Dinuclear Tungsten, Molybdenum, and Ruthenium Complexes Derived from 1,2-Bis(3-indenyl)ethane

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Treatment of dilithiated 1,2-bis(3-indenyl)ethane with $M(CO)_5(THF)$ (M = Mo, W) followed by oxidation provided the metal−metal bonded compounds $M_2(CO)_6\{\mu\text{-}(\eta^5\text{-}C_9H_6)_2C_2H_4\}$ (**1**, M = W; **2**, M = Mo) as a mixture of *meso* and *rac* diastereomers. Under illumination in chlorinated solvents **1** gave $W(CO)_3\{\mu\text{-}(\eta^1{:}\eta^5\text{-}C_9H_5)C_2H_4(\eta^5\text{-}C_9H_6)\}W(CO)_3Cl$ (**3**). Heating a mixture of $Ru_3(CO)_{12}$ and 1,2-bis(3-indenyl)ethane in xylene afforded two dinuclear compounds, $Ru_2(CO)_4\{\mu\text{-}(\eta^5\text{-}C_9H_6)_2C_2H_4\}$ (**4**) and $\{Ru(CO)_2(\eta^5\text{-}C_9H_6C_2H_4C_9H_7)\}_2$ (**5**). The crystal structures of **1-*rac***, **3a**, and **4-*rac*** were determined by X-ray crystallography.

Introduction

The group 6 and group 8 metal carbonyl dimers with cyclopentadienyl-type ligands have been intensively studied as a class of organometallic compounds.[1] Metal−metal bond cleavage occurs frequently, and an important part of this body of chemistry consists of exploring the effects of linking the cyclopentadienyl rings in order to maintain proximity of the two metal centers. Two excellent reviews that summarize the stereochemical features of these dinuclear compounds, both linked and unlinked, in the context of their photochemistry have been published recently.[2,3]

As part of an effort to explore the synthesis and properties of potentially chiral dinuclear metal carbonyl derivatives of 1,2-bis(3-indenyl)ethane, we have described the preparation and subsequent photoinduced transformations of rhenium and manganese compounds.[4] In this paper we report our results with dinuclear metal−metal bonded tungsten, molybdenum, and ruthenium derivatives.

Results and Discussion

Preparation of 1 and 2. The synthesis of the dinuclear compounds $M_2(CO)_6\{\mu\text{-}(\eta^5\text{-}C_9H_6)_2C_2H_4\}$ (**1**, M = W; **2**, M = Mo) is based on considerable literature precedent.[5−10] Lithiation of 1,2-bis(3-indenyl)ethane and addition of $M(CO)_5(THF)$ (M = W or Mo) with heating forms a dianionic, dimetalated intermediate, $[\{M(CO)_3(\eta^5\text{-}C_9H_6)\}_2C_2H_4]^{2-}$, which Alt and co-workers trapped with methyl iodide to give a neutral dimethyl derivative.[8] If the dianionic intermediate is instead oxidized by 2 equiv of ferrocenium ion, a metal−metal bonded derivative, **1** or **2**, is obtained in overall relatively low yield (15−20%). In our hands the Alt trapping procedure gave variable amounts also of a corresponding *mono*methyl derivative, as determined by ^1H NMR spectroscopy, which indicates formation of a monoanionic, *mono*metalated intermediate, presumably due to incomplete lithiation. Oxidation of the monoanionic intermediate apparently forms a dinuclear compound with *two* monometalated bis(indenyl)ethane ligands, as indicated by ^1H NMR spectra of the crude reaction mixtures, but these compounds decomposed during chromatographic separation and were not isolated. The use of ferric sulfate/acetic acid as the oxidant[5−8] or of $M(CO)_3(NCMe)_3$[6,9,10] as precursor gave comparable but not improved yields of **1** or **2**.

The samples of **1** and **2** were prepared as a mixture of *racemic* and *meso* diasteromers in approximately 1:1 ratio. The racemic forms were found to be more soluble in hexane or toluene, and selective extraction of solid mixtures eventually gave a solution of **1-*rac*** sufficiently pure that it could be crystallized for an X-ray diffraction study.

