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Synthetic and structural studies on (η^5:η^5-fulvalene)bimetallic compounds derived from (η^5:η^5-fulvalene)dithallium

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Abstract

A reaction between halide-free solutions of dihydrofulvalene and thallium ethoxide has produced (η^5 : η^5-fulvalene)dithallium (**1**) in 85–100% yield. Reactions of **1** with carbonyl halides of cobalt, rhodium, iridium, manganese and rhenium produce corresponding homobimetallic fulvalene metal carbonyls (**2**, **5**, **9–11**) in yields of 52–94%. The rhodium complex (η^5 : η^5-$C_{10}H_8$)$Rh_2(CO)_4$ (**5**) reacted with trimethylamine-*N*-oxide dihydrate to form a tricarbonyl derivative (η^5 : η^5-$C_{10}H_8$)Rh_2(μ-CO)$(CO)_2$ (**6**) that contained a bridging carbonyl group and a rhodium–rhodium bond. The bridging carbonyl substituent could be replaced by a bridging methylene group by reaction of **6** with *N*-methyl-*N*-nitrosourea. Tetra(η^2-ethylene)-, bis(η^4-1,2,5,6-cyclooctadiene)-, and bis(η^4-1,2,5,6-cyclooctatetraene)(η^5 : η^5-fulvalene)dirhodium (**12–14**) have been prepared in high yields by reactions of **1** with the corresponding chloro(diolefin)rhodium dimers. Variable temperature ^{1}H NMR studies on the tetraethylene complex **12** demonstrated that the ethylene ligands are fluxional, with ΔG^+ 65 ± 1 KJ/mol. Photolysis of **14** with two equivalents of (η^2-C_2H_4)$_2$(η^5-C_5H_5)Rh has afforded the tetranuclear complex bis[(η^5-cyclopentadienyl)rhodium(μ-cyclooctatetraene)](η^5 : η^5-fulvalene)dirhodium (**15**) in 27% yield.

The single crystal X-ray structures of **2**, **5**, **10**, and **12** have been carried out. Each consists of an η^5 : η^5-fulvalene dianion bridging two metal centers which lie on opposite sides on the fulvalene plane. In each case the formula unit resides around a crystallographic center of inversion. **2** and **5** are isostructural crystallizing in the

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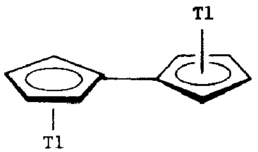
monoclinic space group $P2_1/c$ with a 7.938(6), b 8.223(7), c 10.884(8) Å, β 109.34(4)°, and D_{calc} 1.77 gcm^{-3} for $Z = 2$ (**2**) and a 8.149(1), b 8.420(1), c 10.498(4) Å, β 107.27(2)° and D_{calc} 2.15 gcm^{-3} for $Z = 2$ (**5**). The average M–C(η^5) and M–CO distances are Co–C(η^5) 2.10(2) Å, Co–CO 1.734(6) Å (**2**) and Rh–C(η^5) 2.27(3) Å, Rh–CO 1.864(3) Å (**5**). **10** is monoclinic $P2_1/n$ with a 10.366(6), b 6.986(4), c 11.910(5) Å, β 115.07(4)° and D_{calc} 1.73 gcm^{-3} for $Z = 2$. The average Mn–C(η^5) and Mn–CO distances are 2.115(5) and 1.802(6) Å, respectively. **12** is triclinic, $P\bar{1}$, with a 8.068(1), b 9.998(4), c 11.509(3) Å, α 67.48(2), β 69.01(2), χ 80.51(3)° and D_{calc} 1.85 gcm^{-1} for $Z = 2$. There are two unique molecular units each residing around a crystallographic center of inversion. The two differ by a small rotation of the $Rh(C_2H_4)_2$ fragments. The average Rh–C(η^5) and Rh–C(η^2) separations are 2.25(3) and 2.129(9) Å, respectively.

Introduction

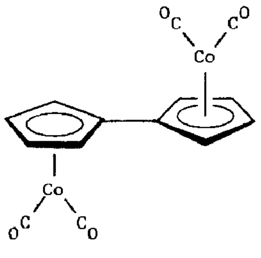
The preparation and properties of organometallic compounds that contain two or more metals in close proximity represent an area that has been extensively studied in recent years, in connection with probing potential electronic and chemical interactions between the metal centers. Fulvalenebimetallic compounds, first described by us in 1969 [1,2], have proved to be very useful in this regard. However, synthetic routes to such compounds developed thus far either lack generality, involve numerous steps, or require generation of the fulvalene reagent immediately prior to use [3]. In an attempt to combine the synthetic utility of the fulvalene dianion [4] with the convenience and reactivity of cyclopentadienylthallium compounds [5–8], we have investigated the preparation of a dithallium derivative of fulvalene. In this article, we report detailed studies concerning a high yield synthetic route to (η^5 : η^5-fulvalene)dithallium (**1**) as well as reactions of this reagent to form fulvalene complexes of cobalt, rhodium, iridium, manganese and rhenium [9,10]. In addition, single crystal X-ray diffraction investigations of 4 of these fulvalene-bimetallic systems [2,5,10,12] are described.

Results and discussion

Vollhardt and Weidman [3,13] have recently developed an efficient synthesis of dihydrofulvalene [4,11,12] and have examined reactions of this reagent with metal carbonyls, leading to a series of new dimetallafulvalene carbonyl complexes. We have found that THF/hexane solutions of dihydrofulvalene prepared in this manner reacted with thallium ethoxide at −78°C to form (η^5 : η^5-fulvalene)dithallium (**1**) in 85–100% yield. Compound **1** is an air-sensitive, chocolate brown solid



1



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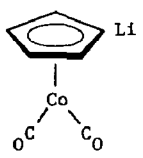

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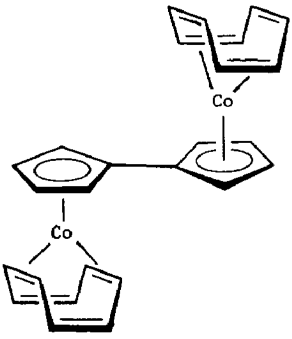

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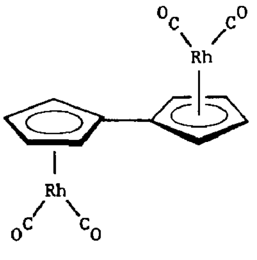
that can be stored under argon at −20 °C for long periods of time without apparent decomposition. Further purification of **1** was not feasible due to its low solubility in organic solvents. However, the product as formed was entirely suitable for further transformations.

A reaction between **1** and $[\mathrm{ICo(CO)}_n]_x$ [14] produced red crystalline $(\eta^5:\eta^5\text{-}C_{10}H_8)(CO)_4Co_2$ (**2**) in moderate yield. The ^1H NMR and IR spectra of **2** were identical to literature data for **2** [3,13]. The product was also identical to **2** which we had prepared in 1981 by the cobalt(II) chloride-induced coupling of $(\eta^5\text{-}C_5H_4Li)(CO)_2Co$ (**3**), derived from $(\eta^5\text{-}C_5H_4Br)(CO)_2Co$ [15,16]. Crystals suitable for X-ray crystallographic studies were obtained by slow crystallization from pentane.

The reaction chemistry of **2** was briefly investigated. An attempt to prepare a tricarbonyl species with a bridging carbonyl group and a Co–Co bond by reaction of **2** with trimethylamine-*N*-oxide dihydrate led only to starting material and decomposition products. However, photolysis of **2** in the presence of excess cyclooctatetraene produced a red-brown, slightly air-sensitive bis(cyclooctatetraene) complex (**4**) in 32% yield. The product was characterized by its ^1H NMR, IR and mass spectra. The latter exhibited a molecular ion peak at m/e 454, the relative intensity of which was 25% of the $(M - C_8H_8)^+$ base peak.

Compound **1** also reacted with dichlorotetracarbonyldirhodium to form the orange dirhodium complex $(\eta^5:\eta^5\text{-}C_{10}H_8)(CO)_4Rh_2$ (**5**) in 72% yield. The ^1H NMR spectrum of **5** exhibited triplet resonances for the fulvalene protons at δ 5.71 and 5.42 ppm, whereas the IR spectrum exhibited terminal carbonyl bands at 2037 and 1978 cm^{-1}. The mass spectrum of **5** contained a weak molecular ion peak at



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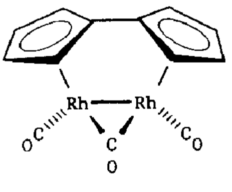


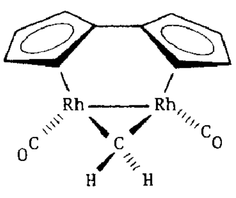
6

m/e 446 and stronger peaks at *m/e* 418, 390, 362 and 334, resulting from successive losses of CO. Crystals of **5** suitable for X-ray crystallography were obtained by slow crystallization from pentane.

Complex **5** reacted with trimethylamine-*N*-oxide dihydrate in benzene to form a bridging carbonyl complex (**6**) in 44% yield. Complex **6** was a dark red, air- and thermally-sensitive compound that reacted readily with carbon monoxide to reform **5** in quantitative yield. The ^{1}H NMR spectrum of **6** exhibited two triplet resonances at δ 5.92 and 5.24 ppm. A static structure for **6** as illustrated should result in a different electronic environment for each of the four protons on a given cyclopentadienyl ring, and hence a more complicated ^{1}H NMR spectrum. The observed result can be explained by a rapid scrambling of the CO ligands which would result in an averaged spectrum. A similar scrambling of CO ligands has been reported for the non-fulvalene analog of **6**, $(\eta^5\text{-Cp})_2(\mu\text{-CO})(CO)_2Rh_2$ [17,18]. Lewis and coworkers [17] examined the variable temperature ^{13}C NMR spectra of a ^{13}CO-enriched sample of $(\eta^5\text{-Cp})_2(\mu\text{-CO})(CO)_2Rh_2$ and found that an averaged carbonyl spectrum was obtained at 20 °C. At −80 °C, the expected static carbonyl spectrum was observed. The rate of CO scrambling was estimated to be at least 10^3/sec at 20 °C.

The IR spectrum of **6** contained bands at 2017, 1979 and 1833 cm^{-1}, assignable to two terminal and one bridging carbonyl ligands, respectively. The mass spectrum exhibited a molecular ion peak of moderate intensity at *m/e* 418. Other strong peaks were observed at *m/e* 390, 362 and 334, resulting from successive losses of CO.

Treatment of **6** with *N*-methyl-*N*-nitrosourea produced a bridging methylene complex (**7**) in 6% yield. The tetracarbonyl compound **5** was also formed in 20% yield, indicating that the formation of the Rh–Rh bond in complexes **6** and **7** creates a considerable degree of strain on the fulvalene ligand. The low yield of **7** can thus be explained in part by the steric strain imposed by the metal–metal bond and by the thermal instability of **6**.



