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Synthesis and photochemistry of ring-coupled heterobimetallic compounds of ruthenium. The molecular structures of $RuM(CO)_5(\mu\text{-}\eta^5,\eta^5\text{-}C_5H_4CR_2C_5H_4)$, where M = Mo, R = CH_3; M = W, R = H, $[Ru(CO)_2][Mo(CO)_3Cl](\mu\text{-}\eta^5,\eta^1{:}\eta^5\text{-}C_5H_4CH_2C_5H_3)$ and $[W(CO)_3][Ru(CO)_2Cl](\mu\text{-}\eta^5,\eta^1{:}\eta^5\text{-}C_5H_4CH_2C_5H_3)$

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Abstract

Reaction of the versatile reagent $Ru(CO)_2(\mu\text{-}\eta^5,\eta^1\text{-}C_5H_4CR_2C_5H_4)$, where R = H or CH_3, with $M(CO)_6$ or $M(CO)_3(CH_3CN)_3$, where M = Mo or W, yields bimetallic compounds of the form $RuM(CO)_5(\mu\text{-}\eta^5,\eta^5\text{-}C_5H_4CR_2C_5H_4)$ in excellent yield, while reaction with $Fe(CO)_5$ yields $RuFe(CO)_2(\mu\text{-}CO)_2[\mu\text{-}\eta^5,\eta^5\text{-}C_5H_4C(CH_3)_2C_5H_4]$ in excellent yield. Reaction with $Ni(CO)_4$ yields thermally unstable $RuNi(CO)_3[\mu\text{-}\eta^5,\eta^5\text{-}C_5H_4C(CH_3)_2C_5H_4]$. These compounds have been characterized by IR and NMR spectroscopies, and, with the exception of the Ru/Ni compound, elemental analysis. Photolysis of $RuMo(CO)_5[\mu\text{-}\eta^5,\eta^5\text{-}C_5H_4C(CH_3)_2C_5H_4]$ in the presence of triphenylphosphine yields both of the simple mono-carbonyl substitution products with the phosphine on Ru and Mo. Photolysis of the derivative with phosphine bound to the molybdenum yields $[Ru(\sigma\text{-}C_6H_5)(CO)][Mo(CO)_2][\mu\text{-}P(C_6H_5)_2](\mu\text{-}\eta^5,\eta^5\text{-}C_5H_4C(CH_3)_2C_5H_4)[Ru\text{–}Mo]$. Photolysis of $RuFe(CO)_2(\mu\text{-}CO)_2[\mu\text{-}\eta^5,\eta^5\text{-}C_5H_4C(CH_3)_2C_5H_4]$ with triphenylphosphine yields $[Ru(CO)]\{Fe[P(C_6H_5)_3]\}(\mu\text{-}CO)_2[\mu\text{-}\eta^5,\eta^5\text{-}C_5H_4C(CH_3)_2C_5H_4][Ru\text{–}Fe]$. Photolysis of the Ru/Mo and Ru/W heterobimetallic compounds in deuterobenzene established that two metal-hydride species were formed, one whose chemical shift was characteristic of a $CpRu(CO)_2H$ and the second typical of a $CpM(CO)_3H$. Photolysis of the Ru/Mo and Ru/W compounds in 20% chloroform in benzene followed by chromatography of the reaction mixtures permitted isolation of the isomeric photoproducts as their chloride derivatives. IR and NMR spectroscopy and X-ray crystallography of these compounds established them to have 'twist' structures in which one cyclopentadienyl ring is η^1 to one of the metals and η^5 to the second. The molecular structures of four compounds were determined: $RuMo(CO)_5[\mu\text{-}\eta^5,\eta^5\text{-}C_5H_4C(CH_3)_2C_5H_4]$: monoclinic, $P2_1/n$, $a = 9.608(3)$, $b = 12.613(4)$, $c = 14.467(5)$ Å, $\beta = 97.59(2)°$, $V = 1738.0(9)$ Å^3, $z = 4$, $R_F = 3.53$. $RuW(CO)_5(\mu\text{-}\eta^5,\eta^5\text{-}C_5H_4CH_2C_5H_4)$: monoclinic, $P2_1/c$, $a = 14.232(5)$, $b = 7.833(3)$, $c = 13.771(5)$ Å, $\beta = 93.22(3)°$, $V = 1533(1)$ Å^3, $z = 4$, $R_F = 3.88$. $[Mo(CO)_3][Ru(CO)_2Cl](\mu\text{-}\eta^5,\eta^1{:}\eta^5\text{-}C_5H_4CH_2C_5H_3)$: monoclinic, $P2_1/c$, $a = 10.259(9)$, $b = 12.666(5)$, $c = 13.451(5(5)$ Å, $\beta = 109.85(4)°$, $V = 1641(1)$ Å^3, $z = 4$, $R_F = 2.72$. $[Ru(CO)_2][W(CO)_3Cl](\mu\text{-}\eta^5,\eta^1{:}\eta^5\text{-}C_5H_4CH_2C_5H_3)$: monoclinic, $P2_1/c$, $a = 12.793(3)$, $b = 9.485(2)$, $c = 13.450(2)$ Å, $\beta = 94.56(1)°$, $V = 1626.8(6)$ Å^3, $z = 4$, $R_F = 3.67$.

Keywords: Heterobimettallic compounds; Ruthenium complexes; Molecular structures; Photochemistry

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1. Introduction

Interest in the synthesis and chemistry of heterobimetallic compounds continues to increase due to a

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widely held belief in the potential for these compounds to exhibit metal cooperativity leading to reaction pathways not otherwise available to mononuclear or homobimetallic compounds. Our work has dealt in large measure with the synthesis of bis(cyclopentadienylmetal) compounds in which the two cyclopentadienyl rings are coupled by a carbon or silicon linkage. While there are many examples of homobimetallic compounds in this class, the synthesis of heterobimetallic compounds has proven to be more challenging.

Vollhardt and Weldman [1] reported the synthesis of $MoRu(CO)_5(\mu\text{-}\eta^5,\eta^5\text{-}C_5H_4C_5H_4)$ in greater than statistical yield by reaction of $Mo(CO)_6$, $Ru_3(CO)_{12}$, and dihydrofulvalene in glyme. Separation of the resultant mixture of Mo_2, Ru_2 and MoRu compounds was achieved by preparative HPLC. Huffman [2] attempted to develop a more rational route to these compounds beginning with $Mo(CO)_2(PMe_3)_2(\eta^4\text{-}C_5H_4C_5H_4)$ with partial success. Far better results were achieved via the synthesis of $M(CO)_3CH_3(\eta^5\text{-}C_5H_4C_5H_5)$, where M = Mo or W, in which the pendant cyclopentadiene ring could be deprotonated and metallated [3]. Vollhardt and coworkers have developed a substantial chemistry of the W/Ru and Mo/Ru compound including acetylene exchange for carbonyl groups [4] and electrochemistry [5].

Heterobimetallic derivatives of bis(cyclopentadienyl)methane have been reported by Härter and Werner and their coworkers. Werner et al. found that it was possible to selectively prepare $(MC_5H_4CH_2C_5H_5)$, where M = Li and Na, then react this species with Group IX metal carbonyl halides to give $M(CO)_2(\eta^5\text{-}C_5H_4CH_2C_5H_5)$ [6]. Subsequent deprotonation of the pendant cyclopentadiene ring followed by metallation yielded heterobimetallic derivatives. Härter et al. [7] adapted a reaction reported by Mueller-Westerhoff and coworkers [8] in which ring lithiated cyclopentadienyl metal derivatives may be reacted with dimethylaminofulvene to yield fulvalene substituted compounds. Reduction of the fulvene yields a pendant cyclopentadienyl anion that may be metallated. Heck and Körnich have prepared unusual heterobimetallic compounds having the cyclopentadienyl and tetramethylcyclopentadienyl rings coupled by a ketone carbonyl. Of immediate relevance to the current work are the compounds $WM(CO)_5(\mu\text{-}\eta^5,\eta^5\text{-}C_5H_4\text{–}C(=O)\text{–}C_5Me_4)$, where M = Fe and Ru [9].

