>
<td>O3</td>
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<td>7.139(22)</td>
</tr>
<tr>
<td>O4</td>
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<td>6.687(21)</td>
</tr>
<tr>
<td>O5</td>
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<td>6.970(20)</td>
</tr>
<tr>
<td>O6</td>
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<td>6.727(22)</td>
</tr>
<tr>
<td>O7</td>
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<td>0.73139(32)</td>
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<td>5.828(18)</td>
</tr>
<tr>
<td>O8</td>
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</tr>
<tr>
<td>O9</td>
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<td>0.97162(32)</td>
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<tr>
<td>O10</td>
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<td>0.32714(32)</td>
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<td>O11</td>
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<td>O12</td>
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<td>0.41156(37)</td>
<td>7.271(22)</td>
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<tr>
<td>O14</td>
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<td>0.07358(26)</td>
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<td>O18</td>
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</tr>
<tr>
<td>O19</td>
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</tr>
<tr>
<td>Cl1</td>
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<tr>
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<tr>
<td>C2</td>
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<tr>
<td>C3</td>
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<tr>
<td>C4</td>
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<td>-0.00430(42)</td>
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</tr>
<tr>
<td>C5</td>
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</tr>
<tr>
<td>C6</td>
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<td>0.08069(41)</td>
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</tr>
<tr>
<td>C7</td>
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<tr>
<td>C8</td>
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<tr>
<td>C9</td>
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<td>C10</td>
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<tr>
<td>C12</td>
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<td>0.76200(37)</td>
<td>0.33435(41)</td>
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</tr>
<tr>
<td>C13</td>
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<td>C14</td>
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<tr>
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<td>C16</td>
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<td>0.54277(30)</td>
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<tr>
<td>C18</td>
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<tr>
<td>C19</td>
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<td>0.64120(29)</td>
<td>0.16025(34)</td>
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<tr>
<td>C20</td>
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<td>C21</td>
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<td>C22</td>
<td>0.13023(142)</td>
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<td>0.89266(89)</td>
<td>10.643(25)</td>
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</table>

* B(eq) is the mean of the principal axes of the thermal ellipsoid.
Table IV. Selected Bond Distances (Å) and Bond Angles (Deg.) of 1 (esd in Parentheses)

<table>
<thead>
<tr>
<th>(A) Metal-metal distances</th>
<th>Ru(1)–Ru(2)</th>
<th>2.7960(9)</th>
<th>Ru(1)–Ru(5)</th>
<th>2.8285(8)</th>
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</thead>
<tbody>
<tr>
<td>Ru(2)–Ru(3)</td>
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<td>Ru(2)–Ru(4)</td>
<td>2.8785(8)</td>
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<tr>
<td>Ru(3)–Ru(4)</td>
<td>2.6874(10)</td>
<td>Ru(3)–Ru(5)</td>
<td>2.8873(10)</td>
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</tr>
<tr>
<td>Ru(4)–Ru(5)</td>
<td>2.8860(10)</td>
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</table>

<table>
<thead>
<tr>
<th>(B) Parameters with the carbide atom</th>
<th>Ru(1)–C(14)</th>
<th>2.059(5)</th>
<th>Ru(2)–C(14)</th>
<th>1.963(5)</th>
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</thead>
<tbody>
<tr>
<td>Ru(3)–C(14)</td>
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<td>Ru(4)–C(14)</td>
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</tr>
<tr>
<td>Ru(5)–C(14)</td>
<td>1.951(5)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \angle \text{Ru}(2)–C(14)–\text{Ru}(5) )</td>
<td>177.6(3)</td>
<td>( \angle \text{Ru}(1)–C(14)–\text{Ru}(3) )</td>
<td>144.8(2)</td>
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</tr>
<tr>
<td>( \angle \text{Ru}(1)–C(14)–\text{Ru}(4) )</td>
<td>135.2(2)</td>
<td>( \angle \text{Ru}(3)–C(14)–\text{Ru}(4) )</td>
<td>79.7(2)</td>
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<table>
<thead>
<tr>
<th>(C) Parameters associated with the alkene ligand</th>
<th>Ru(1)–O(14)</th>
<th>2.145(3)</th>
<th>Ru(1)–O(16)</th>
<th>2.117(3)</th>
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<tbody>
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<td>Ru(2)–C(17)</td>
<td>2.168(5)</td>
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<td>C(16)–C(17)</td>
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<td>C(18)–O(16)</td>
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<td>C(18)–O(17)</td>
<td>1.316(6)</td>
<td>C(15)–O(14)</td>
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<td>C(15)–O(15)</td>
<td>1.315(6)</td>
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<tr>
<td>( \angle \text{C}(15)–\text{C}(16)–\text{C}(17) )</td>
<td>122.7(4)</td>
<td>( \angle \text{C}(16)–\text{C}(17)–\text{C}(18) )</td>
<td>124.4(4)</td>
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<tr>
<td>( \angle \text{Ru}(1)–O(14)–\text{C}(15) )</td>
<td>118.0(3)</td>
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<td>119.9(3)</td>
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</table>