Structure of 1-*rac*. Two views of the molecular structure of **1-*rac*** are shown in Figure 1. The W−W bond distance in **1-*rac*** of 3.158(1) Å is quite comparable to those in related linked compounds, e.g., $W_2(CO)_6(\mu\text{-}(\eta^5\text{-}C_5H_4)_2CH_2)$ with W−W = 3.166(1) Å[9] and $W_2(CO)_6(\mu\text{-}(\eta^5\text{-}C_5H_4)_2SiMe_2)$ with W−W = 3.196 Å.[6] All of these W−W distances are slightly shorter than that shown by the unlinked compound $W_2(CO)_6(\eta^5\text{-}C_5H_5)_2$, with W−W = 3.222 Å.[11] For complex **1**, the torsion angle CNT−W1−W2−CNT of 50.5° (CNT is the centroid of the five-membered ring) is also close to that of similar

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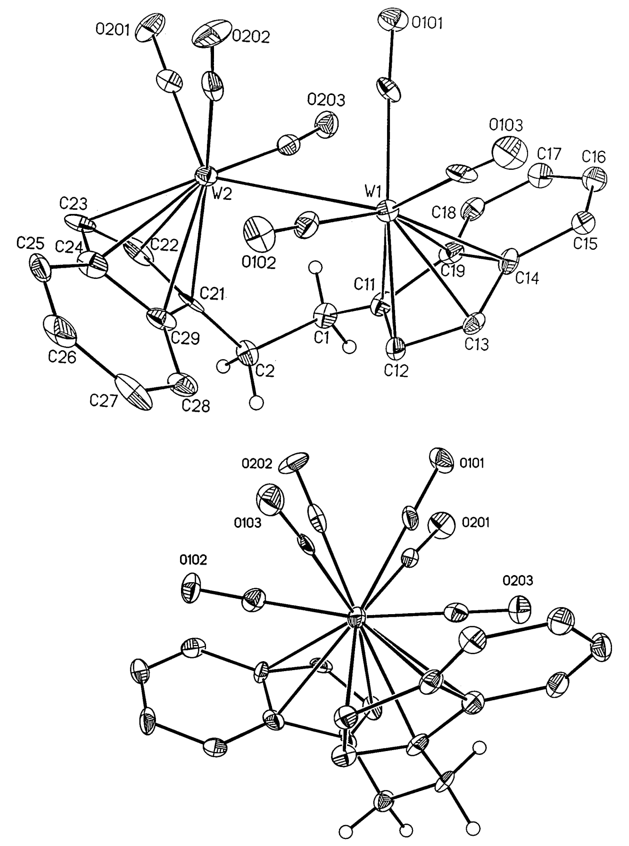
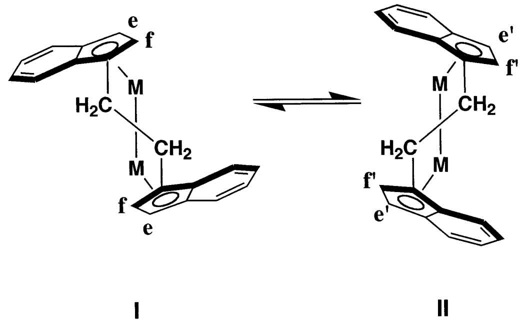


Figure 1. ORTEP diagrams of compound **1-*rac*** (30% thermal ellipsoids). (a) Side view. (b) View along the W1−W2 axis. Bond distances (Å): W1−W2, 3.1581(8); W1−C11, 2.450(14); W1−C12, 2.37(2); W1−C13, 2.293(14); W1−C14, 2.383(14); W1−C19, 2.48(2); W2−C21, 2.342(14); W2−C22, 2.304(14); W2−C23, 2.32(2); W2−C24, 2.46(2); W2−C29, 2.532(14).