Green and coworkers have described the formation of heterobimetallic compounds of (2,2-cyclopentadienyl)(indenyl)propane by reaction of $ClMn(CO)_5$ and $[ClRh(CO)_2]_2$ with $ZrCl(\eta^5\text{-}C_5H_5)[\eta^5,\eta^2\text{-}C_5H_4C(CH_3)_2\text{-}C_9H_6]$ [10]. In this case, the pendant indenyl group is stabilized by a dihapto bond to the zirconium.

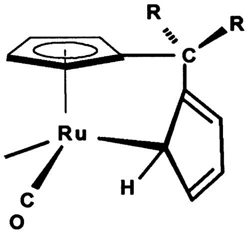
Salzer and coworkers have reported the synthesis of $(\eta^5\text{-}C_5Me_4Et)Mo(CO)_5Ru(\eta^5\text{-}C_5H_5)$ [11].

We have recently described the synthesis of $Ru(CO)_2(\mu\text{-}\eta^5,\eta^1\text{-}C_5H_4CR_2C_5H_4)$, where R = H (**1**) or CH_3 (**2**), which shares with the compound reported by Green the stabilization of a pendant ring by partial metal complexation [12]. Reaction of these compounds with $M(CO)_6$ or $M(CO)_3(CH_3CN)_3$, where M = Mo or W, yields the heterobimetallic compounds $RuM(CO)_5(\mu\text{-}\eta^5,\eta^5\text{-}C_5H_4CH_2C_5H_4)$, where M = Mo (**3**) or W (**4**), and $RuMo(CO)_5[\mu\text{-}\eta^5,\eta^5\text{-}C_5H_4C(CH_3)_2C_5H_4]$ (**5**). Similarly, reaction with $Fe(CO)_5$ or $Ni(CO)_4$ yields the compounds $RuM(CO)_n[\mu\text{-}\eta^5,\eta^5\text{-}C_5H_4C(CH_3)_2C_5H_4]$, where M = Fe, $n = 4$ (**6**) and M = Ni, $n = 3$ (**7**). The characterization and photochemistry of these compounds is reported in this paper.

2. Results and discussion

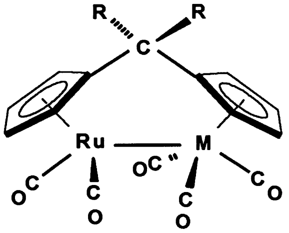
2.1. Synthesis and characterization of $RuM(CO)_n(\mu\text{-}\eta^5,\eta^5\text{-}C_5H_4CR_2C_5H_4)$

Compounds **1** and **2** were prepared as previously reported by reaction of $[Cl_2Ru(CO)_3]_2$ with 1 equiv. of $CR_2(C_5H_4Tl)_2$ in refluxing benzene [12]. Compounds **1** and **2** are isolated by chromatography from the reaction mixtures as air-stable, waxy solids in good yields. Reaction of these compounds with $M(CO)_6$ or $M(CO)_3(CH_3CN)_3$, where M = Mo or W, gave the resulting heterobimetallic compounds **3**, **4**, and **5** in excellent yield after chromatography.



1. R = H

2. R = CH_3



3. M = Mo, R = H

4. M = W, R = H

5. M = Mo, R = CH_3

The compounds are isolated as red to orange–red, air-stable, crystalline solids. IR spectra of **3** and **5** in dichloromethane contain two strong carbonyl bands at

2020, 1957 cm^{-1}, and medium intensity bands at 1900 and 1873 cm^{-1}. RuMo(CO)$_5$(μ-η^5,η^5-$C_5H_4C_5H_4$) is reported to have carbonyl stretching bands at 2020, 1942, 1935, 1868 cm^{-1}. Compound **4** has a similar pattern with two strong bands at 2019 and 1955 cm^{-1}, and medium bands at 1973, 1889, and 1867 cm^{-1}. It is likely that the C_1 symmetry of the solid state (vide infra) of compounds **3**, **4**, and **5** is preserved on the IR time scale in the solution phase. The ^{1}H NMR spectra of the three heterobimetallic compounds are simple with four ring resonances and singlets for the CH_2 or $C(CH_3)_2$ bridges. The ^{13}C NMR spectra are also simple with four ring resonances and two *ipso* ring carbons located. In light of the low symmetry suggested by the IR spectrum and solid state structures, it is likely that the molecules are rapidly twisting about an axis that passes through the bridge carbon and the center of the M–M′ bond. Similar averaging has been observed for $M_2(CO)_6$(μ-η^5,η^5-$C_5H_4CR_2C_5H_4$), where M = Mo or W, and R = H or CH_3, for which the molecules possess C_2 symmetry in the solid state. The carbonyl resonances of **3** and **5** are fully averaged at room temperature (r.t), whereas the carbonyl resonances of **4** are almost at coalesence at r.t. Those resonances are completely averaged at 325 K. A low temperature NMR of **5** (197 K) failed to freeze out the carbonyl averaging. Averaging of the carbonyl resonances has been observed for the Ru, Mo, and W homobimetallic derivatives of bis(cyclopentadienyl)methane and 2,2-bis(cyclopentadienyl)propane.

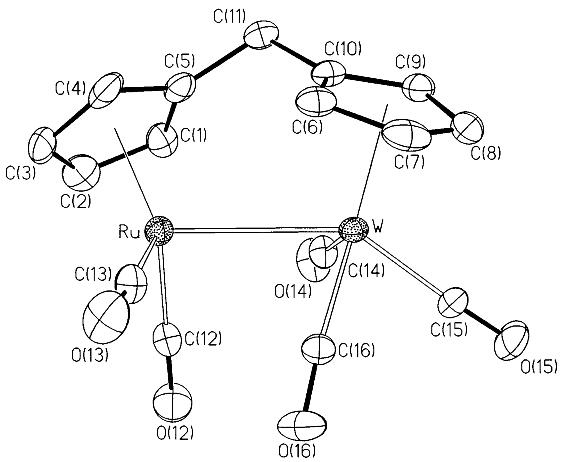


Fig. 1. Molecular structure of **4**.

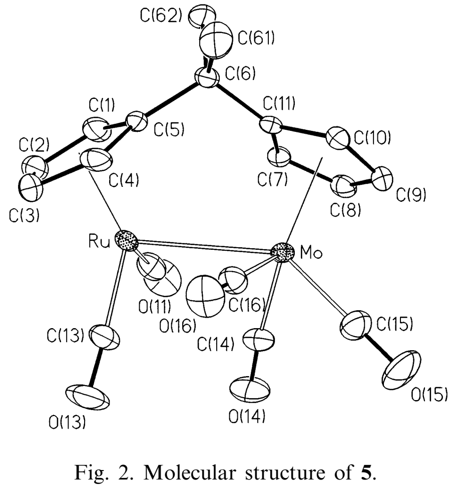
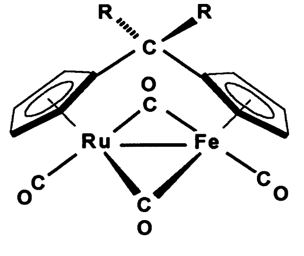


Fig. 2. Molecular structure of **5**.

