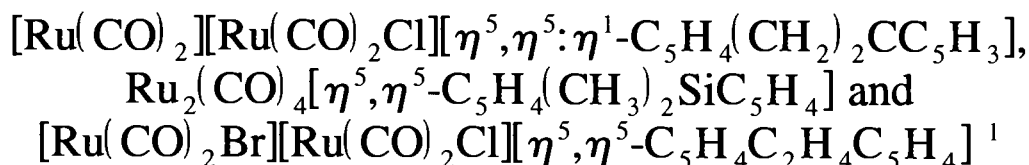


## Synthesis of mono- and bimetallic ruthenium carbonyl compounds from ring-coupled bis(cyclopentadienyl thallium) reagents.

### The molecular structures of



Thomas E. Bitterwolf<sup>a,\*</sup>, Maureen B. Leonard<sup>a</sup>, Pamela A. Horine<sup>a</sup>, Joyce E. Shade<sup>b</sup>,  
Arnold L. Rheingold<sup>c</sup>, Donna J. Staley<sup>c</sup>, Glenn P.A. Yap<sup>c</sup>

<sup>a</sup> Department of Chemistry, University of Idaho, Moscow, ID 83844-2343, USA

<sup>b</sup> Department of Chemistry, U.S. Naval Academy, Annapolis, MD 21402-5026, USA

<sup>c</sup> Department of Chemistry and Biochemistry, University of Delaware, Newark, DE 19716, USA

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### Abstract

Reaction of ring-coupled bis(cyclopentadienylthallium) compounds of the general form  $\text{Tl}_2[\text{C}_5\text{H}_4\text{LC}_5\text{H}_4]$ , where  $\text{L} = \text{CH}_2\text{-}$ ,  $(\text{CH}_3)_2\text{C-}$ ,  $(\text{CH}_3)_2\text{Si-}$ ,  $\text{C}_2\text{H}_4\text{-}$ , with  $[\text{Cl}_2\text{Ru}(\text{CO})_3]_2$  was found to form a family of mono- and bimetallic complexes including compounds of the form:  $\text{Ru}_2(\text{CO})_4(\eta^5, \eta^5\text{-C}_5\text{H}_4\text{LC}_5\text{H}_4)$ ,  $\text{Ru}(\text{CO})_2(\eta^5, \eta^5: \eta^1\text{-C}_5\text{H}_4\text{LC}_5\text{H}_4)$ ,  $[\text{Ru}(\text{CO})_2][\text{Ru}(\text{CO})_2\text{Cl}](\eta^5, \eta^5: \eta^1\text{-C}_5\text{H}_4\text{LC}_5\text{H}_3)$ , and  $[\text{Ru}(\text{CO})_2\text{Cl}](\eta^5, \eta^5\text{-C}_5\text{H}_4\text{LC}_5\text{H}_4)$ . These compounds have been completely characterized by IR,  $^1\text{H}$  and  $^{13}\text{C}$  NMR, mass spectrometry and elemental analysis. The molecular structures of several compounds in this series have been determined:  $[\text{Ru}(\text{CO})_2][\text{Ru}(\text{CO})_2\text{Cl}][\eta^5, \eta^5: \eta^1\text{-C}_5\text{H}_4(\text{CH}_2)_2\text{CC}_5\text{H}_3]$ : triclinic,  $P\bar{1}$ ,  $a = 7.812(3)$  Å,  $b = 9.004(2)$  Å,  $c = 12.773(5)$  Å,  $\alpha = 84.33(3)^\circ$ ,  $\beta = 75.26(3)^\circ$ ,  $\gamma = 80.93(3)^\circ$ ,  $V = 857.3(6)$  Å<sup>3</sup>,  $Z = 2$ ,  $R(F) = 3.52\%$ .  $\text{Ru}_2(\text{CO})_4[\eta^5, \eta^5\text{-C}_5\text{H}_4(\text{CH}_3)_2\text{SiC}_5\text{H}_4]$ : monoclinic,  $P2_1/n$ ,  $a = 11.036(2)$  Å,  $b = 13.660(2)$  Å,  $c = 11.621(2)$  Å,  $\beta = 105.83(2)^\circ$ ,  $V = 1688.6(5)$  Å<sup>3</sup>,  $Z = 4$ ,  $R(F) = 2.68\%$ ;  $[\text{Ru}(\text{CO})_2\text{Cl}][\text{Ru}(\text{CO})_2\text{Br}](\eta^5, \eta^5\text{-C}_5\text{H}_4\text{C}_2\text{H}_4\text{C}_5\text{H}_4)$ : monoclinic,  $C2/c$ ,  $a = 25.237(3)$  Å,  $b = 6.049(1)$  Å,  $c = 12.646(2)$  Å,  $\beta = 109.73(1)^\circ$ ,  $V = 1817(2)$  Å<sup>3</sup>,  $Z = 4$ ,  $R(F) = 4.37\%$ .

**Keywords:** Ruthenium; Thallium; Silicon; Bimetallic; Metal carbonyl; Ring-coupled

### 1. Introduction

Over the course of our studies on bimetallic complexes of ring coupled cyclopentadienyl ligands, we have observed occasional trace reaction sideproducts that appeared to contain both  $\eta^5\text{-C}_5\text{H}_4\text{R}$  and  $\eta^1\text{-C}_5\text{H}_4\text{R}$  ligands. Although we felt that these materials would be interesting in their own right, we recognized that they

might also be effective precursors for heterobimetallic complexes that are otherwise difficult to prepare. We therefore sought to develop synthetic routes that would generate working quantities of these  $(\eta^5\text{-C}_5\text{H}_4\text{R})(\eta^1\text{-C}_5\text{H}_4\text{R})$  species. This communication expands upon our previous reports on the synthesis of ring coupled bimetallic compounds, and also demonstrates the synthesis of monometallic and bimetallic complexes containing  $\eta^5, \eta^1\text{-C}_5\text{H}_4\text{LC}_5\text{H}_4$ , and  $\eta^5, \eta^5: \eta^1\text{-C}_5\text{H}_4\text{LC}_5\text{H}_3$  ligands where  $\text{L} = \text{CH}_2$ ,  $\text{C}(\text{CH}_3)_2$ ,  $\text{Si}(\text{CH}_3)_2$ , and  $\text{C}_2\text{H}_4$ . The facile conversion of these ruthenium  $(\eta^5\text{-C}_5\text{H}_4\text{R})(\eta^1\text{-C}_5\text{H}_4\text{R})$  compounds to heterobimetallic compounds will be reported separately.

\* Corresponding author.

<sup>1</sup> Dedicated to Professor Marvin D. Rausch, friend, mentor and collaborator, on the occasion of his 65th birthday.

## 2. Results and discussion

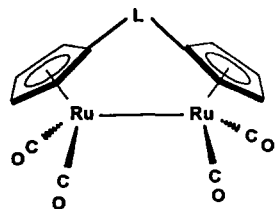
We have previously demonstrated the usefulness of  $\text{Ti}_2(\text{C}_5\text{H}_4\text{CH}_2\text{C}_5\text{H}_4)$  as a reagent in the synthesis of bimetallic complexes [1]. Reaction of  $\text{Ti}_2(\text{C}_5\text{H}_4\text{CH}_2\text{C}_5\text{H}_4)$  with metal complexes of the form  $\text{XML}_n$ , where  $\text{X} = \text{Cl}, \text{Br}, \text{or I}$ , results in the formation of  $(\text{ML}_n)_2(\eta^5, \eta^5\text{-C}_5\text{H}_4\text{CH}_2\text{C}_5\text{H}_4)$  products. Occasionally it has been possible to isolate monosubstituted compounds in which only one cyclopentadienyl ring has been metalated, leaving the second ring as a cyclopentadiene. Werner and coworkers [2] have elegantly demonstrated the use of these compounds as building blocks for heterobimetallic compounds.

$(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{CO})_2(\eta^1\text{-C}_5\text{H}_5)$  has been prepared by reaction of  $(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{CO})_2\text{Cl}$  with  $\text{C}_5\text{H}_5\text{Ti}$  [3] or  $[\text{RuCl}_2(\text{CO})_3]_2$  with  $\text{NaC}_5\text{H}_5$  [4]. The 1,2-shift of the sigma bonded cyclopentadienyl ring has been investigated [3].

