products was formed also when 1 was treated with the isocyanide-platinum dication $[Pt(CNCy)_4]^{2+}$.[32] Most of the products identified from this reaction were known polynuclear rhodium compounds. These included $(\eta\text{-}C_5H_5)_2Rh_2(CO)_2(CF_3C_2CF_3)$ (34% yield), $(\eta\text{-}C_5H_5)_2Rh_2(CO)(CNCy)(CF_3C_2CF_3)$ (three isomers, total yield 20%), and $(\eta\text{-}C_5H_5)_3Rh_3(CO)(CF_3C_2CF_3)$ (6%). No Rh_2Pt clusters could be identified.

Conclusions. The sites of attachment of the hexafluorobut-2-yne and carbonyl ligands to the isosceles Rh_3 triangle in $[(\eta\text{-}C_5H_5)_2Rh_3(CO)(CF_3C_2CF_3)(CNR)_3]^+$ are dependent on the phase. The alkyne always adopts the $\mu_3\text{-}\eta^2\text{-}\parallel$ bonding mode characteristic of 48-electron clusters. However, in the solid state, π-bonding is to the most electron-attracting rhodium center, in contrast with theory and most previous observations. The CO is edge-bridging in the solid state. In solution, two isomers coexist, but in the predominant form, the alkyne has twisted to the predicted position with π-bonding to one or the other of the $(\eta\text{-}C_5H_5)Rh$ centers. The CO has also shifted to a semi-face-bridging position. It is clear that the stabilities of the isomers are very similar. Small differences in the relative electronegativities of the metal centers and weak coordination of solvent molecules can affect the preferred orientation of the ligands in these complexes. These results, and recently published work[29] on the $[FeCo_2(CO)_9(EtC_2Et)]$ cluster, establish that the alkyne orientation in asymmetric trinuclear clusters is extremely sensitive to a range of extraneous factors.

Acknowledgment. This work was assisted by grants from the Australian Research Grants Scheme and the loan of rhodium trichloride from Johnson-Matthey. We thank the Australian Government for the award of an Australian Postgraduate Research Award (to O.M.P.). Technical assistance from D. Bogsanyi (low-temperature IR spectra), M. Liddell (FAB mass spectra), and G. Fallon (X-ray crystallography) is gratefully acknowledged.

Supplementary Material Available: Listings of thermal parameters, bond distances and angles for the ligands, equations of least-squares planes and dihedral angles, and H atom positional parameters (7 pages); a listing of observed and calculated structure factors (8 pages). Ordering information is given on any current masthead page.

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Synthesis of (1*RS*,2*RS*,5*SR*)-3,4,6,7-Tetramethylidene-8-oxobicyclo[3.2.1]-oct-2-yl Acetate and the Chemo- and Stereoselective Coordination of Its Butadiene Functions with Rhodium and Iron Moieties[1]

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Received March 22, 1990

The title compound (**6**) has been derived from 7,8-epoxy-2,3,5,6-tetramethylidenebicyclo[2.2.2]octane. Treatment of **6** with tris(μ_2-carbonyl)tris(η^5-indenyl)-*triangulo*-trirhodium gave first μ-carbonyl(Rh–Rh)bis(η^5-indenyl)[(1*RS*,2*RS*,5*SR*,6*SR*,7*RS*)-*C*,6,7,*C*-η-(3,4,6,7-tetramethylidene-8-oxobicyclo[3.2.1]oct-2-yl acetate)]dirhodium(I)(*Rh–Rh*) (**13**) and then [*cis*-μ-[(1*RS*,2*RS*,3*SR*,4*RS*,5*SR*,6*SR*,7*RS*)-*C*,3,4,*C*-η(*Rh*):*C*,6,7,*C*-η(*Rh–Rh*)-(3,4,6,7-tetramethylidene-8-oxobicyclo[3.2.1]oct-2-yl acetate)]μ-carbonyl(*Rh–Rh*)bis(η^5-indenyl)dirhodium(I)(*Rh–Rh*)](indenylrhodium) (**16**) with high chemo- and stereoselectivity. Treatment of **13** with $Fe_2(CO)_9$ gave first [*trans*-μ-[(1*RS*,2*RS*,4*RS*,5*RS*,6*SR*,7*RS*)-*C*,4-η^2(*Fe*):*C*,6,7,*C*-η^4(*Rh–Rh*)-(3,4,6,7-tetramethylidene-8-oxobicyclo[3.2.1]oct-2-yl acetate)]μ-carbonyl(*Rh–Rh*)bis(η^5-indenyl)dirhodium(I)(*Rh–Rh*)](tetracarbonyliron) (**17**) and then [*cis*-μ[1*RS*,2*RS*,3*SR*,4*RS*,5*RS*,6*SR*,7*RS*)-*C*,3,4,*C*-η^4(*Fe*):*C*,6,7,*C*-η^4(*Rh–Rh*)-(3,4,6,7-tetramethylidene-8-oxobicyclo[3.2.1]oct-2-yl acetate)]μ-carbonyl((Rh–*Rh*)bis(η^5-indenyl)dirhodium(I)(*Rh–Rh*)](tricarbonyliron) (**18**) with good regio- and stereoselectivity. The ketone function in the unstable tetraenone **6** is probably responsible for the selectivities observed in the formation of the rhodium polymetallic complexes.