The molecular structures of **4** and **5** were determined by X-ray crystallography of crystals grown from dichloromethane/petroleum ether by vapor diffusion and are presented in Figs. 1 and 2. Crystallographic data for these compounds are summarized in Table 1. Representative bond length and bond angle data are presented in Tables 2 and 3. As noted previously, the molecules have C_1 symmetry with the carbonyl groups on the Ru(CO)$_2$ and M(CO)$_3$ units twisted in opposite directions. The Ru–Mo and Ru–W bond lengths of 2.9586(1) and 2.970(1) Å, respectively, are almost the exact average of the Ru–Ru, Mo–Mo and W–W bond lengths in the analogous ring-coupled homobimetallic complexes [13,14]. A W–Ru bond length of 2.978 (2) Å was reported by Heck and Körnish for their ketone derivative [9]. Similarly, the ligand bond lengths and angles are very similar to the homobimetallic compounds. In our experience, the M–M bond lengths of the bis(cyclopentadienyl)methane derivatives of molybdenum and tungsten tend to be slightly shorter than the corresponding $M_2(CO)_6$(η^5-C_5H_5)$_2$ compounds. The molecular structure of (η^5-C_5Me_4Et)Mo(CO)$_5$Ru(η^5-C_5H_5) was not reported and the analogous Ru–W compound without ring coupling is not known.

Reaction of **2** with Fe(CO)$_5$ in refluxing xylene resulted in formation of **6** in essentially quantitative yield. The IR spectrum of **6** has strong carbonyl stretching bands at 1995, 1956, 1777 cm^{-1} and a weak shoulder at about 1810 cm^{-1}.



6. R = CH_3

The bands at 1777 and 1810 cm^{-1} are assigned to the asymmetric and symmetric stretching modes of the bridging carbonyls. These are very similar in position to the bands reported for RuFe(CO)$_2$(μ-CO)$_2$(η^5-C_5H_5)$_2$ [15]. The ^{1}H and ^{13}C NMR spectra of **6** are simple with two sets of two ring resonances and a singlet for the bridging $C(CH_3)_2$ group. Metal carbonyl resonances are fully averaged at r.t., consistent with the behavior of

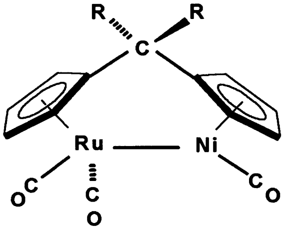
Table 1
Crystallographic data for **4**, **5**, **13**, and **14**

Formula	$C_{18}H_{14}MoO_5Ru$	$C_{16}H_{10}O_5RuW$	$C_{16}H_9ClMoO_5Ru$	$C_{17}H_{12}ClO_5RuW$
Crystal parameters				
Formula weight	507.3	567.2	513.7	616.6
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a (Å)	9.608(3)	14.232(5)	10.259(9)	12.793(3)
b (Å)	12.613(4)	7.833(3)	12.666(5)	9.485(2)
c (Å)	14.467(5)	13.771(5)	13.451(5)	13.450(2)
β (°)	97.59(2)	93.22(3)	109.85(4)	94.56(1)
V (Å^3)	1738.0(9)	1533(1)	1641(1)	1626.8(6)
Z	4	4	4	4
Crystal dimensions (mm)	0.34 × 0.38 × 0.40	0.32 × 0.34 × 0.38	0.23 × 0.25 × 0.30	0.38 × 0.39 × 0.40
Crystal color	red	red	red	yellow
D_{calc} (g cm^{-3})	1.939	2.458	2.079	2.498
μ(Mo Kα) (cm^{-1})	16.15	85.06	18.70	81.20
Temperature (K)	2982	298	244	298
T_{max}/T_{min}	1.29	1.69	1.43	1.89
Data collection				
Diffractometer	Siemens P4			
Monochromator	graphite			
Radiation	Mo Kα ($\lambda = 0.71073$ Å)			
2θ Scan range	4.0–57.0	4.0–62.0	4.0–50.0	4.0–52.0
Data collected (h, k, l)	$\pm 12, +16, +19$	$\pm 20, +11, +19$	$\pm 11, +15, +15$	$\pm 15, +11, +16$
Reflections collected	4562	4982	3009	3371
Independent reflections	4401	4795	2876	3225
Independent reflections ($F_o \geq n\sigma(F_o)$)	3498 ($n = 4$)	3463 ($n = 5$)	2600 ($n = 4$)	2406 ($n = 4$)
Standard/reflections	3/197	3/197	3/197	3/197
Variation in standards (%)	<1	<1	<1	<1
Refinement[a]				
R_F (%)	3.53	3.88	2.72	3.67
R_{wF} (%)	4.54	5.35	4.53	3.68
Δ/σ_{max}	0.002	0.002	0.011	0.004
$\Delta/(\rho)$ (e Å^{-3})	1.03	1.18	0.52	1.11
N_o/N_v	15.5	16.6	11.9	11.1
Goodness-of-fit	1.0	1.0	1.2	1.1

[a] Quantity minimized = $\Sigma w\Delta^2$; $R = \Sigma\Delta/\Sigma(F_o)$; $R_w = \Sigma\Delta w^{0.5}/\Sigma(F_o \cdot w^{0.5})$, $\Delta = |(F_o - F_c)|$.

the corresponding homobimetallic compounds. Ring and carbon resonances were assigned by COSY and $^1H/^{13}C$ correlation spectroscopy. We are not able to establish to which metal the rings were attached.

Reaction of **2** with $Ni(CO)_4$ in xylene, followed by chromatography of the reaction mixture on alumina, resulted in isolation of **7** as a red–brown solid. Over time this compound decomposes to **2** and an unknown nickel containing product. Compound **7** has a strong carbonyl stretching band at 2017 cm^{-1} and a pair of medium intensity bands at 1960 and 1943 cm^{-1}.



7. R = CH$_3$

The ^1H and ^{13}C NMR spectra are consistent with a molecule with C_s symmetry. A broad feature was ob-

Table 2
Bond lengths (Å) and angles (°) for **4**

Bond lengths			
Ru–W	2.970(1)	C(12)–O(12)	1.147(11)
Ru–C(12)	1.862(9)	C(13)–O(13)	1.117(11)
Ru–C(13)	1.878(8)	C(14)–O(14)	1.146(11)
W–C(14)	1.977(8)	C(15)–O(15)	1.157(11)
W–C(15)	1.963(8)	C(16)–O(16)	1.169(11)
W–C(16)	1.962(8)		
Bond angles			
W–Ru–C(12)	91.6(3)	W–Ru–C(13)	90.4(3)
Ru–W–C(14)	70.1(2)	Ru–W–C(15)	137.9(2)
Ru–W–C(16)	77.4(2)	C(12)–Ru–C(13)	91.3(4)
C(14)–W–C(15)	79.4(3)	C(14)–W–C(16)	100.3(3)
C(15)–W–C(16)	80.4(3)	Ru–C(12)–O(12)	179.2(6)
Ru–C(13)–O(13)	175.7(8)	W–C(14)–O(14)	173.8(7)
W–C(15)–O(15)	176.9(8)	W–C(16)–O(16)	175.4(7)

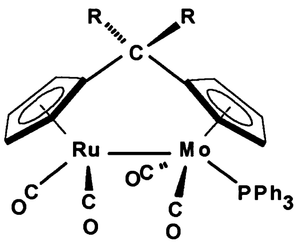
Table 3
Bond lengths (Å) and angles (°) for **5**