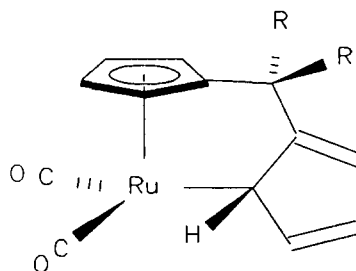
Reaction of  $\text{Ti}_2(\text{C}_5\text{H}_4\text{CH}_2\text{C}_5\text{H}_4)$  with metal com-

plexes of the form,  $\text{X}_2\text{ML}_n$ , might be expected to form bimetallic products such as  $(\text{MXL}_n)_2(\eta^5, \eta^5\text{-C}_5\text{H}_4\text{-CH}_2\text{C}_5\text{H}_4)$ , and indeed such compounds are isolated for both  $[\text{Cl}_2\text{Ru}(\text{CO})_3]_2$  and  $\text{I}_2\text{Fe}(\text{CO})_4$ . In the specific case of Ru, a further process occurs that is presumed to involve oxidation of a cyclopentadienyl anion and reduction of the Ru(II) to Ru(I), leading to the formation of a Ru–Ru bond. Thus reaction of  $\text{Ti}_2(\text{C}_5\text{H}_4\text{CH}_2\text{C}_5\text{H}_4)$  with  $[\text{Cl}_2\text{Ru}(\text{CO})_3]_2$  in a 1:1 ratio results in the formation of both  $\text{Ru}_2(\text{CO})_4(\eta^5, \eta^5\text{-C}_5\text{H}_4\text{CH}_2\text{C}_5\text{H}_4)$ , **I**, and  $[\text{Ru}(\text{CO})_2\text{Cl}]_2(\eta^5, \eta^5\text{-C}_5\text{H}_4\text{CH}_2\text{C}_5\text{H}_4)$ , **II** [1].

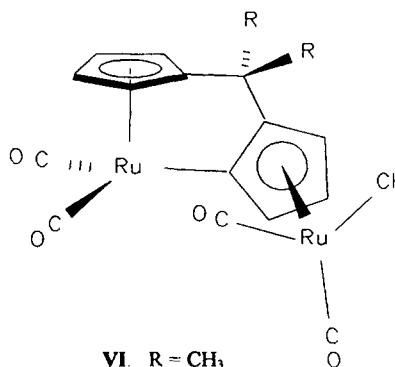
Changing the  $\text{Ti}_2(\text{C}_5\text{H}_4\text{CH}_2\text{C}_5\text{H}_4):[\text{Cl}_2\text{Ru}(\text{CO})_3]_2$  ratio to 2:1 resulted in the formation of a new product that could be easily separated from **I** by column chromatography on alumina or by fractional crystallization from octane. The new yellow, crystalline compound, **III**, was found to have two IR bands in the terminal carbonyl stretching region whose positions were similar to those reported by Campbell and Green for  $(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{CO})_2(\eta^1\text{-C}_5\text{H}_5)$  [3]. The  $^1\text{H}$  NMR spectrum



- I.**  $\text{L} = \text{CH}_2$   
**V.**  $\text{L} = \text{C}(\text{CH}_3)_2$   
**VII.**  $\text{L} = \text{Si}(\text{CH}_3)_2$   
**VIII.**  $\text{L} = \text{C}_2\text{H}_4$



- III.**  $\text{R} = \text{H}$   
**IV.**  $\text{R} = \text{CH}_3$



- VI.**  $\text{R} = \text{CH}_3$

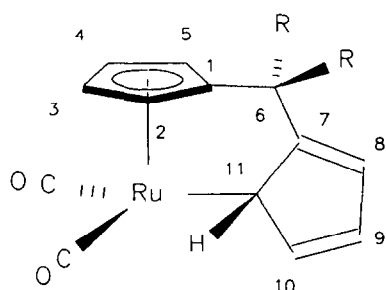


Fig. 1. Numbering scheme for **III** and **IV**.

contained both vinyl and cyclopentadienyl proton resonances. This spectroscopic evidence, along with mass spectrometry, indicates that **III** is best formulated as  $\text{Ru}(\text{CO})_2(\eta^5, \eta^1\text{-C}_5\text{H}_4\text{CH}_2\text{C}_5\text{H}_4)$  in which the pendant cyclopentadiene ring is twisted toward the metal to form a  $\sigma$ -bond. The probable structure predicted from models and the numbering scheme for this compound are presented in Fig. 1. One- and two-dimensional (COSY and NOESY)  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, and proton–carbon correlation spectra allowed all resonances to be assigned in the molecule. For example, NOE interactions between H-11 and H-2 and the connectivity established by COSY allowed assignment of all resonances on the  $\eta^5$ -ring. Further, long-range coupling between H-6<sub>a</sub> and H-11 ('W' pattern) permitted assignment of the two, magnetically inequivalent methylene hydrogens. The (C-11)–(H-11) group sigma bonded to the Ru is strongly shifted upfield relative to the vinyl C–H groups on the mono-hapto ring.

In order to determine whether the  $(\eta^5\text{-C}_5\text{H}_4\text{R})(\eta^1\text{-C}_5\text{H}_4\text{R})$  species are generally accessible products for ring-coupled bis(cyclopentadienyl) ligands, we expanded our investigation to include  $(\text{CH}_3)_2\text{C}$ -,  $(\text{CH}_3)_2\text{Si}$ - and  $\text{C}_2\text{H}_4$ -bridges between the cyclopentadienyl rings. In all cases, the neutral bis(cyclopentadiene) compounds were prepared by standard literature procedures. Bis(cyclopentadienylthallium) reagents were prepared by addition of thallos ethoxide to the bis(cyclopentadiene) compound in ethanol. The resultant thallium compounds precipitated immediately. The reagents were recovered by filtration and were washed with ethanol, ethyl ether and petroleum ether and used in subsequent syntheses without further purification. In the particular case of  $\text{Tl}_2(\text{C}_5\text{H}_4\text{C}_2\text{H}_4\text{C}_5\text{H}_4)$ , it was found late in this work that the thallium reagent was heavily contaminated (about 60%) with  $\text{TlBr}$  which appears to be produced by reaction of thallos ethoxide with residual dibromoethane from the synthesis of the ligand. As a consequence, bromo and mixed chloro–bromo derivatives were isolated from reactions with this material.

Reaction of  $\text{Tl}_2[\text{C}_5\text{H}_4(\text{CH}_3)_2\text{CC}_5\text{H}_4]$ , with  $[\text{Cl}_2\text{Ru}(\text{CO})_3]_2$  resulted in the formation of at least four products (by HPLC), three of which could be isolated and purified by column chromatography and recrystallization. A yellow crystalline compound, **IV**, was recovered from the first chromatographic band and shown by IR, NMR and mass spectrometry to be the analog of **III**. Multinuclear, one- and two-dimensional NMR permitted all resonances to be assigned.

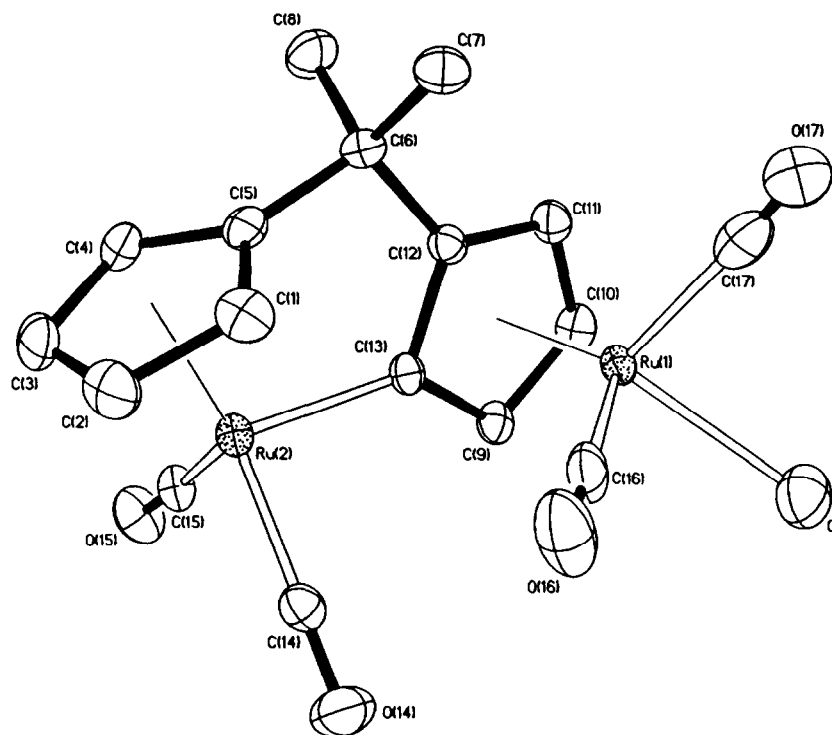


Fig. 2. Molecular structure of  $[\text{Ru}(\text{CO})_2][\text{Ru}(\text{CO})_2\text{Cl}][\eta^5, \eta^5: \eta^1\text{-C}_5\text{H}_4(\text{CH}_2)_2\text{CC}_5\text{H}_3]$ , **VI**.