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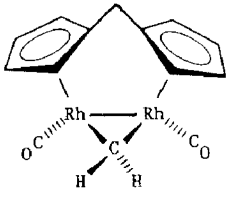

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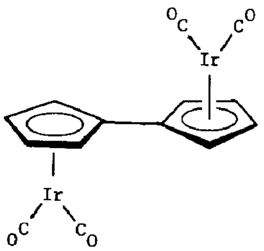
Orange-brown, moderately air-sensitive **7** exhibited resonances in the ^{1}H NMR spectrum at δ 7.24 and 6.41 ppm for the bridging methylene protons, and at δ 6.07, 5.88, 5.42 and 4.03 ppm, assignable to the fulvalene protons. Similar chemical shifts for bridging methylene protons have been observed for the related complex $(\eta^5\text{-Cp})_2(\mu\text{-CH}_2)(CO)_2Rh_2$ [19] and a bis(η^5-cyclopentadienyl)methane analog (**8**) [20]. The four separate resonances for the fulvalene protons in **7** indicate that the bridging methylene group prevents scrambling of the CO ligands, and further supports the postulate that the CO ligands are scrambling in the tricarbonyl complex **6**.

In a manner analogous to the formation of the cobalt and rhodium analogs,



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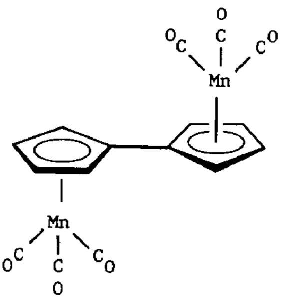


10

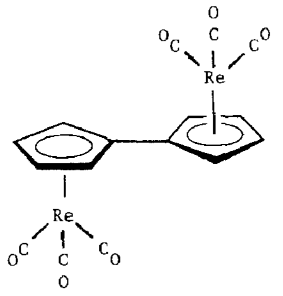
(η^5 : η^5-$C_{10}H_8$)$(CO)_2Ir_2$ (**9**) was obtained in 52% yield from a reaction between dithallium reagent **1** and chlorotricarbonyliridium. The diiridium complex **9** was characterized by its ^1H NMR and IR spectra. The mass spectrum of **9** exhibited weak molecular ion peaks at *m/e* 626, 624 and 622, of 11% relative intensity compared to the $(M - CO)^+$ base peaks at *m/e* 598, 596 and 594. The intensities of these peaks corresponded to the expected isotopic abundances of ^{193}Ir and ^{191}Ir.

A reaction between **1** and bromopentacarbonylmanganese afforded the (fulvalene)dimanganese complex (η^5 : η^5-$C_{10}H_8$)$(CO)_6Mn_2$ (**10**) in excellent yield (86%). This synthetic route compares favorably with an alternative synthesis of **10** involving the lithiation of η^5-$CpMn(CO)_3$ and subsequent oxidative C–C coupling as originally described by Nesmeyanov et al. [21] and developed by Herrmann and coworkers [22]. We also investigated an additional synthesis of **10** involving a reaction between fulvalenedilithium [4,11] and bromopentacarbonylmanganese. This procedure afforded **10** in 71% yield. All three of the above-mentioned routes to **10** are more efficient than the original methods reported by us in 1969, starting from iodocymantrene, dicymantrenylmercury or cymantrenylmagnesium iodide [1,2]. Crystals of **10** suitable for X-ray diffraction studies were grown from dichloromethane/hexane solution.

The rhenium analog of **10**, (η^5 : η^5-$C_{10}H_8$)$(CO)_6Re_2$ (**11**), was previously prepared by Nesmeyanov et al. [23] via Ullmann coupling of (η^5-C_5H_4I)$Re(CO)_3$. In our studies, we have been able to prepare **11** in 94% yield from a reaction between bromopentacarbonylrhenium and thallium reagent **1**. As in the case of **10**, this method represents a considerably improved synthetic route to **11** over the previous procedure. Complex **11** was characterized by its ^1H NMR and IR spectra and by its melting point, which was in accord with the literature data.

In addition to reactions of **1** with carbonyl metal halides, it was of interest to examine a series of reactions of **1** with chloro(diolefin)rhodium dimers, leading hopefully to fulvalenedimetallo complexes that contain olefin ligands. An initial reaction between **1** and dichlorotetraethylenedirhodium formed the desired tetraethylene complex (**12**) in 73% yield as a yellow, slightly air-sensitive crystalline solid. Single crystals of **12** suitable for X-ray crystallography were obtained by slow crystallization from diethyl ether/pentane. The mass spectrum of **12** contained a molecular ion peak at *m/e* 446.

The ^1H NMR spectrum of **12** at 20 °C exhibited triplet resonances at δ 5.15 and



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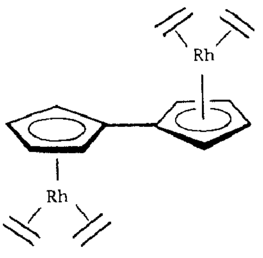


12

4.67 ppm, assignable to the fulvalene protons, and two broad multiplets at δ 2.58 and 1.19 ppm, assignable to the ethylene protons. The broadness of the coordinated ethylene protons suggested that the ethylene ligands in **12** were fluxional on the NMR timescale, as has been observed earlier by Cramer and coworkers [24,25] for η^5-CpRh(C_2H_4)$_2$. A variable temperature ^1H NMR study was therefore undertaken on a concentrated sample of **12** in toluene-d_8 solution between −40 °C and +70 °C. The ^1H NMR spectra of the ethylene region of **12** at various temperatures are shown in Fig. 1. The ΔG^{+} for the rotation of the ethylene ligands was estimated to be 65 ± 1 kJ/mol by the method of Cramer and Mrowca [26]. This value compares favorably with the calculated value of 65.7 kJ/mol [26] for η^5-CpRh(C_2H_4)$_2$, indicating that the electron-donating characteristics of the fulvalene ligand are virtually identical to those of the cyclopentadienyl ligand. Furthermore, any steric interaction between the ethylene ligands on the different rhodium atoms in **12** must be negligible. This conclusion is in agreement with results of a single-crystal X-ray diffraction study of **12** as described below.

The fulvalenedirhodium complexes ($\eta^5:\eta^5$-$C_{10}H_8$)(η^4-C_8H_{12})$_2$Rh$_2$ (**13**) and

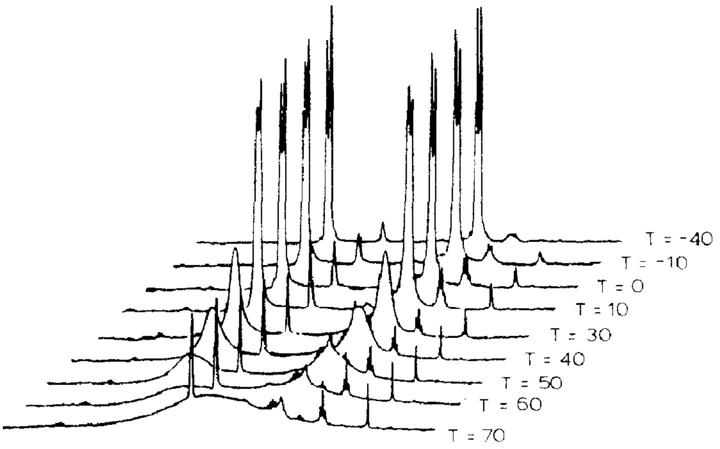
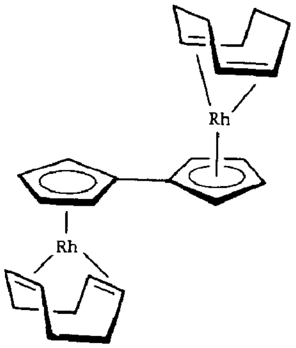


Fig. 1. Variable temperature ^1H NMR spectra of the ethylene region of ($\eta^5:\eta^5$-$C_{10}H_8$)(η^2-C_2H_4)$_2$Rh$_2$ (**12**) in toluene-d_8. A minor peak due to the solvent appears between the two ethylene resonances at δ 2.58 and 1.19 ppm, and two minor peaks due to impurities appear at slightly higher field relative to the δ 1.19 ppm resonance.



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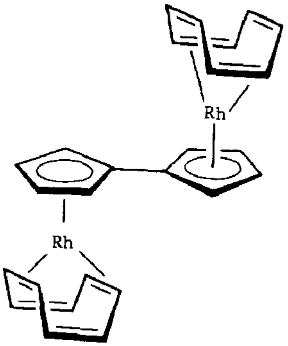

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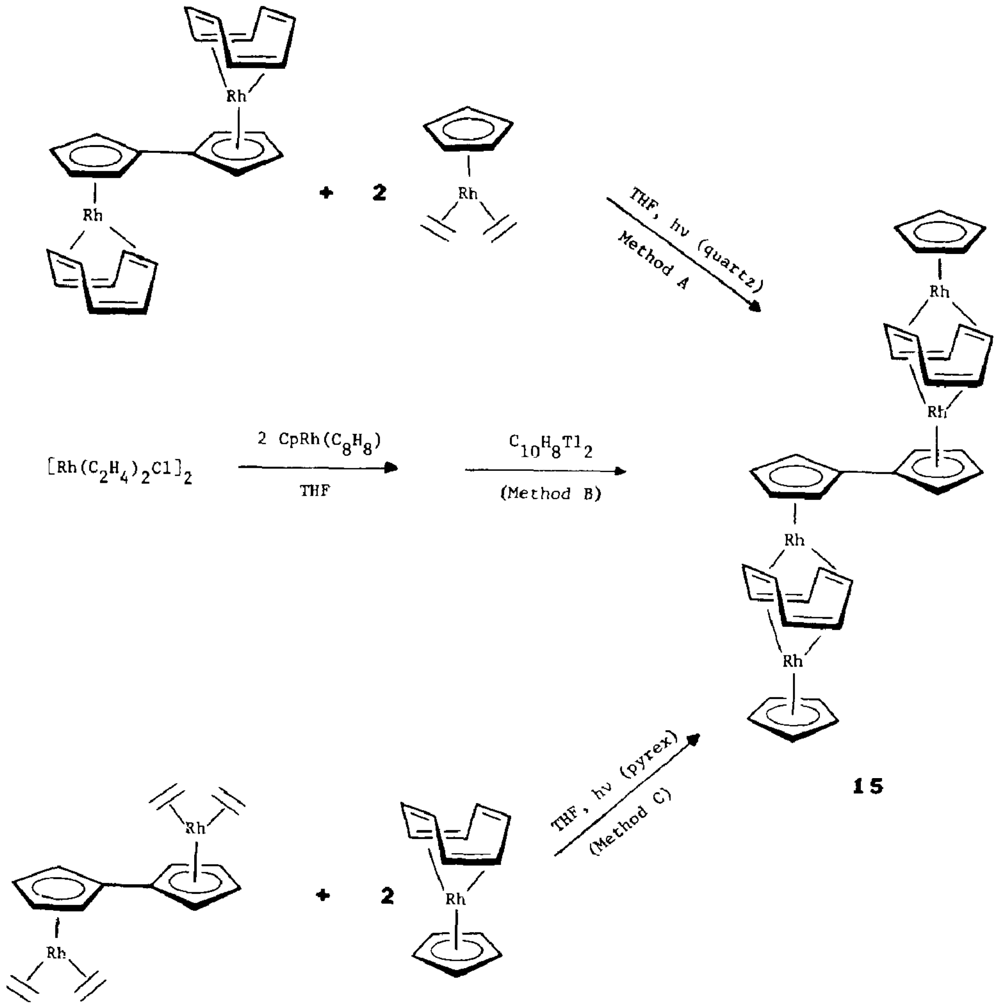
Rh
Rh
+ 2
Rh
THF, hν (quartz)
Method A
$[Rh(C_2H_4)_2Cl]_2$
2 $CpRh(C_8H_8)$
THF
$C_{10}H_8Tl_2$
(Method B)
Rh
Rh
Rh
Rh
THF, hν (pyrex)
(Method C)
Rh
Rh
+ 2
Rh

15

($\eta^5:\eta^5$-$C_{10}H_8$)(η^4-C_8H_8)$_2Rh_2$ (**14**) were produced in yields of 80 an 75%, respectively, from reactions between **1** and either dichlorobis(1,5-cyclooctadiene)dirhodium or dichlorobis(cyclooctatetraene)dirhodium. Both **13** and **14** were obtained as golden-yellow crystalline solids, and were fully characterized by elemental analyses as well as by their ^1H NMR, IR and mass spectra.