Bond lengths			
Ru–Mo	2.958(1)	C(12)–O(11)	1.144(7)
Ru–C(12)	1.876(6)	C(13)–O(13)	1.131(7)
Ru–C(13)	1.873(5)	C(14)–O(14)	1.143(6)
W–C(14)	1.977(5)	C(15)–O(15)	1.149(7)
W–C(15)	1.956(5)	C(16)–O(16)	1.159(6)
W–C(16)	1.966(4)		
Bond angles			
Mo–Ru–C(12)	86.7(2)	Mo–Ru–C(13)	94.7(2)
Ru–Mo–C(14)	76.9(1)	Ru–Mo–C(15)	138.6(2)
Ru–Mo–C(16)	72.2(1)	C(12)–Ru–C(13)	92.3(2)
C(14)–Mo–C(15)	78.1(2)	C(14)–Mo–C(16)	98.1(2)
C(15)–Mo–C(16)	79.4(2)	Ru–C(12)–O(11)	176.2(5)
Ru–C(13)–O(13)	177.7(5)	Mo–C(14)–O(14)	175.5(5)
Mo–C(15)–O(15)	177.0(5)	Mo–C(16)–O(16)	174.9(4)

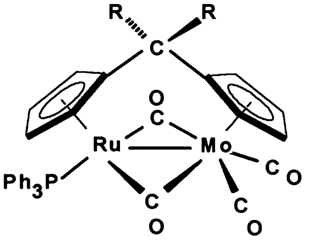
served at 201 ppm in the ^{13}C spectrum which may be due to averaging metal carbonyl groups. Stone and coworkers have reported the synthesis of what was believed to be RuNi(CO)$_3$(η^5-C$_5$H$_5$)$_2$ by reaction of Ru$_3$(CO)$_{12}$ and nickelocene [16]. The compound was too unstable for isolation and decomposed during work-up to give Ru$_2$(CO)$_4$(η^5-C$_5$H$_5$)$_2$ and Ni$_2$(CO)$_2$(η^5-C$_5$H$_5$)$_2$. IR bands attributable to the Ru/Ni compound were found at 2005 and 1822 cm^{-1}. We shall continue to examine the chemistry of the ring-coupled Ru/Ni compounds in the hope of developing a derivative chemistry of this unique material.

2.2. Solution photolyses with triphenylphosphine

Photolysis of **5** in benzene with an equivalent of triphenylphosphine followed by chromatographic separation was found to yield three products, **8**, **9**, and **10**. Two of these products, **8** and **9**, were established by spectral analysis and elemental analysis to be isomeric carbonyl exchange products, while the third, **10**, was shown independently to arise from secondary photolysis of **8**.



8. R = H



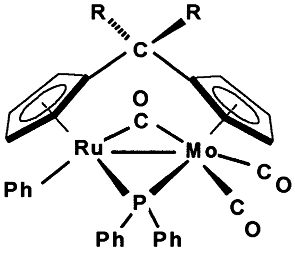
9. R = H

^{1}H and ^{13}C NMR spectra of **8** are consistent with a species having C_s symmetry (or averaging on the NMR time scale). Two sets of metal carbonyl resonances are observed with one set at 238.2 split by a phosphine while the second set at 205.6 is not. The ^{31}P NMR spectrum of **8** has a single resonance at 77.22 ppm. The analogous homobimetallic compounds, Mo$_2$(CO)$_{6-n}$(PPh$_3$)$_n$(μ-η^5,η^5-C$_5$H$_4$CH$_2$C$_5$H$_4$), where $n = 1$ or 2, have metal carbonyl resonances in the 234 ppm region and phosphine resonance at about 75 ppm [17], thus we believe that the triphenylphosphine resides on the molybdenum atom in **8**.

The IR spectrum of **8** contains bands at 1992, 1933, 1877, and 1814 cm^{-1} while that of **9** has bands at 1949, 1909, 1852, and 1734 cm^{-1}. Like **8**, the ^{1}H and ^{13}C NMR spectra of **9** require either a C_s symmetry or averaging on the NMR time scale. Two sets of metal carbonyl resonances are observed at 239.5 and 238.1 ppm with the higher field resonance split by the phosphine. A singlet at 48.5 ppm was observed in the ^{31}P NMR spectrum which is characteristic of a ruthenium bound triphenylphosphine (vide infra). Coupling between the phosphine and the ring protons of one ring allowed complete ring assignments to be made. A ^{1}H/^{13}C correlation spectrum permitted the ring carbons to be assigned to the two rings.

The spectral data suggest that the triphenyl phosphine unit is bound to the molybdenum in compound **8** and to the ruthenium in compound **9**. The IR data are consistent with structures in which there is a semibridging carbonyl in **8** and a bridging carbonyl group in **9**.

Photolysis of **8** results in formation of a new product, **10**, that may be separated by chromatography. Compound **10** is isolated as an intensely purple oil. Small amounts of this compound are also isolated from the synthesis of **8** and **9**.

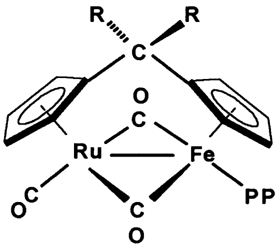


10. R = CH$_3$

The ^{1}H spectrum of **10** is complex with separate resonances for the three phenyl groups, and seven resonances (one overlapping) for the ring protons. Two methyl resonances are observed. The ^{13}C NMR spectrum is also consistent with a highly asymmetric structure with all eight ring resonances being resolved. Three sets of resonances for the phenyl groups are observed as well as three sets of carbonyl resonances, two of which couple with phosphorus. A single phosphorus resonance is observed at 188.5 ppm. The IR spectrum contains three bands at 1968, 1920, and 1849 cm^{-1}. The NMR spectra of **10** bear a striking resemblance to those of Ru$_2$(CO)(μ-CO)(σ-C$_6$H$_5$)[μ-P(C$_6$H$_5$)$_2$](μ-η^5,η^5-C$_5$H$_4$CH$_2$C$_5$H$_4$) which is formed upon photolysis of

$Ru_2(CO)_4(\mu\text{-}\eta^5,\eta^5\text{-}C_5H_4CH_2C_5H_4)$ with triphenylphosphine [18]. We have proposed that the ruthenium compound is formed in a stepwise manner with initial carbonyl loss leading to formation of a simple triphenylphosphine derivative, followed by loss of a second carbonyl and oxidative addition of a P–C bond to the electron deficient metal atom. It may be important to note that it is the ruthenium that would be expected to lose a carbon monoxide from **8**, thus the oxidative addition steps in the diruthenium and ruthenium/molybdenum cases would be identical.

Photolysis of **6** in benzene with an excess of triphenylphosphine gave, after work-up, a single product, **11**, as purple–red flakes. We were unable to obtain crystallographic quality crystals from this material.



11. R = CH_3

The IR spectrum of **11** contains strong bands at 1948 and 1728 cm^{-1} and a weak band at 1767 cm^{-1}. The ^1H NMR spectrum is slightly broadened with four sets of ring resonances and a singlet for the bridge methyl groups consistent with a C_s symmetry. The ^{13}C NMR spectrum reveals both terminal and bridging CO resonances. The bridging carbonyl resonances couple with the phosphine ligand. As for the ^1H spectrum, the ring carbon and bridge regions require C_s symmetry.