The second, orange band from chromatography yielded an orange crystalline solid, **V**, that was shown to be an analog of **I**, on the basis of spectral and mass spectrometric data. Like **I**, **V** strongly favors a conformation in which all carbonyls are terminal, although the observation of carbonyl averaging in the  $^{13}\text{C}$  NMR spectrum (and a weak IR band in the bridging carbonyl region) indicates that a terminal-to-bridging equilibrium does occur.

In one synthetic batch we were able to isolate and purify a small quantity of a third component of the reaction mixture. An IR spectrum of the yellow, crystalline compound, **VI**, showed it to have four bands in

the carbonyl stretching region that suggested the presence of both  $\text{CpRu}(\text{CO})_2\text{R}$  and  $\text{CpRu}(\text{CO})_2\text{Cl}$  groups in the molecule. The  $^1\text{H}$  NMR spectrum of **VI** contained seven, well-defined multiplet resonances in the ring proton region and two distinct methyl resonances. COSY revealed that the four lower field resonances belonged to one ring, and long range coupling between two of these protons and the methyl groups allowed assignment of the protons  $\alpha$  and  $\beta$  to the bridge. The three upfield ring resonances are assigned to a second ring which must be  $\eta^1$  to one ruthenium and  $\eta^5$  to the second. The  $^{13}\text{C}$  NMR spectrum shows seven hydrogen substituted ring resonances and three *ipso* resonances, which are

Table 1  
Crystallographic data for **VI**, **VII**, and **XI**

	<b>VI</b>	<b>VII</b>	<b>XI</b>
<i>Crystal parameters</i>			
Formula	$\text{C}_{17}\text{H}_{13}\text{ClO}_4\text{Ru}_2$	$\text{C}_{16}\text{H}_{14}\text{O}_4\text{Ru}_2\text{Si}$	$\text{C}_{16}\text{H}_{12}\text{BrClO}_4\text{Ru}_2$
Formula weight	518.9	500.5	585.76
Crystal system	triclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/n$	$C2/c$
<i>a</i> (Å)	7.812(3)	11.036(2)	25.237(3)
<i>b</i> (Å)	9.004(2)	13.660(2)	6.049(1)
<i>c</i> (Å)	12.773(5)	11.621(2)	12.646(2)
$\alpha$ (deg)	84.33(3)	—	—
$\beta$ (deg)	75.26(3)	105.83(2)	109.73(1)
$\gamma$ (deg)	80.93(3)	—	—
<i>V</i> (Å <sup>3</sup> )	857.3(6)	1688.6(5)	1817(2)
<i>Z</i>	2	4	4
Crystal dimensions (mm <sup>3</sup> )	0.22 × 0.24 × 0.32	0.21 × 0.30 × 0.35	0.23 × 0.32 × 0.35
Crystal color	yellow	orange	red
<i>D</i> (calc) (g cm <sup>-3</sup> )	2.010	1.969	1.999
( <i>Mo K α</i> ) (cm <sup>-1</sup> )	19.34	18.4	38.51
Temp. (K)	298	293	298
<i>T</i> (max)/ <i>T</i> (min)	1.42	1.21	2.34
<i>Data collection</i>			
Diffractometer	Siemens P4	Nicolet R3m/μ	Siemens P4
Monochromator		graphite	
Radiation		<i>Mo K α</i> ( $\lambda = 0.71073 \text{ \AA}$ )	
2 $\theta$ scan range (deg)	4–60	4–60	4–55
Data collected ( <i>h</i> , <i>i</i> , <i>l</i> )	± 10, ± 12, + 17	± 15, + 17, + 13	± 32, + 7, + 15
Reflections collected	5201	5330	2138
Independent reflections	4993	4909	2095
Independent observed	4094 ( <i>n</i> = 4)	4111 ( <i>n</i> = 3)	1649 ( <i>n</i> = 5)
reflections			
$F_o \geq n\sigma(F_o)$			
Std./rfln	3/197	3/197	3/197
var. in stds. (%)	< 1	< 1	1
<i>Refinement</i>			
<i>R</i> ( <i>F</i> ) (%)	3.52	2.68	4.37
<i>R</i> ( <i>wF</i> ) (%)	4.77	3.22	5.87
$\Delta\sigma$ (max)	0.004	0.01	0.00
$\Delta(\rho)$ (e Å <sup>-3</sup> )	0.85	0.63	0.66
<i>N</i> <sub>o</sub> / <i>N</i> <sub>v</sub>	18.9	18.9	15.1
GOF	1.14	0.963	1.41

<sup>a</sup> Quantity minimized =  $\Sigma w\Delta^2$ ;  $R = \Sigma\Delta/\Sigma(F_o)$ ;  $R(w) = \Sigma\Delta w^{1/2}/\Sigma(F_o w^{1/2})$ ,  $\Delta = |F_o - F_c|$ .

Table 2  
Selected bond lengths (Å) and angles (deg) for VI

Bond lengths			
Ru(1)–C(16)	1.933(6)	C(14)–O(14)	1.126(7)
Ru(1)–C(17)	1.991(6)	C(15)–O(15)	1.146(5)
Ru(1)–Cl	2.428(2)	C(16)–O(16)	1.058(7)
Ru(1)–CNT <sup>a</sup>	1.888	C(17)–O(17)	0.885(8)
Ru(2)–C(14)	1.887(5)		
Ru(2)–C(15)	1.883(4)		
Ru(2)–C(13)	2.054(3)		
Ru(2)–CNT	1.891		
Bond angles			
C(16)–Ru(1)–Cl	91.5(1)	C(13)–Ru(2)–C(14)	92.3(2)
C(17)–Ru(1)–Cl	89.3(2)	C(13)–Ru(2)–C(15)	93.5(1)
C(16)–Ru(1)–C(17)	90.6(2)	C(14)–Ru(2)–C(15)	90.2(2)

<sup>a</sup> CNT is the centroid of  $\eta^2$ -C<sub>5</sub> ring.

consistent with the presence of an  $\eta^5$ -Cp and an  $\eta^1$ : $\eta^5$ -Cp. Four resonances were observed in the Ru–CO region arising from two distinct ruthenium carbonyl environments as well as the chiral nature of the molecule.

Crystals of VI were grown by vapor diffusion of pentane into a dichloromethane solution of VI. An X-ray crystallographic analysis of the crystals revealed the 'twisted' structure shown in Fig. 2. Selected bond lengths and angles for VI are presented in Table 1 and crystallographic data is presented in Table 2. The two cyclopentadienyl rings are found to be effectively perpendicular to one another. The average of the interligand angles on the two ruthenium atoms are about 90°. No bond metric shows any significant deviation from the norm as a result of the formation of the Ru–Cp  $\sigma$ -bond.

We presume that [Ru(CO)<sub>2</sub>Cl]<sub>2</sub>( $\eta^5$ , $\eta^5$ -C<sub>5</sub>H<sub>4</sub>(CH<sub>3</sub>)<sub>2</sub>-CC<sub>5</sub>H<sub>4</sub>) is also formed in this reaction but were unable to isolate an uncontaminated sample of this material.