Table V. Selected Bond Distances (Å) and Bond Angles (Deg.) of 2 (esd in Parentheses)

<table>
<thead>
<tr>
<th>(A) Metal-metal distances</th>
<th>Ru(1)–Ru(2)</th>
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<th>Ru(1)–Ru(5)</th>
<th>2.920(1)</th>
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<td>Ru(3)–Ru(4)</td>
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<td>Ru(3)–Ru(5)</td>
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<td>Ru(4)–Ru(5)</td>
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<table>
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<tr>
<th>(B) Parameters associated with the carbide atom</th>
<th>Ru(1)–C(16)</th>
<th>2.096(5)</th>
<th>Ru(2)–C(16)</th>
<th>1.967(5)</th>
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</thead>
<tbody>
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<td>Ru(4)–C(16)</td>
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<tr>
<td>Ru(5)–C(16)</td>
<td>1.99(5)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \angle \text{Ru}(2)–\text{C}(16)–\text{Ru}(5) )</td>
<td>176.4(3)</td>
<td>( \angle \text{Ru}(1)–\text{C}(16)–\text{Ru}(3) )</td>
<td>123.1(3)</td>
<td></td>
</tr>
<tr>
<td>( \angle \text{Ru}(1)–\text{C}(16)–\text{Ru}(4) )</td>
<td>151.1(3)</td>
<td>( \angle \text{Ru}(3)–\text{C}(16)–\text{Ru}(4) )</td>
<td>85.7(2)</td>
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</table>

<table>
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<tr>
<th>(C) Parameters associated with the alkyne ligand</th>
<th>Ru(1)–C(17)</th>
<th>2.135(5)</th>
<th>Ru(1)–O(17)</th>
<th>2.147(6)</th>
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<td>C(17)–C(20)</td>
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</tr>
<tr>
<td>( \angle \text{C}(18)–\text{C}(17)–\text{C}(20) )</td>
<td>122.7(4)</td>
<td>( \angle \text{C}(17)–\text{C}(20)–\text{C}(21) )</td>
<td>124.4(4)</td>
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<tr>
<td>( \angle \text{Ru}(1)–\text{C}(17)–\text{C}(20) )</td>
<td>123.9(4)</td>
<td>( \angle \text{Ru}(3)–\text{C}(20)–\text{C}(17) )</td>
<td>121.5(4)</td>
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</tr>
</tbody>
</table>
pure dichloromethane as eluent, affording yellow orange Ru₂(μ₅-C)(CO)₁₅
[C₂(CO₂Me)₂] (2, 17.6 mg, 0.016 mmol, 8 %) as the major isolable cluster
product. Single crystals suitable for X-ray diffraction study were obtained
from a mixture of CH₂Cl₂ and methanol at −20°C.

Spectral data for 2: MS spectrum (FAB, ¹⁰²Ru), m/z 1038(M⁺).
IR(CH₂Cl₂): ν(CO), 2111 (w), 2081 (s), 2073 (vs), 2068 (s), 2051 (s), 2024
(br, m), 1946 (br, vw) cm⁻¹; ν(ester-CO), 1690 (br, w) cm⁻¹. ¹H NMR
(CD₂Cl₂, 294 K): δ 3.52 (s, 3H), 3.48 (s, 3H). (d, 1H, Jₕ₋ₕ = 9.4 Hz), 3.96
(s, 3H), ¹³C NMR (CD₂Cl₂, 294 K): δ 440.7 (μ₅-C), 194.9 (2CO), 193.6
(2CO), 192.9 (2CO), 192.6 (CO), 190.9 (3CO), 190.6 (2CO), 189.2 (2CO),
188.3 (CO), 181.7 (CO₂Me), 171.4 (CO₂Me), 170.2 (C₂), 160.4 (C₂), 189.0
(CO₂Me), 182.5 (CO₂Me), 51.7 (OCH₃), 51.5 (OCH₃). Elemental analysis
for C₂₂H₂₂O₁₉Ru₂: Calcd.: C, 24.48, H, 0.56. Found: C, 24.11; H, 0.72.