Introduction

2,3,6,7-Tetramethylidenebicyclo[3.2.1]octane (**1**)[3] and its derivatives[4] are potential synthetic intermediates for the preparation of naphthocyclinones[5] and analogues via tandem Diels–Alder additions.[6] In 1980, Gabioud et al.[7] developed a quick access to 7,8-epoxy-2,3,5,6-tetramethylidenebicyclo[2.2.2]octane (**2**). Since bicyclo[2.2.2]oct-2-yl ester[8] and halide derivatives[9] are known to

(1) Preliminary communication: Autumn meeting of the Swiss Chemistry Society, Bern, Switzerland, Oct 20, 1989.
(2) Part of the planned Ph.D. thesis of F. Claret, University of Lausanne.
(3) Gabioud, R.; Vogel; P. *J. Org. Chem.* **1986**, *51*, 2385.
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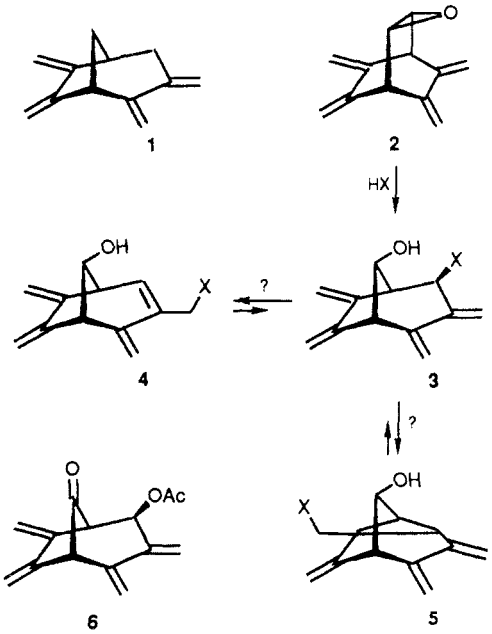
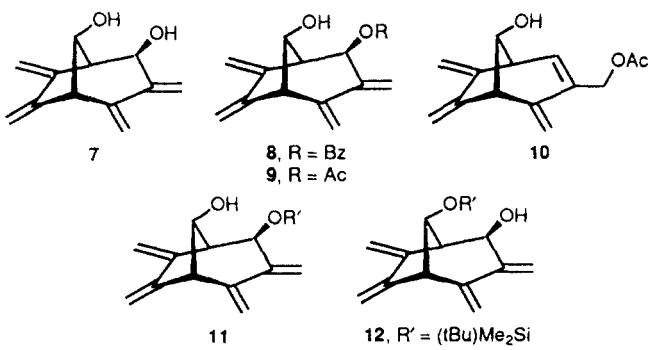


undergo facile Wagner–Meerwein rearrangements into bicyclo[3.2.1]oct-2-yl derivatives[10] under conditions of S_N1 solvolysis, we have examined the possibility of applying that principle to epoxy tetraene **2** for generating 2,8-disubstituted 3,4,6,7-tetramethylidenebicyclo[3.2.1]octane derivatives of type **3**. A priori, the main difficulty was to find conditions under which the allylic rearrangement of type **3** → **4** or/and the homoallylic rearrangement of type **3** → **5** would not compete significantly with the desired reaction **2** + HX → **3**. As we shall see, such conditions have been found. The 8-hydroxy-3,4,6,7-tetramethylidenebicyclo[3.2.1]oct-2-yl derivatives **3** so obtained underwent quick polymerization, thus limiting their potential as synthetic intermediates. For that reason, we have explored the possibility of selectively protecting one or two of their *s-cis*-butadiene functions by coordination with transition-metal complexes. Indeed, we have discovered highly chemo- and stereoselective methods for the complexation of the diene units in 3,4,6,7-tetramethylidene-8-oxobicyclo[3.2.1]oct-2-*exo*-yl acetate (**6**) with rhodium and iron moieties and wish to report these results here.

Results and Discussion

Treatment of epoxy tetraene **2** with aqueous 1 N $HClO_4$ in $CF_3CH(OH)CF_3$ (HFIP) at 0°C (4 h) gave the rearranged diol **7** in 91% yield. Only traces of isomeric alcohols were present in the crude reaction mixture (360-MHz ^1H NMR spectroscopy). In the presence of 1 equiv of benzoyl chloride (BzCl) in pyridine (20 °C, 0.5 h), diol **7** was monoesterified selectively into the allylic benzoate **8** (68%). Similarly, the allylic acetate **9** (60%) was obtained with acetyl chloride in pyridine (20 °C, 0.5 h). The monoacetate **9** could be prepared in a slightly better isolated yield (65%) by acetolysis of **2** (AcOH/HFIP 1:2, 20 °C, 40 h). In this case, the reaction was accompanied by the formation of the rearranged acetate **10** (21%), which could be separated from **9** by column chromatography on silica gel. Oxidation of **9** with pyridinium chlorochromate (PCC) gave the corresponding ketone **6**. The yield of **6** could not be determined, as this compound polymerized quickly on concentrating its solutions at room temperature.