Scheme 1



ditungsten complexes; for example, the value for $W_2(CO)_6(\mu\text{-}(\eta^5\text{-}C_5H_4)_2CH_2)$ is 47.8°.[9]

NMR Data for 1 and 2. Two possible conformations for the *rac* diastereomer are depicted in Scheme 1. One conformation (I) is that seen in Figure 1b; the second conformation (II) is related by rotations about the metal−metal bond and the C−C bonds of the linking unit. Proton NMR signals due to both I and II (e.g., **e**/**f** and **e′**/**f ′**) are seen upon dissolving crystals of **1-rac**; the relative populations are nearly equal. Similarly, the mixture of diastereomers for **1** also shows two pairs of signals for the *meso* form. The linked cyclopentadienyl dimers $W_2(CO)_6(\mu\text{-}(\eta^5\text{-}C_5H_4)_2SiMe_2)$[7] and $W_2(CO)_6(\mu\text{-}(\eta^5\text{-}C_5H_4)_2CH_2)$[9] exist in the solid as a mixture of two gauche enantiomers, and their interconversion in solution can be observed by equilibration of enantiotopic proton NMR signals for the Cp rings. However, the corresponding two rotamers for **1** are not enantiomers and hence generate separate NMR signals. Up to the stability limit of **1** in toluene (ca. 90 °C), there is modest broadening of its ^1H NMR spectrum, but no definite signal averaging can be discerned.

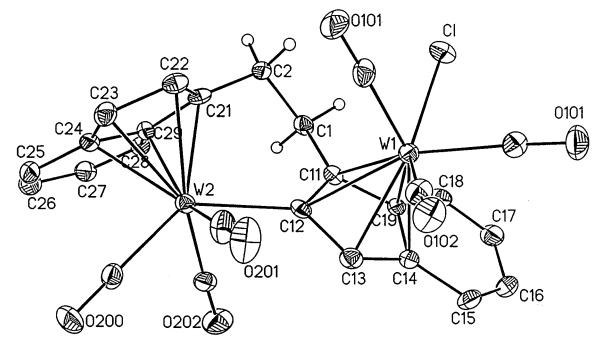


Figure 2. ORTEP diagram of compound **3a** (30% thermal ellipsoids). Bond distances (Å): W1−Cl, 2.505(2); W1−C11, 2.376(6); W1−C12, 2.419(6); W1−C13, 2.285(6); W1−C14, 2.395(6); W1−C19, 2.402(6); W2−C12, 2.247(6); W2−C21, 2.379(6); W2−C22, 2.317(6); W2−C23, 2.298(7); W2−C24, 2.366(7); W2−C29, 2.435(6).

In contrast, the ^1H NMR spectrum of **2** undergoes dramatic changes with temperature. At room temperature, the **e** and **f** ring proton signals for **2** consist of two broad peaks per diastereomer. Lowering the temperature reveals one set of four doublets, assigned to the *rac* diastereomer, and a second set of two doublets, assigned to the *meso* diastereomer. Apparently, the four distinct signals possible for the *meso* conformers are not resolved under these conditions; however, both conformers must be present to explain the line broadening effects seen near room temperature and above. The free energy of activation for interconversion of the *rac* conformers of **2** is estimated as $\Delta G^\ddagger = 14$ kcal mol^{-1}. This barrier is quite comparable with those measured previously for rotamer conversion in linked Mo_2 compounds,[7,9,10] with a higher barrier for W_2 analogues also precedented.

Formation and Structure of 3. A $CDCl_3$ solution of **1** in an NMR tube under nitrogen was observed to change color from red to orange over the course of several hours when exposed to room illumination; no change was observed over the same time period in the dark. The ^1H NMR spectrum of the isolated orange compound (**3**) showed evidence for two isomers, and its mass spectrum indicated incorporation of chlorine. Monitoring the disappearance of **1** showed that the *meso* isomer reacted approximately twice as fast as the *rac* isomer. The transformation was also observed in CH_2Cl_2, however, at a slower rate. Under similar conditions we did not observe this transformation for the Mo analogue **2**; strong irradiation with a mercury lamp simply caused general decomposition.