X-Ray Crystallography. Diffraction measurements were carried out
on a Nonius CAD-4 or a Siemens R3m/V diffractometer. Lattice parameters
of 1 were determined from 25 randomly selected high angle reflections
with 20 angles in the range 18.50–23.32, whereas the corresponding cell
dimensions of complex 2 were determined from 23 reflections with 20 angle
in the range of 13.21–27.55. All reflections were corrected for Lorentz,
polarization, and absorption effects. All data reduction and refinement were
performed using the NRCC-SDP-VAX and Siemens SHELXTL PLUS
(VMS) packages. The structures were refined by full-matrix least squares,
all nonhydrogen atoms were refined with anisotropic thermal parameters
and the hydrogen atoms on organic ligands were calculated in idealized
positions and included in the structure factor calculation. The combined
data collection and refinement parameters are given in Table I. Atomic
positional parameters for complexes 1 and 2 are found in Tables II and III,
whereas the selected bond angles and lengths appear in Tables IV and V,
respectively.

RESULTS AND DISCUSSION

Synthesis and Characterization of 1. The carbido cluster Ru₂(μ₅-C)
(CO)₁₅ reacts with two equiv. of the oxidative decarbonylation reagent
Me₃NO in acetonitrile solution at room temperature to afford an unstable
light red complex which is tentatively assigned to have an empirical for-
mula Ru₂(μ₅-C)(CO)₁₃(NCMe)₂. No attempt is made to isolate and
characterize this material. However, upon the addition of excess of
dimethyl maleate, it was converted to an orange cluster Ru₂(μ₅-C)(CO)₁₃
[C₂H₂(CO₂Me)₂] (1) in 51 % yield by the incorporation of one dimethyl
maleate molecule. The direct reaction of Ru₂(μ₅-C)(CO)₁₅ with excess
dimethyl maleate in dichloromethane containing two equiv. of Me₃NO
also affords the maleate cluster 1, but the yield is substantially lower. These
employed conditions differ from that utilized for the reactions of Ru₆(μ₃-C)
(CO)₁₇ with dienes in producing the arene clusters, where no acetonitrile
solvent was added in stabilizing the intermediate [8].

On the contrary, treatment of Ru₆(μ₃-C)(CO)₁₅ with dimethyl
fumarate, in which the CO₂Me functional groups adopt trans-disposition
at the carbon–carbon double bond, does not produce the corresponding
fumarate complex but cluster decomposition. This dramatic diversity in
reactivity provides the first indication to the possible involvement of both
CO₂Me functional groups in stabilizing the maleate complex 1.

The maleate cluster 1 is characterized by spectroscopic methods and
X-ray diffraction study. The FAB mass spectrum displays a parent
molecular ion at m/z 1029, showing the existence of 13 CO ligands and one
ligated olefin fragment. The ¹H NMR spectrum is very simple, showing two
doublets at δ 4.12 and 3.68 with a coupling constant ³JH-H = 9.4 Hz and
two singlet signals at δ 3.96 and 3.62, an indicative of a dimethyl maleate
ligand. From these spectroscopic data we can assume that the vacant coor-
dination sites generated by the elimination of two CO ligands is filled by
the maleate ligand, which is coordinated to the ruthenium atoms through
the carbon–carbon double bond and the oxygen atoms of the carbonyl
ligands.