The relative proportions of IV and V can be shifted by altering the ratio of thallium and ruthenium reagents in the initial synthesis, but both compounds are isolated from 2:1 and 1:1 reactions. In contrast, only I has been observed in 1:1 reactions. Similarly, reaction of Tl<sub>2</sub>[C<sub>5</sub>H<sub>4</sub>(CH<sub>3</sub>)<sub>2</sub>SiC<sub>5</sub>H<sub>4</sub>] with [Cl<sub>2</sub>Ru(CO)<sub>3</sub>]<sub>2</sub> in a 1:1 ratio yields only the bimetallic compound, VII, as a yellow crystalline solid. In contrast to II and IV, VII was found by IR to strongly favor a conformation with two terminal and two bridging carbonyl groups. Again <sup>13</sup>C NMR indicates that carbonyl averaging does occur. An X-ray crystallographic analysis established that VII retains the bridging carbonyl form in the solid state, with the bridging dimethylsilyl group shifted slightly off the vertical, perhaps to accommodate the short Ru–Ru distance. The structure of VII is shown in Fig. 3 and bond lengths and angles are presented in Table 3. Crystallographic data is presented in Table 2. By way of comparison, Ru<sub>2</sub>(CO)<sub>4</sub>( $\eta^5$ , $\eta^5$ -C<sub>5</sub>H<sub>4</sub>CH<sub>2</sub>C<sub>5</sub>H<sub>4</sub>) [5] and

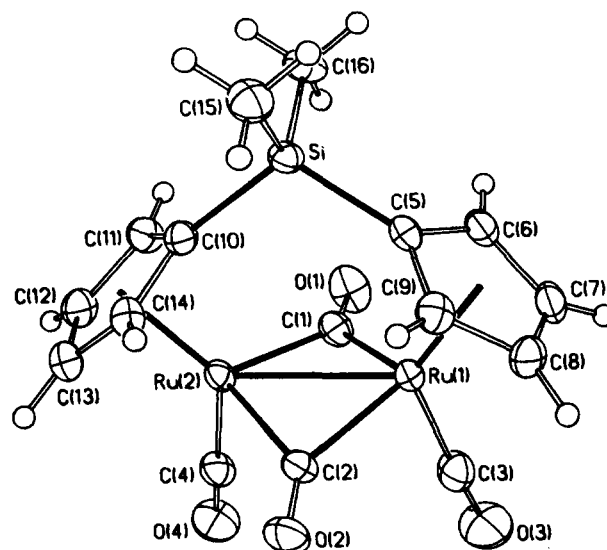


Fig. 3. Molecular structure of [Ru<sub>2</sub>(CO)<sub>4</sub>][ $\eta^5$ , $\eta^5$ -C<sub>5</sub>H<sub>4</sub>(CH<sub>3</sub>)<sub>2</sub>SiC<sub>5</sub>H<sub>4</sub>], VII.

W<sub>2</sub>(CO)<sub>6</sub>[ $\eta^5$ , $\eta^5$ -C<sub>5</sub>H<sub>4</sub>(CH<sub>3</sub>)<sub>2</sub>SiC<sub>5</sub>H<sub>4</sub>] [6] have been found to have C<sub>2</sub> symmetry. The observed ring-silicon and silicon–methyl bond lengths in VII are almost identical to those reported for the tungsten compound. The Ru–Ru distance in VII, 2.7042 Å, is shorter than that of *trans*-Ru<sub>2</sub>(CO)<sub>4</sub>( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub> [7], 2.735 Å, which we attribute to bond compression caused by the coupled rings. A similar bond compression is observed for the W–W bond when one compares the unbridged com-

Table 3  
Bond lengths (Å) and angles (deg) for VII

Bond distances			
Ru(1)–Ru(2)	2.7042(4)	C(1)–O(1)	1.176(4)
Ru(1)–C(1)	2.027(3)	C(2)–O(2)	1.168(4)
Ru(1)–C(2)	2.036(3)	C(3)–O(3)	1.143(6)
Ru(1)–C(3)	1.865(4)	C(4)–O(4)	1.132(5)
Ru(1)–CNT <sup>a</sup>	1.905(3)	Si–C(5)	1.889(3)
Ru(2)–C(1)	2.040(3)	Si–C(10)	1.875(3)
Ru(2)–C(2)	2.054(3)		
Ru(2)–C(4)	1.868(4)		
Ru(2)–CNT	1.920(3)		
Bond angles			
CNT(1)–Ru(1)–Ru(2)	126.9(1)	C(1)–Ru(2)–C(4)	87.5(1)
CNT(1)–Ru(1)–C(1)	121.3(2)	C(2)–Ru(2)–C(4)	89.3(1)
CNT(1)–Ru(1)–C(2)	122.8(2)	Ru(1)–C(1)–Ru(2)	83.3(1)
CNT(1)–Ru(1)–C(3)	128.9(2)	Ru(1)–C(2)–Ru(2)	82.8(1)
C(1)–Ru(1)–C(2)	94.2(1)	Ru(1)–C(1)–O(1)	138.3(3)
C(1)–Ru(1)–C(3)	89.2(1)	Ru(1)–C(2)–O(2)	138.3(3)
C(2)–Ru(1)–C(3)	90.6(2)	Ru(1)–C(3)–O(3)	177.8(4)
CNT(2)–Ru(2)–Ru(1)	126.9(1)	Ru(2)–C(1)–O(1)	137.8(3)
CNT(2)–Ru(2)–C(1)	122.9(2)	Ru(2)–C(2)–O(2)	138.5(3)
CNT(2)–Ru(2)–C(2)	121.6(2)	Ru(2)–C(4)–O(4)	178.3(3)
CNT(2)–Ru(2)–C(4)	131.4(2)	C(5)–Si–C(10)	109.7(2)
C(1)–Ru(2)–C(2)	93.5(1)	C(15)–Si–C(16)	114.3(2)

<sup>a</sup> CNT is the centroid of  $\eta^5$ -C<sub>5</sub> ring.

compound with its  $(\text{CH}_3)_2\text{Si}$  and  $\text{CH}_2$  bridged analogs [6,8].

Reaction of the  $\text{Ti}_2(\eta^5, \eta^5\text{-C}_5\text{H}_4\text{C}_2\text{H}_4\text{C}_5\text{H}_4)\text{-TiBr}$  mixture with  $[\text{Cl}_2\text{Ru}(\text{CO})_3]_2$  yielded a product mixture that was shown by HPLC to contain at least six components, only four of which were obtained in sufficient quantity to characterize. Column chromatography of the reaction mixture yielded a faint initial band that was shown by IR to contain a compound with terminal carbonyl bands similar in position to those of **III** and **IV**. There was insufficient sample for NMR analysis.

The second, orange band yielded the bimetallic compound, **VIII**. **VIII** adopts a conformation that favors bridging carbonyl groups that were found by  $^{13}\text{C}$  NMR to undergo exchange at room temperature. The room temperature  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra are simple, with two ring proton resonances and a singlet for the bridge resonances indicating fluxional averaging of ring and bridge proton environments at this temperature.

The third, orange band, **IX**, yielded a compound that was found by IR to have four bands in the terminal carbonyl region, whose positions, like those of **VI** described above, indicated that the molecule contains both  $\text{CpRu}(\text{CO})_2\text{R}$  and  $\text{CpRu}(\text{CO})_2\text{Halide}$  components. Continuing the analogy with **VI**,  $^1\text{H}$  NMR of **IX** indicated no resonances in the vinyl region, but rather seven cyclopentadienyl resonances were observed. The  $\text{C}_2\text{H}_4$ -bridge resonances appeared as four well-resolved multiplets that were shown to be doublets of doublets of doublets. A COSY spectrum permitted identification of the geminal resonances on the bridge, and a Karplus analysis of the coupling constants yielded a self-consistent conformation of the  $\text{C}_2\text{H}_4$  bridge. COSY also allowed the cyclopentadienyl resonances to be divided into two sets, of four and three resonances respectively. COSY and NOESY spectra provided additional evidence for interactions between ring and bridge resonances that established the connectivity of the bridge. NOE interactions between H-5, H-4 and H-11 aided in establishing both the conformation of the molecule and also the complete proton resonance assignments. Fi-

nally,  $^1\text{H}$ - $^{13}\text{C}$  correlation spectra were used to assign the carbon resonances.

Mass spectrometry and elemental analysis of this sample revealed unequivocally that the parent mass corresponded to a compound of formula  $\text{C}_{16}\text{H}_{11}\text{BrO}_4\text{-Ru}_2$ , rather than the chloro derivative as anticipated. The bromide is believed to come from halide exchange between the TiBr contaminant and the various Ru-Cl compounds during synthesis.

