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Ligand exchange photochemistry of $M_2(CO)_4(\mu\text{-}\eta^5,\eta^5\text{-}C_5H_4CH_2C_5H_4)$ (M = Fe or Ru) and thermal acetylene exchange of $Ru_2(CO)(\mu\text{-}CO)[\mu\text{-}\eta^1\text{:}\eta^1\text{-}(C_6H_5)_2C_2](\mu\text{-}\eta^5,\eta^5\text{-}C_5H_4CH_2C_5H_4)$ The molecular structures of $Ru_2(CO)(\sigma\text{-}C_6H_5)(\mu\text{-}CO)[\mu\text{-}P(C_6H_5)_2](\mu\text{-}\eta^5,\eta^5\text{-}C_5H_4CH_2C_5H_4)$ and $Ru_2(CO)(\mu\text{-}CO)[\mu\text{-}\eta^1,\eta^3\text{-}C_6H_5C{=}C(C_6H_5)O](\mu\text{-}\eta^5,\eta^5\text{-}C_5H_4CH_2C_5H_4)$

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Abstract

Photolysis of $Fe_2(CO)_4(\mu\text{-}\eta^5,\eta^5\text{-}C_5H_4CH_2C_5H_4)$ in the presence of phosphines or phosphites results in the formation of simple carbonyl substitution products $Fe_2(CO)(\mu\text{-}CO)_2L(\mu\text{-}\eta^5,\eta^5\text{-}C_5H_4CH_2C_5H_4)$ or $Fe_2(\mu\text{-}CO)_2L_2(\mu\text{-}\eta^5,\eta^5\text{-}C_5H_4CH_2C_5H_4)$. Acetylenes react photochemically with the diiron compound to give vinylketone-bridged derivatives of the form $Fe_2(CO)(\mu\text{-}CO)[\mu\text{-}\eta^1\text{:}\eta^3\text{-}RC{=}C(R)CO](\mu\text{-}\eta^5,\eta^5\text{-}C_5H_4CH_2C_5H_4)$, where R = CH_3O_2C and C_6H_5. Reaction of $Ru_2(CO)_4(\mu\text{-}\eta^5,\eta^5\text{-}C_5H_4CH_2C_5H_4)$ with triphenylphosphine under photochemical conditions resulted in loss of two carbon monoxide ligands and P–C insertion by ruthenium to yield $Ru_2(CO)(\sigma\text{-}C_6H_5)(\mu\text{-}CO)[\mu\text{-}P(C_6H_5)_2](\mu\text{-}\eta^5,\eta^5\text{-}C_5H_4CH_2C_5H_4)$. Photolysis of $Ru_2(CO)_4(\mu\text{-}\eta^5,\eta^5\text{-}C_5H_4CH_2C_5H_4)$ with diphenylacetylene gave the previously reported $Ru_2(CO)_2(\mu\text{-}CO)[\mu\text{-}\eta^1\text{:}\eta^1\text{-}(C_6H_5)_2C_2](\mu\text{-}\eta^5,\eta^5\text{-}C_5H_4CH_2C_5H_4)$ and an air oxidation product, $Ru_2(CO)(\mu\text{-}CO)[\mu\text{-}\eta^1\text{:}\eta^3\text{-}C_6H_5C{=}C(C_6H_5)O](\mu\text{-}\eta^5,\eta^5\text{-}C_5H_4CH_2C_5H_4)$. The diphenylacetylene derivative underwent acetylene exchange, but did not undergo exchange with triphenylphosphine. All compounds have been characterized by spectroscopic methods, elemental analysis and/or mass spectroscopy. The molecular structures of two ruthenium compounds were determined by X-ray crystallography. $Ru_2(CO)(\sigma\text{-}C_6H_5)(\mu\text{-}CO)[\mu\text{-}P(C_6H_5)_2](\mu\text{-}\eta^5,\eta^5\text{-}C_5H_4CH_2C_5H_4)$: monoclinic, $P2_1/c$, a = 13.902(3) Å, b = 13.283(3) Å, c = 14.426(4) Å, β = 101.62(2)°, V = 2609(1) Å^3, z = 4, $R(F)$ = 3.98%. $Ru_2(CO)(\mu\text{-}CO)[\mu\text{-}\eta^1\text{:}\eta^3\text{-}C_6H_5C{=}C(C_6H_5)O](\mu\text{-}\eta^5,\eta^5\text{-}C_5H_4CH_2C_5H_4)$: orthorhombic, $Pccn$, a = 15.000(4) Å, b = 15.662(4) Å, c = 19.053(4) Å, V = 4476(2) Å^3, z = 8, $R(F)$ = 3.05%. © 1997 Elsevier Science S.A.

Keywords: Iron; Ruthenium; Cyclopentadienyls; Carbonyls; Bimetallic complexes; Photochemistry; Acetylenes

1. Introduction

In earlier papers we have described the synthesis of the ring-coupled homobimetallic derivatives $M_2(CO)_4(\mu\text{-}\eta^5,\eta^5\text{-}C_5H_4CH_2C_5H_4)$ [1,2], where M = Fe (**1**) and Ru (**2**), and we have recently described the surprising photochemically induced rearrangement of **2** to the structurally twisted isomer, $[Ru(CO)_2][Ru(CO)_2H](\eta^5,\eta^5\text{:}\eta^1\text{-}C_5H_4CH_2C_5H_3)$, **3** [3]. Knox et al. [4] have reported that **2** reacts with diphenylacetylene under photochemical conditions to produce $Ru_2(CO)(\mu\text{-}CO)[\mu\text{-}\eta^1\text{:}\eta^1\text{-}(C_6H_5)_2C_2](\mu\text{-}\eta^5,\eta^5\text{-}C_5H_4CH_2C_5H_4)$, **4**.

A number of photochemical ligand exchange reactions of ring-coupled bimetallic iron and ruthenium compounds have been reported. Vollhardt and cowork-

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ers [5] have examined the photochemistry of the fulvalene compound, $Ru_2(CO)_4(\mu\text{-}\eta^5,\eta^5\text{-}C_5H_4C_5H_4)$, with acetylenes. Wright and coworkers [6] have examined the substitution photochemistry of $Fe_2(CO)_4[\mu\text{-}\eta^5,\eta^5\text{-}C_5H_4(CH_3)_2SiC_5H_4]$ with various diphosphines, while Bursten and coworkers have recently described the photolysis of this compound with acetylenes and have discussed the possible mechanism of the acetylene substitution reaction [7]. Cotton et al. [8] prepared $Fe_2(CO)[P(OC_6H_5)_3](\mu\text{-}CO)_2[\mu\text{-}\eta^5,\eta^5\text{-}C_5H_4(CH_3)_4\text{-}C_2C_5H_4]$ by photolysis. Knox [9] has examined the acetylene substitution chemistry of unbridged $M_2(CO)_4(\eta^5\text{-}C_5H_5)_2$, where M = Fe and Ru.

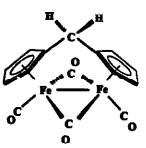
As part of our continuing investigation of the chemistry of ring-coupled bimetallic compounds, we have examined the photochemical reactions of **1** and **2** with various ligands, including phosphines, phosphites, and acetylenes. The results of these studies are reported in this paper.