Surprisingly, the monosilylation of diol **7** with (tBu)Me_2SiCl and imidazole showed selectivity opposite that of the benzoylation and acetylation and led to a 1:2 mixture of the silyl ethers **11** and **12**.

Polyenes **2**, **6**, and **7**–**12** in dilute solutions (hexane, benzene, MeOH) gave mixtures of mono- and dimetallic complexes in the presence of $Fe_2(CO)_9$ (20–60 °C)[11] together with polymeric materials. Neither irradiation with $Fe(CO)_5$[12] nor treatment with $[Fe(CO)_3(\eta^2\text{-cyclooctene})_2]$ in hexane at low temperature (−40 to 0 °C)[13] did lead to better results. Treatment of these polyenes with tris-(μ_2-carbonyl)tris(η^5-indenyl)-*triangulo*-trirhodium[14,15]was not much more successful except for tetraenone **6**. Heating **6** with 1 equiv of the trirhodium cluster in toluene (50 °C, 15 h) furnished selectively the dinuclear complex **13** in 92% yield. The strikingly high chemo- (diene at C(6), C(7) vs diene at C(3), C(4)) and stereoselectivity (face of the diene moiety syn vs anti to the CO function at C(8)) of that reaction is difficult to explain. The carbonyl group at C(8) in **6** may play a decisive role as the other polyenes **2**, and **7**–**12** did not lead to selective complex formation under similar conditions. Furthermore, the readily polymerized 7-oxa[2.2.1]hericene (2,3,5,6-tetramethylidenebicyclo-[2.2.1]heptan-7-one), which gave mixtures of exo and endo mono- and dimetallic complexes in low yield with iron carbonyl, also led to good yields of the exo-dinuclear and exo,exo-tetranuclear rhodium complexes **14** and **15**, respectively, when treated with $(indenyl)_3Rh_3(CO)_3$.[16]

Prolonged heating of the dirhodium complex **13** with 1 equiv of $(indenyl)_3Rh_3(CO)_3$ in toluene at 55 °C for 10 days afforded the trinuclear rhodium complex **16** in 55% yield together with 22% of unreacted starting material. The greater distance between the carbonyl group at C(8) and the diene moiety at C(3), C(4) compared with that separating the ketone function from the diene moiety at C(6), C(7) in **6** might be the origin of the chemoselectivity of the reaction **6** → **13**. This hypothesis, however, does not explain the fact that no trace of a tetranuclear rhodium complex could be observed in the crude reaction mixture transforming **13** into **16**.

When argon was bubbled through a benzene solution of **13** and $Fe_2(CO)_9$ (20 °C, 10 h), (alkene)$Fe(CO)_4$ complex **17** was formed and could be isolated pure in 63% yield

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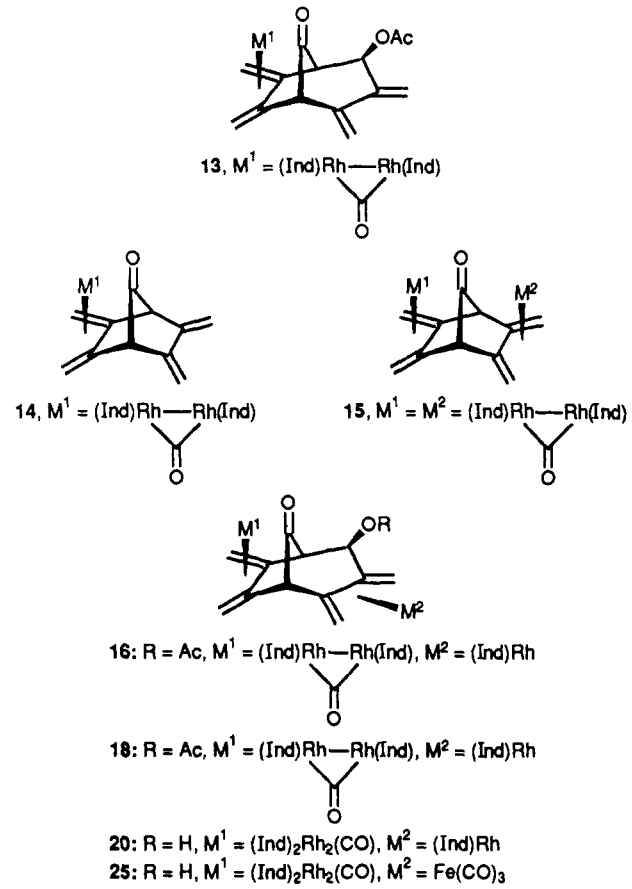
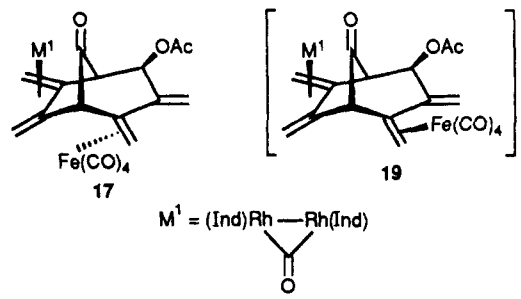