The availability of these new fulvalenedirhodiumbis(diolefin) complexes suggested that they could be utilized in the formation of polynuclear analogs. Three methods were examined as possible routes to a tetrarhodium complex (**15**) as shown below. The product was characterized by its ^1H NMR and mass spectra and by elemental analysis. Of the 3 routes to form **15**, the most satisfactory appeared to be Method A. Methods A and C both involved photochemical reactions. The most important difference between them was that Method A was performed in quartz whereas Method C was conducted in pyrex. The absence of byproducts resulting from Method A is in agreement with a recent literature report on the photolysis of η^5-CpRh(C_2H_4)$_2$, which indicated that the photolysis must be undertaken in quartz in order to eliminate both ethylene ligands [27].

X-Ray crystallographic studies

The crystal structures of **2**, **5**, **10**, and **12** have several features in common, and present a reasonably detailed picture of the expected bonding of the fulvalene dianion to metal fragments. In all four structures, the fulvalene ligand is nearly planar and each five-membered ring is η^5-coordinated to a metal center on opposite sides of the anion. Crystallographically, each molecule resides around a center of inversion. Small distortions of the fulvalene ligands, both in M–C distances and in C–C separations around the ring, are noted as observed for their cyclopentadienyl and cyclopentadienyl-like analogs. Major distortions observed when the bonded metal centers are forced on the same side of the fulvalene ligand (e.g., the 65° twist of C_5 fragments in ($\eta^5:\eta^5$-$C_{10}H_8$)$Mn_2(CO)_4$dppm [22] or the severe bending along the C–C bond joining the C_5 rings observed for ($\eta^5:\eta^5$-$C_{10}H_8$)$Mo_2(CO)_6$ [28] were not observed in the title compounds. The individual structures are described below.

2 and **5** are isostructural and are depicted in Fig. 2 (top view of **2**) and 3 (side view of **5**). Bond distances and angles are given in Table 1 for both compounds. In these compounds the M–C(1)–O(1) bonds are eclipsed by C(7) while the M–C(2)–O(2) interactions lies between the C(4)–C(5) bond. Analysis of the M–C(η^5) distances reveals that the M–C(7) distance is the shortest of the five η^5-separations: Co–C(7) 2.056(6) Å; Rh–C(7) 2.223(3) Å. The averages of all five M–C separations are Co–C 2.10(2) Å (0.08 Å range) and Rh–C 2.27(3) Å (0.05 Å range). For comparison, M–C(η^5) separations observed for similar compounds include (η^5-C_5Me_5)M(CO)$_2$ (M = Co, 2.09(2) Å [29]; M = Rh, 2.26(2) Å [30,31]), (η^5-C_5Ph_5M(CO)$_2$ (M = Co, 2.10(1) Å [32]; M = Rh 2.29(3) Å [33]), (η^5-C_5Bz_5)Co(CO)$_2$ (2.08(2) Å [32]) (Bz = Benzyl), and (η^5-$C_5H_4NO_2$)Rh(CO)$_2$ (2.270(8) Å [34]).

The fulvalene anions are planar to within 0.036 Å in **2** and 0.053 Å in **5**. The five-membered rings are only slightly better at 0.025 (**2**) and 0.035 Å (**5**). In each case, the largest deviation of any atom from the planes corresponds to the C(7) position which deviates out of the plane toward to metal position. The metal-centroid values are 1.71 Å (**2**) and 1.92 Å (**5**). The planes defined by the C_5 rings and those defined by the M(CO)$_2$ fragments intersect at angles 90.5° for both compounds.

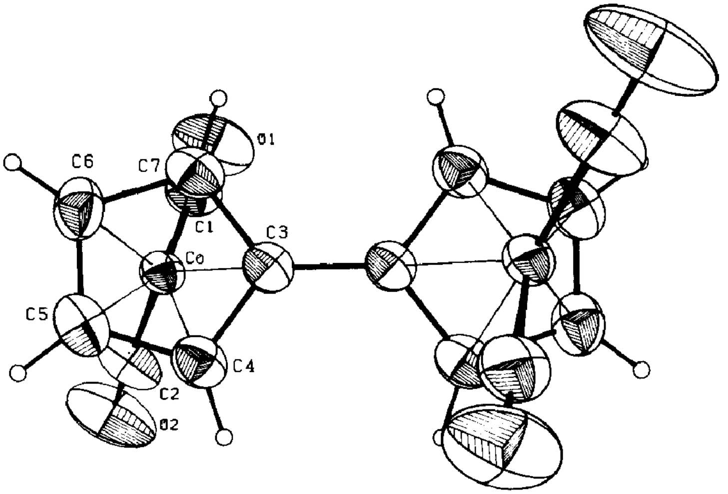

Fig. 2. Top view of **2**.

As observed in many of the η^5-C_5 compounds of this type [29–34], small variations in C–C bond distances around the C_5 rings are observed in **2** and **5**. **5** was determined at −150 °C and presents a slightly more accurate picture of the variation. There is a pattern of short, long, short, long, medium around the ring. The C(5)–C(6) bond is short (1.395(5) Å), opposite the joining carbon C(3) (as is C(3)–C(4) (1.403(5) Å). The two longer distances are 1.448(5) Å (C(4)–C(5)) and 1.446(4) Å (C(3)–C(7)). The C(6)–C(7) distance is 1.422(4) Å. The variations amount to 0.05 Å. In the Co compound, **2**, the range in C–C separations is also 0.05 Å and C(5)–C(6) and C(3)–C(4) are again short, however, the remaining three distances are less distinct at 1.455(9), 1.437(9), and 1.446(9) Å. Interestingly, the eclipsed carbon C(7) has the most unique environment. It is the only carbon

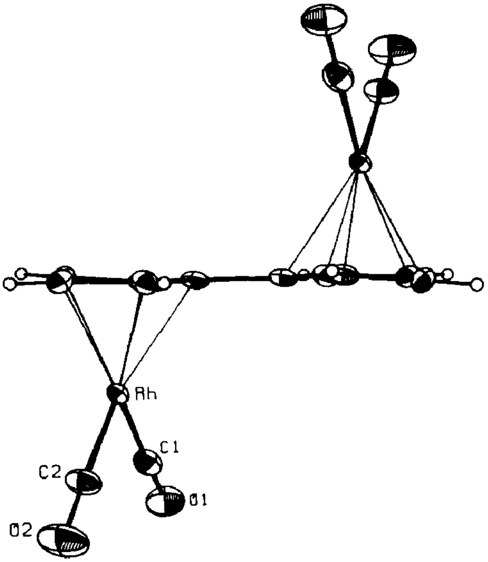

Fig. 3. Side view of **5**.

Table 1

Bond distances (Å) and angles (°) for **2** and **5**

Atoms	Distance(**2**)	Distance(**5**)	Atoms	Angle (**2**)	Angle (**5**)
M–C(1)	1.728(8)	1.861(4)	C(1)–M–C(2)	92.6(4)	89.8(1)
M–C(2)	1.740(8)	1.866(4)	M–C(1)–O(1)	178.2(7)	179.4(3)
M–C(3)	2.131(6)	2.312(3)	M–C(2)–O(2)	177.9(8)	178.3(3)
M–C(4)	2.099(6)	2.279(3)	C(3)′–C(3)–C(4)	126.9(6)	127.3(3)
M–C(5)	2.085(7)	2.245(3)	C(3)′–C(3)–C(7)	126.5(7)	126.0(4)
M–C(6)	2.108(6)	2.277(3)	C(4)–C(3)–C(7)	106.5(5)	106.7(3)
M–C(7)	2.056(6)	2.223(3)	C(3)–C(4)–C(5)	108.4(6)	108.3(3)
O(1)–C(1)	1.150(8)	1.141(5)	C(4)–C(5)–C(6)	109.0(6)	108.5(3)
O(2)–C(2)	1.133(8)	1.138(5)	C(5)–C(6)–C(7)	106.5(6)	107.6(3)
C(3)–C(3)′ [a]	1.46(1)	1.472(6)	C(3)–C(7)–C(6)	109.3(6)	108.7(3)
C(3)–C(4)	1.405(8)	1.403(5)	Cent–M–C(1)	134.1	134.7
C(3)–C(7)	1.437(9)	1.446(4)	Cent–M–C(2)	133.3	135.4
C(4)–C(5)	1.455(9)	1.448(5)			
C(5)–C(6)	1.392(9)	1.395(5)			
C(6)–C(7)	1.446(9)	1.422(4)			
Cent [b]–M	1.71	1.92			

[a] Primed atoms are related by the crystallographic center of inversion. [b] Cent refers to the centroid of the C(3)–C(7) ring.

position having one long and one medium C–C bond and has the largest C–C–C angle (109.3(6)° in **2** and 108.7(3)° in **5**). The other four carbon atoms each have one long and one short C–C bond. The bonds joining the C_5 rings (C(3)-C(3)′) are 1.46(1) Å in **2** and 1.472(6) Å in **5**.

The $M(CO)_2$ fragments are normal. The M–CO distances average 1.734(6) Å (**2**) and 1.864(3) Å (**5**), the C–O bond lengths, 1.142(8) Å (**2**) and 1.140(2) Å (**5**), the

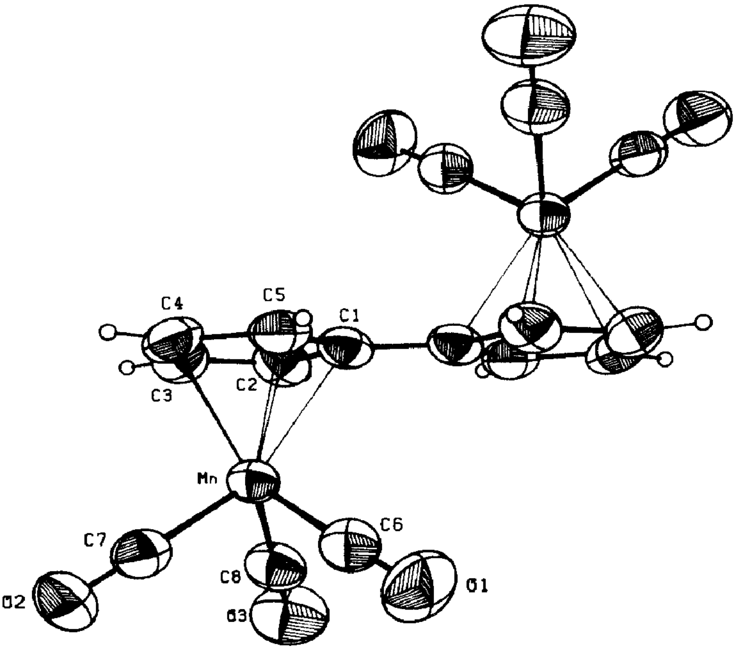

Fig. 4. Side view of **10**.