The molecular structure of isomer **3a** is shown in Figure 2. Relative to **1** the W−W bond has been replaced by a W−Cl bond and a W−C σ bond. The length of the latter is 2.247(6) Å, which is comparable to the W−C σ bond distances of 2.18(3) Å in $W_2(\mu\text{-}\eta^1{:}\eta^5\text{-}C_5H_4)(C_5H_5)(\mu\text{-}H)(CN^tBu)(CO)_2(\mu\text{-dppm})$[12] and of 2.22(2) Å in $[\{W(\eta^5\text{-}C_5H_5)(\mu\text{-}\eta^1{:}\eta^5\text{-}C_5H_4)(NCMe)\}_2][PF_6]_2$;[13] however, the tritungsten compound $W_3(\eta^5\text{-}C_5H_5)_2(\mu\text{-}\eta^1{:}\eta^5\text{-}C_5H_4)(CO)_6$ shows a shorter distance of 2.13(2) Å.[14] In two analogous compounds derived from a bis(cyclopentadienyl)methane linker, $W(CO)_3\{\mu\text{-}(\eta^1{:}\eta^5\text{-}C_5H_4)CH_2(\eta^5\text{-}C_5H_3)\}Ru(CO)_2Cl$ shows $W-C(\sigma)$ = 2.211(8) Å[15] and $Mo(CO)_3\{\mu\text{-}(\eta^1{:}\eta^5\text{-}C_5H_4)CH_2(\eta^5\text{-}C_5H_3)\}Mo(CO)_3Cl$ has $Mo-C(\sigma)$ = 2.210(4) Å.[16]

Bitterwolf and co-workers have characterized a number of compounds similar to **3** that have been formed by photoinduced "twist" rearrangements of dinuclear compounds with linked cyclopentadienyl ligands.[2,3,15-17] The chlorinated solvent is clearly trapping an intermediate metal hydride, and photochemical studies for Mo_2 and W_2 compounds indicate that the reaction is initiated by CO loss.[3,16] However, the wavelength dependence exhibited by a Ru_2 compound instead suggests initiation by metal−metal bond cleavage.[18] We have no evidence in our case that bears on these mechanistic details, but the differences observed between **1** and **2** as well as between the individual diastereomers of **1** are intriguing and may warrant further study.

Synthesis and Characterization of 4 and 5. The reaction of $Ru_3(CO)_{12}$ with 1,2-bis(3-indenyl)ethane in refluxing xylenes affords not only **4**, $Ru_2(CO)_4\{\mu\text{-}(\eta^5\text{-}C_9H_6)_2(CH_2)_2\}$, in which two Ru centers are attached to one ligand, but also **5**, $\{Ru(CO)_2(\eta^5\text{-}C_9H_6C_2H_4C_9H_7)\}_2$, in which one Ru center is attached to each ligand. The analogous reaction conducted in heptane is much more complicated, producing only small amounts of **4** and **5** together with several other products. Under these conditions, isomerization of the reactant 1,2-bis(3-indenyl)ethane into the conjugated diene (*E*,*E*)-bis(indanylidenyl)ethane, as noted previously,[4] is also evident.

Compounds **4** and **5** are readily characterized and differentiated by the molecular ions in their mass spectra as well as by their IR and ^1H NMR spectra. The IR ν(CO) spectrum of **5** shows three comparably strong bands at 1994, 1953, and 1780 cm^{-1}. This pattern is very similar to that reported for the unlinked indenyl compound $Ru_2(CO)_4(\eta^5\text{-}C_9H_7)_2$,[19] which has been shown to be a mixture of *cis* and *trans* bridged isomers by ^{13}C NMR studies.[20] In contrast the IR ν(CO) spectrum of **4** shows a pattern of major bands at 1999 (vs), 1958 (m), and 1777 (s) cm^{-1} that is very close to that of $Ru_2(CO)_4\{\mu\text{-}(\eta^5\text{-}C_5H_4)_2(CH_2)_2\}$[21] as well as that of $Ru_2(CO)_4\{\mu\text{-}(\eta^5\text{-}C_9H_6)_2CHCH_3\}$,[22] both of which are constrained to the *cis* configuration only.

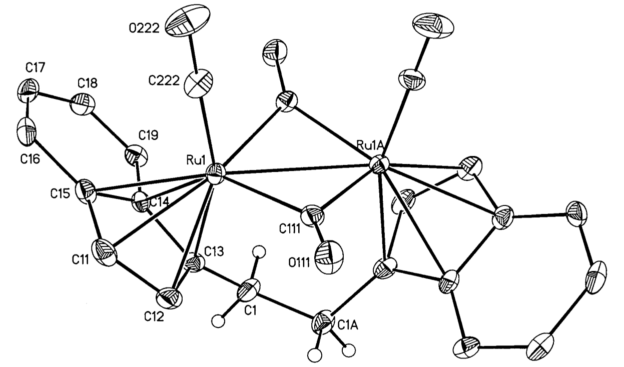
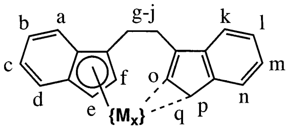