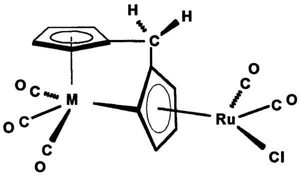
We have recently reported [18] the synthesis of the triphenylphosphine derivative of $Fe_2(CO)_4(\mu\text{-}\eta^5,\eta^5\text{-}C_5H_4CH_2C_5H_4)$ using the same methods as used in the present work. Two strong bands were readily assigned as corresponding to the terminal CO (1950 cm^{-1}) located along the molecular mirror plane and the asymmetric stretching band of the bridging carbonyl groups (1725 cm^{-1}). A weak band at 1763 cm^{-1} was assigned to the symmetric stretch of the bridging carbonyls. These band positions correspond almost exactly to bands observed for **11**. Perhaps more diagnostic is that the ^{31}P NMR chemical shift of **11** is 72.33 ppm while that of the homobimetallic iron triphenylphosphine derivative is 71.88 ppm, suggesting that the triphenylphosphine in **11** is on the iron. By way of comparison, the ^{31}P NMR chemical shifts for $M(CO)(PPh_3)(Cl)(\eta^5\text{-}C_5H_5)$, where M = Fe and Ru, are 64.06 and 49.29 ppm, respectively (J.E. Shade, personal communication, 1996).

2.3. Solution photolyses without ligands

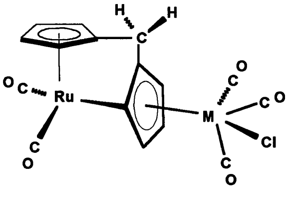
Brief photolysis of **4** in an NMR tube in deuterobenzene was shown by ^1H NMR to form products in which two strong metal hydride resonances were observed at -6.35 and -10.18 ppm with an integration ratio of approximately 2:1. The resonance at -6.35 ppm has a pair of satellites ($J = 38.1$ Hz) identifying it as belonging to a W–H group. In addition, a number of new resonances appeared in the ring proton region and two sets of AB resonances appeared in the region of the ring-bridging methylenes. Photolysis of **3** or **5** under identical conditions produced new hydride resonances at -4.87 and -10.22 ppm, and -4.99 and -10.15 ppm, respectively. New ring resonances were observed in the spectra of the photoproducts, and two sets of AB quartets for the CH_2 resonances were found for **3** and **4**. Two methyl resonances were observed for the photoproduct of **5**. Extended photolysis of these compounds led to the appearance of additional hydride resonances and increasingly complex ring and bridge regions.

We have previously reported [19] that ring-coupled bimetallic ruthenium compounds of the form, $Ru_2(CO)_4(\eta^5,\eta^5\text{-}C_5H_4\text{–}L\text{–}C_5H_4)$, where L = CH_2, $C(CH_3)_2$, C_2H_4, or $Si(CH_3)_2$, undergo a ‘twist’ photochemical rearrangement to form $[Ru(CO)_2][Ru(CO)_2H](\mu\text{-}\eta^5,\eta^5\text{:}\eta^1\text{-}C_5H_4\text{–}L\text{–}C_5H_3)$. Clearly an identical reaction is occurring in the case of compounds **3**, **4**, and **5** leading to both possible ‘twist’ isomers.

In order to trap and isolate these twisted hydride species, compounds **3** and **4** were photolyzed in benzene containing 20% $CHCl_3$. Small amounts of compounds **14** and **15** were also obtained by addition of $CHCl_3$ to a solution of the twist hydrides produced by photolysis in deuterobenzene. Chromatography separated two products in each case (**12**, **13** and **14**, **15**) and these products were characterized by IR, ^1H and ^{13}C NMR spectroscopies.



12. M = Mo
14. M = W



13. M = Mo
15. M = W

The very small quantities of samples precluded elemental analysis. In both cases the isomer with the $Ru(CO)_2Cl$ moiety was isolated in much smaller yield than the isomer with the $M(CO)_3Cl$ group indicating that the preference for the $M(CO)_3H$ product indicated by NMR is preserved in the isolated chlorides. Finally, single crystals of **13** and **14** were grown and the molecular structures determined by X-ray crystallography

(Figs. 3 and 4). The crystallographic and refinement data are presented in Table 1 and selected bond lengths and angles are presented in Tables 4 and 5. The η^5:η^1-C_5H_3 ring in these compounds is nearly perpendicular to the η^5-C_5H_4 rings (87.0 and 94.0°, respectively). All bond lengths and angles are within normal ranges indicating that the twisted conformation has no apparent bond strain.

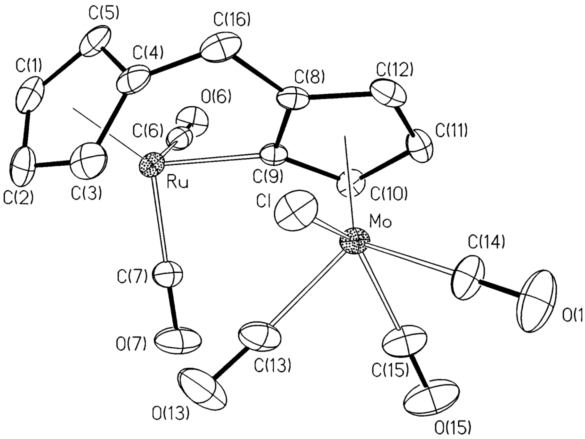


Fig. 3. Molecular structure of **13**.

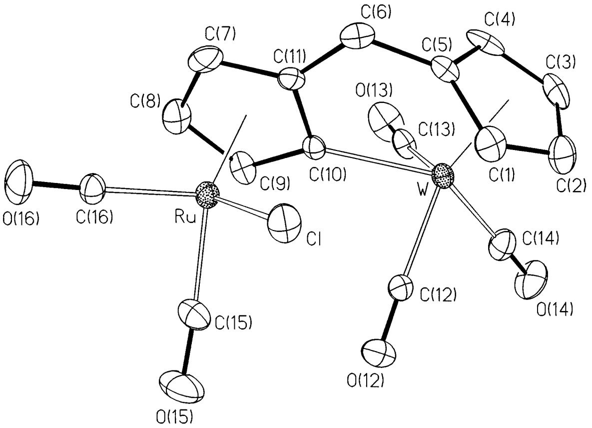


Fig. 4. Molecular structure of **14**.

Table 4
Bond lengths (Å) and angles (°) for **13**

Bond lengths			
Ru–C(9)	2.061(4)	Mo–Cl	2.516(2)
Ru–C(6)	1.876(4)	C(6)–O(6)	1.141(5)
Ru–C(7)	1.869(5)	C(7)–O(7)	1.148(6)
Mo–C(13)	2.005(4)	C(13)–O(13)	1.147(6)
Mo–C(14)	2.004(6)	C(14)–O(14)	1.114(7)
Mo–C(15)	1.995(6)	C(15)–O(15)	1.135(8)
Bond angles			
C(9)–Ru–C(6)	93.5(2)	C(9)–Ru–C(7)	91.4(2)
C(13)–Mo–C(14)	109.0(2)	C(13)–Mo–C(15)	77.5(2)
C(14)–Mo–C(15)	75.8(2)	C(13)–Mo–Cl	77.9(1)
C(14)–Mo–Cl	78.1(1)	C(15)–Mo–Cl	135.6(2)
Ru–C(6)–O(6)	177.1(5)	Ru–C(7)–O(7)	178.1(4)
Mo–C(13)–O(13)	177.2(6)	Mo–C(14)–O(14)	178.4(4)
Mo–C(15)–O(15)	176.8(5)	Ru–C(9)–Mo	128.2(2)