2. Results and discussion

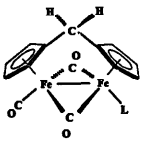
2.1. Photochemical substitution of $Fe_2(CO)_4(\mu\text{-}\eta^5,\eta^5\text{-}C_5H_4CH_2C_5H_4)$, 1

We have previously reported the synthesis of $Fe_2(CO)_4(\mu\text{-}\eta^5,\eta^5\text{-}C_5H_4CH_2C_5H_4)$ by reduction of $[Fe(CO)_2I]_2(\mu\text{-}\eta^5,\eta^5\text{-}C_5H_4CH_2C_5H_4)$ [1]. This inefficient route has now been replaced by a direct synthesis of **1** by reaction of bis(cyclopentadienyl)methane with $Fe(CO)_5$ in refluxing xylene to which norbornene is added as a hydrogen scavenger. Photolysis of **1** in benzene solution under an atmosphere of ^{13}CO gave a ^{13}CO-enriched product. ^{13}C NMR of this compound established that the carbon monoxide groups were exchanging between terminal and bridging positions, as has been previously observed for similar compounds. A variable-temperature NMR study of **1** in toluene established a coalescence temperature of 257 K and a $\Delta G^{\ddagger}$ of 43.0 kJ mol^{-1}. This exchange barrier compares favorably with a value of 46.0 kJ mol^{-1} reported by Cotton et al. for $Fe_2(CO)_4[\mu\text{-}\eta^5,\eta^5\text{-}C_5H_4(CH_3)_4C_2C_5H_4]$ [8]. Bridging-to-terminal carbonyl exchange in the cis conformations of $Fe_2(CO)_4(\eta^5\text{-}C_5H_4R)_2$, where R = H and CH_3, have been reported to have free energies of activation of 51.9 kJ mol^{-1} and 56.5 kJ mol^{-1} respectively [10]. While contributions to these free energy of activation values from solvent effects cannot be entirely ruled out, it would appear that coupling the cyclopentadienyl rings slightly lowers the barrier to carbonyl exchange.

Photolysis of **1** in benzene with $P(C_6H_5)_3$, $P(CH_3)_3$, or $P(OCH_2)_3CC_2H_5$ results in good yields of singly substituted products, $Fe_2L(CO)(\mu\text{-}CO)_2(\mu\text{-}\eta^5,\eta^5\text{-}C_5H_4CH_2C_5H_4)$, where $L = P(C_6H_5)_3$ (**5**), $P(CH_3)_3$ (**6**), and $P(OCH_2)_3CC_2H_5$ (**7**) respectively. Traces of air-sensitive products, presumed to be doubly substituted derivatives, were occasionally observed during chromatography, but were not isolated. IR spectra of compounds **5**, **6**, and **7** contained one band in the terminal carbonyl region and two bands, a weak symmetric and a strong asymmetric stretch, in the bridging carbonyl region. NMR spectra of these compounds were simple, indicating that the molecules either possess a mirror plane, or that the magnetic environments of the ring protons and carbons α and β to the bridge were being averaged by a rocking of the bis(cyclopentadienyl)methane ligand. The resonances of the bridging carbonyl groups were split by coupling to the phosphorus ligand.



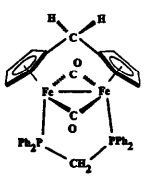
1



5 L = PPh_3

6 L = PMe_3

7 L = $P(OCH_2)_3CCH_2CH_3$



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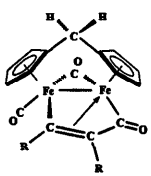


9 R = Ph

10 R = CO_2CH_3

Photolysis of **1** with bis(diphenylphosphino)methane, dppm, gave $Fe_2(\mu\text{-dppm})(\mu\text{-}CO)_2(\mu\text{-}\eta^5,\eta^5\text{-}C_5H_4CH_2C_5H_4)$, **8**, in good yield. IR, ^1H and ^{13}C NMR spectra of this compound were consistent with the expected molecular structure and with the analogous $(CH_3)_2Si$-bridged compound reported by Wright and coworkers [6]. Bridging carbonyl resonances of **8** were not observed.

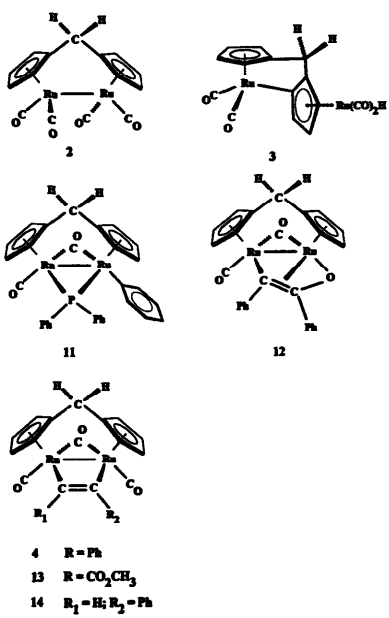
Photolyses of **1** with diphenylacetylene or dimethyl acetylenedicarboxylate (DMAD) gave products of the form $Fe_2(CO)(\mu\text{-}CO)[\mu\text{-}\eta^1\text{:}\eta^3\text{-}RC{=}C(R)CO](\mu\text{-}\eta^5,\eta^5\text{-}C_5H_4CH_2C_5H_4)$, where R = C_6H_5 (**9**) or CH_3O_2C (**10**). Traces of additional products were isolated in the case of DMAD, but were not completely

characterized. Knox [9] has previously reported that acetylenes react with $Fe_2(CO)_4(\eta^5\text{-}C_5H_5)_2$ under photochemical conditions to give products in which carbonyl insertion into an acetylene–iron bond produces a five-membered dimetallacyclopentenone ring such as observed for **9** and **10**. Bursten and coworkers [7] have reported the synthesis and molecular structure of $Fe_2(CO)(\mu\text{-}CO)[\mu\text{-}\eta^1{:}\eta^3\text{-}HC{=}C(C_6H_5)CO][\mu\text{-}\eta^5,\eta^5\text{-}C_5H_4Si(CH_3)_2C_5H_4]$ in which this same feature was observed. IR spectra of **9** and **10** have weak bands in the ketone stretching region consistent with a dimetallacyclopentenone core structure. Room temperature ^1H and ^{13}C NMR spectra of **9** and **10** are broadened, suggesting that a slow equilibrium is occurring in which the terminal carbonyl and the ketone carbonyl groups exchange through a shuttling motion of the acetylene. The spectra of both compounds were significantly sharpened at 260 K. The highly asymmetric geometries of **9** and **10** are reflected in the fact that the resonances of all eight cyclopentadienyl ring proton resonances are clearly resolved at low temperature. The resonances associated with the bridging methylene group appear as an AB quartet. Two sets of resonances are observed for the phenyl groups in **9** and the methyl esters in **10**. A low temperature COSY 2-D analysis of **9** permitted resonances to be assigned to protons on the two cyclopentadienyl rings. The numbering scheme used for all compounds described in this paper is presented in Fig. 1.

2.2. Photochemical substitution of $Ru_2(CO)_4(\mu\text{-}\eta^5,\eta^5\text{-}C_5H_4CH_2C_5H_4)$, 2

In contrast to $Fe_2(CO)_4(\eta^5\text{-}C_5H_5)_2$, the phosphine and phosphite chemistry of $Ru_2(CO)_4(\eta^5\text{-}C_5H_5)_2$ is quite limited. $P(OCH_3)_3$ [11] and PPh_3 [12] derivatives have been prepared by exchange for acetylene in $Ru_2(CO)_2[\mu\text{-}\eta^1{:}\eta^3\text{-}C(O)C_2Ph_2](\eta^5\text{-}C_5H_5)_2$, while the $P(C_3H_7)_3$ [13] derivative was prepared by direct reaction with $Ru_2(CO)_4(\eta^5\text{-}C_5H_5)_2$ in refluxing xylene. Only the phosphite derivative, $Ru_2(CO)_3P[OCH(CH_3)_2]_3(\eta^5\text{-}C_5H_5)_2$, has been prepared photochemically [14].