Using the spectral data and Dreiding stereomodels, a probable conformation of **IX** with one  $\eta^5\text{-Cp}$  and one  $\eta^1:\eta^5\text{-Cp}$  was developed, Fig. 4. The numbering scheme for this molecule is also presented. The relative orientations of the  $\eta^5$ - and  $\eta^1\text{-C}_5\text{H}_4$  rings in **IX** differ substantially from those in **III**, **IV**, or **VII** in that the single carbon bridge in these compounds requires that the  $\eta^1:\eta^5\text{-Cp}$  ring be almost perpendicular to the  $\eta^5\text{-Cp}$  ring while the two carbon bridge in **IX** permits the planes of the two rings to be effectively parallel to one another.

Continued elution of the mixtures from the reactions of the  $\text{Ti}_2(\text{C}_5\text{H}_4\text{C}_2\text{H}_4\text{C}_5\text{H}_4)\text{-TiBr}$  and  $[\text{ClRu}(\text{CO})_3]_2$  isolated two compounds, **X** and **XI**. **X** was found by IR to have bands diagnostic of a  $\text{CpRu}(\text{CO})_2\text{halide}$  moiety and subsequent mass spectrometry found a fragmentation pattern consistent with **X** being  $[\text{Ru}(\text{CO})_2\text{Br}]_2(\eta^5, \eta^5\text{-C}_5\text{H}_4\text{C}_2\text{H}_4\text{C}_5\text{H}_4)$  although the parent fragment was not observed. Attempts to employ fast atom bombardment mass spectrometry (FABMS) were unsuccessful, apparently due to the ready exchange of halide ions with the alcohol matrix. Negative ion mass spectrometry confirmed the presence of Br in the sample.  $^1\text{H}$  NMR of **X** is simple, consisting of two ring proton resonances and a singlet resonance for the bridge indicating a symmetric molecule that is experiencing rapid averaging of the ring and bridge environments.

Curiously, the IR and EI/CI mass spectrometry of **XI** appeared initially to be identical to those of **X**. Again, FABMS was unsuccessful because of halide exchange with the alcohol matrix. Ultimately, negative ion mass spectrometry demonstrated that Br was present

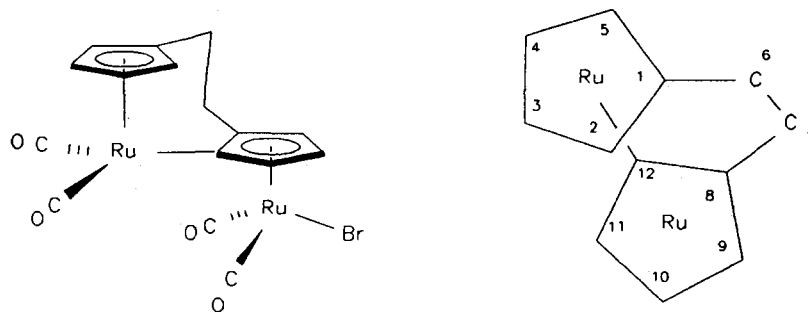


Fig. 4. Proposed conformation and numbering scheme for **IX**.

Table 4  
Bond lengths (Å) and angles (deg) for **XI**

Bond lengths			
Ru–CNT	1.871	C(3)–C(8)	1.487(10)
Ru–Br/Cl	2.477(1)	C(8)–C(8a)	1.510(15)
Ru–C(1)	1.891(6)	C(1)–O(1)	1.142(9)
Ru–C(2)	1.876(7)	C(2)–O(2)	1.126(10)
Bond angles			
CNT–Ru–Br/Cl	122.0	C(1)–Ru–C(2)	90.3(3)
CNT–Ru–C(1)	125.5	C(1)–Ru–Br/Cl	91.9(3)
CNT–Ru–C(2)	125.6	C(2)–Ru–Br/Cl	91.5(3)
C(3)–C(8)–C(8a)	113.7(7)		

<sup>a</sup> CNT is the centroid of  $\eta^5$ -C<sub>5</sub> ring.

in the compound, but Cl was below the mass resolution minimum of the instrument. A molecular structure (vide infra) provides evidence that **XI** is the mixed halide analog of **X**. The similarity in mass spectrometry arises from the absence of a parent mass and the coincidental overlap of the envelopes of the Cl-containing fragments with those of other fragments. The plethora of isotopes for Ru, Cl, and Br make for very broad envelopes that cannot be effectively teased apart.

X-ray crystallography was performed on a crystal of **XI** grown by vapor phase diffusion of pentane into a dichloromethane solution. **XI** was found to assume the expected conformation with the two Ru(CO)<sub>2</sub>X groups anti to one another (Fig. 5). Br and Cl are found to have equal occupancy at each metal, resulting in an apparent C<sub>2</sub> symmetry. Bond lengths and angles are presented in Table 4 and crystallographic data are presented in Table 2. The structure of **XI** appears to be unexceptional in the solid state.

The <sup>1</sup>H NMR spectrum of **XI** is consistent with expectations, having four resonances in the ring proton

region and a complex AA'BB' pattern for the bridge protons. In the <sup>13</sup>C NMR spectrum, four hydrogen-bearing ring carbon resonances and two Ru–CO resonances are consistent with expectations; however, both *ipso* resonances are split and there are four, not two, resonances for the C<sub>2</sub>H<sub>4</sub>-bridge carbons. These features persist even for NMR samples made from single crystals of highly purified material. Although we might speculate about possible dipolar contacts between the dissimilar ends of the molecule, such contacts seem unlikely to persist at room temperature in a polar solvent (CDCl<sub>3</sub>). We presently have no explanation for these observations.

### 3. Experimental

Bis(cyclopentadienyl) compounds (CH<sub>3</sub>)<sub>2</sub>C(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub> [9], (CH<sub>3</sub>)<sub>2</sub>Si(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub> [10], and C<sub>2</sub>H<sub>4</sub>(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub> [11] were prepared by literature procedures. Bis(cyclopentadienylthallium)methane was prepared as previously reported [1]. <sup>29</sup>Si NMR spectra were recorded using a Bruker 250 MHz NMR at the University of Maryland.

#### 3.1. General synthesis of bis(cyclopentadienylthallium) reagents

(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>L, where L = (CH<sub>3</sub>)<sub>2</sub>C, (CH<sub>3</sub>)<sub>2</sub>Si, or C<sub>2</sub>H<sub>4</sub>, (20 mmol) were taken up in ethanol (50 ml) in a 100 ml round bottom flask equipped with a septum and nitrogen purge. Thallous ethoxide (10.0 g, 40 mmol) was added dropwise with stirring. Formation of a cloudy precipitate was immediate. After addition of the thallium ethoxide, the mixture was stirred for 1 h. It was occasionally necessary to break up the heavy precipitate

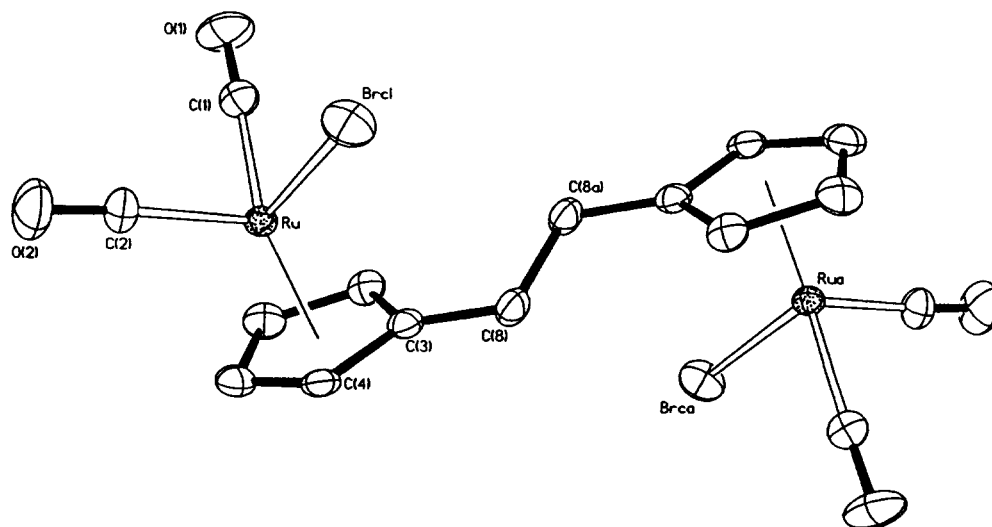


Fig. 5. Molecular structure of [Ru(CO)<sub>2</sub>Br][Ru(CO)<sub>2</sub>Cl][ $\eta^5$ , $\eta^5$ -C<sub>5</sub>H<sub>4</sub>C<sub>2</sub>H<sub>4</sub>C<sub>5</sub>H<sub>4</sub>], **XI**.

with a spatula and complete the final mixing with mechanical stirring. The resulting precipitate was collected by filtration, washed with ethanol, followed by ethyl ether and pentane. The resulting solid was dried under vacuum and used without further purification. Yields:  $(\text{CH}_3)_2\text{C}(\text{C}_5\text{H}_4\text{Tl})_2$ , 72%;  $(\text{CH}_3)_2\text{Si}(\text{C}_5\text{H}_4\text{Tl})_2$ , 85%.  $\text{C}_2\text{H}_4(\text{C}_5\text{H}_4\text{Tl})_2$  was subsequently found to be contaminated with about 60%  $\text{TlBr}$ .