Table 2

Bond distances (Å) and angles (°) for **10**

Atoms	Distance	Atoms	Angle
Cent [b]-Mn	1.780	C(1)-Mn-C(6)	92.8(2)
Mn-C(2)	2.149(5)	C(3)-Mn-C(6)	156.0(3)
Mn-C(4)	2.156(6)	C(5)-Mn-C(6)	91.9(3)
Mn-C(6)	1.795(6)	C(1)-Mn-C(7)	153.3(3)
Mn-C(8)	1.810(7)	C(3)-Mn-C(7)	101.4(3)
Mn-O(2)	2.941(5)	C(5)-Mn-C(7)	115.3(3)
C(1)-C(1)′ [a]	1.44(1)	Cent-Mn-C(7)	123.3(2)
C(1)-C(5)	1.428(9)	C(2)-Mn-C(8)	91.0(3)
C(3)-C(4)	1.42(1)	C(4)-Mn-C(8)	142.8(3)
C(6)-O(1)	1.142(7)	C(6)-Mn-C(8)	92.0(3)
C(8)-O(3)	1.128(8)	Cent-Mn-C(8)	124.5(2)
		C(1)-C(2)-C(3)	109.8(6)
Mn-C(1)	2.158(5)	C(3)-C(4)-C(5)	108.1(6)
Mn-C(3)	2.161(6)	Mn-C(6)-O(1)	177.5(6)
Mn-C(5)	2.149(6)	Mn-C(8)-O(3)	178.9(6)
Mn-C(7)	1.800(7)	C(2)-Mn-C(6)	126.4(3)
Mn-O(1)	2.936(5)	C(4)-Mn-C(6)	124.8(3)
Mn-O(3)	2.938(5)	Cent-Mn-C(6)	121.5(2)
C(1)-C(2)	1.417(8)	C(2)-Mn-C(7)	138.9(3)
C(2)-C(3)	1.428(9)	C(4)-Mn-C(7)	89.8(3)
C(4)-C(5)	1.440(9)	C(6)-Mn-C(7)	94.5(3)
C(7)-O(2)	1.141(7)	C(1)-Mn-C(8)	112.8(3)
		C(3)-Mn-C(8)	105.1(3)
		C(5)-Mn-C(8)	151.5(3)
		C(7)-Mn-C(8)	92.6(3)
		C(2)-C(1)-C(5)	106.9(5)
		C(2)-C(3)-C(4)	107.0(5)
		C(1)-C(5)-C(4)	108.2(6)
		Mn-C(7)-O(2)	178.5(6)

[a] Primed atoms are related by the crystallographic center of inversion. [b] Cent refers to the centroid of the C(1)-C(5) ring.

OC-M-CO angles are 92.6(4)° (**2**) and 89.8(1)° (**5**), and the Centroid-M-CO angles average 133.7(4)° (**2**) and 135.0(4)° (**5**). M-CO and OC-M-CO parameters for reference compounds include (η^5-C_5Me_5)M(CO)$_2$ (M = Co, 1.728(4) Å, 93.7(2)° [29]; M = Rh, 1.854(9) Å, 90.1(3)° [30,31]) and (η^5-C_5Ph_5)M(CO)$_2$ (M = Co, 1.70(1) Å, 89.5(5)° [32]; M = Rh 1.835(3) Å, 88.3(5)° [33]).

A side view of ($\eta^5:\eta^5$-$C_{10}H_8$)$Mn_2(CO)_6$ (**10**) is depicted in Fig. 4, bond distances and angles are given in Table 2. The overall structure is much more regular than observed for **2** or **5**, and discernable trends in ligand bonding distortion are absent. While this may be a consequence of the true structure, it may also be a result of fairly high standard deviations in the bonding parameters. Localization of electron density in the η^5-C_5 ring has been noted for the similar (η^5-C_5H_5)Mn(CO)$_3$ [35].

The fulvalene dianion is planar to within 0.010 Å, and each C_5 ring to within 0.002 Å. The Mn-C(η^5) distances average 2.155(5) Å and have a range of only 0.012 Å. The Mn atom lies 1.780 Å from the Centroid of the C_5 ring. The three Mn-CO separations average 1.802(6) Å and the OC-Mn-CO and Centroid-Mn-CO angles

Table 3

Bond Distances (Å) and Angles (°) for **12**

Atoms	Distance	Atoms	Angle
Rh(1)–C(1)	2.121(4)	C(1)–Rh(1)–C(2)	38.6(2)
Rh(1)–C(3)	2.138(4)	C(2)–Rh(1)–C(3)	98.5(2)
Rh(1)–C(5)	2.215(4)	C(2)–Rh(1)–C(4)	88.5(2)
Rh(1)–C(7)	2.256(4)	C(10)–Rh(2)–C(11)	38.4(2)
Rh(1)–C(9)	2.263(4)	C(11)–Rh(2)–C(12)	99.3(2)
Rh(2)–C(11)	2.127(4)	C(11)–Rh(2)–C(13)	89.5(2)
Rh(2)–C(13)	2.141(4)	Rh(1)–C(1)–C(2)	70.7(2)
Rh(2)–C(15)	2.250(4)	Rh(1)–C(3)–C(4)	70.9(2)
Rh(2)–C(17)	2.275(4)	C(5)′–C(5)–C(6)	126.5(5)
C(1)–C(2)	1.401(6)	C(6)–C(5)–C(9)	107.0(3)
C(5)–C(5)′ [a]	1.446(7)	C(6)–C(7)–C(8)	109.1(3)
C(5)–C(9)	1.443(5)	C(5)–C(9)–C(8)	108.4(3)
C(7)–C(8)	1.425(5)	Rh(2)–C(11)–C(10)	70.6(2)
C(10)–C(11)	1.398(6)	Rh(2)–C(13)–C(12)	70.1(3)
C(14)–C(14)′	1.456(7)	C(14)′–C(14)–C(18)	125.6(5)
C(14)–C(18)	1.441(5)	C(14)–C(15)–C(16)	106.6(4)
C(16)–C(17)	1.405(6)	C(16)–C(17)–C(18)	108.3(4)
Cent1 [b]–Rh(1)	1.90	Cent1–Rh(1)–C(1)	127.7
M(12) [c]–Rh(1)	2.00	Cent1–Rh(1)–C(3)	131.4
M(1011)–Rh(2)	2.01	Cent1–Rh(1)–M(12)	131.7
Rh(1)–C(2)	2.121(4)	M(12)–Rh(1)–M(34)	95.0
Rh(1)–C(4)	2.138(4)	Cent2–Rh(2)–C(11)	129.7
Rh(1)–C(6)	2.264(4)	Cent2–Rh(2)–C(13)	128.6
Rh(1)–C(8)	2.269(4)	Cent2–Rh(2)–M(1213)	132.7
Rh(2)–C(10)	2.123(4)	C(1)–Rh(1)–C(3)	88.1(2)
Rh(2)–C(12)	2.123(4)	C(1)–Rh(1)–C(4)	102.9(2)
Rh(2)–C(14)	2.215(4)	C(3)–Rh(1)–C(4)	38.1(2)
Rh(2)–C(16)	2.220(4)	C(10)–Rh(2)–C(12)	88.5(2)
Rh(2)–C(18)	2.272(4)	C(10)–Rh(2)–C(13)	103.7(2)
C(3)–C(4)	1.397(7)	C(12)–Rh(2)–C(13)	38.5(2)
C(5)–C(6)	1.443(5)	Rh(1)–C(2)–C(1)	70.7(2)
C(6)–C(7)	1.404(5)	Rh(1)–C(4)–C(3)	70.9(2)
C(8)–C(9)	1.388(5)	C(5)′–C(5)–C(9)	126.3(4)
C(12)–C(13)	1.405(7)	C(5)–C(6)–C(7)	107.1(3)
C(14)–C(15)	1.424(6)	C(7)–C(8)–C(9)	108.2(3)
C(15)–C(16)	1.426(6)	Rh(2)–C(10)–C(11)	71.0(2)
C(17)–C(18)	1.409(6)	Rh(2)–C(12)–C(13)	71.4(3)
Cent2–Rh(2)	1.89	C(14)′–C(14)–C(15)	126.2(4)
M(34)–Rh(1)	2.02	C(15)–C(14)–C(18)	108.1(3)
M(1213)–Rh(2)	2.01	C(15)–C(16)–C(17)	109.4(4)
		C(14)–C(18)–C(17)	107.6(4)
		Cent1–Rh(1)–C(2)	130.0
		Cent1–Rh(1)–C(4)	129.4
		Cent1–Rh(1)–M(34)	133.3
		Cent2–Rh(2)–C(10)	127.7
		Cent2–Rh(2)–C(12)	131.0
		Cent2–Rh(2)–M(1011)	131.5
		M(1011)–Rh(2)–M(1213)	95.9

[a] Primed atoms are related by the crystallographic center of inversion. [b] Cent1 refers to the centroid of the C(5)–C(9) ring, Cent2 to the C(14)–C(18) ring. [c] M(12) refers to the midpoint of the C(1)–C(2) bond, M(34) to that of C(3)–C(4), M(1011) to that of C(10)–C(11), and M(1213) to that of C(12)–C(13).

average 92(1) and 123(1)°, respectively. The largest Centroid–Mn–CO angle occurs for C(8), the only carbonyl carbon to eclipse a C_5 ring atom (C(2)). In two structures available for comparison, the Mn–C(η^5), Mn–CO and OC–Mn–CO values are: (η^5-C_5H_5)Mn$(CO)_3$ [35] 2.214(4) Å, 1.780(6) Å, 92.02(5)° and (η^5-C_5H_4COMe)Mn$(CO)_3$ [36] 2.14 Å, 1.80 Å, 92°.

Within each C_5 ring the range in C–C bond distances is 0.023 Å. The C–C bonds average 1.43(1) Å, the C–C–C internal angles 108(1)°. The C(1)–C(1)′ bond length joining the two C_5 fragments is 1.44(1) Å.

The structure of **12** consists of two unique molecules, each of which resides around a crystallographic center of inversion. Side views of the two molecules are presented in Fig. 5 and top views in Fig. 6. Bond distances and angles are given in Table 3.

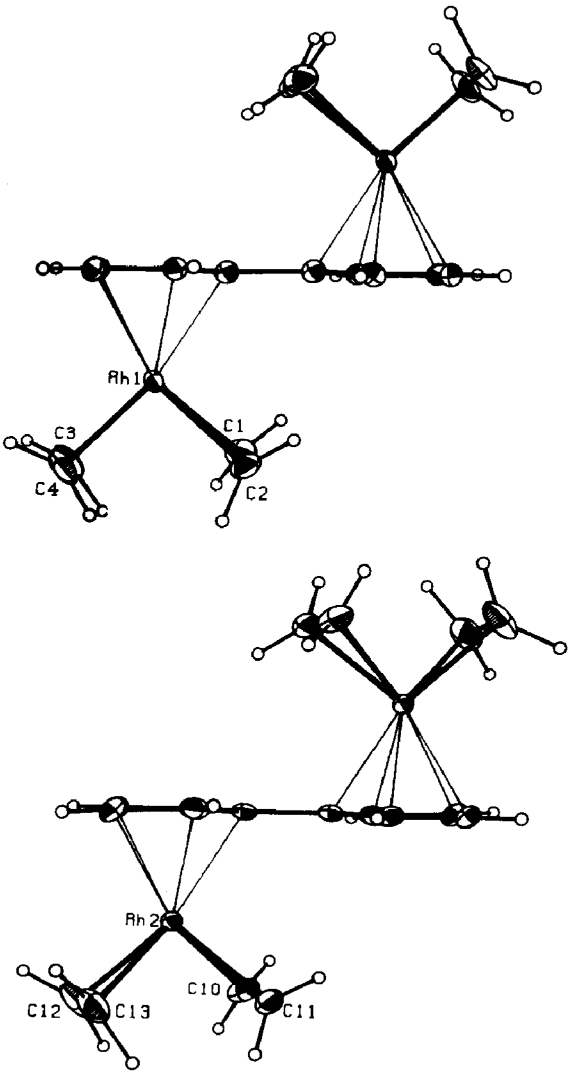

Fig. 5. Side views of the two independent molecules in **12**.