Figure 3. ORTEP diagram of compound **4-*rac*** (30% thermal ellipsoids). Bond distances (Å): Ru1−Ru1A, 2.7185(7); Ru1−C11, 2.231(5); Ru1−C12, 2.268(5); Ru1−C13, 2.288(5); Ru1−C14, 2.365(5); Ru1−C15, 2.326(5); Ru1−C111, 2.014(5); Ru1A−C111, 2.063(5); Ru1−C222, 1.869(5); C111−O111, 1.184(6); C222−O222, 1.148(7).

Chart 1



Both compounds **4** and **5** are prepared as a mixture of diastereomers, as is apparent from their ^1H NMR spectra. Separation of the diastereomers could be effected due to the higher solubilities of the racemic forms in hydrocarbon solvents. The ^1H NMR spectrum of **4-*rac*** was established from crystals used for X-ray analysis. Each diastereomer of **4** exhibits a pair of doublets due to ring protons **e** and **f** (see Chart 1), which are diagnostic of η^5 coordination of each indenyl group. These shifts are similar to ones reported for related indenyl-ruthenium compounds.[23] The protons in the C_2H_4 linker exhibit a separate AA′BB′ pattern for each diastereomer. The ^1H NMR spectrum of **5** shows diagnostically useful peaks near δ 6.2, which are due to the vinylic protons **o** in the uncoordinated five-membered ring of the dangling indenyl group.

An interesting feature of this reaction is the relative yield of the diastereomers of **4**, which was 2:1 in favor of the *meso* form. The ethylidene-linked dimer $Ru_2(CO)_2(\mu\text{-}CO)_2\{\mu\text{-}(\eta^5\text{-}C_9H_6)_2CHCH_3\}$ was obtained as a 4:1 mixture of diastereomers, with the *meso* form predominating.[22]

Crystal Structure of 4-*rac*. The molecular structure of **4-*rac*** is shown in Figure 3. The molecule possesses crystallographically imposed C_2 symmetry. The Ru−Ru bond length of 2.7185(7) Å is similar to the value of 2.735(2) Å for the *trans* configuration of $Ru_2(CO)_2(\mu\text{-}CO)_2(\eta^5\text{-}C_5H_5)_2$24 as well as that of 2.704(1) Å for the *cis* configuration in the linked analogue $Ru_2(CO)_2(\mu\text{-}CO)_2\{\mu\text{-}(\eta^5\text{-}C_5H_5)_2(CH_2)_2\}$.[21] An analogous compound with one intervening carbon in the linking group, $Ru_2(CO)_2(\mu\text{-}CO)_2\{\mu\text{-}(\eta^5\text{-}C_9H_6)_2CHCH_3\}$, shows a significantly shorter distance of 2.656(2) Å,[22] but a single linking silicon center allows an expanded distance of 2.7042(4) Å.[25] All of these carbonyl-bridged structures show

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shorter Ru−Ru distances than related nonbridged compounds, for example, $Ru_2(CO)_4\{\mu\text{-}(\eta^5\text{-}C_5H_5)_2CH_2\}$, wherein Ru−Ru = 2.766(1) Å.[26]

The structure of **4** closely resembles that of $Ru_2(CO)_2(\mu\text{-}CO)_2\{\mu\text{-}(\eta^5\text{-}C_5H_5)_2(CH_2)_2\}$[21] in several other ways. The bond angle at the bridging carbon in **4** of 117.1(5)° is only slightly larger than that of 116.5(10)° for the latter compound. Also the CNT−Ru−Ru−CNT torsion angle is 4.7° in **4**, which is comparable to the 0.9° value observed for the cyclopentadienyl analogue. The bond lengths between Ru centers and the bridging carbonyl carbons are similar as well: 2.014(5) and 2.063(5) Å for **1** and 2.041(8) and 2.053(8) Å in the cyclopentadienyl analogue. The dihedral angles formed between the planes defined by the Ru centers and the bridging carbonyl carbons are also quite similar: 158.2° for **4** and 156.6° for $Ru_2(CO)_2(\mu\text{-}CO)_2\{\mu\text{-}(\eta^5\text{-}C_5H_5)_2(CH_2)_2\}$.