Photolysis of **2** with $P(C_6H_5)_3$ followed by chromatographic work-up of the resultant reaction mixture yielded an orange band as the major product. Other products were shown by HPLC to be present in lesser amounts, but could not be isolated as pure materials by preparative chromatography. The IR spectrum of the new compound, **11**, consisted of a strong band at 1951 cm^{-1} and a broad, medium band at 1793 cm^{-1}. In marked contrast to the simple spectra of the iron compound, **5**, the ^1H and ^{13}C NMR spectra of **11** were very complex. Three distinct sets of phenyl resonances were observed. The proton and carbon chemical shifts of one of these sets of resonances were shifted quite dramatically from the other two. Although the carbon atoms of all three phenyl groups were still magnetically coupled to the phosphorus atom, the *ipso*-carbon coupling constant of the unique phenyl ring was found to be 10.5 Hz, while the two other rings had more typical coupling constants of 34.1 and 32.2 Hz. Separate resonances for all eight ring hydrogen atoms of the bis(cyclopentadienyl)methane unit were observed. Ten separate cyclopentadienyl ring carbon resonances (two *ipso*) were also observed, four of which (two on each ring) were coupled to the phosphorus atom. Two phosphorus-coupled carbonyl resonances were observed. COSY and NOESY spectra, coupled with $^1H/^{13}C$ correlation spectra, permitted every resonance to be assigned. In the absence of a long range NOE interaction between the phenyl rings and the cyclopentadienyl ring protons we are unable to arrive at an absolute assignment of ring protons relative to the other metal ligands. Finally, mass spectrometry established a parent mass for the compound that corresponded to one $P(C_6H_5)_3$ unit and two carbonyl groups.



2 **3**

11 **12**

4 R = Ph
13 R = CO_2CH_3
14 R_1 = H; R_2 = Ph

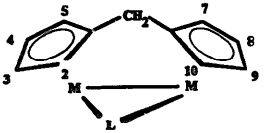


Fig. 1. General numbering scheme for bis(cyclopentadienyl)methane rings. Where NOE interactions between a bridging ligand and the rings permitted full assignment, the ligand was assigned to be proximate to positions 2 and 10.

Crystals of **11** were grown from dichloromethane–petroleum ether by vapor diffusion in the cold, and the molecular structure determined by X-ray crystallography. Crystallographic data are presented in Table 1 and selected bond lengths and angles for **11** are presented in Table 2. The structure of **11**, Fig. 2, revealed that one of the phenyl groups from the $P(C_6H_5)_3$ had migrated to a ruthenium as the result of a ruthenium insertion into a P–C bond. The remaining $P(C_6H_5)_2$ moiety bridges the two ruthenium atoms with the two phenyl rings in magnetically distinct environments. P–C bond cleavage is well known, particularly for ruthenium compounds, and has been reviewed up to 1985 [15].

The bimetallic core of the molecule has a 34 electron count. The Ru–Ru distance, 2.744(1) Å, is consistent with the presence of a single bond between the metals. The Ru–P bond lengths and Ru–centroid distances are almost identical. The terminal carbonyl bonded to Ru(2) has a normal Ru–C bond length of 1.855(7) Å, while the second carbonyl is semi-bridging with Ru(2)–C(2) of 2.218(7) Å and Ru(1)–C(2) of 1.935(6) Å. The Ru(1)–C(2)–O(2) bond angle is 149.3(5)°, while that of Ru(2)–C(2)–O(2) is 128.0(5)°.

We tentatively suggest that **11** arises from secondary photolysis of the expected product, $Ru_2[P(C_6H_5)_3](CO)(\mu\text{-}CO)_2(\mu\text{-}\eta^5,\eta^5\text{-}C_5H_4CH_2C_5H_4)$, by way of carbonyl loss and insertion of the electron deficient ruthenium into a P–phenyl bond. We have thus far been unable to halt the photolysis at the tricarbonyl, triphenylphosphine stage using conventional methods. We are presently exploring the use of a flow photochemical cell to prepare photochemically sensitive products.

Table 1
Crystallographic data for **11** and **12**

	11	**12**
Formula	$C_{31}H_{25}O_2PRu_2$	$C_{27}H_{20}O_3Ru_2$
Formula weight	662.6	594.6
Space group	$P2_1/c$	*Pccn*
a (Å)	13.902(3)	15.000(4)
b (Å)	13.283(3)	15.662(4)
c (Å)	14.426(4)	19.053(4)
β (deg)	101.62(2)	
V (Å^3)	2609(1)	4476(2)
Z	4	8
Crystal color	red	deep red
D(calc) (g cm^{-3})	1.687	1.765
μ(Mo Kα) (cm^{-1})	12.46	13.5
Temperature	298	297
$R(F)$ (%)	3.98	3.05
$R(wF)$ (%)	4.74	4.31

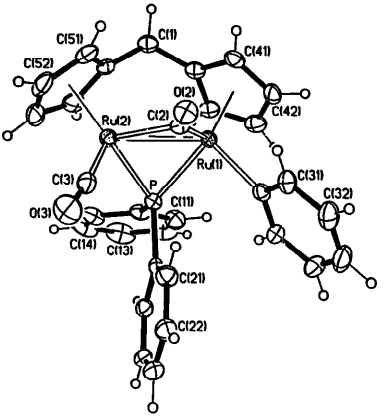


Fig. 2. Molecular structure of **11**.

Knox et al. [4] have reported that photolysis of **2** in the presence of diphenylacetylene results in the formation of **4**. We had also carried out this reaction and isolated **4** as well as two other products from the reaction mixture. One product, that was shown to not be an acetylene derivative, was subsequently identified as a photoinduced rearrangement product, **3**, and has been reported elsewhere [3]. Another minor product, **12**, was only found in occasional batches of the reaction, and its origins were traced to the presence of adventitious oxygen in either the solvents or the flush gases. All three compounds could be easily separated by column chromatography.

12 was recovered as dark red crystals. The IR spectrum of **12** contained a terminal carbonyl band and a bridging carbonyl band whose stretching frequency (1820 cm^{-1}) was unusually high. The ^{1}H and ^{13}C NMR spectra were complex with unique resonances for all ring proton and carbon atoms of the bis(cyclopentadienyl)methane unit, and resonances for two phenyl rings in slightly different environments. The methylene proton resonances form an AB quartet. These features require **12** to have an overall asymmetric structure. A COSY NMR spectrum permitted ring proton resonances to be assigned, and a unique NOESY interaction be-

Table 2
Selected bond lengths and angles for **11**

Bond lengths (Å)			
Ru(1)–Ru(2)	2.744(2)	Ru(1)–P	2.277(2)
Ru(2)–P	2.304(2)	Ru(1)–C(2)	1.935(6)
Ru(2)–C(2)	2.218(7)	Ru(2)–C(3)	1.855(7)
Ru(1)–C(36)	2.138(5)	C(2)–O(2)	1.174(8)
C(3)–O(3)	1.150(9)	C(16)–P	1.822(5)
C(26)–P	1.843(5)		
Bond angles (deg)			
Ru(1)–P–Ru(2)	73.6(1)	Ru(1)–C(2)–Ru(2)	82.4(2)
Ru(1)–C(2)–O(2)	149.3(5)	Ru(2)–C(2)–O(2)	128.0(5)
C(3)–Ru(2)–Ru(1)	114.8(2)	Ru(2)–Ru(1)–C(36)	121.7(1)
C(2)–Ru(2)–C(3)	85.7(3)	Ru(2)–C(3)–O(3)	173.8(7)
C(45)–C(1)–C(55)	114.7(6)		

tween one of the phenyl rings and one ring proton allowed assignment of ring protons relative to the diphenylacetylene fragment.

X-ray crystallography of **12** revealed the structure presented in Fig. 3. Crystallographic data are presented in Table 1 and selected bond lengths and angles are presented in Table 3. Reaction with oxygen during photolysis results in removal of a CO moiety and the effective insertion of an oxygen atom into an acetylene–ruthenium bond to yield a bridging group that is best described as a μ-vinyloxide, μ-η^1:η^3-PhC=C(Ph)O. It has been reported [16] that the non-bridged analog of this compound is the product of an unusual reaction sequence involving reaction of $Ru_2(CO)_4(\eta^5\text{-}C_5H_5)_2$ with phenyl lithium and HBF_4. The torsion angle, CNT(1)–Ru1–Ru2–CNT(2), for **12** is found to be $-8.6°$.