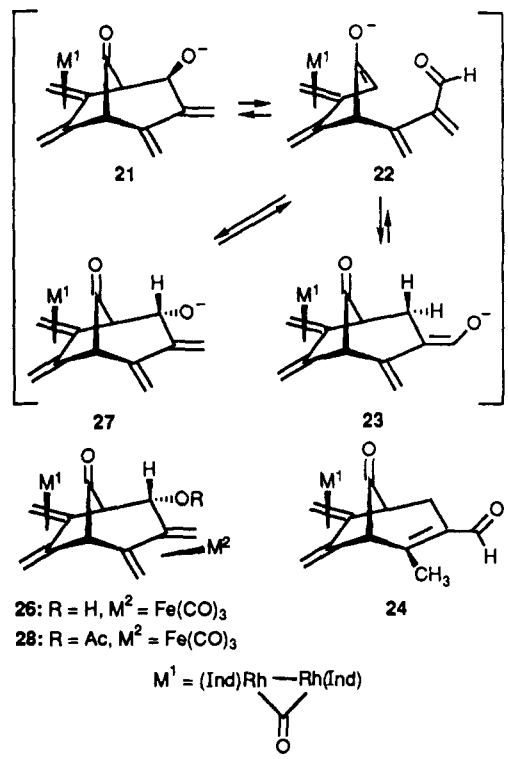
together with 21% of the unreacted starting material and 4–5% of the (diene)$Fe(CO)_3$ complex 18. Heating a



benzene solution of 13 + $Fe_2(CO)_9$ to 40 °C for 24 h afforded 18 in 79% yield. When diluted benzene or $CDCl_3$ solutions of 17 were heated to 40 °C, quick demetalation and recovery of 13 were observed. No significant formation of the *syn*-$Fe(CO)_4$ complex 19 (or a regioisomer) could be seen under these conditions. The transformation of 17 into 18 required the presence of $Fe_2(CO)_9$. These observations suggested that 17 is not an intermediate in the process 13 → 18. They can be interpreted in the following way. The transient $Fe(CO)_4$ species formed at 20 °C is quenched by the less hindered face of the less crowded methylidene group C(4). Complexation of the methylidene moiety at C(3) is disfavored for steric reasons (conformation of the cyclohexane ring,[3] 2-*syn*-acetoxy substituent). The face of CH_2=C(4) or of CH_2=C(3), syn to C(8) in 13, is quenched by the $Fe(CO)_4$ moiety competitively at 40 °C only, a temperature at which the *anti*-(alkene)$Fe(CO)_4$ complex 17 is not stable. The intermediate complex so obtained has the time to be decarbonylated and generates the more stable (η^4-diene)$Fe(CO)_3$ complex 18.

The dirhodium complex 13 and the trinuclear Rh_2Fe complex 18 were not stable under acidic conditions. For instance, tetraenone 6 was recovered nearly quantitatively on treating 13 with a 2:1 mixture of THF and 1 N aqueous

Scheme I



HCl at 20 °C for 90 min. Under the same conditions, 18 was also demetalated, somewhat more slowly than 13. The deprotection was complete, though, after 8 h at 20 °C.

Structural Determinations. The structures of the new compounds 7–13 and 16–18 were given by their elemental analyses, their spectral data (see Experimental Section), their mode of formation, and their transformation into products described below. The ^1H NMR spectrum assignments were confirmed by double-resonance experiments and nuclear Overhauser effect (NOE) measurements. The syn relationship of the two hydroxyl groups in diol 7 was given by the observation of the typical[3,17] W-type H,H coupling constant ^4J = 1.5 Hz between HC(2) and HC(8). A distinction between the signals of HC(2) and HC(8) in 7–9, 11, and 12 was suggested by the difference in the vicinal coupling constants with the bridgehead proton HC(1) (^3J(HC(1),HC(2)) ≅ 3.5 Hz, ^3J(HC(1),HC(8)) ≅ 5 Hz) and confirmed by observing NOE's between HC(2) and the adjacent olefinic protons of H_2C=C(3). The HOC(8) group in 9–11 was confirmed by the ^3J(OH,HC(8)) coupling constant (9–10 Hz). The syn configuration of the (indenyl)$_2Rh_2$(CO) moiety in 13 was given by the observation of NOE's between proton signals (δ_H = 5.68 ppm) of the indenyl group and of the bridgehead proton HC(5) (δ_H = 2.15 ppm). Molecular models showed that these hydrogen atoms are oriented toward the face syn to C(8) (dihedral angle H–C(5)–C(6)–C(7) = 140–150°). The distinction between the diene moieties at C(3), C(4) and C(6), C(7) was also based on NOE measurements. In the case of the trirhodium complex 16, NOE's were observed between HC(1), HC(5), and the indenyl proton signals. This did not allow us to assign the syn configuration of the (diene)Rh(indenyl) moiety, as the signals of this group overlapped with those of the (indenyl)$_2Rh_2$(CO) moiety.