Experimental Section

General Procedures. Experimental procedures and instrumentation were given in detail previously.[4] The reagents were commercial samples used as received, including 1,2-bis(3-indenyl)ethane, *n*-butyllithium (1.6 M in hexanes), and ferrocenium tetrafluoroborate from Aldrich Chemical Co.

Synthesis of 1 and 2. To a 1.00 g (3.87 mmol) sample of 1,2-bis(3-indeny)lethane dissolved in 50 mL of THF in a 250 mL round-bottom flask under nitrogen was added dropwise by syringe 4.84 mL (7.74 mmol) of *n*-butyllithium in hexanes (1.6 M), and the resulting mixture was stirred for 2 h. In a separate 100 mL quartz Schlenk flask, a sample of $W(CO)_6$ (3.0 g, 8.5 mmol) was dissolved in 50 mL of THF, and the flask was irradiated with a mercury lamp for 3 h while open to a nitrogen flush. Periodic examinination of the IR spectrum showed growth of the bands due to $W(CO)_5(THF)$, which were at a maximum by the end of this period. The second solution was added via cannula to the first, and the resulting mixture was heated under reflux for 12 h. The intense red solution was then cooled to −78 °C with a dry ice/acetone bath, and solid $[FeCp_2][BF_4]$ (2.11 g, 7.73 mmol) was quickly added in one portion. The solution was stirred for 1 h at low temperature, and then it was evaporated in vacuo. The residue was extracted with hexane (3 × 100 mL), and the solution was filtered through a short pad of alumina. The filtrate was evaporated, and the residue was dissolved in dichloromethane for chromatography over a 3 cm × 20 cm column of neutral alumina. Elution with 4:1 C_6H_{14}/CH_2Cl_2 gave a fast moving, rapidly decomposing red band, which contained $\{W(CO)_3(\eta^5\text{-}C_9H_6C_2H_4C_9H_7)\}_2$ on the basis of its ^1H NMR spectrum (cf. **5**, below) and a slow moving red band. The latter band was collected by eluting with dichloromethane, and evaporation of the solvent gave 0.43 g (0.54 mmol, 14%) of compound **1**. Anal. Calcd for $C_{26}H_{16}O_6W_2$: C, 39.42; H, 2.04. Found: C, 39.61; H, 2.21. MS (FAB, ^{184}W): *m/z* 792 (M^+). IR (CH_2Cl_2): ν(CO), 2009 (s), 1955 (s), 1915 (br,m), 1892 (sh), 1870 (sh,w) cm^{-1}. ^1H NMR ($CDCl_3$, 22 °C, four isomers: two ***rac*** (r) and two ***meso*** (m); see Chart 1 for key to assignments): δ 7.6−7.1 (16H, m, **a**−**d**), 5.90 (1H, d, *J* = 3 Hz, **e**-r), 5.89 (1H, d, *J* = 3 Hz, **e**-m), 5.87 (1H, d, *J* = 3 Hz, **e′**-m), 5.81 (1H, d, *J* = 3 Hz, **e′**-r), 5.75 (1H, d, *J* = 3 Hz, **f**-m), 5.43 (1H, d, *J* = 3 Hz, **f**-r), 5.41 (1H, d, *J* = 3 Hz, **f ′**-m), 5.17 (1H, d, *J* = 3 Hz, **f ′**-r), 3.7−2.2 (8H, m, **g**−**j**).