Comparing **12** with the unbridged analog, it is found that the Ru–Ru bond distance, 2.632(1) Å, is shorter than that reported, 2.717(1) Å, by Knox, but that all

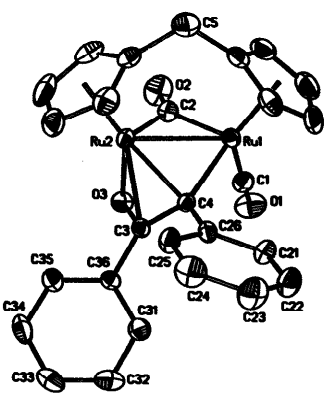


Fig. 3. Molecular structure of **12**.

other bond lengths in the dimetallavinyloxide ring are nearly identical. The Ru–Ru bond of **12** is also shorter than that in **2**, 2.767(1) Å [4], and in $Ru_2(CO)_2(\mu\text{-}CO)_2[\mu\text{-}\eta^5,\eta^5\text{-}C_5H_3(CH_3)_2SiC_5H_4]$, 2.7042 Å [2]. Particularly surprising is the fact that the Ru–Ru bond in **12** with a three atom vinyloxide bridge is shorter than that of **11** with a single phosphorus atom bridge. The bridging carbonyl group is symmetrical between the two ruthenium atoms and shows no sign of semi-bridging behavior. The observed high stretching frequency of this carbonyl may arise from a reduction of the M–C(O)–M bond angle, ultimately due to electron withdrawal by the oxygen atom, which would be expected to shift the carbonyl to higher stretching frequencies.

2.3. Acetylene exchange reactions of 4

In contrast to the observations of Knox and coworkers, reaction of **4** with an excess of DMAD or phenylacetylene in refluxing toluene for 2 h gave the acetylene exchange products **13** and **14** in moderate yields. Repeated attempts to effect a similar exchange reaction with triphenylphosphine were unsuccessful. **13** and **14** were fully characterized by IR, ^{1}H and ^{13}C NMR (1-D and 2-D techniques), as well as by mass spectroscopy and elemental analysis. Elemental analysis and ^{1}H NMR indicate that **14** is isolated with a dichloromethane of crystallization. Knox has made a similar observation for **4**.

The IR spectra of compounds **4**, **13**, and **14** contain three carbonyl bands in the metal carbonyl region consistent with a bridging carbonyl and two terminal carbonyl groups. The acetylene groups are oriented in the 'parallel' mode [17]. All carbonyl bands are sensitive to the electronic character of the bridging acetylene with the terminal stretching frequencies being in the order

$$(MeO_2C)_2C_2 > PhC_2H > Ph_2C_2$$

whereas the order of bridging stretching frequencies is

$$PhC_2H > (MeO_2C)_2C_2 > Ph_2C_2$$

Table 3
Selected bond lengths and angles for **12**

Bond lengths (Å)			
Ru(1)–Ru(2)	2.632(1)	Ru(2)–C(3)	2.215(4)
Ru(1)–C(1)	1.862(4)	Ru(2)–C(4)	2.134(4)
Ru(1)–C(2)	2.008(4)	Ru(2)–O(3)	2.143(3)
Ru(1)–C(4)	2.102(4)	C(3)–O(3)	1.308(5)
Ru(2)–C(2)	2.050(5)	C(3)–C(4)	1.435(5)
Ru(1)–CNT(1)	1.916(5)	Ru(2)–CNT(2)	1.836(5)
Bond angles (deg)			
CNT(1)–Ru(1)–C(1)	131.0(3)	Ru(1)–C(1)–O(1)	177.2(4)
CNT(1)–Ru(1)–C(2)	117.6(3)	Ru(1)–C(2)–O(2)	141.7(4)
CNT(1)–Ru(1)–C(4)	126.8(3)	Ru(2)–C(2)–O(2)	137.4(4)
CNT(1)–Ru(1)–Ru(2)	117.3(1)	Ru(1)–C(4)–Ru(2)	76.8(1)
CNT(2)–Ru(2)–C(2)	117.1(3)	Ru(2)–O(3)–C(3)	75.5(2)
CNT(2)–Ru(2)–C(3)	145.1(3)	Ru(1)–C(4)–C(3)	122.4(3)
CNT(2)–Ru(2)–C(4)	137.6(3)	Ru(2)–C(4)–C(3)	73.8(2)
CNT(2)–Ru(2)–O(3)	146.3(3)	C(4)–C(3)–O(3)	118.9(3)
CNT(2)Ru(2)–Ru(1)	126.8(1)		
Torsion angle (deg)			
CNT(1)–Ru(1)–Ru(2)–CNT(2)	−8.6		

As expected for a molecule with a mirror plane perpendicular to the Ru–Ru bond, the ^{1}H NMR spectrum of **13** contains four well-defined cyclopentadienyl ring resonances, an AB pattern for the methylene group, and a sharp singlet for the methyl ester. The ^{13}C NMR spectrum is equally well defined. A COSY spectrum revealed weak couplings between the methylene bridge protons and the two most downfield ring proton resonances, suggesting that these ring protons are α to the bridge. Although the ring resonances could be fully assigned to the ring hydrogens, the absence of a NOE interaction between the methyl groups and the rings precluded a definitive assignment of ring resonances relative to the acetylene bridge.

14 has C_1 symmetry and its ^{1}H and ^{13}C NMR spectra were consistent with the expected structure. A COSY spectrum permitted assignment of the proton resonances of ring hydrogens on the two rings, while a NOESY spectrum identified those bis(cyclopentadienyl)methane ring hydrogens closest to the phenyl and acetylenic hydrogen, thus making possible an absolute assignment of all of the hydrogen atom resonances within the two cyclopentadienyl rings. All cyclopentadienyi ring carbon atoms were assigned on the basis of a ^{1}H–^{13}C correlation spectrum.

14 is chiral, and the racemic mixture could be resolved into its enantiomers on an analytical scale by HPLC using a Chiralcel chromatographic column. We have previously described the use of these columns for the resolution of planar chiral complexes of chromium tricarbonyl with 1,2- and 1,3-asymmetrically disubstituted arenes [18].

Attempts to form **14** by direct photolysis of **4** with phenylacetylene in a ten-fold excess gave only a small amount of **14** along with the photochemical rearrangement product, **3**. It has previously been observed that only the reaction of diphenylacetylene with $Ru_2(CO)_4(\eta^5\text{-}C_5H_5)_2$ results in the formation of significant yields of substitution product. The reason for this high order of selectivity is not apparent.

Vollhardt and coworkers [5] have examined the photolysis of $Ru_2(CO)_2(\mu\text{-}\eta^5,\eta^5\text{-}C_5H_4C_5H_4)$ with acetylenes and also find that 'parallel' acetylene derivatives are formed. These workers note that $Ru_2(CO)_2(\eta^5,\eta^5\text{-}C_5H_4C_5H_4)$ undergoes facile conversion to $Ru_2(CO)_4(\mu\text{-}\eta^5{:}\eta^1\text{-}C_5H_4)_2$ under conditions of the photolysis and suggest that it is this rearranged species that undergoes secondary photolysis to yield the intermediate that ultimately reacts with acetylene. In the case of **2**, a photochemical rearrangement to form **3** is observed, but there is no evidence to implicate this species as an intermediate in acetylene substitution. To the contrary, we have previously established in matrix studies [19] that **1** and **2** lose carbon monoxide to form species with three terminal carbonyl groups that are the more likely intermediate for acetylene or phosphine complexation.