Saponification of the acetate 16 (K_2CO_3/MeOH/CH_2Cl_2) gave the expected alcohol 20 together with a mixture of compounds containing mostly the α,β-unsatu-

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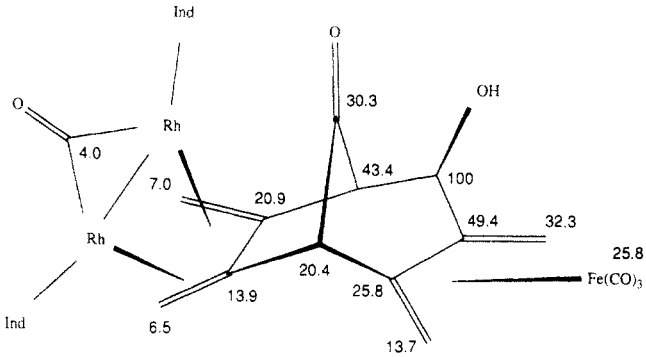

Figure 1. Relative $Yb(thd)_3$ (tris(2,2,6,6-tetramethyl-3,5-heptanedionato)ytterbium) induced δ_C shift of the syn alcohol **25** in $CDCl_3$ (90.55-MHz ^{13}C NMR spectroscopy). Linear LIS values were obtained for seven successive additions of 0.1 equiv of $Yb(thd)_3$.

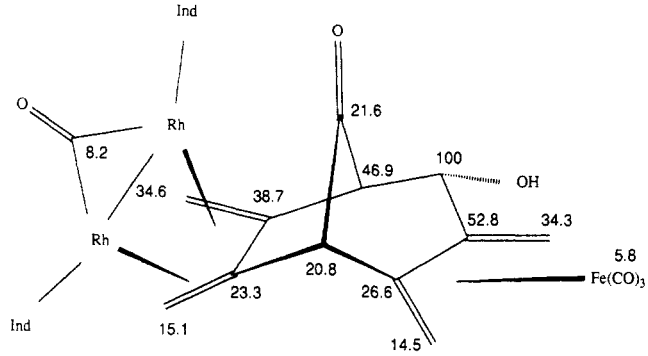

Figure 2. Relative $Yb(thd)_3$-induced δ_C shifts of the anti alcohol **26** in $CDCl_3$ (90.55-MHz ^{13}C NMR spectroscopy). Linear LIS values were obtained for five successive additions of 0.1 equiv of $Yb(thd)_3$.

rated aldehyde **24**. The latter compound was obtained in 90% yield on treating pure **13** with $K_2CO_3/MeOH/CH_2Cl_2$. This result can be interpreted in terms of the retroaldolization process **21** ⇄ **22**; the enolate intermediate **22** then undergoes an intramolecular Michael addition to form dienolate **23**, which finally affords **24** (Scheme I). The formation of **24** from **16** implies loss of the (indenyl)Rh moiety under the conditions used for the saponification of the acetate. Irradiation of the OH signal (δ_H = 0.68 ppm) of **20** led to observable NOE's at the signals of the indenyl groups. The syn configuration of the OH group in **20** was confirmed by acetylation (Ac_2O, pyridine) of **20** into **16**. Irradiation of the HC(2) signal (δ_H = 4.11 ppm) of **20** did not lead to any observable NOE at the signals of the indenyl groups, thus confirming the syn configuration of the (diene)Rh(indenyl) function of **20** and of **16**.

NOE measurements between HC(2), HC(5), and the methylidene protons H_2C=C(3) and H_2C=C(4) in **17** allowed us to establish that the less sterically hindered H_2C=C(4) methylidene group was coordinated to $Fe(CO)_4$. The anti relative configuration of the iron was suggested by the reactivity of **17** (see above) and confirmed by measurements of the $Yb(thd)_3$-induced shifts (LIS) on the ^{13}C chemical shifts of **17** (see Experimental Section). Coordination of the lanthanide complex implied mostly the ester function of **17**, thus leading to an insignificant induced shift at the carbonyl signals of the $Fe(CO)_4$ moiety, the latter group being in the anti face of the three-membered bridge of the bicyclic system.

The syn relative configuration of the $Fe(CO)_3$ moiety in **18** was established by comparing the $Yb(thd)_3$-induced shifts on the δ_C resonance of the carbonyl group of the $Fe(CO)_3$ group in alcohols **25** (Figure 1) and **26** (Figure 2). Treatment of **18** with $K_2CO_3/MeOH/CH_2Cl_2$ gave a mixture of alcohols, from which **25** (37%) and **26** (48%) could be isolated by column chromatography on silica gel. The syn/anti isomerization of these alcohols can be interpreted in terms of a retroaldolization/aldolization process of the type **21** ⇄ **22** ⇄ **27** (Scheme I). The intramolecular Michael addition of **22** invoked to explain the transformation **13** → **24** does not occur in this case, as the dienol moiety is coordinated to $Fe(CO)_3$. Acetylation (Ac_2O, pyridine) of **25** and **26** gave **18** and **28**, respectively.