Bis(cyclopentadienylthallium) compounds are too insoluble in common organic solvents to permit solution NMR spectral studies. Caution: thallium compounds are highly toxic and should only be handled with appropriate safety precautions.

### 3.2. Synthesis of $\text{Ru}_2(\text{CO})_4(\eta^5, \eta^5\text{-C}_5\text{H}_4\text{CH}_2\text{C}_5\text{H}_4)$ , **I**, and $\text{Ru}(\text{CO})_2(\eta^5, \eta^1\text{-C}_5\text{H}_4\text{CH}_2\text{C}_5\text{H}_4)$ , **III**

$\text{Tl}_2(\text{C}_5\text{H}_4\text{CH}_2\text{C}_5\text{H}_4)$  (2.0 g, 3.6 mmol) and  $[\text{RuCl}_2(\text{CO})_3]_2$  (0.93 g, 3.6 mmol) were taken up in benzene and refluxed overnight. After filtration and removal of solvent, the orange oil was chromatographed on alumina using benzene as an eluant. A single golden band was eluted and was shown by HPLC to consist of two components. After removal of solvent, the mixture was rechromatographed on alumina using petroleum ether as an eluant. A yellow band was rapidly eluted from the column followed by a golden band. Removal of solvent from the first band recovered **III** as yellow plates. M.p. 118–120 °C. Yield: 0.22 g, 21%. IR:  $(\text{CH}_2\text{Cl}_2)$  2018, 1960  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR:  $(\text{C}_6\text{D}_6)$  6.80 (d,  $J_{9-10} = 5$  Hz, H-9), 6.40 (dd,  $J_{9-10} = 5$  Hz,  $J_{10-11} = 2$  Hz, H-10), 5.62 (b singlet, H-8), 5.46 (m, H-2), 5.29 (m, H-5), 5.07 (m, H-4), 4.81 (m, H-3), 4.51 (b singlet, H-11), 3.33 (d, AB,  $J = 14.0$  Hz,  $\text{CH}_2$ , H-6<sub>a</sub>), 3.01 (d, AB,  $J = 14.0$  Hz,  $\text{CH}_2$ , H-6<sub>b</sub>).  $^{13}\text{C}$  NMR:  $(\text{C}_6\text{D}_6)$  201.7 (Ru–CO), 200.4 (Ru–CO), 155.7 (*ipso*  $\eta^1\text{-C}_5\text{H}_5$ ), 142.8 ( $\eta^1\text{-C}_5\text{H}_5$ , C-10), 123.4 ( $\eta^1\text{-C}_5\text{H}_5$ , C-9), 115.0 (*ipso* Cp), 112.9 ( $\eta^1\text{-C}_5\text{H}_5$ , C-8), 89.2 (Cp), 88.7 (Cp), 83.1 (Cp), 81.4 (Cp), 37.4 ( $\eta^1\text{-C}_5\text{H}_5$ , C-11), 27.1 ( $\text{CH}_2$ ). Mass spectrometry: (EI,  $^{101}\text{Ru}$ ) 299 (20,  $\text{M}^+$ ), 271 (1,  $\text{M}^+ - \text{CO}$ ), 243 (55,  $\text{M}^+ - 2\text{CO}$ ). Anal. Found: C, 52.43; H, 3.17.  $\text{C}_{13}\text{H}_{10}\text{O}_2\text{Ru}$ . Calc. C, 52.16; H, 3.34%. Second band was shown to be identical to an authentic sample of  $\text{CH}_2[\eta^5\text{-C}_5\text{H}_4\text{Ru}(\text{CO})_2]_2$ . Yield: 40 mg, 2%.

### 3.3. Synthesis of $\text{Ru}(\text{CO})_2[\eta^5, \eta^1\text{-C}_5\text{H}_4(\text{CH}_3)_2\text{CC}_5\text{H}_4]$ , **IV**, $\text{Ru}_2(\text{CO})_4[\eta^5, \eta^5\text{-C}_5\text{H}_4(\text{CH}_3)_2\text{CC}_5\text{H}_4]$ , **V**, and $[\text{Ru}(\text{CO})_2][\text{Ru}(\text{CO})_2\text{Cl}]_2[\eta^5, \eta^5\text{-C}_5\text{H}_4(\text{CH}_3)_2\text{CC}_5\text{H}_4]$ , **VI**

$\text{Tl}_2[\text{C}_5\text{H}_4(\text{CH}_3)_2\text{CC}_5\text{H}_4]$  (2.24 g, 3.9 mmol) and  $[\text{RuCl}_2(\text{CO})_3]_2$  (1.97 g, 3.9 mmol) were taken up in benzene and refluxed for 12 h. After filtration and removal of solvent the dark brown oily residue was taken up in benzene and chromatographed on alumina using benzene as the eluant. A yellow band eluted

quickly followed by a second yellow band that was collected separately.

HPLC of the yellow solid from the first band indicated two components. Fractional crystallization from hot octane recovered **V** as dark yellow needles that were shown to be pure by HPLC. M.p. 217–219 °C. Yield: 120 mg, 6%. IR:  $(\text{CH}_2\text{Cl}_2)$  2013 (s), 1961 (s), 1941 (s), 1920 (sh), 1775 (w)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR:  $(\text{C}_6\text{D}_6)$  4.79 (t, 4H, Cp), 4.39 (t, 4H, Cp), 0.93 (s, 6H,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR:  $(\text{C}_6\text{D}_6)$  205.7 (Ru–CO), 105.2 (*ipso* Cp), 84.4 (Cp), 80.8 (Cp), 35.1 ( $\text{C}(\text{CH}_3)_2$ ), 29.8 ( $\text{CH}_3$ ). Mass spectrometry: (EI,  $^{101}\text{Ru}$ ) 484 (52,  $\text{M}^+$ ), 456 (26,  $\text{M}^+ - \text{CO}$ ), 428 (60,  $\text{M}^+ - 2\text{CO}$ ), 400 (71,  $\text{M}^+ - 3\text{CO}$ ), 372 (90,  $\text{M}^+ - 4\text{CO}$ ), 327 (13,  $\text{Me}_2\text{CCp}_2\text{Ru}(\text{CO})_2^+$ ), 299 (9,  $\text{Me}_2\text{CCp}_2\text{RuCO}^+$ ), 272 (34,  $\text{Me}_2\text{CCp}_2\text{RuH}^+$ ). Anal. Found: C, 42.44; H, 2.89.  $\text{C}_{17}\text{H}_{14}\text{O}_4\text{Ru}_2$ . Calc. C, 42.14; H, 2.89%.