The photochemical substitution of carbonyl groups on **1** and analogous ring-coupled or non-ring-coupled compounds by phosphines and phosphites appears to proceed with formation of monosubstitution products and traces of somewhat more air-sensitive disubstitution products. The dearth of simple photochemical phosphine substitution products on ruthenium compounds, and the observation here of a facile secondary reaction in the triphenylphosphine reaction of **2**, requires additional study to determine the mechanism of these secondary reactions.

Acetylene substitution in iron compounds yields products in which dimetallacyclopentenone core struc-

tures are preferentially formed. Substitution of acetylenes on non-ring-coupled ruthenium compounds also preferentially yield dimetallacyclopentenone cores, while substitutions on ring-coupled compounds, such as **2** and its fulvalene analog, yield simple 'parallel' bridged acetylene products. For ruthenium compounds it appears that the preference for the dimetallacyclopentenone or parallel structures may depend upon minor geometric constraints imposed by the rings.

3. Experimental

2 and bis(cyclopentadienyl)methane were prepared by published procedures [1]. All solvents were dried and distilled under nitrogen. Chiral chromatography was conducted on a Chiralcel OD analytical column using nitrogen-flushed 5% isopropanol in heptane as an eluant. Preparative chromatography was conducted using nitrogen flushed solvents and neutral (CAMAG) alumina. Microscale photochemistry was carried out using Ace 'Micro No-Air' apparatus illuminated with a 350 W high pressure mercury lamp. Preparative photochemistry was carried out in a 250 ml Ace Hanovia doubly jacketed apparatus using a Pyrex filter.

Infrared spectra were recorded on a Bio-Rad Qualimatic FTIR spectrometer operating at 2 cm^{-1} resolution. ^{1}H and ^{13}C NMR spectra were recorded on an IBM NR-300 MHz NMR spectrometer (Idaho) or a QE-300 NMR spectrometer (US Naval Academy) and were referenced to appropriate solvent resonances. Mass spectrometry was carried out by Dr. Gary Knerr of the University of Idaho on a VG 7070-HS GC/MS using direct insertion. Elemental analyses were carried out by Galbraith Laboratories, Inc. of Knoxville, TN and Desert Analytics of Tuscon, AZ.

3.1. Synthesis of $Fe_2(CO)_4(\mu\text{-}\eta^5,\eta^5\text{-}C_5H_2CH_2C_5H_4)$. 1

Bis(cyclopentadienyl)methane, 1.80 g (12.7 mmol), an approximate 40% solution in hydrocarbon, $Fe(CO)_5$, 13.6 g (69 mmol), and norbornene, 7.0 g (74.4 mmol), were taken up in xylene, 200 ml, and refluxed under nitrogen for 1 day. At the end of this time a dull metal mirror had formed on the inside of the flask. The contents of the flask were filtered through Celite, and the flask rinsed with xylene. After removal of xylene under vacuum the remaining residue was extracted with hot petroleum ether. The black-purple insoluble solid that remained from this extraction was almost pure (by HPLC) **1** and was used in subsequent reactions without additional purification. The petroleum ether extracts were chromatographed on alumina using petroleum ether as an eluant. A yellow band consisting of norbornene and norbornene was eluted from the column followed by a red band that appears to be a norbornene–iron carbonyl complex. A third red band containing **1** was eluted and combined with the insoluble portion to give 1.30 g (30%). IR: (CH_2Cl_2) 1995(s), 1957(w), 1800(sh), 1777(s) cm^{-1}.

3.2. Synthesis of ^{13}C labeled $Fe_2(CO)_4(\mu\text{-}\eta^5,\eta^5\text{-}C_5H_4CH_2C_5H_4)$. 1

1, 70 mg (0.19 mmol), was taken up in benzene, 5 ml, in a Griffin–Worden tube and degassed by three freeze–pump–thaw cycles. ^{13}CO (about 700 mm at 23 °C) was introduced to the tube, and the sample photolyzed overnight using an Ace Hanovia medium pressure mercury lamp inside of a water-cooled quartz jacket. After removal of solvent, the purple residue was chromatographed on alumina with dichloromethane to give a single band. Recovery was essentially quantitative. IR: (CH_2Cl_2) 1995(sh), 1982(s), 1950(s), 1925(m), 1882(w), 1793(sh), 1777(m), 1739(s), 1698(w) cm^{-1}.

3.3. Synthesis of $Fe_2(CO)L(\mu\text{-}CO)_2(\mu\text{-}\eta^5,\eta^5\text{-}C_5H_4CH_2C_5H_4)$, where $L = P(C_6H_5)_3$ (5), $P(CH_3)_3$ (6) $P(CH_3O)_3CC_2H_5$ (7), and $Fe_2(\mu\text{-dppm})(\mu\text{-}CO)_2(\mu\text{-}\eta^5,\eta^5\text{-}C_5H_4CH_2C_5H_4)$ 8

1, 0.5 g (1.36 mmol) and $P(C_6H_5)_3$, 1.00 g (3.82 mmol), were taken up in benzene, 250 ml, in an Ace Hanovia water-jacketed photolysis vessel equipped with a quartz cold finger. Nitrogen was bubbled through the reaction mixture and the reaction mixture was photolyzed overnight. Solvent was removed to give a dark solid that was washed with petroleum ether to remove unreacted phosphine, then chromatographed on alumina using dichloromethane as an eluant. A large blue band was preceded by a faint red band. The red band was shown (IR and HPLC) to be **1**. After removal of solvent the blue band yielded **5** as a solid, m.p.: decomp. above 200 °C. Yield: 488 mg, 66%. IR: (CH_2Cl_2) 1950(s), 1763(w), 1725(s) cm^{-1}. ^{1}H NMR: ($CDCl_3$) 7.58 (br s, 6H, o-Ph), 7.31 (br s, 9H, m- and p-Ph), 4.91 (br s, 6H, Cp), 4.02 (s, 2H, Cp), 2.61 (s, 2H, CH_2). ^{13}C NMR: ($CDCl_3$) 213.0 (d, $J_{P-C} = 2$ Hz, terminal CO), 188.6 (d, $J_{P-C} = 14.0$ Hz, μ-CO), 135.4 (d, $J_{P-C} = 41.3$ Hz, *ipso*-Ph), 133.9 (d, $J_{P-C} = 9.5$ Hz, o-Ph), 129.5 (d, $J_{P-C} = 2.0$ Hz, p-Ph), 127.8 (d, $J_{P-C} = 9.0$ Hz, m-Ph), 100.6 (*ipso*-Cp), 94.7 (d, $J_{P-C} = 2.0$ Hz, *ipso*-Cp), 93.0 (Cp), 91.8 (Cp), 85.1 (Cp), 81.7 (Cp), 22.9 (CH_2). ^{31}P NMR: ($CDCl_3$) 71.88 ppm. Anal. Found: C, 63.64; H, 4.13; P, 5.41. $C_{32}H_{25}Fe_2O_3P$. Calc.: C, 64.03; H, 4.17; P, 5.17%. **5** was also prepared by reaction of **1** with $P(C_6H_5)_3$ in refluxing toluene.

6 and **7** were prepared by identical procedures. **6** was isolated as a red solid, m.p.: decomp. above 250 °C. IR: (CH_2Cl_2) 1934(s), 1762(w), 1726(s) cm^{-1}. ^{1}H NMR: ($CDCl_3$) 5.01 (s, 2H, Cp-a), 4.87 (s, 2H, Cp-a), 4.69 (s, 2H, Cp-b), 4.56 (s, 2H, Cp-b), 2.59 (s, 2H, CH_2), 1.00

(d, J_{P-H} = 9.0 Hz, P–CH_3). ^{13}C NMR: ($CDCl_3$) 283.1 (d, J_{P-C} = 16.8 Hz, μ-CO), 217.1 (s, terminal CO), 100.6 (*ipso*-Cp), 94.5 (*ipso*-Cp), 92.8 (Cp-a, H – 4.87 ppm), 92.2 (Cp-b, H – 4.67 ppm), 81.6 (Cp-b, H – 4.56 ppm), 81.1 (Cp-a, H – 5.01 ppm), 23.0 (CH_2), 18.0 (d, J_{P-C} = 28.6 Hz, P–CH_3). ^{31}P NMR: ($CDCl_3$) 36.77 ppm. Anal. Found: C, 48.80; H, 4.56; P, 7.79. $C_{17}H_{19}Fe_2O_3P$. Calc.: C, 49.31; H, 4.60; P, 7.49%.