Conclusion

The trinuclear rhodium cluster $(indenyl)_3Rh_3(CO)_3$ is a useful agent for the selective protection of complicated, unstable exocyclic polyenones. In the case of (1*RS*,1*RS*,5*SR*)-3,4,6,7-tetramethylidene-8-oxobicyclo-[3.2.1]oct-2-yl acetate (**6**) the diene unit at C(6), C(7) is coordinated stereoselectively through its syn face to a $(indenyl)_2Rh_2(CO)$ moiety, giving the dinuclear complex **13**. Complexation of the exocyclic butadiene group C(3), C(4) of **13** is a much slower process and leads to the exclusive formation of the *syn*-(η^4-diene)Rh(indenyl) system **16**. The ketone at C(8) is probably responsible for these chemo- and stereoselectivities. In the presence of $Fe_2(CO)_9$ at room temperature, the diene moiety at C(3), C(4) of **13** is coordinated first by its CH_2=C(4) methylidene group, leading to the isolable (η^2-alkene)$Fe(CO)_4$ complex **17**. At 40 °C, the more stable *syn*-(η^4-diene)$Fe(CO)_3$ complex **18** is formed. Although no satisfactory explanation can be given for the observed selectivities, interesting trinuclear transition-metal complexes (e.g. **16**, **18**) have been prepared in good yields. The exploration of their chemistry may lead to new families of unusual polymetallic systems.

Experimental Section

For general remarks, see ref 18. Solvents were either reagent or technical grade (Fluka, Aldrich, or Merck) and when necessary were purified and dried by distillation from an appropriate desiccant under an atmosphere of N_2. Concentration of solutions after reactions and extractions involved use of a rotary evaporator operating at a reduced pressure of approximately 20 Torr. Liquid/solid flash chromatography (FC) used columns of silica gel (0.040–0.063 mm, Merck 7734 or 9385) or Lobar columns (Merck SiO_2 or RP-8). None of the procedures reported here have been optimized.

(1*RS*,2*SR*,5*RS*,8*SR*)-3,4,6,7-Tetramethylidenebicyclo-[3.2.1]octane-2,8-diol (7). 7,8-Epoxy-2,3,5,6-tetramethylidenebicyclo[2.2.2]octane (**2**; 807 mg, 4.69 mmol)[7] was dissolved in a stirred mixture of $CF_3C(OH)HCF_3$ (40 mL) and aqueous 1 N $HClO_4$ (20 mL) cooled to 0 °C. After the mixture was stirred at 0 °C for 4 h, CH_2Cl_2 (50 mL) and H_2O (100 mL) were added. The aqueous phase was extracted with CH_2Cl_2 (100 mL, three times). The organic extracts were combined and washed with saturated aqueous $NaHCO_3$ solution (100 mL, twice). After drying ($MgSO_4$) and solvent evaporation, the residue was purified by FC (CH_2Cl_2/Et_2O 3:1): yield 700 mg (91%); colorless crystals; mp 250 °C dec. UV (isooctane): λ_{max} 233 nm (ϵ 9800). UV (95% EtOH): λ_{max} 201 (ϵ 7250), 233 nm (ϵ 10 500). IR (KBr): 3400, 3280, 3080, 2980, 2940, 2880, 1845, 1815, 1800, 1780, 1630, 1620, 1455, 1420, 1340, 1295, 1275, 1255, 1220, 1200, 1175, 1095, 1000, 960, 915, 905, 895, 885, 855, 835, 800, 770, 740, 665, 655, 630 cm^{-1}. ^1H NMR (360 MHz, $CDCl_3$): δ 5.45 (br s), 5.43 (d, J_{gem} = 1.5 Hz), 5.39 (s), 5.26 (d, J_{gem} = 1.5), 5.08 (d, J_{gem} = 1.5), 5.03 (s), 4.99 (s), 4.94 (d, J_{gem} = 1.5), 4.31 (ddd, J(HC(1),HC(8)) = 5, J(HC(5),-HC(8)) = 5, J(HC(2),HC(8)) = 1.5, HC(8)), 4.28 (dd, J = 3.6, 1.5, HC(2)), 3.35 (br d, J = 5, HC(5)), 3.12 (m, HC(1)). ^{13}C NMR (90.55 MHz, $CDCl_3$): δ 146.3, 145.8, 145.3, and 144.0 (4 s, C(3), C(4), C(6), C(7)), 117.2, 111.4, 107.4, and 106.5 (4 t, ^1J(CH) = 157–159 Hz, H_2C=C(3), H_2C=C(4), H_2C=C(6), H_2C=C(7)), 78.5 (d, ^1J(C,H) = 156, C(2)), 74.5 (d, ^1J(C,H) = 152, C(8)), 56.9 (d,

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^1J(C,H) = 144, C(1)), 49.9 (d, ^1J(C,H) = 144, C(5)). MS (70 eV; *m/e* (relative intensity)): 191 (0.47, $M^{\bullet+}$ + 1), 189 (0.49, $M^{\bullet+}$ - 1), 172 (19.5, $M^{\bullet+}$ - 18), 157 (10.4), 143 (13), 141 (10), 129 (32), 128 (38), 127 (10), 115 (21), 91 (36), 77 (18), 65 (48), 63 (38), 58 (87), 51 (100). MS (CI, NH_3): 208 (25.7, $M^{\bullet+}$ + 18), 191 (33, $M^{\bullet+}$ + 1), 190 (90, $M^{\bullet+}$), 178 (10), 177 (26), 176 (16), 175 (29), 174 (23), 173 (100), 172 (55), 171 (12), 161 (21), 157 (24), 145 (23), 144 (22), 143 (32), 142 (28), 141 (26), 129 (31), 128 (34), 119 (27), 91 (33). Anal. Calcd for $C_{12}H_{14}O_2$ (M_r 190.244): C, 75.76; H, 7.42; O, 16.82. Found: C, 75.71; H, 7.44.