Subsequent column chromatography of the octane soluble material on alumina with petroleum ether cleanly separated a rapidly moving yellow band from a small additional amount of **V**. Removal of solvent from the rapidly moving band recovered **IV** as yellow plates. M.p. 73–77 °C. Yield: 64 mg, 6%. IR:  $(\text{CH}_2\text{Cl}_2)$  2017, 1959  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR:  $(\text{C}_6\text{D}_6)$  6.72 (d,  $J_{9-10} = 5$  Hz, H-10), 6.45 (q,  $J_{9-10} = 5$  Hz,  $J_{10-11} = 2$  Hz, H-9), 5.74 (b singlet, H-8), 5.44 (m, H-4), 5.28 (m, H-3), 5.23 (m, H-5), 4.82 (m, H-2), 4.40 (m, H-11), 1.65 (s,  $\text{CH}_3$ ), 1.23 (s,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR:  $(\text{C}_6\text{D}_6)$  202.3 (Ru–CO), 201.0 (Ru–CO), 166.2 (*ipso*  $\eta^1\text{-C}_5\text{H}_4$ ), 142.8 ( $\eta^1\text{-C}_5\text{H}_4$ , C-10), 123.4 ( $\eta^1\text{-C}_5\text{H}_4$ , C-9), 122.6 (*ipso* Cp), 108.5 ( $\eta^1\text{-C}_5\text{H}_4$ , C-8), 88.4 (Cp), 88.1 (Cp), 80.5 (Cp), 78.5 (Cp), 34.6 ( $\eta^1\text{-C}_5\text{H}_4$ , C-11), 32.1 ( $\text{CMe}_2$ ), 26.3 ( $\text{CH}_3$ ), 24.0 ( $\text{CH}_3$ ). Mass spectrometry: (CI,  $^{101}\text{Ru}$ ) 327 (30,  $\text{M}^+$ ), 299 (12,  $\text{M}^+ - \text{CO}$ ), 271 (77,  $\text{M}^+ - 2\text{CO}$ ). Anal. Found: C, 54.97; H, 4.32.  $\text{C}_{15}\text{H}_{14}\text{O}_2\text{Ru}$ . Calc.: C, 55.03; H, 4.28%.

The second, rapidly moving band from the column of the original reaction mixture was shown by HPLC to consist of a complex mixture of products. IR  $(\text{CH}_2\text{Cl}_2)$  of the mixture contained bands at 2051, 2033, 1999, and 1982  $\text{cm}^{-1}$ , indicating the presence of species with  $\text{Ru}(\text{CO})_2\text{Cl}$  and  $\text{Ru}(\text{CO})_2\text{R}$  functions. Careful chromatography of this mixture on alumina using 20% dichloromethane in petroleum ether eluted a broad yellow band within which was a distinct orange band. Isolation of this orange band, followed by rechromatography under identical conditions, gave a small amount of yellow solid that was further purified by recrystallization from dichloromethane by solvent exchange with pentane to give **VI** as yellow crystals. M.p. 180 °C with decomp. Yield: 25 mg, 1%. IR:  $(\text{CH}_2\text{Cl}_2)$  2047, 2033, 1998, 1983  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR:  $(\text{CDCl}_3)$  5.76 (m, H-2), 5.71 (m, H-3), 5.59 (m, H-4), 5.26 (m, H-5), 4.97 (m, Cp-2), 4.91 (m, Cp-2), 4.85 (m, Cp-2), 1.60 (s, 3H,  $\text{CH}_3$ ), 1.50 (s, 3H,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR:  $(\text{CDCl}_3)$  198.6 (Ru–CO), 197.9 (Ru–CO), 197.6 (Ru–CO), 197.2



(Ru–CO), 137.7 (*ipso* Cp), 137.0 (*ipso* Cp), 132.5 (*ipso* Cp) 93.0 (Cp), 87.4 (Cp), 84.7 (Cp), 84.2 (Cp), 82.7 (Cp), 81.5 (Cp), 36.8 (C(CH<sub>3</sub>)<sub>2</sub>), 32.4 (CH<sub>3</sub>), 29.1 (CH<sub>3</sub>).

### 3.4. Synthesis of Ru<sub>2</sub>(CO)<sub>4</sub>[η<sup>5</sup>,η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>(CH<sub>3</sub>)<sub>2</sub>SiC<sub>5</sub>H<sub>4</sub>], VII

Tl<sub>2</sub>[C<sub>5</sub>H<sub>4</sub>(CH<sub>3</sub>)<sub>2</sub>SiC<sub>5</sub>H<sub>4</sub>] (5.4 g, 9.1 mmol) and [RuCl<sub>2</sub>(CO)<sub>3</sub>]<sub>2</sub> (4.73 g, 9.1 mmol) were refluxed in benzene overnight. After filtration and removal of solvent, the resultant brown oil was chromatographed on alumina with 1:1 petroleum ether:dichloromethane to yield a single golden band that was shown by HPLC to consist of a mixture in which Ru<sub>2</sub>(CO)<sub>4</sub>(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub> was present as a contaminant. Chromatography of the mixture on alumina with 15% dichloromethane in petroleum ether eluted two yellow bands, the first of which was shown to be VII. After removal of solvent and recrystallization from heptane, VII was recovered as yellow needles. M.p. 154–156 °C. Yield: 0.36 g, 7.9%. IR: (CH<sub>2</sub>Cl<sub>2</sub>) 2012, 2002, 1963, 1939, 1776 cm<sup>-1</sup>. <sup>1</sup>H NMR: (CDCl<sub>3</sub>) 5.70 (t, 4H, Cp, H-3, H-4), 5.19 (t, 4H, Cp, H-2, H-5), 0.42 (s, 6H, Si(CH<sub>3</sub>)<sub>2</sub>, J<sub>Si-H</sub> = 10 Hz). <sup>13</sup>C NMR: (CDCl<sub>3</sub>) 95.3 (Cp), 88.9 (Cp), 86.0 (*ipso* Cp), -2.53 (Si(CH<sub>3</sub>)<sub>2</sub>). <sup>29</sup>Si NMR: (CDCl<sub>3</sub>) -10.93. Mass spectrometry: (EI, <sup>101</sup>Ru) 500 (40, M<sup>+</sup>), 472 (21, M<sup>+</sup>-CO), 444 (45, M<sup>+</sup>-2CO), 416 (73, M<sup>+</sup>-3CO), 388 (73, M<sup>+</sup>-4CO). Anal. Found: C, 38.34; H, 2.89. C<sub>16</sub>H<sub>14</sub>O<sub>4</sub>Ru<sub>2</sub>Si. Calc.: C, 38.40; H, 2.80%.

### 3.5. Synthesis of Ru<sub>2</sub>(CO)<sub>4</sub>(η<sup>5</sup>,η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>C<sub>2</sub>H<sub>4</sub>C<sub>5</sub>H<sub>4</sub>), VIII, [Ru(CO)<sub>2</sub>][Ru(CO)<sub>2</sub>Br](η<sup>5</sup>,η<sup>5</sup>:η<sup>1</sup>-C<sub>5</sub>H<sub>4</sub>C<sub>2</sub>H<sub>4</sub>-C<sub>5</sub>H<sub>3</sub>), IX, [Ru(CO)<sub>2</sub>Br]<sub>2</sub>(η<sup>5</sup>,η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>C<sub>2</sub>H<sub>4</sub>C<sub>5</sub>H<sub>4</sub>), X, and [Ru(CO)<sub>2</sub>Br][Ru(CO)<sub>2</sub>Cl](η<sup>5</sup>,η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>C<sub>2</sub>H<sub>4</sub>C<sub>5</sub>-H<sub>4</sub>), XI

Tl<sub>2</sub>(C<sub>5</sub>H<sub>4</sub>C<sub>2</sub>H<sub>4</sub>C<sub>5</sub>H<sub>4</sub>) (2.18 g, 1.54 mmol corrected for TlBr) and [RuCl<sub>2</sub>(CO)<sub>3</sub>]<sub>2</sub> (2.0 g, 3.9 mmol) were taken up in benzene and refluxed for 24 h. After filtration and removal of solvent, the residue was chromatographed on alumina with benzene as an eluant. Three yellow bands could be eluted in succession from the column. A faint, fourth band was observed, but was not isolated.

The first yellow band was shown by HPLC to contain two components, thus this band was rechromatographed on alumina with 1:1 benzene:petroleum ether to give two yellow bands. Removal of solvent from the first of these bands gave VIII as a yellow powder. M.p. 210 °C with decomp. Yield: 0.67 g, 37%. IR: (CH<sub>2</sub>Cl<sub>2</sub>) 1998, 1958, 1771 cm<sup>-1</sup>. <sup>1</sup>H NMR: (CDCl<sub>3</sub>) 5.54 (t, AA'BB', Cp), 5.26 (t, AA'BB', Cp), 2.45 (s, 4 H, C<sub>2</sub>H<sub>4</sub>). <sup>13</sup>C NMR: (CDCl<sub>3</sub>) 105.4 (*ipso* Cp), 94.4 (Cp), 83.9 (Cp), 25.6 (C<sub>2</sub>H<sub>4</sub>). Mass Spec-

trometry: (EI, <sup>101</sup>Ru) 470 (34, M<sup>+</sup>), 442 (12, M<sup>+</sup>-CO) 414 (28, M<sup>+</sup>-2CO), 386 (62, M<sup>+</sup>-3CO), 358 (100, M<sup>+</sup>-4CO). High resolution mass spectrometry: Calculated for C<sub>16</sub>H<sub>12</sub>O<sub>4</sub><sup>100</sup>Ru, <sup>102</sup>Ru: 469.88212. Found: 469.88212. Calculated for C<sub>16</sub>H<sub>12</sub>O<sub>4</sub><sup>101</sup>Ru, <sup>102</sup>Ru: 470.88349. Found: 470.88349.