The molecular structure of 1 is shown in Fig. 1 together with the
atomic numbering scheme. The selective bond angles and distances are
presented in Table IV. The metal core structure is closely related to the
“wingtip-bridged butterfly” structure adopted by several analogous pen-
taruthenium and osmium carbido derivatives [9]. In this molecule, all
carbonyl ligands adopt the terminal bonding mode with almost linear
Ru–CO angles in the range 173.4–179.0°. The Ru–Ru distances are of three
types. The shortest is the Ru(hinge)–Ru(hinge) bond (Ru(3)–Ru(4) =
2.6874(10) Å), then the Ru(bridge)–Ru(wingtip) bonds (Ru(1)–Ru(2) =
2.7960(9) Å and Ru(1)–Ru(5) = 2.8285(8) Å and the longest are the
Ru(wingtip)–Ru(hinge) bonds at 2.8860(10)–2.9056(8) Å. The Ru(wingtip)–
C(14)–Ru(wingtip) angle is nearly linear with angle 177.6(3)°. The carbide
carbon distances to the wingtip ruthenium atoms (Ru(2)–C(14) = 1.963(5) Å
and Ru(5)–C(14) = 1.951(6) Å are significantly shorter than those to the
hinge and bridged ruthenium atoms (2.059(5) Å–2.098(5) Å).

The most striking feature is the bonding of the dimethyl maleate
ligand. The alkene portion is coordinated to the Ru(2) atom with distance
C(16)–C(17) = 1.438(7) Å, which is similar to that observed in the Mo
maleate complexes [10]. The carbonyl functional groups are extended
across the Ru(1)–Ru(2) bond and coordinated to the adjacent Ru(1) atom
with distances Ru(1)–O(14) = 2.145(3) Å and Ru(1)–O(16) = 2.117(3) Å.
These values are typical for the O → Ru dative bond in triruthenium complexes containing such \( \eta^2 \)-carbonyl group [11], but are slightly shorter than that observed in dinuclear (C\(_5\)Me\(_5\))\(_2\)Ru\(_2\)\(\mu\)-H][C\(_2\)H\(_2\)(CO\(_2\)Me)\(_2\)] [C\(_2\)H(CO\(_2\)Me)\(_2\)] (2.23(1) Å) [12] and mononuclear (Ph\(_3\)P)\(_3\)RuH[CH = CMe(CO\(_2\)Bu)] (2.246(7) Å) [13], in which the carbonyl oxygen is also coordinated to ruthenium atom. Therefore, the structure of I represents the first example in which the dimethyl maleate ligand serves as a six-electron donor through the coordination of its carbon–carbon double bond and both carbonyl fragments.

After understanding the structure of I, the mechanism leading to the generation of such novel cluster compound can be envisioned. Basically, formation of I may be viewed as an initial coordination by the olefinic portion of the dimethyl maleate, followed by bending of both carbonyl oxygen atoms to the ligand sphere of an adjacent Ru atom. In this case, one oxygen donor replaces the second weakly coordinated acetonitrile ligand, whereas in the formation of the second oxygen to ruthenium atom donor interaction, a Ru–Ru bond is broken. The cis-disposition of the carbonyl
groups is important in stabilizing this particular metal framework, as the
direct reaction with dimethyl fumarate, which contains two trans CO$_2$Me
functional groups, failed to produced the alkene adduct. It seems that the
direct linkage with the second carbonyl group and the subsequent cleavage
of the Ru–Ru bond are of importance in stabilizing the cluster.

*Synthesis and Characterization of 2.* Treatment of Ru$_3$(μ$_5$-C)(CO)$_{15}$
with stoichiometric amount of Me$_3$NO in acetonitrile followed by addition
of dimethyl acetylene dicarboxylate results in the formation of pen-
taruthenium compound Ru$_3$(μ$_5$-C)(CO)$_{15}$[C$_2$(CO$_2$Me)$_2$] (2) in 8 % yield
as an orange material. The IR spectrum in CH$_2$Cl$_2$ solution shows only
terminal CO stretches at 2111–1946 cm$^{-1}$. The $^1$H NMR spectrum consists
of two methyl resonance signals at δ 3.52 and 3.48, suggesting the presence
of one dimethyl acetylene dicarboxylate molecule.

In attempts to explore the possible reaction mechanism, we have
varied the conditions by addition of two equivalents of Me$_3$NO instead.