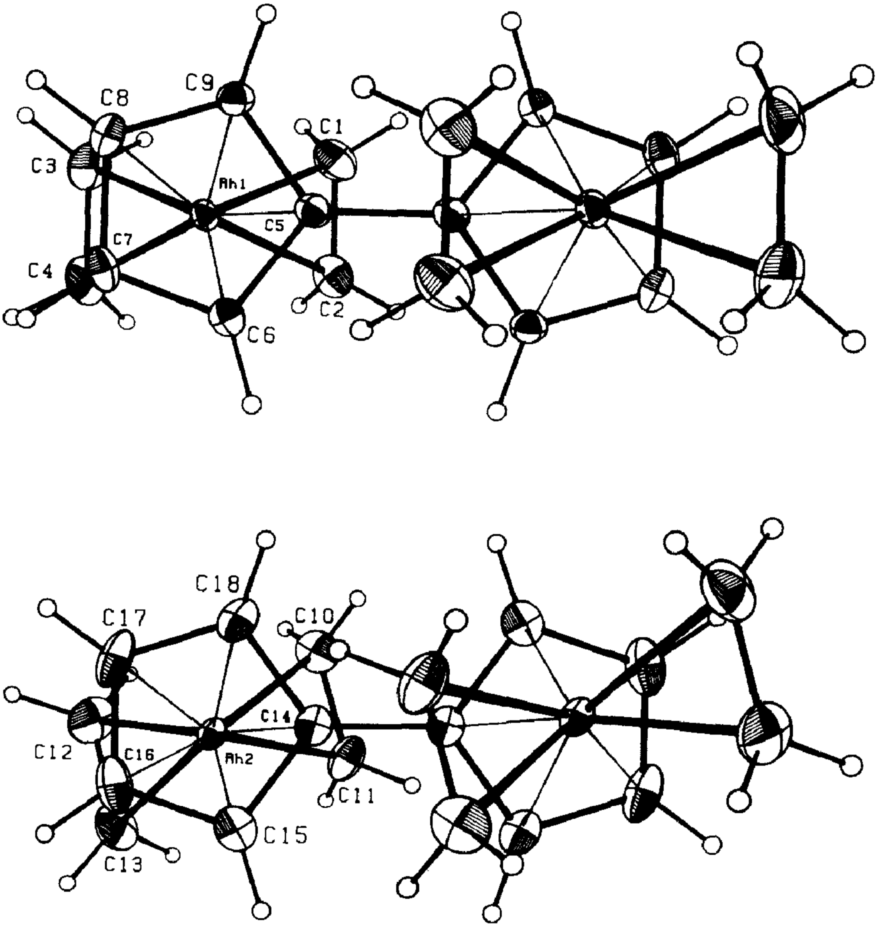

Fig. 6. Top views of the two independent molecules in **12**.

It is immediately obvious from Fig. 5 that the two unique molecules are in fact different. The difference is manifest in a slight twist of the $Rh(C_2H_4)_2$ fragments relative to one another. In molecule 1 (Rh(1)), C(3) and C(4) nearly eclipse ring carbon atoms while the midpoint of the C(1)–C(2) bond is centered over ring carbon atom C(5). In molecule 2, three of the ethylene carbon atoms are staggered, and only C(13) could be considered to be eclipsing a ring carbon atom (C(16)). If we consider the planes defined by the metal atom and the midpoints of the C–C bonds in the C_2H_4 ligands, we find that these planes are 90° to those defined by the fulvalene ligands.

The different relative orientations of the $Rh(C_2H_4)_2$ fragments result in small variations between the two molecules. First we will consider those parameters which are similar in both molecules. The two fulvalene anions are planar to within 0.032 Å (0.025 Å for each C_5 ring), with the largest deviations occurring for the carbon at the ring bridging site and one carbon next to it. C(5) and C(14) deviate from their respective planes toward the metal atoms, C(6) and C(15) deviate away from the metal atoms. The Rh–C(η^5) distances average 2.25(3) Å in both molecules with a 0.06 Å range. In both cases the shortest Rh–C separation occurs for the bridging carbons (C(5), C(14)). The longest Rh–C(η^5) contacts are across the ring at C(8) and C(17). The Centroid distances are 1.90 Å for Rh(1) and 1.89 Å for Rh(2).

We begin to see variations between the two molecules as we look at the Rh$(C_2H_4)_2$ fragments. For molecule 1, C(3) and C(4) eclipse ring carbon atoms, C(1) and C(2) do not. The Rh–C(3) and Rh–C(4) distances are both 2.138(4) Å, while C(1) and C(2) make a closer approach, each 2.121(4) Å from Rh(1). In molecule 2, only C(13) eclipses a ring carbon, and the Rh(2)–C(13) separation is the longest of the four at 2.141(4) Å. The three remaining distances are nearly equivalent and average 2.124(2) Å. When averaged over all values for both molecules, the bonding parameters are nearly identical: Rh(1)–C_2 2.130(9) Å, Rh(2)–C_2 2.128(7) Å, Centroid–Rh(1)–C_2 130(1)°, Centroid–Rh(2)–C_2 129(1)°, M(12) (midpoint of the C(1)–C(2) bond)–Rh(1)–M(34) 95°, M(1112)–Rh(2)–M(1213) 96°, C=C(Rh(1)) 1.399(2) Å, C=C(Rh(2)) 1.402(4) Å. In (η^5-C_5H_5)Rh$(C_2F_4)(C_2H_4)$, the Rh–C separations average 2.024(2) Å (C_2F_4) and 2.167(2) Å (C_2H_4) [37].

As observed in the low temperature structure of **5**, the low temperature structure of **12** reveals interesting variations in bonding parameters of the fulvalene ligands. Again, when averaged the two unique fulvalene ligands appear identical: C–C 1.42(2) Å and C–C–C 108.0(9)° for both. Closer examination of these values, however, reveals different trends in the two unique molecules. In the Rh(1) ligand, there are two short C–C bonds (C(6)–C(7) and C(8)–C(9)) separated by one of medium length (C(7)–C(8)) and two which are long (C(5)–C(6), C(5)–C(9)). In the Rh(2) fulvalene molecule, there are two short C–C bonds next to each other (C(16)–C(17), C(17)–C(18)), and two medium length bonds next to each other (C(15)–C(16), C(14)–C(15)) with the largest C–C bond between C(14) and C(18). The C–C bonds joining the two C_5 fragments are also slightly different, C(5)–C(5)′ 1.446(7) Å for Rh(1) and C(14)–C(14)′ 1.456(7) Å for Rh(2).

Experimental

General

All operations were carried out under an argon atmosphere using standard Schlenk, vacuum line or glovebox techniques except where specified. The argon was dried with magnesium perchlorate, molecular sieves and phosphorus pentoxide, and trace oxygen was removed with activated BTS catalyst. Diethyl ether, tetrahydrofuran (THF) and 1,2-dimethoxyethane (DME) were predried over sodium wire and distilled from sodium-benzophenone ketyl. Hexane and benzene were distilled from calcium hydride. Column chromatography was carried out under argon using CAMAG alumina. The alumina was heated under vacuum on a rotary evaporator to remove oxygen and water, then deactivated with 5% (by weight) of argon-saturated water and stored under argon until used.

Cyclopentadiene was obtained from Eastman Kodak Co. and was cracked immediately prior to use. Cyclooctatetraene was obtained from Aldrich Chemical Co. and was distilled prior to use. 1,5-Cyclooctadiene, trimethylamine-*N*-oxide dihydrate and thallium ethoxide were obtained from Aldrich. Ethylene and carbon monoxide were obtained from Matheson Gas Products and were used without further purification. Dicobalt octacarbonyl and chlorotricarbonyliridium were purchased from Strem Chemicals, Inc.

Bromopentacarbonylmanganese was prepared by a literature method [41]. Bromopentacarbonylrhenium was prepared from dirhenium decacarbonyl by an analogous procedure. Dichlorotetracarbonyldirhodium [42], dichlorotetra(ethylene) dirhodium [43], bis(η^2-ethylene)(η^5-cyclopentadienyl)rhodium [24], dichlorobis(1,5-cyclooctadiene)dirhodium [44], and cyclopentadienylsodium (DME) [4] were prepared by literature methods. Dichlorobis(cyclooctatetraene)dirhodium was prepared in 87% yield via a similar route to that used by Bennett and Saxby [45], utilizing dichlorotetra(ethylene)dirhodium in place of chlorobis(cyclooctene)rhodium.

Photochemical reactions were performed using a 450W Hanovia lamp in a water-cooled quartz or pyrex well. The solutions to be photolyzed were placed in either a quartz or a water-cooled pyrex Schlenk tube, and were positioned as close to the lamp as possible. In those instances where a quartz Schlenk tube was used, both the lamp well and the Schlenk tube were placed in a bath through which cold water was constantly flowing.

^{1}H NMR spectra were obtained on Varian A-60, JEOL FX-90Q or Varian XL-300 spectrometers. Infrared spectra were recorded on Perkin–Elmer 1310 or Beckmann IR-10 spectrometers. Mass spectra were recorded on a Perkin–Elmer–Hitachi RMU 6L mass spectrometer, or on a Varian CH7 mass spectrometer at the Universität Bayreuth, Bayreuth, W. Germany. Melting points were obtained on a Mel-Temp apparatus (Laboratory Devices, Inc.) and are uncorrected. Microanalyses were performed by the Microanalytical Laboratory, University of Massachusetts, Amherst, MA.

(η^5 : η^5-Fulvalene)dithallium (1)

Into an argon-flushed, 500-ml Schlenk flask was placed 6.98 g (39.2 mmol) of cyclopentadienylsodium(DME). THF (200 ml) was added and the solution was cooled to −78 °C. A solution of iodine (4.97 g, 19.6 mmol) in 50 ml of THF was added via a cannula to the cooled solution with stirring. The solution was allowed to warm for 25 min and 200 ml of cold (0 °C) hexane was then added with rapid stirring. The milky solution was rapidly transferred to an argon-flushed, 1000-ml separatory funnel containing 200 ml of degassed 1% aqueous sodium thiosulfate. After shaking several times, the lower aqueous solution was discarded and the organic layer was transferred to an argon-flushed Schlenk tube containing 50 g of anhydrous sodium sulfate. After 2 min of vigorous shaking, the clear yellow solution was decanted into an argon-flushed Schlenk tube and cooled to −78 °C. Diethyl ether (ca. 75 ml) was added with stirring, and thallium ethoxide (2.00 ml, 7.04 g, 28.2 mmol) was added dropwise via a pipette. The resulting curdy yellow slurry was stirred at −78 °C for 1 h and was then allowed to warm to room temperature for 5 h, during which time it turned to chocolate brown. The product was allowed to settle and the supernatant liquid was decanted. The remaining brown solid was washed six times with diethyl ether and dried for 12 h under high vacuum to produce 14.38 g (95% yield based on thallium ethoxide) of chocolate brown, air-sensitive (η^5 : η^5-fulvalene)dithallium. (Found: C, 22.33; H, 1.54. $C_{10}H_8Tl_2$ calcd.: C, 22.37; H, 1.50%).