The second band from rechromatography on alumina gave IX as a yellow powder. M.p. 137–140 °C. Yield: 20 mg, 1%. IR: (CH<sub>2</sub>Cl<sub>2</sub>) 2043, 2029, 1986, 1976 cm<sup>-1</sup>. <sup>1</sup>H NMR: (CDCl<sub>3</sub>) 5.48 (t, 1H, H-11), 5.40 (m, 3H, H-3, H-4, H-12), 5.13 (m, 2H, H-2, H-5), 4.68 (t, 1H, H-10), 2.78 (1 H, H-6a, ddd, J<sub>6a-7a</sub> = 3.5 Hz, J<sub>6a-7b</sub> = 4.0 Hz, J<sub>6a-6b</sub> = 14.7 Hz), 2.63 (ddd, H-7b, J<sub>7b-7a</sub> = 15.4 Hz, J<sub>7b-6b</sub> = 3.3 Hz), 2.34 (ddd, H-7a, J<sub>7a-6b</sub> = 12.3 Hz), 2.05 (ddd, H-6b). <sup>13</sup>C NMR: (CDCl<sub>3</sub>) 199.5 (Ru–CO), 199.0 (Ru–CO), 198.4 (Ru–CO), 198.2 (Ru–CO), 117.5 (*ipso* Cp), 114.3 (*ipso* Cp), 108.6 (*ipso* Cp), 91.6 (Cp), 90.6 (Cp, C-11), 88.4 (Cp), 87.3 (Cp), 85.0 (Cp, C-10), 85.7 (Cp, C-2), 76.6 (Cp, C-5), 29.4 (C<sub>2</sub>H<sub>4</sub>, C-7), 25.4 (C<sub>2</sub>H<sub>4</sub>, C-6). Mass Spectrometry: (CI, <sup>101</sup>Ru) 549 (7, M<sup>+</sup>), 521 (20, M<sup>+</sup>-CO), 493 (41, M<sup>+</sup>-2CO), 469 (100, M<sup>+</sup>-Br), 465 (55, M<sup>+</sup>-3CO), 441 (59, M<sup>+</sup>-CO, Br), 437 (48, M<sup>+</sup>-4CO), 413 (24, M<sup>+</sup>-Br, 2CO), 392 (36, M<sup>+</sup>-Ru, 2CO), 385 (9, M<sup>+</sup>-Br, 3CO), 357 (25, M<sup>+</sup>-Br, 4CO). Anal. Found: C, 35.26; H, 2.02; Br, 14.19. C<sub>16</sub>H<sub>11</sub>BrO<sub>4</sub>Ru<sub>2</sub>. Calc.: C, 34.97; H, 2.00; Br, 14.55%.

The second band from chromatography of the initial reaction mixture yielded X as a yellow powder. M.p. 176–180 °C. Yield 30 mg, 2%. IR: (CH<sub>2</sub>Cl<sub>2</sub>) 2051, 2001 cm<sup>-1</sup>. <sup>1</sup>H NMR: 5.26 (t, 4H, Cp), 5.16 (t, 4H, Cp), 2.65 (s, 4H, C<sub>2</sub>H<sub>4</sub>). <sup>13</sup>C NMR: (CDCl<sub>3</sub>) 195.4 (Ru–CO), 117.7 (*ipso* Cp), 84.3 (Cp), 82.8 (Cp), 27.2 (C<sub>2</sub>H<sub>4</sub>). Mass spectrometry: (CI and EI) (M<sup>+</sup>-not observed), 550 (7, M<sup>+</sup>-Br); 522 (100, M<sup>+</sup>-Br, CO); 494 (46, M<sup>+</sup>-Br, 2CO); 470 (52, M<sup>+</sup>-2Br); 466 (38, M<sup>+</sup>-Br, 3CO); 442 (45, M<sup>+</sup>-2Br, CO); 438 (95, M<sup>+</sup>-Br, 4CO); 414 (10, M<sup>+</sup>-2Br, 2CO); 386 (2, M<sup>+</sup>-2 Br, 3 CO); 358 (9, M<sup>+</sup>-2Br, 4CO); 257 (72, C<sub>2</sub>H<sub>4</sub>(C<sub>5</sub>H<sub>4</sub>)<sub>2</sub>Ru<sup>+</sup>).

The third band from chromatography of the initial column yielded XI as a yellow powder. M.p. 177–181 °C. Yield 30 mg, 2%. IR: (CH<sub>2</sub>Cl<sub>2</sub>) 2052, 2001 cm<sup>-1</sup>. <sup>1</sup>H NMR: (CDCl<sub>3</sub>) 5.26 (2H, Cp), 5.24 (2H, Cp), 5.15 (2H, Cp), 5.10 (2H, Cp), 2.65 and 2.52 (4 H, AA'BB' multiplet, C<sub>2</sub>H<sub>4</sub>). <sup>13</sup>C NMR: (CDCl<sub>3</sub>) 195.8 (Ru–CO), 195.44 (Ru–CO), 120.6 (*ipso* Cp), 120.5 (*ipso* Cp), 117.9 (*ipso* Cp), 117.7 (*ipso* Cp), 84.2 (Cp), 83.6 (Cp), 82.8 (Cp), 82.0 (Cp), 27.2 (C<sub>2</sub>H<sub>4</sub>), 26.7 (C<sub>2</sub>H<sub>4</sub>), 26.5 (C<sub>2</sub>H<sub>4</sub>), 26.0 (C<sub>2</sub>H<sub>4</sub>). Mass spectrometry: (CI and EI) (M<sup>+</sup>-not observed), 550 (7, M<sup>+</sup>-Br); 522 (100, M<sup>+</sup>-Br, CO); 494 (46, M<sup>+</sup>-Br, 2CO); 470 (52, M<sup>+</sup>-2Br); 466 (38, M<sup>+</sup>-Br, 3CO); 442 (45, M<sup>+</sup>-2Br, CO); 438 (95, M<sup>+</sup>-Br, 4CO); 414 (10, M<sup>+</sup>-2Br, 2CO); 386 (2, M<sup>+</sup>-2Br, 3CO); 358 (9, M<sup>+</sup>-2Br, 4CO); 257 (72, C<sub>2</sub>H<sub>4</sub>(C<sub>5</sub>H<sub>4</sub>)<sub>2</sub>Ru<sup>+</sup>).

#### 4. Crystallographic studies

Crystal, data collection and refinement parameters are given in Table 1. Suitable crystals were selected and mounted with epoxy cement to glass fibers. The unit cell parameters were obtained by the least squares refinement of the angular settings of 24 reflections ( $20^\circ \leq 2\theta \leq 25^\circ$ ).

The photographic data indicated monoclinic crystal systems for **VII** and **XI** and triclinic for **VI**. *E*-statistics suggested the centrosymmetric space group for **VI**. Systematic absences in the diffraction data unambiguously indicated  $P2_1/c$  for **VII** and either of the C-centered space groups  $Cc$  and  $C2/c$  for **XI**. The *E*-statistics strongly suggested the centrosymmetric option for **XI**. The space group choices were subsequently confirmed by the resulting computationally stable and chemically reasonable structures obtained. Structures were solved using direct methods, completed by subsequent difference Fourier syntheses and refined by full-matrix least squares procedures. No absorption corrections were applied for **VII** because of the less than 10% variation in the  $\psi$ -scan integrated intensities. Semi-empirical ellipsoid absorption corrections were applied on the data sets of **VI** and **XI**. There are two crystallographically independent molecules of **VII** which are chemically identical. The molecule in **XI** is located on an inversion center which causes the halide atoms to be disordered. The averaged unique halide atom was computationally treated as a bromine atom at 74.3% occupancy assuming an overall 50:50 Br:Cl ratio. All non-hydrogen atoms were refined with anisotropic displacement coefficients. Hydrogen atoms were treated as idealized contributions.

All software and sources of the scattering factors are contained in either the SHELXTL (5.1) or the SHELXTL PLUS (4.2) program libraries [12].

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