(1*RS*,2*SR*,5*RS*,8*SR*)-8-Hydroxy-3,4,6,7-tetramethylidenebicyclo[3.2.1]oct-2-yl Benzoate (8). A mixture of **7** (132 mg, 0.69 mmol), anhydrous pyridine (3 mL), and benzoyl chloride (97 mg, 80 μL, 0.7 mmol) was stirred at 20 °C for 0.5 h (control of the end of the reaction with SiO_2 TLC (Et_2O/petroleum ether 1:1)). H_2O (30 mL) and Et_2O (30 mL) were added. The aqueous phase was extracted with Et_2O (30 mL, three times). The organic extracts were combined and washed successively with aqueous 1 N HCl (30 mL, twice) and saturated aqueous $NaHCO_3$ solution (30 mL). After drying ($MgSO_4$) and solvent evaporation, the residue was purified by FC (Lobar, column B, CH_2Cl_2, 4 mL/min): yield 139 mg (68%), colorless oil that polymerizes quickly on concentrating its solutions. UV (isooctane): λ_{max} 202 (ε 42700), 229 (15200), 250 (5700), 261 (3900), 281 nm (1100). UV (CH_3CN): 229 (15700), 250 (6900), 261 (4700), 281 nm (1650). ^1H NMR (360 MHz, $CDCl_3$): δ 7.98 (dt, 2 H, *J* = 7, 1.5 Hz), 7.55 (tt, 1 H, *J* = 7, 1.5), 7.43 (dd, 2 H, *J* = 7.1, 7.0), 5.71 (dd, *J*(HC(1),HC(2)) = 3.5, *J*(HC(2),HC(8)) = 1.0, HC(2)), 5.56 (d, J_{gem} = 1.3, H of H_2C=C(3) cis to C(4)), 5.55 (s, H of H_2C=C(7) cis to C(6)), 5.44 (s, H of H_2C=C(6) cis to C(7)), 5.34 (br s, H of H_2C=C(3) trans to C(4)), 5.28 (d, J_{gem} = 1.5, H of H_2C=C(4) cis to C(3)), 5.19 (s, H of H_2C=C(7) trans to C(6)), 5.03 (s, H of H_2C=C(6) trans to C7)), 5.01 (d, J_{gem} = 1.2, H of H_2C=C(4) trans to C(3)), 4.25 (dddd, *J*(OH,HC(8)) = 10, *J*(HC(1),HC(8)) = 5.0, *J*(HC(5),HC(8)) = 4.9, *J*(HC(2),HC(8)) = 1.0, HC(8)), 3.40 (d, *J* = 4.9, HC(5)), 3.22 (dd, *J* = 5, 3.5, HC(1)), 2.89 (d, *J* = 10, OH; this signal disappears on adding D_2O and the signal at 4.25 ppm becomes a ddd, *J* = 5.0, 4.9, 1.0 Hz). ^{13}C NMR (90.55 MHz, $CDCl_3$): δ 165.4 (s, COO), 145.8, 144.6, 143.3, and 140.9 (4 s, C(3), C(4), C(6), C(7)), 133.2 (dt, ^1J(C,H) = 150, ^3J(C,H) = 7 Hz), 129.6 (dt, *J* = 162, 6), 128.6 (dt, *J* = 154, 7, C_{arom}), 120.8, 112.5, 108.6, and 106.7 (4 t, *J* = 160, 4 CH_2 = C), 78.0 (d, *J* = 150, C(2)), 73.7 (d, *J* = 152, C(8)), 56.5 (d, *J* = 143, C(1)), 49.0 (d, *J* = 143, C(5)). MS (70 eV; *m/e* (relative intensity)): 173 (9, $M^{\bullet+}$ - $OCOC_6H_5$), 172 (60), 157 (6), 144 (11), 129 (21), 128 (15), 115 (10), 105 (100), 91 (11), 77 (60), 51 (21).