Tetracarbonyl(η^5 : η^5-fulvalene)dicobalt (2)

Method A. A solution of (η^5-lithiocyclopentadienyl)dicarbonylcobalt was generated at −78 °C under the previously described conditions [7] using 0.96 g (3.7

mmol) of (η^5-bromocyclopentadienyl)dicarbonylcobalt, 2.00 ml (3.7 mmol) of n-butyllithium in hexane, and 40 ml of diethyl ether. Immediately upon completion of the addition of the n-butyllithium, 4.83 g (37.0 mmol) of anhydrous cobalt(II) chloride was added together with 40 ml of THF. The reaction mixture was stirred at −78 °C for 2 h, allowed to warm to 25 °C, and stirred for an additional 16 h. The mixture was then filtered through a glass frit, treated with 10 g of alumina and concentrated to dryness in vacuo. The resulting residue was added to an alumina column (3 × 45 cm). Elution with pentane produced an orange band, which after removal of the solvent afforded 0.28 g (41%) of (η^5-cyclopentadienyl)dicarbonylcobalt. Continued elution with pentane and pentane/diethyl ether produced a red band, which after removal of the solvent gave 0.24 g (28%) of **2** as a deep red solid. An analytical sample was prepared by vacuum sublimation, m.p. 95–96 °C (lit. [13] m.p. 97–98 °C). (Found: C, 47.05; H, 2.33. $C_{14}H_8Co_2O_4$ calcd.: C, 46.96; H, 2.25%). ^1H NMR (C_6D_6) (t, 4 H), 4.32 (t, 4 H). IR (KBr): ν(CO) 2010 (vs), 1950 (vs) cm^{-1}.

Method B. Into an argon-flushed 300-ml Schlenk tube were added dicobalt octacarbonyl (1.50 g, 4.40 mmol) and 100 ml of THF. To the stirred solution was added iodine (1.12 g, 4.41 mmol) slowly. The green solution was allowed to stir at room temperature for 1 h, and then transferred via a cannula to a stirred slurry of (η^5 : η^5-fulvalene)dithallium (2.30 g, 4.28 mmol) in 100 ml of THF in a 500-ml argon-flushed Schlenk flask. The reaction mixture was stirred at room temperature for 20 h. The solvent was removed and the residue was chromatographed on a 3 × 3 cm plug of alumina contained on a frit. Removal of the solvent afforded 1.53 g (52%) of **2** as a dark red solid. The ^1H NMR and IR spectra of the product were identical to those described in Method A and to literature data [13,15,16].

Bis(η^4-1,2,5,6-cyclooctatetraene)(η^5 : η^5-fulvalene)dicobalt (4)

A solution of tetracarbonyl(η^5 : η^5-fulvalene)dicobalt (0.36 g, 1.00 mmol) in 100 ml of diethyl ether was placed in an argon-flushed quartz Schlenk tube. Cyclooctatetraene (0.34 ml, 0.31 g, 3.00 mmol) was added via a syringe and the red solution was photolyzed for 72 h at 15 °C. A red-brown precipitate was collected on a Celite plug on a frit, and was washed several times with diethyl ether. The solid was then washed through the frit with boiling THF, and the resulting red solution was concentrated until the solid just dissolving on boiling. The solution was cooled to room temperature and placed in a −20 °C freezer overnight. The resulting red-brown solid was collected and dried to yield 0.14 g (32%) of a slightly air-sensitive solid. An analytical sample was prepared by recrystallization from THF, dec. > 150 °C. (Found: C, 68.53; H, 5.57. $C_{26}H_{24}Co_2$ calcd.: C, 68.73; H, 5.33%). ^1H NMR ($CDCl_3$): δ 5.46 (s, 8 H), 5.24 (m, 4 H), 4.39 (m, 4 H), 3.18 (s, 8 H). IR (KBr): 2990 (s), 2968 (m), 2919 (vw), 1630 (m), 1422 (w), 1410 (w), 1395 (s), 1360 (m), 1345 (vs), 1150 (w), 1125 (s), 1054 (m), 1042 (w), 988 (m), 940 (m), 921 (sh), 908 (s), 881 (m), 869 (w), 850 (vw), 830 (sh), 820 (vs), 739 (w), 720 (m), 602 (m) cm^{-1}. MS: m/e 454 (M^+).

Tetracarbonyl(η^5 : η^5-fulvalene)dirhodium (5)

Into an argon-flushed 250-ml Schlenk flask were added (η^5 : η^5-fulvalene)dithallium (2.72 g, 5.07 mmol) and 150 ml of THF. Dichlorotetracarbonyldirhodium (1.97 g, 5.07 mmol) was added and the reaction mixture was stirred at room temperature for 22 h. The solvent was removed and the residue was chromatographed on a 3 × 3 cm alumina plug with pentane, producing an orange band. The pentane was removed to yield 1.64 g (72%) of orange-red crystals. An analytical sample was obtained by vacuum sublimation (90 °C, 10^{-3} torr) followed by crystallization from pentane; m.p. 99–101 °C. (Found: C, 37.66; H, 1.89. $C_{14}H_8O_4Rh_2$ calcd.: C, 37.70; H, 1.81%). ^{1}H NMR ($CDCl_3$): δ 5.17 (t, 4 H), 5.42 (t, 4 H). IR (Et_2O): ν(CO) 2037 (vs), 1978 (vs) cm^{-1}. MS: *m/e* 446 (M^+).

(μ-Carbonyl)dicarbonyl(η^5 : η^5-fulvalene)dirhodium (6)

Into a 100-ml 3-neck flask fitted with reflux condenser, gas inlet and magnetic stirrer were added tetracarbonyl(η^5 : η^5-fulvalene)dirhodium (1.24 g, 2.78 mmol) and 50 ml of benzene. Trimethylamine-*N*-oxide dihydrate (0.31 g, 2.79 mmol) was added and the mixture was heated at reflux for 8 h. After cooling to room temperature, the solvent was removed and the residue was chromatographed on a dry-packed alumina column. Elution with pentane produced an orange band which upon evaporation afforded 0.39 g (31%) of starting material. Further elution with diethyl ether produced a dark red band which upon evaporation of the solvent yielded 0.51 g (44%) of **6** as a dark red solid. An analytical sample was prepared by recrystallization from diethyl ether/hexane at −78 °C; dec. > 100 °C. (Found: C, 37.41; H, 2.10. $C_{13}H_8O_3Rh_2$ calcd.: C, 37.35; H, 1.93%). ^{1}H NMR ($CDCl_3$): δ 5.92 (t, 4 H), 5.24 (t, 4 H). IR (Et_2O): ν(CO) 2017 (vs), 1979 (s), 1833 (s) cm^{-1}. MS: *m/e* 418 (M^+).

Reaction of 6 with carbon monoxide

A small sample of **6** was dissolved in diethyl ether in an argon-flushed Schlenk tube. Carbon monoxide was bubbled through the red solution for 30 min. The Schlenk tube was flushed with argon and IR analysis indicated a slight decrease in the intensity of the bridging carbonyl band. After stirring for 12 h under a CO atmosphere, the color had changed to orange and IR analysis indicated the sample was completely converted into (tetracarbonyl)(η^5 : η^5-fulvalene)dirhodium.

(μ-Methylene)dicarbonyl(η^5 : η^5-fulvalene)dirhodium (7)

To a solution of (μ-carbonyl)dicarbonyl(η^5 : η^5-fulvalene)dirhodium (0.41 g, 0.98 mmol) in 50 ml of benzene was added *N*-methyl-*N*-nitrosourea (0.84 g, 8.15 mmol) with stirring. The solution was heated at reflux for 4 h and the solvent was removed in vacuo. The residue was chromatographed on a dry-packed alumina column with methylene chloride-pentane (1 : 1), producing an orange band. Removal of the solvent and crystallization from diethyl ether-pentane afforded 25 mg (6%) of red-brown crude product (**7**). Removal of the solvent from the mother liquor gave 90 mg (20%) of tetracarbonyl(η^5 : η^5-fulvalene)dirhodium, as identified by IR analysis. The crude product (**7**) was recrystallized from diethyl ether/pentane to produce a slightly purer product. (Found: C, 39.21; H, 2.78. $C_{13}H_{10}O_2Rh$ calcd.: C, 38.64; H, 2.50%). ^{1}H NMR ($CDCl_3$): δ 7.24 (m, 1 H), 6.41 (m, 1 H), 6.07 (m, 2 H), 5.88 (m, 2 H), 5.42 (m, 2 H), 4.03 (m, 2 H). IR (Et_2O): ν(CO) 2002 (s), 1964 (m) cm^{-1}. MS: *m/e* 404 (M^+).

Tetracarbonyl(η^5 : η^5-fulvalene)diiridium (9)

Into an argon-flushed 300-ml Schlenk flask were placed (η^5 : η^5-fulvalene)dithallium (1.40 g, 2.61 mmol) and 150 ml of THF. To this suspension was added chlorotricarbonyliridium (1.62 g, 5.20 mmol) and the reaction mixture was stirred for 48 h at room temperature. The brown solution was filtered through a Celite plug and the solvent was removed in vacuo. The residue was chromatographed on a dry-packed alumina column (1 × 30 cm). Diethyl ether produced an orange band and THF produced a small orange-red band that were identical by IR spectroscopy. Removal of the solvent from both bands produced **9** as an orange solid in a combined yield of 0.85 g (52%). An analytical sample was prepared by recrystallization from diethyl ether/pentane as orange microcrystals, m.p. 149–151 °C (dec). (Found: C, 26.29; H, 1.47. $C_{14}H_8Ir_2O_4$ calcd.: C, 26.92;. H, 1.29%). ^{1}H NMR ($CDCl_3$): δ 5.69 (t, 4 H), 5.47 (t, 4 H). IR (Et_2O): ν(CO) 2025 (vs), 1965 (vs) cm^{-1}. MS: *m/e* 626 (39%, ^{193}Ir), 624 (47%, ^{193}Ir, ^{191}Ir), 622 (14%, ^{191}Ir) (M^+).

Hexacarbonyl(η^5 : η^5-fulvalene)dimanganese (10)

Method A. (η^5 : η^5-Fulvalene)dithallium (2.47 g, 4.60 mmol) was placed in a 300-ml argon-flushed Schlenk flask followed by benzene (60 ml). To the stirred suspension was added bromopentacarbonylmanganese (2.53 g, 9.20 mmol). The brown mixture was heated at reflux for 20 h during which time it turned orange. After cooling, the mixture was filtered through a Celite plug and the solvent was removed under high vacuum. The residue was placed on a 2 × 3 cm alumina plug and washed with pentane to remove any dimanganese decacarbonyl. Further elution with benzene produced an orange band which upon removal of the solvent gave 1.61 g (86%) of **10**. Sublimation at 140 °C/10^{-3} torr produced **10** as an air-stable yellow solid, m.p. 143–146 °C (dec). (lit. [2] 145–146 °C). ^{1}H NMR ($CDCl_3$): δ 4.95 (t, 4 H), 4.75 (t, 4 H). IR (THF): ν(CO) 2010 (vs), 1935 (vs) cm^{-1}.