7 was isolated as a red solid after chromatography of the reaction mixture on alumina using 2:1 petroleum ether:CH_2Cl_2 as an eluant. M.p.: darkens, but no melting up to 250 °C. Yield: 245 mg, 36%. IR: (CH_2Cl_2) 1958 (s) 1775(sh), 1746(s) cm^{-1}. ^1H NMR: ($CDCl_3$) 5.06 (t, 2H, Cp), 4.91–4.88 (m, 4H, Cp), 4.72 (q, 2H, Cp), 3.97 (d, J_{P-H} = 4.8 Hz, P–O–CH_2), 2.61 (s, Cp–CH_2–Cp), 1.04 (q, J = 7.7 Hz, CH_3), 0.70 (t, J = 7.7 Hz, CH_3). ^{13}C NMR: ($CDCl_3$) 278.7 (d, J_{P-C} = 23.2 Hz, μ-CO), 213.5 (terminal CO), 99.4 (*ipso*-Cp), 96.7 (d, J_{P-C} = 4.8 Hz, *ipso*-Cp), 94.0 (Cp), 93.1(Cp), 81.3 (Cp), 80.8 (Cp), 74.0 (d, J_{P-C} = 7.1 Hz, P–O–CH_2), 34.8 (d, J_{P-C} = 31.8 Hz, (O–CH_2)$_3$–CCH_2), 23.3 (CH_2), 22.9 (CH_2), 7.0 (CH_3). ^{31}P NMR: ($CDCl_3$) 164.5 ppm. Anal. Found: C, 47.75; H, 4.09. $C_{20}H_{21}Fe_2O_6P$. Calc.: C, 48.03; H, 4.20%.

8 was isolated by extraction of the reaction mixture with 15% dichloromethane in petroleum ether, followed by recrystallization of the insoluble material from dichloromethane–heptane. **8** was recovered as a dark green solid, m.p.: decomp. above 250 °C. Yield: 180 mg, 19%. IR: (CH_2Cl_2) 1729(w), 1683(s) cm^{-1}. ^1H NMR: ($CDCl_3$) 7.36 (m, 6H, Ph), 7.27 (m, 9H, Ph), 4.78 (Cp), 4.56 (Cp), 2.77 (CH_2), 1.63 (t, J_{P-H} = 9.7 Hz, P–CH_2–P). ^{13}C NMR: ($CDCl_3$) 137.6 (t, J_{P-C} = 21.1 Hz, *ipso*-Ph), 132.6 (t, J_{P-C} = 4.9 Hz, o-Ph), 129.6 (s, p-Ph), 128.1 (t, J_{P-C} = 4.4 Hz, m-Ph), 94.9 (Cp), 92.2 (*ipso*-Cp), 82.5 (Cp), 29.9 (t, J_{P-C} = 24.6 Hz, P–CH_2–P), 24.5 (CH_2). ^{31}P NMR: ($CDCl_3$) 87.2 ppm. Anal. Found: C, 65.49; H, 4.59; P, 8.73. $C_{38}H_{32}Fe_2O_2P_2$. Calc.: C, 65.73; H, 4.61; P, 8.94%.

3.4. Synthesis of $Fe_2(CO)(\mu\text{-}CO)(\mu\text{-}\eta^1{:}\eta^3\text{-}RC{=}C(R)CO)(\mu\text{-}\eta^5,\eta^5\text{-}C_5H_4CH_2C_5H_4)$, where $R = C_6H_5$ (9) and CH_3O_2C (10)

1, 0.50 g (1.37 mmol), and $(C_6H_5)_2C_2$, 1.0 g (5.61 mmol), were taken up in benzene, 250 ml, and photolyzed overnight in an Ace Hanovia water-jacketed reaction vessel. The reaction mixture was continuously purged with nitrogen. After removal of benzene, the solid residue was chromatographed on alumina with 1:1 dichloromethane:petroleum ether. Bands of unreacted acetylene and **1** were eluted from the column. The elution solvent was changed to neat dichloromethane and a brown band was eluted. Removal of solvent and recrystallization from dichloromethane–petroleum ether gave **9** as a brown solid, m.p.: 153 °C with decomp. Yield: 137 mg, 19.4%. IR: (CH_2Cl_2) 1980(s), 1799(s), 1734(w), 1722(w) cm^{-1}. ^1H NMR: ($CDCl_3$, 270 K) 7.70 (d, 1H, Ph), 7.45 (t, 1H, Ph), 7.23 (d, 2H, Ph), 7.13 (s, 2H, Ph), 6.95 (s, 2H, Ph), 6.75 (s, 2H, Ph), 6.12 (s, 1H, Cp, H-4), 5.86 (s, 1H, Cp, H-8), 5.30 (s, 1H, Cp, H-9), 5.09 (s, 1H, Cp, H-5), 4.69 (s, 1H, Cp, H-7), 4.59 (s, 1H, Cp, H-2), 4.43 (s, 1H, Cp, H-3), 4.11 (s, 1H, Cp, H-10), 3.13 and 3.03 (AB quartet, J = 14.2 Hz, CH_2). ^{13}C NMR: ($CDCl_3$, 260 K) 263.0 (μ-CO), 229.0 (ketonic CO), 211.7 (terminal CO), 193.6 (C=C adjacent to ketone), 153.1 (*ipso*-Ph), 136.4 (*ipso*-Ph), 131.9 (Ph), 130.8 (Ph), 128.3 (Ph), 127.3 (Ph), 126.8 (Ph), 126.0 (Ph), 100.0 (Cp), 94.3 (*ipso*-Cp), 90.3 (2C, Cp) 89.2 (Cp), 88.1 (Cp), 87.0 (Cp), 86.3 (Cp), 85.4 (Cp), 39.2 (C=C), 24.4 (CH_2). Mass spectrometry: (EI) 432 ($M^+ - 3CO$), 366 ($CpCH_2CpFePh_2C_2$), 338 ($M^+ - Ph_2C_2$), 310 ($M^+ - Ph_2C_2 - CO$), 282 ($M^+ - Ph_2C_2 - 2CO$), 254 ($M^+ - Ph_2C_2 - 3CO$), 198 ($CpCH_2CpFe$), 178 (Ph_2C_2). Anal. Found: C, 65.07; H, 3.89. $C_{28}H_{20}Fe_2O_3$. Calc.: C, 65.15; H, 3.88%.