Table 5
Bond lengths (Å) and angles (°) for **14**

Bond lengths			
Ru–Cl	2.417(3)	W–C(10)	2.211(8)
Ru–C(15)	1.884(10)	C(15)–O(15)	1.152(14)
Ru–C(16)	1.876(9)	C(16)–O(16)	1.126(12)
W–C(12)	2.004(10)	C(12)–O(12)	1.130(13)
W–C(13)	1.971(9)	C(13)–O(13)	1.171(13)
W–C(14)	2.015(11)	C(14)–O(14)	1.136(14)
Bond angles			
C(15)–Ru–C(16)	89.6(4)	Cl–Ru–C(15)	89.3(3)
Cl–Ru–C(16)	94.0(3)	C(10)–W–C(12)	79.1(3)
C(10)–W–C(13)	77.4(3)	C(10)–W–C(14)	137.4(4)
C(12)–W–C(13)	110.5(4)	C(12)–W–C(14)	78.0(4)
C(13)–W–C(14)	78.0(4)	Ru–C(15)–O(15)	177.0(9)
Ru–C(16)–O(16)	176.7(8)	W–C(12)–O(12)	176.4(8)
W–C(13)–O(13)	174.9(8)	W–C(14)–O(14)	177.0(9)
W–C(10)–Ru	134.5(4)		

Evidence that will be reported elsewhere supports a mechanism for the 'twist' reaction in which photolysis results in carbonyl loss to form a coordinatively unsaturated bimetallic species. Oxidative addition of a C–H bond gives an intermediate which has M–H, M–Cp, and M–M bonds. Reductive elimination of a M–H and recapture of a carbon monoxide completes the reaction sequence. In the case of the heterobimetallic compounds described above, we have direct observation of the carbonyl loss intermediate in a Nujol matrix [20], and have captured the carbonyl-loss intermediate with triphenylphosphine. It is interesting that triphenylphosphine appears to prefer adding to the Group VI metal side of the molecule, while the 'twist' reaction products would suggest that oxidative addition to the ruthenium is preferred. Work on the reaction of these heterobimetallic compounds with other ligands, particularly acetylene, is proceeding.

3. Experimental

All synthesis were carried out under an atmosphere of dinitrogen using standard Schlenk techniques. All purification chromatography was performed using reagent grade solvents and neutral alumina provided by CAMAG Inc. or silica gel (Fisher Scientific). All preparative solvents were dried and distilled under nitrogen.

^1H, ^{13}C, and ^{13}P NMR spectra were recorded on an Bruker NR-300 spectrometer (University of Idaho) or a QE300 NMR spectrometer (US Naval Academy). Chemical shifts were recorded in ppm relative to tetramethylsilane using appropriate solvent resonances as internal standards. IR spectra were obtained using a

Bio-Rad Qualimatic FTIR spectrometer or a Perkin–Elmer Spectrum 1000 FTIR. Elemental analyses were performed by Desert Analysis of Tucson, AZ.

Compounds **1** and **2** were prepared as previously described. Metal carbonyls were purchased from Strem Chemicals, Inc. and used as received.

3.1. Synthesis of $RuMo(CO)_5(\mu\text{-}\eta^5,\eta^5\text{-}C_5H_4CH_2C_5H_4)$ *(**3**)*

Compound **1** (159 mg, 0.67 mmol) and $Mo(CO)_6$ (165 mg, 0.67 mmol) were taken up in butyl ether (16 ml) in a 25 ml Schlenk flask. The contents of the flask were freeze–pump–thawed three times and then sealed under vacuum and heated at 120°C overnight. After removal of the solvent the remaining red residue was washed with petroleum ether. The resulting residue was shown by HPLC and subsequent analysis to be pure **3** as a red–orange solid, 110 mg, 34%. M.p. 180°C decomp. IR (CH_2Cl_2): 2020, 1957, 1900 (sh), 1873 cm^{-1}. ^1H NMR (C_6D_6): 4.67 (m, 4H, Cp), 4.30 (m, 4H, Cp), 2.71 (s, 2H, CH_2). ^{13}C NMR (C_6D_6): 220.0 (M–CO averaged signal), 105.3 (*ipso* Cp), 101.2 (*ipso* Cp), 89.3 (Cp), 87.5 (Cp), 86.8 (Cp), 84.5 (Cp), 26.3 (CH_2).

3.2. Synthesis of $RuW(CO)_5[\eta^5,\eta^5\text{-}C_5H_4CH_2C_5H_4]$ *(**4**)*

Compound **1** (200 mg, 0.67 mmol) and $W(CO)_3(CH_3CN)_3$ (318 mg, 0.67 mmol) were charged into a 100 ml Schlenk flask. The flask was evacuated and backfilled with nitrogen, then xylene (50 ml) was added. The flask was fitted with a condenser and the reaction mixture refluxed overnight under nitrogen. After removal of the xylene under vacuum, the red crystalline residue was taken up in dichloromethane and chromatographed on alumina using dichloromethane as the eluant. A single band was eluted. Removal of solvent yielded **4** as an orange–red solid, 200 mg, 53%. M.p. 211–213°C. IR (CH_2Cl_2): 2019, 1973 (sh), 1955, 1889 (sh), 1867 cm^{-1}. ^1H NMR ($CDCl_3$): 5.44 (t, 2H, Cp), 5.27 (t, 2H, Cp), 5.15 (t, 2H, Cp), 4.96 (t, 2H, Cp), 3.77 (s, CH_2). All Cp resonances were clean AA′BB′ triplets. ^{13}C NMR ($CDCl_3$, 298°C): 104.5 (*ipso* Cp), 102.2 (*ipso* Cp), 88.6 (Cp), 87.9 (Cp), 85.9 (Cp), 85.2 (Cp), 27.1 (CH_2). M–CO found at 212.3 ppm at 325°C.

3.3. Synthesis of $RuMo(CO)_5[\mu\text{-}\eta^5,\eta^5\text{-}C_5H_4C(CH_3)_2C_5H_4]$ *(**5**)*

Compound **2** (494 mg, 1.51 mmol) and $Mo(CO)_6$ (397 mg, 1.51 mmol) were taken up in xylene as described for **4** and refluxed overnight. After removal of solvent, the residue was chromatographed on alumina with petroleum ether:dichloromethane (3:1) as an eluant. A single red–orange band was eluted which yielded **5** as a red–orange crystalline solid, 605 mg, 79%. M.p. 180°C decomp. IR (CH_2Cl_2): 2019, 1956, 1900 (sh), 1873 cm^{-1}. ^1H NMR ($CDCl_3$): 5.40 (t, 2H, Cp), 5.24 (t, 2H, Cp), 5.10 (t, 2H, Cp), 5.08 (t, 2H, Cp), 1.49 (CMe_2). ^{13}C NMR ($CDCl_3$): 219.4 (M–CO averaged signal), 117.4 (*ipso* Cp), 111.5 (*ipso* Cp), 86.7 (Cp), 86.4 (Cp), 85.0 (Cp), 84.5 (Cp), 35.5 (*C*Me_2), 30.8 (CH_3).