Method B. To a stirred solution of cyclopentadienylsodium (DME) (0.51 g, 2.86 mmol) in 75 ml of THF at −78 °C was added a solution of iodine (0.36 g, 1.43 mmol) in 20 ml of THF via a cannula. After the addition was complete, the solution was allowed to warm for 25 min and then cooled to −78 °C. n-Butyllithium (2.86 mmol, 2.86 ml of a 1.0 *M* solution) was added via a syringe, and the reaction mixture was allowed to warm to room temperature over a 5 h period. The pale yellow, cloudy solution was cooled to −78 °C and bromopentacarbonylmanganese (0.78 g, 2.83 mmol) was added with stirring. The reaction mixture was heated at reflux for 20 h, cooled, and filtered through a Celite plug on a frit. Alumina (ca. 5 g) was added and the solvent was removed under high vacuum. The solid was placed on a 1 × 30 cm dry-packed alumina column and eluted with pentane to remove dimanganese decacarbonyl. Further elution with benzene and THF produced two bands. Removal of the solvent from the combined bands gave 0.45 g (70%) of **10** as a yellow-orange solid. Recrystallization from methylene chloride/hexane afforded **10** as yellow platelets, whose ^{1}H NMR and IR spectra were identical to the product described in Method A.

Hexacarbonyl(η^5 : η^5-fulvalene)dirhenium (11)

(η^5 : η^5-Fulvalene)dithallium (1.85 g, 3.45 mmol) was placed in a 300-ml argon-flushed Schlenk flask followed by 200 ml of benzene. To the stirred suspension was added bromopentacarbonylrhenium (2.79 g, 6.87 mmol). The brown mixture was heated at reflux for 20 h during which time it turned yellow. After cooling to room temperature, the mixture was filtered through a Celite plug and the solvent was removed under high vacuum. The residue was placed on a 2 × 3 cm alumina plug and washed with pentane to remove any dirhenium decacarbonyl. Further elution with benzene produced a yellow band which upon removal of the solvent afforded 2.16 g (94%) of **11** as a yellow solid. Sublimation at 140 °/10^{-3} torr produced **11** as an off white, air-stable solid, m.p. 172–174 °C (lit. [23] 173–174.5 °C). ^{1}H NMR ($CDCl_3$) δ 5.55 (t, 4 H), 5.33 (t, 4H). IR (THF): ν(CO) 2010 (vs), 1928 (vs) cm^{-1}.

*Tetra(η^2-ethylene)(η^5 : η^5-fulvalene)dirhodium (**12**)*

Into an argon-flushed 300-ml Schlenk flask were placed (η^5 : η^5-fulvalene)dithallium (2.07 g, 3.86 mmol) and 150 ml of THF. Dichlorotetra(ethylene)dirhodium (1.50 g, 3.86 mmol) was added and the mixture was stirred at room temperature for 12 h. The mixture was filtered through a Celite plug on a frit and the solvent was removed in vacuo. The residue was placed on a dry-packed alumina column and eluted with diethyl ether/pentane (1/1) to produce a yellow band. Removal of the solvent gave 1.26 g (73%) of **12** as a yellow-tan solid. An analytical sample was prepared by recrystallization from diethyl ether, dec > 145 °C. (Found: C, 48.60; H, 5.25. $C_{18}H_{24}Rh_2$ calcd.: C, 48.45; H, 5.42%). ^{1}H NMR (20 °C, toluene-d_8) δ 5.15 (t, 4H), 4.67 (t, 4H), 2.58 (m, 8H), 1.19 (m, 8H). IR (KBr): 3074 (vw), 3040 (m), 3005 (vw), 2978 (w), 1495 (w), 1488 (sh), 1430 (m), 1418 (m), 1411 (m), 1354 (w), 1197 (s), 1188 (vs), 1052 (w), 1039 (m), 988 (w), 965 (w), 823 (w), 800 (vs), 715 (w) cm^{-1}.

*Variable Temperature ^{1}H NMR Study of **12***

The ethylene region of the ^{1}H NMR spectrum of **12** in $CDCl_3$ exhibited two broad featureless peaks at 20 °C, as observed on a Varian XL-300 spectrometer. A variable temperature study was undertaken in which the ^{1}H NMR spectra of a concentrated toluene-d_8 solution of **12** were observed at 10 °C intervals over a temperature range of -40 to $+70$ °C. At -40 °C, two sharp doublets were observed at δ 2.60 and 1.22 ppm. The lines began to broaden at $+10$ °C and coalescence was observed at ca. $+70$ °C, resulting in a single peak at δ 1.91 ppm. The free energy of activation, ΔG^+, was estimated to be 65 ± 1 kJ/mol by the method of Cramer and Mrowca [26].

*Bis(η^4-1,2,5,6-cyclooctadiene)(η^5 : η^5-fulvalene)dirhodium (**13**)*

Into an argon-flushed 250-ml Schlenk flask were added (η^5 : η^5-fulvalene)dithallium (0.95 g, 1.77 mmol), THF (100 ml), and dichlorobis(1,5-cyclooctadiene)dirhodium (0.87 g, 1.76 mmol). After stirring at room temperature for 18 h, the mixture was filtered through an alumina plug (3 × 2 cm) and the solvent was removed under a high vacuum to yield 0.78 g (80%) of **13** as a yellow-tan solid. Recrystallization from THF gave analytically pure golden-yellow needles, m.p. 257–258 °C. (Found: C, 56.40; H, 5.93. $C_{26}H_{32}Rh_2$ calcd.: C, 56.74; H, 5.86%). ^{1}H NMR ($CDCl_3$): δ 5.38 (t, 4 H), 4.99 (m, 4 H), 3.64 (m, 8 H), 2.16 (m, 8 H), 1.87 (m, 8 H). IR (KBr): 2998 (m), 2975 (m), 2930 (s), 2870 (s), 2825 (s), 1443 (m), 1418 (w), 1402 (w), 1350 (w), 1320 (s), 1235 (w), 1153 (w), 1108 (w), 1068 (w), 1038 (m), 992 (m), 982 (m), 961 (m), 873 (m), 865 (sh), 818 (m), 784 (vs) cm^{-1}. MS: m/e 550 (M^+).

*Bis(η^4-1,2,5,6-cyclooctatetraene)(η^5 : η^5-fulvalene)dirhodium (**14**)*

Into an argon-flushed 300-ml Schlenk flask were added (η^5 : η^5-fulvalene)dithallium (0.55 g, 1.03 mmol) and 150 ml of diethyl ether. Dichlorobis(cyclooctatetraene)dirhodium (0.50 g, 1.03 mmol) was added and the mixture was stirred for 18 h. The solvent was evaporated and 150 ml of THF was added. After stirring for 30 min, the reaction mixture was filtered through a 2 × 3 cm alumina plug. The solvent was concentrated until the solid just dissolved on boiling, and the mixture was cooled to -20 °C for 12 h. The resulting precipitate was collected to yield 0.41 g

Table 4

Crystal data and summary of intensity data collection and structure refinement

	2	**5**	**10**	**12**
Color/Shape	red/plate	orange/plate	yellow/plate	yellow/plate
Form.Wt.	358.08	446.03	406.11	446.2
Space group	$P2_1/c$	$P2_1/c$	$P2_1/n$	$P\bar{1}$
Temp., °C	20	−150	20	−150
Cell Constants [a]				
a, Å	7.938(6)	8.149(1)	10.366(6)	8.068(1)
b, Å	8.223(7)	8.420(1)	6.986(4)	9.998(4)
c, Å	10.884(8)	10.498(4)	11.910(5)	11.509(3)
α, deg				67.48(3)
β, deg	109.34(4)	107.27(2)	115.07(4)	69.01(2)
γ, deg				80.51(3)
Cell vol, Å^3	670.4	687.8	781.2	800.3
Formula units/unit cell	2	2	2	2
D_{calc}, gcm^{-3}	1.77	2.15	1.73	1.85
μ_{calc}, cm^{-1}	25.7	23.3	15.6	19.9
Diffractometer/Scan	Enraf-Nonius CAD-4/θ-2θ			
Range of relative transm. factors, %	90/100	46/100		82/100
Radiation, graphite monochromator	Mo-K_α (λ = 0.71073)			
Max crystal dimensions, mm	0.15×0.25×0.25	0.20×0.53×0.53	0.32×0.33×0.40	0.20×0.30×0.45
Scan width	0.80 + 0.35 tan θ			
Standard reflections	400;040;004	10,0,0;0,14,0;0,0,14	400;040;004	800;0,11,0;008
Decay of standards	±2%	±2%	±1%	±2%
Reflections measured	1020	1401	1650	2846
2θ range, deg	$2 \leq 2\theta \leq 44$	$2 \leq 2\theta \leq 50$	$2 \leq 2\theta \leq 50$	$2 \leq 2\theta \leq 50$
Range of h, k, l	+9, +10, ±12	+9, +10, ±12		+9, ±11, ±13
Reflections observed $[F_o \geq 5\sigma(F_o]$[b]	666	1173	1296	2702
Computer programs [c]	SHELX [38]			
Structure solution	Heavy atom techniques	coordinates from **2**	Heavy atom techniques	MULTAN [39]
No. of parameters varied	91	91	109	181
Weights	unit	$[\sigma(F_0)^2]^{-1}$	unit	$[\sigma(F_0)^2]^{-1}$
GOF	0.77	3.2	1.27	4.2
$R = \Sigma \|\| F_o \| - \| F_c \|\| / \Sigma \| F_o \|$	0.029	0.024	0.045	0.027
R_w	0.035	0.027	0.056	0.033
Largest feature final diff. map	0.3 e Å^{-3}	0.3 e Å^{-3}	0.3 e Å^{-3}	0.2 eÅ^{-3}

[a] Least-squares refinement of $((\sin\theta)/\lambda)^2$ values for 25 reflections $\theta > 20°$. [b] Corrections: Lorentz-polarization and absorption (empirical, psi scan; compounds **2**, **5**, **12**). [c] Neutral scattering factors and anomalous dispersion corrections from ref. 40.

(75%) of **14** as golden-yellow, air-stable platelets. An analytical sample was obtained by recrystallization from THF, m.p. 261–264 °C (dec). (Found: C, 57.36; H, 4.40. $C_{26}H_{24}Rh_2$ calcd.: C, 57.58; H, 4.46%). ^{1}H NMR ($CDCl_3$): δ 5.66 (s, 8 H), 5.58 (m, 4 H), 5.08 (m, 4 H), 3.84 (m, 8 H). IR (KBr): 3005 (w), 2995 (s), 2975 (m), 2925 (w), 1630 (m), 1420 (w), 1409 (w), 1395 (sh), 1383 (m), 1355 (sh), 1346 (s), 1126 (m), 1054 (m), 1042 (m), 984 (m), 955 (w), 912 (m), 870 (w), 851 (vw), 804 (vs), 787 (vs), 752 (w), 728 (w), 619 (w) cm^{-1}. MS: *m/e* 542 (M^+).