10 was prepared as described for **9**. Chromatography of the reaction mixture on alumina using 1:1 petroleum ether:dichloromethane. A red band that was subsequently shown to be **1** was eluted with the solvent mixture, then the eluant was changed to neat dichloromethane and a green band was removed from the column. HPLC of this green band showed that it consisted of two components; thus, it was re-chromatographed using dichloromethane to give a brown band and a green band. Removal of solvent from the brown band gave **10** as a brown solid, m.p.: 187 °C with decomp. Yield: 61 mg, 9%. IR: (CH_2Cl_2) 1997(s), 1818(s), 1744(s), 1710(m) cm^{-1}. ^1H NMR: ($CDCl_3$, 230 K) 6.18 (1H, Cp), 5.76 (1H, Cp), 5.52 (1H, Cp), 5.29 (1H, Cp), 4.90 (1H, Cp), 4.85 (1H, Cp), 4.71 (1H, Cp), 4.27 (1H, Cp), 4.13 (3H, CH_3), 3.71 (3H, CH_3), 3.14 and 2.94 (AB quartet, J = 13.3 Hz, CH_2). ^1H NMR: ($CDCl_3$, 335 K) 5.85 (2H, Cp), 5.00 (2H, Cp), 4.92 (2H, Cp), 4.72 (2H, Cp), 3.88 (6H, CH_3), 3.16 and 2.97 (AB quartet, J = 13.9 Hz, CH_2). ^{13}C NMR: ($CDCl_3$) 258.1 (μ-CO), 221.6 (ketonic CO), 209.0 (terminal CO), 179.2 (C=C adjacent to ketone), 178.7 (CO_2), 171.4 (CO_2), 100.3 (Cp), 95.7 (*ipso*-Cp), 92.7 (*ipso*-Cp), 91.4 (Cp), 90.6 (Cp), 89.8 (Cp), 88.2 (Cp), 86.9 (Cp), 85.0 (Cp), 84.6 (Cp), 53.9 (CH_3), 53.1 (CH_3), 23.5 (CH_2), 20.9 (C=C). Mass spectrometry: (EI) 480 (M^+), 452 ($M^+ - CO$), 449 ($M^+ - CH_3O$), 424 ($M^+ - 2CO$), 396 ($M^+ - 3CO$), 365 ($M^+ - 3CO - CH_3O$). Anal. Found: C, 49.86; H, 3.33. $C_{20}H_{16}Fe_2O_7$. Calc.: C, 50.03; H, 3.34%.

3.5. Synthesis of $Ru_2(CO)(\mu\text{-}CO)(\sigma\text{-}C_6H_5)[\mu\text{-}P(C_6H_5)_2](\mu\text{-}\eta^5,\eta^5\text{-}C_5H_4CH_2C_5H_4)$, 11

2, 0.50 g (1.14 mmol), and $P(C_6H_5)_3$, 0.30 g (1.14 mmol), were taken up in benzene, 250 ml, and

photolyzed overnight with a constant nitrogen purge. After removal of solvent, the reaction mixture was chromatographed on alumina with 1:1 petroleum ether:benzene. A small amount of starting material was eluted, followed by an orange-red band. Recrystallization of this band from dichloromethane–petroleum ether gave **11** as an orange crystalline solid, m.p.: 229–230 °C. Yield: 40 mg, 5%. IR: (CH_2Cl_2) 1951(s), 1805(m) cm^{-1}. ^1H NMR: ($CDCl_3$) 8.00 (m, 2H, o-Ph-a), 7.55 (m, 3 H, m- and p-Ph-a), 7.43 (m, 2H, σ-Ph), 6.72 (m, H, p-Ph-b), 6.71 (m, 2H, m-Ph-b), 6.69 (m, 3H, σ-Ph), 6.20 (m, 2H, o-Ph-b), 5.63 (m, 1H, H-3), 5.39 (m, 1H, H-4), 5.21 (m, 1H, H-9), 5.18 (m, 1H, H-2), 5.11 (m, 1H, H-10), 5.10 (m, 1H, H-8), 4.31 (m, 1H, H-5), 4.17 (m, 1H, H-7), 3.37 (s, 2H, CH_2). ^{13}C NMR: ($CDCl_3$) 226.7 (d, J_{P-C} = 10 Hz, η-CO), 205.1 (d, J_{P-C} = 14 Hz, terminal CO), 148.3 (d, J_{P-C} = 10.5 Hz, *ipso*-σ-Ph), 144.7 (d, J_{P-C} = 3.6 Hz, o-σ-Ph), 142.2 (d, J_{P-C} = 34.1 Hz, *ipso*-Ph-a), 139.7 (d, J_{P-C} = 32.2 Hz, *ipso*-Ph-b), 134.4 (d, J_{P-C} = 10.4 Hz, o-Ph-a), 132.3 (d, J_{P-C} = 9.6 Hz, o-Ph-b), 129.7 (s, p-Ph-a), 128.0 (d, J_{P-C} = 9.1 Hz, m-Ph-a), 127.6 (d, J_{P-C} = 3.2 Hz, p-Ph-b), 126.3 (d, J_{P-C} = 14.3 Hz, m-Ph-b), 125.9 (s, m-σ-Ph), 121.2 (s, p-σ-Ph), 95.9 (s, C-7), 94.9 (s, *ipso*-Cp), 93.4 (s, C-5), 92.7 (d, J_{P-C} = 5.4 Hz, C-2), 89.5 (s, *ipso*-Cp), 89.2 (d, J_{P-C} = 5.0 Hz, C-10), 86.8 (d, J_{P-C} = 3.5 Hz, C-9), 86.2 (s, C-8), 85.8 (d, J_{P-C} = 3.0 Hz, C-3), 78.0 (s, C-4), 25.3 (s, CH_2). ^{31}P NMR: ($CDCl_3$) −56.1 ppm (s). MS: (EI, ^{101}Ru) 662 (M^+), 632 (M^+ − CO), 606 (M^+ − 2CO), 585 (M^+ − Ph), 529 (M^+ − 2CO and Ph), 498 ($CH_2Cp_2Ru_2PPh_2^+$), 452 (M^+ − 2CO and 2 Ph), 428 ($CH_2Cp_2RuPPh_2$), 421 ($CH_2Cp_2Ru_2Ph^+$).

3.6. Synthesis of $Ru_2(CO)(\mu\text{-}CO)[\mu\text{-}\eta^1\text{:}\eta^1\text{-}(C_6H_5)_2C_2](\mu\text{-}\eta^5,\eta^5\text{-}C_5H_4CH_2C_5H_4)$, 4, and $Ru_2(CO)(\mu\text{-}CO)(\mu\text{-}\eta^1\text{:}\eta^3\text{-}C_6H_5C{=}C(C_6H_5)O](\mu\text{-}\eta^5,\eta^5\text{-}C_5H_4CH_2C_5H_4)$, 12

2, 0.40 g (0.87 mmol), and Ph_2C_2, 0.15 g (0.87 mmol), were taken up in benzene and photolyzed at room temperature for 8 h with a nitrogen trickle purge. The resulting red solution was stripped of solvent, and the red residue was dissolved in a minimal quantity of dichloromethane and chromatographed on a 40 cm × 2 cm alumina column using 1:1 petroleum ether:dichloromethane. An initial yellow band was shown to be unreacted **2**. Continued elution recovered 73 mg of **4** as an orange solid, m.p. 197–199 °C with decomp. (156–160 °C with decomp. [4]) Yield: 14%.

In occasional preparations, a slowly moving red band was observed on the alumina column. Elution with acetone removed the red band which gave a red solid upon solvent removal. Recrystallization from dichloromethane–petroleum ether gave a few crystals of **12**, m.p. 228–229 °C. IR:($CHCl_3$) 1978, 1820 cm^{-1}. ^1H NMR: ($CDCl_3$) 7.02–6.96 (m, 10H, Ph), 5.98 (m, 1H, Cp, H-4), 5.80 (m, 1H, Cp, H-8), 5.15 (m, 1H, Cp, H-9), 5.00 (m, 1H, Cp, H-3), 4.94 (m, 2H, Cp, H-7 and H-5), 2.39 (m, 1H, Cp, H-2), 4.00 (m, 1H, Cp, H-10), 3.26 (AB quartet, J_{A-B} = 14.7 Hz.), 3.11 (AB quartet, J_{A-B} = 14.7 Hz). ^{13}C NMR: ($CDCl_3$) 233.4 (μ-CO), 201.3 (Ru–CO terminal), 156.8 (PhCCPh), 154.4 (PhCCPh), 140.1 (*ipso*-Ph), 136.0 (*ipso*-Ph), 129.9 (Ph), 128.0 (Ph), 127.0 (Ph), 125.2 (Ph), 104.0 (*ipso*-Cp), 95.8 (*ipso*-Cp), 89.5 (Cp), 89.1 (Cp), 87.8 (Cp), 85.5 (Cp), 85.5 (Cp), 84.2 (Cp), 84.1 (Cp), 83.5 (Cp), 79.1 (Cp), 25.1 (CH_2). MS: (CI) 594 (M^+), 566 (M^+ − CO), 538(M^+ − 2CO), 510 (M^+ − 3CO).