3.4. Synthesis of $RuFe(CO)_4[\mu\text{-}\eta^5,\eta^5\text{-}C_5H_4C(CH_3)_2C_5H_4]$ *(**6**)*

Compound **2** (150 mg, 0.46 mmol) and $Fe(CO)_5$ (450 mg, 2.3 mmol) were charged into a 100 ml Schlenk flask. After addition of xylene (50 ml) the reaction mixture was refluxed overnight under nitrogen. Removal of the xylene under vacuum yielded a dark brown residue which was taken up in a minimum quantity of petroleum ether:dichloromethane (1:1) and chromatographed on alumina using the same solvent as the eluant. A single band was eluted. Removal of solvent yielded **6** as an orange–red solid, 164 mg, 87%. M.p. 193–194°C. IR (CH_2Cl_2): 1997, 1955, 1777 cm^{-1}. ^1H NMR ($CDCl_3$): 5.51 (β protons, ring 1), 5.46 (α protons, ring 1), 5.09 (β protons, ring 2) 4.09 (α protons, ring 2), 1.47 (s, CH_3). ^{13}C NMR ($CDCl_3$): 229.2, 109.8 (*ipso* Cp), 108.8 (*ipso* Cp), 91.3 (α carbon, ring 1), 89.1 (α carbon, ring 2), 85.2 (β carbon, ring 1), 81.2 (β carbon, ring 2), 32.5 (*C*Me_2), 29.4 (CH_3). MS (FAB): 439 (M^+), 411 (M^+–CO), 383 (M^+–2CO), 355 (M^+–3CO), 327 (M^+–4CO or –$Fe(CO)_2$).

3.5. Synthesis of $RuNi(CO)_3[\mu\text{-}\eta^5,\eta^5\text{-}C_5H_4C(CH_3)_2C_5H_4]$ *(7)*

Compound **2** (50 mg, 0.15 mmol) and xylene (10 ml) were added to a 25 ml Schlenk flask and freeze–pump–thawed three times. An excess of $Ni(CO)_4$ was condensed into the flask and the flask sealed under vacuum. The reaction mixture was heated overnight at 87°C. Removal of solvent and unreacted $Ni(CO)_4$ under vacuum gave a brown residue that was taken up in petroleum ether:dichloromethane (10:1) and chromatographed on alumina with the same solvent as eluant. A single red–brown band was eluted which gave a red–brown solid upon removal of solvent. IR showed traces of **2** in this material and subsequent studies demonstrated that **7** decomposes over time at r.t. to give **2** and an unidentified nickel product. IR (CH_2Cl_2): 2017, 1959, 1943 (sh) cm^{-1}. ^1H NMR (C_6D_6): 5.54 (t, 2H, Cp), 4.93 (t, 2H, Cp), 4,65 (t, 2H, Cp), 4.40 (t, 2H, Cp), 1.06 (CMe_2). ^{13}C NMR (C_6D_6): 201.3 (M–CO averaged signal), 97.5 (*ipso* Cp), 93.7 (Cp), 87.4 (Cp), 84.8 (Cp), 80.0 (Cp), 34.8 (*C*Me_2), 29.6 (CH_3).

3.6. Synthesis of $[Ru(CO)_2][Mo(CO)_2P(C_6H_5)_3][\mu\text{-}\eta^5,\eta^5\text{-}C_5H_4C(CH_3)_2C_5H_4][Ru\text{–}Mo]$ (**8**), $[RuP(C_6H_5)_3][Mo(CO)_2](\mu\text{-}CO)_2[\mu\text{-}\eta^5,\eta^5\text{-}C_5H_4C(CH_3)_2C_5H_4][Ru\text{–}Mo]$ (**9**), and $[Ru(\sigma\text{-}C_6H_5)(CO)][Mo(CO)][\mu\text{-}P(C_6H_5)_2](\mu\text{-}CO)[\mu\text{-}\eta^5,\eta^5\text{-}C_5H_4C(CH_3)_2C_5H_4][Ru\text{–}Mo]$ (**10**)

Compound **5** (100 mg, 0.21 mmol) and triphenylphosphine (55 mg, 0.21 mmol) were taken up in benzene and photolyzed for 30 min in a water-jacketed Pyrex cell. During photolysis the solution turned from orange to red. After removal of solvent the residue was taken up in petroleum ether:dichloromethane (5:2) and chromatographed on alumina. Four bands were eluted from the column. In order, the bands were found to be: **5** (orange), **8** (red–orange), **10** (purple), and **9** (orange).

Compound **8** was isolated as a red–orange solid. M.p. 219–221°C. IR (CH_2Cl_2): 1992 (s), 1933 (s), 1876 (m), 1814 (s) cm^{-1}. ^1H NMR ($CDCl_3$): 7.35 (m, 15H, Ph), 5.39 (m, 2H, Cp), 5.03 (m, 2H, Cp), 4.82 (m, 2H, Cp), 4.47 (m, 2H, Cp), 1.44 (s, CH_3). ^{13}C NMR ($CDCl_3$): 238.1 (d, $J_{P-C} = 22.7$ Hz, Mo–CO), 205.6 (Ru–CO), 137 (broad, *ipso* Ph), 133.3 (d, $J_{P-C} = 10.2$ Hz, *o*-Ph), 129.6 (s, *p*-Ph), 128.0 (d, $J_{P-C} = 9.7$ Hz, *m*-Ph), 115.7 (*ipso* Cp), 115.1 (*ipso* Cp), 88.6 (Cp), 85.8 (Cp), 84.4 (Cp), 84.0 (Cp), 35.8 (CMe$_2$), 31.0 (CH_3). ^{31}P NMR ($CDCl_3$): 77.2 ppm.

Compound **9** was isolated as an orange solid. M.p. 213–217°C. IR (CH_2Cl_2): 1949 (s), 1909 (s), 1852 (m), 1730 (m) cm^{-1}. ^1H NMR: ($CDCl_3$): 7.33 (m, 15H, Ph), 5.39 (AA′BB′, 2H, ring 1a), 5.15 (m, 2H, ring 2a), 5.04 (AA′BB′, 2H, ring 1b), 4.58 (m, 2H, ring 2b), 1.53 (CH_3). ^{13}C NMR ($CDCl_3$): 236.7 (d, $J_{P-C} = 31.5$ Hz, terminal M–CO), 134.6 (d, $J_{P-C} = 43.3$ Hz, *ipso* Ph), 133.5 (d, $J_{P-C} = 11.1$ Hz, *o*-Ph), 129.9 (d, $J_{P-C} = 2$ Hz, *p*-Ph), 128.0 (d, $J_{P-C} = 10.1$ Hz, *m*-Ph), 108.4 (*ipso* Cp), 108.2 (*ipso* Cp), 90.4 (ring 2a), 87.7 (ring 1a), 87.4 (ring 2b), 85.8 (ring 1b), 34.1 (CMe$_2$), 31.1 (CH_3). ^{31}P NMR ($CDCl_3$): 48.2 ppm.

Compound **10** was recovered as a purple solid both from the photolysis of **5** in the presence of triphenylphosphine and photolysis of **8** in the absence of additional ligands. IR (CH_2Cl_2): 1968, 1920, 1844 cm^{-1}. ^1H NMR ($CDCl_3$): 7.80 (m, 2H, *ortho* protons σ phenyl), 7.43 (m, 3H, *meta*, *para* protons σ phenyl), 7.20 (m, 2H, *para* protons PPh_2), 6.90 (m, 4H, *ortho* protons PPh_2), 6.58 (m, 4H, *meta* protons PPh_2), 5.60 (m, 1H, H-2), 5.27 (1H, H-10), 5.21 (m, 1H, H-9), 5.12 (m, 2H, H-3 and H-11), 4.91 (m, 1H, H-4), 4.51 (m, 1H, H-8), 4.02 (m, 1H, H-5), 1.62 (s, 3H, CH_3-12), 1.33 (s, 3H, CH_3-13). ^{13}C NMR ($CDCl_3$): 240.8 (d, $J_{P-C} = 25.4$ Hz, Mo–CO), 239.4 (s, Mo–CO), 205.4 (d, $J_{P-C} = 8.8$ Hz, Ru–CO), 144.6 (s, *ortho* σ-Ph), 142.5 (d, $J_{P-C} = 30.75$ Hz, *ipso* Ph), 140.0 (d, $J_{P-C} = 16.3$ Hz, *ipso* σ-Ph), 140.6 (d, $J_{P-C} = 42.8$ Hz, *ipso* Ph), 133.4 (d, $J_{P-C} = 9.5$ Hz, *o*-Ph a), 132.3 (d, $J_{P-C} = 11.0$ Hz, *o*-Ph b), 129.2 (s, *p*-Ph a), 128.3 (s, *p*-Ph b), 127.9 (d, $J_{P-C} = 9.1$ Hz, *m*-Ph a), 126.8 (s, *m* σ-Ph), 126.7 (d, $J_{P-C} = 9.6$ Hz, *m*-Ph b), 121.7 (s, *p* σ-Ph), 115.8 (*ipso* Cp), 102.0 (*ipso* Cp), 96.0 (Cp), 92.4 (Cp), 88.7 (Cp), 88.1 (Cp), 88.0 (Cp), 85.2 (Cp), 82.5 (Cp), 79.6 (Cp), 35.5 (CMe$_2$), 35.0 (CH_3), 29.6 (CH_3). ^{31}P NMR ($CDCl_3$): 188.5 ppm.