![Perspective drawing of Ru$_3$(μ$_5$-C)(CO)$_{15}$[C$_2$(CO$_2$Me)$_2$] (2)](image)

*Fig. 2. Perspective drawing of Ru$_3$(μ$_5$-C)(CO)$_{15}$[C$_2$(CO$_2$Me)$_2$] (2) showing the crystallographic labeling scheme with thermal ellipsoids at the 30 % probability level.*
However, we were unable to isolate compound 2 during this investigation. This observation probably suggests that its formation is the consequence of the coordination of dimethyl acetylene dicarboxylate to the monocacetonitrile cluster complex Ru3(μ5-C)(CO)14(NCMe) to give an intermediate Ru3(μ5-C)(CO)14[C2(CO2Me)2], followed by recapture of an additional CO ligand in solution. Direct formation of 2 by addition of dimethyl acetylene dicarboxylate across the Ru–Ru bond of Ru3(μ5-C) (CO)12 is precluded because no cluster compound 2 can be isolated in the absence of Me3NO reagent under similar conditions.

The compound 2 was examined by single-crystal X-ray analysis to determine its molecular structure. The ORTEP diagram is presented in Fig. 2 and the selective distances and angles are given in Table V. The cluster framework is related to that of the previously reported complex 1, exhibiting the same kind of “wingtip-bridged butterfly” geometry, in which the butterfly fragment is defined the atoms Ru(2), Ru(3), Ru(4), and Ru(5). The alkyne fragment adopts the novel μ-η¹, η¹-bonding mode [14] and spans the nonbonding Ru(1) and Ru(3) atoms. The C(17)–C(20) distance (1.354(9) Å), which falls in the range for a formal carbon–carbon double bond, is slightly longer than the C = C distances (1.27–1.34 Å) seen for the dimetallacylobutene complexes [15], while the angles (∠Ru(1)–C(17)–C(20) = 123.9(4)° and ∠Ru(3)–C(20)–C(17) = 121.6(4)°) are also consistent with the sp² hybridization of the alkene carbons. Thus this alkyne fragment is bound as the cis-dimetallated alkene [16]. In addition, all carbonyl ligands adopt a terminal mode, except that the carbonyl ligand C(15)O(15) which bridges the Ru(hinge)–Ru(hinge) bond asymmetrically, ∠Ru(3)–C(15)–O(15) = 167.6(6)°. The presence of this bridging CO ligand may be responsible for the slight increase of this Ru(hinge)–Ru(hinge) distance (Ru(3)–Ru(4) = 2.828(1) Å) with respect to the respective hinge Ru–Ru bond in 1. Moreover, the pattern of the ruthenium–carbide distances is also akin to that of the previous discussed complex 1, with the distances to the wingtip ruthenium atoms being slightly shorter than those to the hinge and the bridged ruthenium atoms.

**SUMMARY AND CONCLUSIONS**

The alkene and alkyne derivatives of Ru3(μ5-C)(CO)15, which adopt the wingtip-bridged butterfly geometry, have been synthesized and characterized. Our experimental result suggests that the chemical activation of the parent cluster Ru3(μ5-C)(CO)15 via addition of Me3NO in the presence of acetonitrile is critical to the successful preparation of these derivatives, although the stoichiometry for the alkyne derivative 2 implies that no prior CO dissociation is required. For the maleate derivative 1, in addition to the
carbon–carbon double bond, both oxygen atoms of the carbonyl functional
groups are linked to a ruthenium atom to compensate for the unsaturation
generated by loss of two CO ligands and cleavage of one Ru–Ru bond. The
combined interaction from the maleate ligand to the Ru₅ cluster core is still
not very effective, as treatment of 1 with CO regenerated the carbonyl
cluster Ru₅(μ₂-C)(CO)₁₅ in 49% yield. In contrast, the dimethyl acetylene
dicarboxylate derivative 2, in which the alkyne is coordinated to the cluster
via μ-η¹,η¹-bonding, shows no such carbonyl O → Ru dative interaction
due to the unfavorable position of CO₂Me functional groups. Work is
currently in progress to investigate the coupling of electron deficient
alkenes and alkynes on such pentaruthenium platform. Full details will be
presented in forthcoming publications.

SUPPLEMENTARY MATERIALS AVAILABLE

A complete listing of thermal parameters, tables of nonessential bond
distances and hydrogen atom coordinates for complexes 1 and 2 are
available from the author (Y. C.).

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