3.7. Microscale photolysis of 2 with diphenylacetylene

2, 50 mg (0.11 mmol), and diphenylacetylene, 0.195 g (1.1 mmol), were taken up in dry THF (20 ml) with no protection from air. The sample was divided into two portions for photolysis in an Ace Microscale photolysis apparatus using a Pyrex tube. One sample was rigorously degassed using three freeze–pump–thaw cycles, while the other sample was not degassed in any way. The samples were photolyzed using a 350 W high pressure mercury lamp for 4.5 h. The color of the degassed sample was observed to be a lighter red than that of the oxygen-containing sample. HPLC analysis of the contents of these photolysis tubes demonstrated that compound **12** appeared only in the oxygenated sample.

3.8. Synthesis of $Ru_2(CO)(\mu\text{-}CO)[\mu\text{-}\eta^1\text{:}\eta^1\text{-}(CH_3O_2C)_2C_2](\mu\text{-}\eta^5,\eta^5\text{-}C_5H_4CH_2C_5H_4)$, 13

4, 54 mg (89 mmol), and $(MeO_2C)_2C_2$, 0.10 g (700 mmol), were taken up in toluene (5 ml) and refluxed under nitrogen for 2 h. The solvent was removed under vacuum and the resulting residue was chromatographed on a 25 cm × 1 cm alumina column using 1:1 petroleum ether:dichloromethane as an eluant. After removal of a faint yellow band, believed to be mixed acetylenes, an intense yellow band was eluted from the column. Recrystallization from dichloromethane–petroleum ether gave 40 mg of **13** as yellow crystals, m.p. 205–210 °C. Yield: 78%. IR: (CH_2Cl_2) 2010(s), 1981(m), 1790(m), 1700(m, MeO_2C) cm^{-1}. ^1H NMR: ($CDCl_3$) 5.94 (m, 2H, Cp-α), 5.52 (m, 2H, Cp-α), 5.18 (m, 2H, Cp-β), 4.78 (m, 2H, Cp-β), 3.87 (AB quartet, J_{A-B} = 14.7 Hz, 1H, CH_2), 3.75 (s, 6H, CH_3O_2C), 3.64 (AB quartet, J_{A-B} = 14.7 Hz, 1H, CH_2). ^{13}C NMR: ($CDCl_3$) 199.2 (Ru–CO terminal), 170.0 (CH_3O_2C), 99.4 (Cp), 91.6 (Cp), 88.3 (Cp), 87.7 (*ipso*-Cp), 84.3 (Cp), 52.0 (CH_3O_2C), 25.3 (CH_2). (Note: μ-CO and acetylenic carbons were not observed.) MS: (CI mode) 570 (M^+), 543 (M^+ − CO), 514 (M^+ − 2CO), 486 (M^+ − 3CO), 454 (M^+ − 3CO − OCH_3), 428 (M^+ − $(CH_3O_2C)_2C_2$), 400 (M^+ − $(CH_3O_2C)_2C_2$ − CO), 372 (M^+ − $(CH_3O_2C)_2C_2$ − 2CO), 344 ($CH_2Cp_2Ru_2^+$).

(Note: the isotopic pattern of Ru_2 complexes are observed as complex envelopes. Fragments selected are based on ^{101}Ru.) Anal. Found, C, 41.99; H, 3.00. $C_{20}H_{16}O_7Ru_2$. Calc.: C, 42.11; H, 2.81%.

3.9. Synthesis of $Ru_2(CO)(\mu\text{-}CO)[\mu\text{-}\eta^1:\eta^1\text{-}(C_6H_5C_2H)](\mu\text{-}\eta^5,\eta^5\text{-}C_5H_4CH_2C_5H_4)$, 14

4, 25 mg (41 mmol), and PhC_2H, 0.10 g (100 mmol), were taken up in toluene (5 ml) and refluxed under nitrogen for 2 h. The solvent was removed under vacuum and the resulting brown-orange oil was chromatographed on a 25 cm × 1 cm alumina column using 1:1 petroleum ether:dichloromethane as an eluant. After removing a brown band, which was presumed to be Ph_2C_2 and excess PhC_2H, a canary-yellow band was eluted from the column. Removal of solvent from this band gave **14** as a yellow solid which could be recrystallized from dichloromethane–petroleum ether to give 16 mg of golden yellow plates, m.p. 180 °C with decomp. Yield: 45%. IR: (CH_2Cl_2) 1994(s), 1960(m), 1799(m) cm^{-1}. ^1H NMR: ($CDCl_3$) 7.72 (s, 1H, acetylenic C–H), 7.60 (dd, 2H, ortho H, J_{o-m} = 7.30 Hz., J_{o-p} = 1.28 Hz.), 7.30 (t, 2H, meta H, J_{m-p} = 7.29 Hz.), 7.11 (tt, 1H, para H), 5.84 (m, 1H, Cp-H-7), 5.73 (m, 1H, Cp-H-5), 5.70 (m, 1H, Cp-H-2), 5.62 (m, 1H, Cp-H-10), 5.17 (m, 1H, Cp-H-3), 5.10 (m, 2H, Cp-H-4 and Cp-H-8), 5.01 (m, 1H, Cp-H-9), 3.24 and 3.22 (AB quartet, J_{A-B} = 14.6 Hz., 2H, CH_2). ^{13}C NMR: ($CDCl_3$) 244.9 (μ-CO), 199.6 (Ru–CO), 199.0 (Ru–CO), 139.8 (PhC=*C*H), 138.6 (*ipso*-Ph), 128.2 (m-Ph), 125.0 (o-Ph), 124.9 (p-Ph), 119.6 (Ph*C*=CH), 98.4 (Cp, C-3), 96.3 (Cp, C-8), 95.4 (Cp, C-4), 95.0 (*ipso*-Cp), 94.7 (Cp, C-9), 94.0 (*ipso*-Cp), 87. 1 (Cp, C-10), 86.0 (Cp, C-7), 85.8 (Cp, C-2), 85.4 (Cp, C-5), 23.7 (CH_2). Chiral HPLC: first band, $t_{R'1}$ = 68 min; second band, $t_{R'2}$ = 78 min; α = 1.14. Anal. Found: C, 45.00; H, 3.30. $C_{22}H_{16}O_3Ru_2 \cdot CH_2Cl_2$ (CH_2Cl_2 of crystallization confirmed by ^1H NMR). Calc.: C, 44.89; H, 2.93%.

A small quantity of unreacted **4** was recovered by continued elution.

3.10. Structural characterization of 11 and 12

Crystallographic data are collected in Table 1. For compound **11**, the systematic absences in the diffraction data are uniquely consistent for the $P2_1/c$ space group. The structure was solved using direct methods, completed by subsequent difference Fourier synthesis and refined by full-matrix least squares procedures. Semi-empirical absorption corrections were not required because of the less than 10% variation in the integrated ψ-scan intensities. Phenyl groups were treated as rigid bodies. All non-hydrogen atoms were refined with anisotropic displacement coefficients. Hydrogen atoms were treated as idealized contributions.

For compound **12**, photographic work found *mmm* Laue symmetry, and systematic absences in the data uniquely determined the space group. ψ-scan data indicated that no correction for absorption was required. The structure was solved by direct methods. The phenyl rings were constrained to rigid hexagons during refinement. All non-hydrogen atoms were anisotropically refined and hydrogen atoms were treated as idealized, isotropic contributions. A correction for secondary extinction was refined.

Selected bond distances and angles for compound **11** are presented in Table 2 and those for compound **12** are in Table 3.

All computations used the SHELXTL library of programs [20].

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