Table 1. Crystallographic Data for Compounds 1-*rac*, 3a, and 4-*rac*

	1-*rac*	**3a**	**4-*rac***
formula	$C_{26}H_{16}O_6W_2$	$C_{26}H_{15}Cl_1O_6W_2$	$C_{24}H_{16}O_4Ru_2$
fw	792.09	826.53	570.51
space group	$P\bar{1}$	$P\bar{1}$	$C2/c$
cryst syst	triclinic	triclinic	monoclinic
a (Å)	8.9036(6)	8.3000(3)	7.1851(2)
b (Å)	9.9093(6)	11.9302(4)	15.1052(4)
c (Å)	14.5955(3)	12.8564(5)	17.8691(1)
α (deg)	101.247(1)	69.244(1)	90
β (deg)	97.428(1)	89.373(1)	92.491(1)
γ (deg)	115.489(1)	88.482(1)	90
V, $Å^3$	1106.52(12)	1190.01(7)	1937.54(8)
Z	2	2	4
temp (K)	173 (2)	198 (2)	198 (2)
wavelength (Å)	0.71073	0.71073	0.71073
ρ_{calc} (g cm^{-1})	2.377	2.307	1.956
μ (mm^{-1})	10.430	9.812	1.589
transmn coeff			
max.	0.8164	0.5921	0.9514
min.	0.2080	0.1216	0.8027
no. reflns collected	7229	7841	6185
no. ind reflns	5004	5409	2309
R_{int}	0.0733	0.0509	0.0496
R_1 [$I > 2\sigma(I)$][a]	0.0623	0.0328	0.0364
wR_2[b]	0.1371	0.0735	0.0997
goodness of fit	1.163	1.081	0.879

[a] $R_1 = \Sigma|(F_o - F_c)|/\Sigma F_o$. [b] $wR_2 = \{\Sigma w(F_o^2 - F_c^2)^2/\Sigma(w(F_o)^2)^2\}^{1/2}$.

An analogous reaction starting with 410 mg (1.55 mmol) of $Mo(CO)_6$ and 200 mg (0.77 mmol) of 1,2-bis(3-indenyl)ethane gave 170 mg (0.280 mmol, 18%) of compound **2**. Anal. Calcd for $C_{26}H_{16}O_6Mo_2$: C, 50.67; H, 2.62. Found: C, 50.53; H, 2.70. MS (FAB, ^{96}Mo): *m/z* 616 (M^+). IR ($CHCl_3$): ν(CO), 2020 (s), 1959 (br,s), 1919 (br,m), 1899 (br, m) cm^{-1}. ^1H NMR (CD_2Cl_2, −60 °C, three isomers; see Chart 1 for key to assignments): δ 7.66−7.05 (16H, m, **a**−**d**), 5.95 (2H, d, *J* = 3 Hz, **e**-m), 5.86 (1H, d, *J* = 3 Hz, **e**-r), 5.78 (1H, d, *J* = 3 Hz, **e′**-r), 5.33 (2H, d, *J* = 3 Hz, **f**-m), 5.32 (1H, d, *J* = 3 Hz, **f**-r), 5.05 (1H, d, *J* = 3 Hz, **f′**-r), 3.45−2.65 (8H, m, **g**−**j**).

Isolation of 3. A 20 mg sample of **1** was dissolved in 5 mL of $CHCl_3$ in a round-bottom flask, and the solution was stirred under nitrogen but exposed to room illumination for several hours. The solution was then concentrated and deposited on a silica TLC plate. Elution with 1:1 C_6H_{14}/CH_2Cl_2 gave an orange band, which provided 6 mg (0.0073 mmol, 29%) of compound **3**. Anal. Calcd for $C_{26}H_{15}O_6ClW_2$: C, 37.78; H, 1.83. Found: C, 37.92; H, 1.94. MS (FAB, ^{184}W, ^{35}Cl): *m/z* 826 (M^+). IR (CH_2Cl_2): ν(CO), 2035 (s), 2022 (s), 1945 (s), 1921 (s) cm^{-1}. ^1H NMR ($CDCl_3$, two isomers, see Chart 1 for key to assignments): δ 7.6−7.1 (16H, m, **a**−**d** and **k**−**n**), 5.88 (1H, dd, *J* = 3.0, 0.5 Hz, **e**), 5.87 (1H, dd, *J* = 3.0, 0.5 Hz, **e′**), 5.83 (1H, d, *J* = 3 Hz, **f**), 5.81 (1H, d, *J* = 3 Hz, **f′**), 4.85 (1H, d, *J* = 0.5 Hz, **i**), 4.76 (1H, d, *J* = 0.5 Hz, **i′**), 3.7−2.2 (8H, m, 8H, **g**−**j**).