Bis[(η^5-cyclopentadienyl)rhodium(μ-cyclooctatetraene)](η^5 : η^5-fulvalene)dirhodium (15)

Method A. Into an argon-flushed quartz Schlenk tube were added bis(η^4-1,2,5,6-cyclooctatetraene)(η^5 : η^5-fulvalene)dirhodium (0.27 g, 0.50 mmol), bis-(η^2-ethylene)(η^5-cyclopentadienyl)rhodium (0.28 g, 1.0 mmol) and THF (300 ml). The mixture was photolyzed with stirring for 6 h at 15 °C with a Hanovia lamp contained in a quartz well. The red solution was stirred at room temperature for 13 h and filtered through Celite. The solvent was removed under high vacuum and the residue was chromatographed on a dry-packed alumina column. Elution with pentane produced no bands. Elution with diethyl ether afforded a red band. The solvent was removed and the residue was dissolved in boiling hexane and rapidly filtered through Celite. The filtrate was cooled to −78 °C and bis[(η^5-cyclopentadienyl)rhodium(μ-cyclooctatetraene)](η^5 : η^5-fulvalene)dirhodium was collected as a red-brown solid (0.12 g, 27%). An analytical sample was obtained by recrystallization from hexane; dec. > 80 °C. Found: C, 49.73; H, 4.16. $C_{36}H_{34}Rh_4$ calcd.: C, 49.23; H, 3.90%. ^{1}H NMR ($CDCl_3$): δ 5.38 (m, 26 H), 5.20 (m, 4 H), 5.05 (m, 4 H). IR (KBr): 2980 (s), 2920 (sh), 2360 (w), 1654 (m), 1635 (m), 1456 (w), 1418 (m), 1385 (w), 1342 (m), 1320 (w), 1260 (w), 1105 (m), 1075 (m), 1005 (w), 992 (w), 950 (vw), 904 (w), 825 (sh), 790 (vs), 772 (s) cm^{-1}. MS: *m/e* 878 (M^+).

Method B. Into an argon-flushed 200-ml Schlenk flask were added (η^5-cyclopentadienyl)(η^4-1,2,5,6-cyclooctatetraene)rhodium [46] (0.30 g, 1.10 mmol; prepared in 90% yield from the reaction of (η^5-cyclopentadienyl)thallium with dichlorobis(cyclooctatetraene)dirhodium), dichlorotetra(ethylene)dirhodium (0.21 g, 0.54 mmol),

Table 5

Final fractional coordinates for **2**

Atom	*x/a*	*y/b*	*z/c*
Co	0.7593(1)	0.2075(1)	0.86154(8)
O(1)	0.4688(8)	0.1915(8)	0.9639(6)
O(2)	0.757(1)	0.5568(7)	0.8676(8)
C(1)	0.5839(9)	0.1957(9)	0.9219(7)
C(2)	0.758(1)	0.4191(9)	0.8629(8)
C(3)	0.9589(8)	0.0254(7)	0.9325(6)
C(4)	1.0190(8)	0.1483(8)	0.8675(6)
C(5)	0.8983(9)	0.1564(9)	0.7337(7)
C(6)	0.765(1)	0.0403(8)	0.7161(6)
C(7)	0.7965(9)	−0.0371(8)	0.8410(6)
H(1)[C(4)]	1.120	0.215	0.905
H(1)[C(5)]	0.909	0.229	0.669
H(1)[C(6)]	0.671	0.017	0.637
H(1)[C(7)]	0.722	−0.117	0.860

Table 6

Final fractional coordinates for **5**

Atom	x/a	y/b	z/c
Rh	0.75007(3)	0.21400(3)	0.85617(2)
O(1)	0.4540(4)	0.1992(3)	0.9708(3)
O(2)	0.7236(4)	0.5698(3)	0.8507(3)
C(1)	0.5664(5)	0.2040(4)	0.9270(4)
C(2)	0.7332(5)	0.4350(4)	0.8507(3)
C(3)	0.9623(4)	0.0243(4)	0.9300(3)
C(4)	1.0218(4)	0.1433(4)	0.8613(3)
C(5)	0.9116(4)	0.1462(4)	0.7248(3)
C(6)	0.7874(5)	0.0280(4)	0.7097(3)
C(7)	0.8091(4)	−0.0411(4)	0.8372(3)
H(1)[C(4)]	1.118	0.210	0.898
H(1)[C(5)]	0.922	0.217	0.657
H(1)[C(6)]	0.703	−0.001	0.629
H(1)[C(7)]	0.736	−0.118	0.858

and 75 ml of THF. The mixture was stirred for 3 h and was poured rapidly into a 500 ml Schlenk flask containing a stirred slurry of (η^5 : η^5-fulvalene)dithallium (0.29 g, 0.54 mmol) in 100 ml of THF. The mixture was heated at reflux for 36 h, cooled, and filtered through a Celite plug. The residue was chromatographed on a dry-packed alumina column. Elution with pentane produced a yellow band identified as (η^5-C_5H_5)(η^4-C_8H_8) by its ^{1}H NMR spectrum. Further elution with pentane gave a small pink band that was not identified. Elution with pentane/diethyl ether (2/1) produced a yellow band identified as (η^2-C_2H_4)$_2$(η^5-C_5H_5)Rh by ^{1}H NMR. Elution with diethyl ether afforded a red-brown band that upon removal of the solvent yielded 60 mg (13%) of a red-brown solid. This product was identical by ^{1}H NMR spectroscopy to **15** obtained by Method A.

Table 7

Final fractional coordinates for **10**

Atom	x/a	y/b	z/c
Mn	0.95547(9)	0.0147(1)	0.70268(7)
O(1)	1.2678(5)	0.0380(9)	0.8175(5)
O(2)	0.9171(6)	0.1680(8)	0.9165(4)
O(3)	0.9597(7)	−0.3842(7)	0.7823(5)
C(1)	0.9469(6)	0.0358(9)	0.5188(5)
C(2)	0.8257(6)	−0.065(1)	0.5136(5)
C(3)	0.7445(6)	0.056(1)	0.5564(5)
C(4)	0.8160(7)	0.235(1)	0.5880(5)
C(5)	0.9416(6)	0.2228(9)	0.5652(5)
C(6)	1.1463(7)	0.029(1)	0.7755(5)
C(7)	0.9338(7)	0.108(1)	0.8345(6)
C(8)	0.9583(7)	−0.230(1)	0.7529(6)
H(1)[C(1)]	0.800	−0.202	0.483
H(2)[C(2)]	0.653	0.019	0.563
H(3)[C(3)]	0.7839	0.351	0.620
H(4)[C(4)]	1.0143	0.328	0.579

Method C. A solution of tetra(η^2-ethylene)(η^5 : η^5-fulvalene)dirhodium (0.50 g, 1.12 mmol) and (η^5-cyclopentadienyl)(η^4-1,2,5,6-cyclooctatetraene)rhodium (0.61 g, 2.24 mmol) in 30 ml of THF was photolyzed in a quartz Schlenk tube with a Hanovia lamp in a pyrex immersion well for 12 h at 15 °C. The solvent was

Table 8

Final fractional coordinates for **12**

Atom	*x/a*	*y/b*	*z/c*
Rh(1)	0.80838(4)	0.56181(3)	0.29901(3)
Rh(2)	0.34066(4)	0.07941(3)	0.21241(3)
C(1)	0.7851(6)	0.3599(4)	0.2866(4)
C(2)	0.7007(6)	0.4689(4)	0.2050(4)
C(3)	1.0814(5)	0.5585(5)	0.1806(4)
C(4)	0.9911(6)	0.6723(5)	0.1084(4)
C(5)	0.5735(5)	0.5463(4)	0.4778(4)
C(6)	0.5856(5)	0.6966(4)	0.3923(4)
C(7)	0.7479(5)	0.7445(4)	0.3788(4)
C(8)	0.8343(5)	0.6298(4)	0.4584(4)
C(9)	0.7276(5)	0.5101(4)	0.5209(4)
C(10)	0.0919(6)	0.0213(5)	0.2245(4)
C(11)	0.1839(6)	−0.1039(4)	0.2807(4)
C(12)	0.2040(7)	0.1653(5)	0.3654(4)
C(13)	0.3107(7)	0.0458(5)	0.4140(4)
C(14)	0.5148(5)	0.0541(4)	0.0229(4)
C(15)	0.6244(5)	0.0359(5)	0.1016(4)
C(16)	0.6105(6)	0.1685(5)	0.1241(4)
C(17)	0.5063(6)	0.2698(4)	0.0534(4)
C(18)	0.4459(5)	0.2016(4)	−0.0102(4)
H(1)[C(1)]	0.709	0.295	0.374
H(2)[C(1)]	0.891	0.329	0.253
H(1)[C(2)]	0.769	0.494	0.108
H(2)[C(2)]	0.572	0.468	0.241
H(1)[C(3)]	1.106	0.455	0.150
H(2)[C(3)]	1.174	0.571	0.213
H(1)[C(4)]	1.016	0.777	0.093
H(2)[C(4)]	0.958	0.658	0.040
H(1)[C(6)]	0.499	0.752	0.353
H(1)[C(7)]	0.793	0.839	0.325
H(1)[C(8)]	0.946	0.634	0.467
H(1)[C(9)]	0.751	0.419	0.582
H(1)[C(10)]	0.086	0.047	0.140
H(2)[C(10)]	−0.006	0.054	0.279
H(1)[C(11)]	0.142	−0.150	0.379
H(2)[C(11)]	0.244	−0.173	0.235
H(1)[C(12)]	0.053	0.152	0.391
H(2)[C(12)]	0.252	0.273	0.342
H(1)[C(13)]	0.443	0.059	0.412
H(2)[C(13)]	0.231	−0.057	0.481
H(1)[C(15)]	0.693	−0.049	0.133
H(1)[C(16)]	0.663	0.185	0.179
H(1)[C(17)]	0.480	0.367	0.049
H(1)[C(18)]	0.373	0.244	−0.065

removed and the residue was chromatographed on a dry-packed alumina column. Elution with pentane produced a yellow band that contained 0.20 g of (η^5-C_5H_5)(η^4-C_8H_8)Rh. Further elution with pentane gave a small pink band that was not identified. Elution with pentane/diethyl ether (1/1) produced a yellow band that contained 0.25 g of (η^2-C_2H_4)$_4$(η^5 : η^5-$C_{10}H_8$)Rh_2 by ^{1}H NMR. Elution with diethyl ether yielded a red band that afforded 0.39 g (40%) of a red-brown solid. This product was identical by ^{1}H NMR spectroscopy to **15** obtained by Method A.

X-ray data collection, structure determination and refinement

Single crystals of the title compounds were mounted on pins or in thin-walled glass capillaries under Ar and transferred to the goniometer. **5** and **12** were cooled to $-150\,^\circ$C during data collection by using a stream of cold nitrogen gas. The space groups for **2**, **5**, and **10** were determined from the systematic absences. Solution and successful refinement of **12** was carried out in the space group $P\bar{1}$. A summary of data collection parameters is given in Table 4.

The geometrically constrained hydrogen atoms were placed in calculated positions 0.95 Å from the bonded carbon atom and allowed to ride on that atom with B fixed at 5.5 Å^2. The remaining hydrogen atoms in **12** were located from a difference Fourier map and included with fixed contributions (B 5.5 Å^2). Refinement of nonhydrogen atoms with anisotropic temperature factors led to the final values of R and R_w given in Table 4. The final values of the positional parameters are given in Tables 5–8.

Tables listing thermal parameters, least-squares planes results, and observed and calculated structure factors are available from R.D.R.

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