3.7. Synthesis of $RuFe(CO)_3[P(C_6H_5)_3][\mu\text{-}\eta^5,\eta^5\text{-}C_5H_4C(CH_3)_2C_5H_4]$ (**11**)

Compound **6** (100 mg, 0.227 mmol) and triphenylphosphine (60 mg, 0.229 mmol) were taken up in benzene (15 ml) and photolyzed in a Pyrex water-jacketed cell for 30 min. During photolysis the solution turned from brown to red. After removal of solvent the residue was taken up in petroleum ether:dichloromethane (10:1) and chromatographed on an alumina column. A single rose band was eluted. Removal of solvent gave **11** as a purple–red solid, 42 mg, 44%. IR (CH_2Cl_2): 1950 (s), 1763 (w), 1725 (s) cm^{-1}. ^1H NMR ($CDCl_3$): 7.53 (3H, PPh_3), 7.31 (12H, PPh_3), 5.48 (2H, Cp), 5.32 (2H, Cp), 4.88 (2H, Cp), 3.94 (2H, Cp), 1.49 (s, 6H, CH_3). Note: all resonances in the proton spectrum were broadened obscuring fine structure. ^{13}C NMR ($CDCl_3$): 270.8 (d, $J_{P-C} = 15$ Hz, μ-CO), 202.2 (terminal CO), 134.8 (d, $J = 42.8$ Hz, *ipso* Ph), 133.8 (d, $J_{P-C} = 9.2$ Hz, *o*-Ph), 129.6 (s, *p*-Ph), 127.9 (d, $J_{P-C} = 9.4$ Hz, *m*-Ph), 110.6 (*ipso* Cp), 104.8 (*ipso* Cp), 91.4 (Cp), 88.0 (Cp), 84.0 (Cp), 83.7 (Cp), 31.9 (CMe$_2$), 30.0 (CH_3). ^{31}P NMR ($CDCl_3$): 72.33 ppm.

3.8. Photolysis of **3** and **4** in benzene:$CHCl_3$ (3:1)

Compound **3** (100 mg, 0.21 mmol) was taken up in benzene:$CHCl_3$ (3:1), 10 ml, in an Ace quartz miniphotochemical reactor equipped with a cold finger and photolyzed for 15 min with a 350 W high pressure mercury lamp. Column chromatography on alumina using petroleum ether:dichloromethane (3:1) as an eluant yielded two bands. The first orange band was stripped of solvent to give **13** as an orange crystalline solid. IR (CH_2Cl_2): 2048, 2029, 1981, 1959, 1943 sh cm^{-1}. ^1H NMR: ($CDCl_3$) 5.79 (1H, m, ring 1), 5.63 (1H, m, ring 1), 5.55 (1H, m, ring 1), 5.43 (1H, m, ring 2), 5.28 (1H, m, ring 1), 5.01 (1H, m, ring 2), 4.63 (1H, m, ring 2), 3.33 and 3.10 (AB quartet, $J = 16.8$ Hz). ^{13}C NMR ($CDCl_3$): 243.1 (*axial* Mo–CO), 227.9 (*equatorial* Mo–CO), 224.2 (*equatorial* Mo–CO), 199.3 (Ru–CO), 198.5 (Ru–CO), 157.3 (*ipso* Cp), 130.2 (*ipso* Cp), 114.0 (*ipso* Cp), 92.3 (Cp), 91.1 (Cp), 90.8 (Cp), 87.0 (Cp), 86.9 (Cp), 85.3 (Cp), 83.9 (Cp), 82.3 (Cp), 81.9 (Cp), 27.3 (CH_2). The second yellow band was collected and removal of solvent gave **12** as a yellow powder. IR (CH_2Cl_2): 2050, 2031, 2000, 1966, 1943 cm^{-1}.

Compound **4** was photolyzed in a manner identical to **3**. Chromatography yielded two bands. The first yellow band yielded **14** as yellow crystals. IR (CH_2Cl_2): 2047, 2028, 1999, 1953, 1931 cm^{-1}. ^{1}H NMR ($CDCl_3$): 6.65 (1H, m), 6.05 (1H, m), 5.30 (1H, m), 5.04 (1H, m), 5.00 (1H, m), 4.82 (1H, m), 4.70 (1H, m), 3.29 and 3.02 (AB quartet, $J = 27.3$ Hz). ^{13}C NMR ($CDCl_3$): 225.0 (Mo–CO), 214.5 (Mo–CO), 198.0 (Ru–CO), 197.7 (Ru–CO), (*ipso* not located), 92.8 (Cp), 92.6 (Cp), 92.1 (Cp), 83.8 (Cp), 82.2 (Cp), 81.8 (Cp), 77.2 (Cp), 25.7 (CH_2). The second orange band yielded **15** as orange crystals. M.p. 165–167°C. IR (CH_2Cl_2): 1944, 1927, 1980, 1944 cm^{-1}. ^{1}H NMR ($CDCl_3$): 5.73 (1H, m), 5.63 (1H, m), 5.56 (1H, m), 5.53 (1H, m), 5.27 (1H, m), 5.19 (1H, m), 4.67 (1H, m), 2.29 and 3.5 (AB quartet, $J = 16.7$ Hz). ^{13}C NMR ($CDCl_3$): 232.0 (*axial* W–CO), 219.3 (*equatorial* W–CO), 218.0 (*equatorial* W–CO), 199.3 (Ru–CO), 198.6 (Ru–CO), 154.7 (*ipso*), 129.9 (*ipso*), 111.7 (*ipso*), 91.3 (Cp), 90.2 (Cp), 88.9 (Cp), 85.4 (Cp), 85.1 (Cp), 84.1 (Cp), 81.7 (Cp), 27.2 (CH_2).

3.9. Crystallographic studies

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

The systematic absences in the diffraction data are uniquely consistent for space groups $P2_1/c$ for **3**, **13**, and **14**; and for $P2_1/n$ for **4**. The structures were solved using direct methods, completed by subsequent difference Fourier synthesis and refined by full-matrix least-squares procedures. Semi-empirical ellipsoid absorption corrections were applied. All non-hydrogen atoms were refined with anisotropic displacement coefficients. Hydrogen atoms were treated as idealized contributions. The largest remaining peaks in the difference map for **3**, **4**, and **14** (1.0–1.2 e Å^{-3}) occur at chemically unreasonable positions and were treated as noise.

All software and sources of the scattering factors are contained in the SHELXTL PLUS (4.2) program library (G. Sheldrick, Siemens XRD, Madison, WI).

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