Reaction of $Ru_3(CO)_{12}$ with 1,2-Bis(3-indenyl)ethane. A 100 mg (0.156 mmol) sample of $Ru_3(CO)_{12}$ was added to 30 mg (0.116 mmol) of 1,2-bis(3-indenyl)ethane in 15 mL of xylenes in a round-bottom flask, and the solution was heated to reflux under nitrogen for 24 h. The red solution was evaporated in vacuo, and the residue was extracted with dichloromethane for separation by TLC (silica, 1:2 C_6H_{14}/CH_2Cl_2). The first two bands eluted were unreacted starting materials; the following two orange bands were due to products. The product band of lower R_f provided 36 mg (0.063 mmol, 18%) of $Ru_2(CO)_4\{\mu\text{-}(\eta^5\text{-}C_9H_6)_2(CH_2)_2\}$ (**4**), and the band of higher R_f contained 64 mg of $\{Ru(CO)_2(\eta^5\text{-}C_9H_6C_2H_4C_9H_7)\}_2$ (**5**) (0.077 mmol, 22%).

Data for 4. Anal. Calcd for $C_{24}H_{16}O_4Ru_2$: C, 50.53; H, 2.83. Found: C, 50.82; H, 3.08. MS (FAB, ^{102}Ru): *m/z* 572 (M^+). IR (CH_2Cl_2): ν(CO), 2045 (vw), 1999 (vs), 1958 (m), 1810 (w,sh), 1777 (s) cm^{-1}. ^1H NMR ($CDCl_3$, see Chart 1 for key to assignments): (i) ***meso*** isomer, δ 7.56 (2H, dt, *J* = 8.4, 1.0 Hz, **a**), 7.47 (2H, ddd, *J* = 8.6, 5.7, 1.2 Hz, **b** or **c**), 7.34 (2H, ddd, *J* = 8.6, 1.8, 0.9 Hz, **b** or **c**), 7.25 (2H, m, **d**), 6.18 (2H, dd,

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J = 2.9, 0.6 Hz, **e**), 5.54 (2H, d, *J* = 2.9 Hz, **f**), 2.93 (4H, m, **g**−**j**); (ii) ***rac*** isomer, δ 7.55 (2H, dt, *J* = 8.4, 1.0 Hz, **a**), 7.46 (4H, dd, *J* = 3.4, 1.0 Hz, **b**, **c**), 7.24 (2H, m, **d**), 6.20 (2H, dd, *J* = 2.9, 0.6 Hz, **e**), 5.49 (2H, d, *J* = 2.9 Hz, **f**), 3.31 (2H, m, **g**−**j**), 2.71 (2H, m, **g**−**j**).

Data for 5. Anal. Calcd for $C_{44}H_{34}O_4Ru_2$: C, 63.76; H, 4.13. Found: C, 63.92; H, 4.42. MS (FAB, ^{102}Ru): *m*/*z* 830 (M^+). IR (CH_2Cl_2): ν(CO), 2050 (vw), 1994 (s), 1953 (s), 1820 (w,sh), 1780 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$, two isomers, see Chart 1 for key to assignments): δ 7.5−7.0 (16H, m, **a**−**d**, **k**−**n**), 6.21 (2H, s(br), **o**), 6.19 (2H, s(br), **o′**), 5.51 (2H, d, *J* = 2.7 Hz, **e**); 5.49 (2H, d, *J* = 2.7 Hz, **e′**), 5.09 (2H, d, 2H, *J* = 2.7 Hz, **f**), 4.95 (d, 2H, *J* = 2.7 Hz, *f′*), 3.3 (m, 4H, **p**, **q**), 3.25−3.05 (m, 4H, **g**−**j**), 3.00−2.85 (m, 4H, **g**−**j**).

X-ray Crystallographic Studies. Crystals of **1-*rac***, **3a**, and **4-*rac*** suitable for X-ray crystallography were grown at −14 °C from dichloromethane by slow interdiffusion of hexane. X-ray diffraction data were obtained on a Siemens Platform/CCD automated diffractometer by the staff of the Materials Chemistry Laboratory of the School of Chemical Sciences. All data processing was performed with the integrated program package SHELXTL.[27] The structures were solved by direct methods,[28] and refinements were made by full-matrix least squares based on F^2. Hydrogen atoms were fixed on calculated positions. Crystallographic details for the studies of **1-*rac***, **3a**, and **4-*rac*** are summarized in Table 1.

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Supporting Information Available: Details of the crystallographic investigations for compounds **1**, **3**, and **4** are available via the Internet at http://pubs.acs.org.

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