(1*RS*,2*SR*,5*RS*,8*SR*)-8-Hydroxy-3,4,6,7-tetramethylidenebicyclo[3.2.1]oct-2-yl Acetate (9) and (1*RS*,5*RS*,8*RS*)-(8-Hydroxy-4,6,7-trimethylidenebicyclo[3.2.1]oct-2-en-3-yl)methyl Acetate (10). A mixture of **2** (666 mg, 3.9 mmol), $CF_3CH(OH)CF_3$ (40 mL), and CH_3COOH (20 mL) was allowed to stand at 20 °C for 40 h. CH_2Cl_2 (100 mL), H_2O (100 mL), and a saturated aqueous $NaHCO_3$ solution (100 mL) were added. The aqueous phase was extracted with CH_2Cl_2 (100 mL, twice). The organic extracts were combined and washed with a saturated aqueous $NaHCO_3$ solution (100 mL, four times) and then with brine (100 mL, twice). After drying ($MgSO_4$) and solvent evaporation, the residue was purified by FC (Lobar, column C, CH_2Cl_2/Et_2O 9:1), giving a first fraction containing 61 mg (9%) of **2**, a second fraction yielding 580 mg (65%) of **9**, and a third fraction yielding 192 mg (21%) of **10**. Characteristics of **9**: colorless oil, polymerizes quickly in the condensed state. UV (isooctane): λ_{max} 203 (ε 17000), 221 (11200), 230 (10800), 240 (10450), 251 (9000), 261 nm (5700). UV (CH_3CN): 221 (9800), 236 (10300), 240 (10250), 251 (8500), 261 nm (5150). ^1H NMR (360 MHz, $CDCl_3$): δ 5.51 (br s, 2 H, H of H_2C=C(3) cis to C(4), H of H_2C=C(7) cis to C(6)), 5.47 (dd, *J*(HC(1),HC(2)) = 3.5, *J*(HC(2),CH(8)) = 1.5 Hz, HC(2)), 5.41 (s, H of H_2C=C(6) cis to C(7)), 5.25 (d, J_{gem} = 1.5, H of H_2C=C(4) cis to C(3)), 5.21 (d, J_{gem} = 1.5, H of H_2C=C(3) trans to C(4)), 5.13 (s, H of H_2C=C(7) trans to C(6)), 5.0 (s, H of H_2C=C(6) trans to C(7)), 4.98 (d, J_{gem} = 1.5, H of H_2C=C(4) trans to C(3)), 4.18 (dddd, *J*(OH,HC(8)) = 10, *J*(HC(5),HC(8)) = 5.0, *J*(HC(1),HC(8)) = 4.5, *J*(HC(2),-HC(8)) = 1.5, HC(8)), 3.36 (d, *J*(HC(5),HC(8)) = 5, HC(5)), 3.09 (dd, *J*(HC(1),HC(2)) = 3.5, *J*(HC(1),HC(8)) = 4.5, HC(1)), 2.87 (d, *J*(OH,HC(8)) = 10; this signal disappears on adding D_2O), 2.09 (s, AcO). ^{13}C NMR (90.55 MHz, $CDCl_3$): δ 169.1 (s, COO), 145.5, 144.4, 142.9, and 140.8 (4 s, C(3), C(4), C(6), C(7)), 120.1, 112.0, 108.2, and 106.5 (4 t, ^1J(C,H) = 160 Hz, 4 H_2C=C), 76.4 (d, *J* = 130, C(2)), 73.5 (d, *J* = 152, C(8)), 56.2 (dd, ^1J(C,H) = 152, ^3J(C,H) = 5, C(1)), 48.3 (d, *J* = 141, C(5)), 21.2 (q, *J* = 130, CH_3CO). MS (70 eV; *m/e* (relative intensity)): 232 (0.1, $M^{\bullet+}$), 207 (1.2), 173 (16), 172 (100), 171 (10), 157 (16), 144 (30), 143 (32), 141 (18), 130 (10), 129 (69), 128 (68), 127 (16), 115 (31), 91 (42), 77 (23), 65 (20), 51 (22).

Characteristics of **10**: colorless oil that polymerizes quickly in the condensed state. UV (isooctane): λ_{max} 203 (ε 49400), 238 nm (17800). UV (CH_3CN): 239 nm (18100). ^1H NMR (360 MHz, $CDCl_3$): δ 6.03 (d, *J*(HC(1),HC(2)) = 6 Hz, HC(2)), 5.46, 5.30, 5.15, and 5.03 (4 s), 5.08 (d, J_{gem} = 2), 4.91 (br s), 4.78 and 4.68 (2 dd, J_{gem} = 13.5, ^4J(HC(2),H_2CC(3)) = 2, H_2CC(3)), 4.18 (ddd, *J* = 9, 5.0, 4.5, HC(8)), 3.38 (d, *J* = 4.5, HC(5)), 3.22 (dd, *J* = 6, 4.5, HC(1)), 2.09 (s, Ac), 1.94 (d, *J*(OH,HC(8)) = 9, OH; this signal disappears on adding D_2O and the signal at 4.18 ppm becomes a dd, *J* = 5.0, 4.5). ^{13}C NMR (90.55 MHz, $CDCl_3$): δ 170.7 (s, COO), 147.4, 147.3, 142.2, and 131.3 (4 s, C(3), C(4), C(6), C(7)), 129.5 (d, *J* = 165 Hz, C(2)), 111.5, 107.6, and 103.7 (3 t, *J* = 158, 3 H_2C=C), 72.6 (d, *J* = 156, C(8)), 63.6 (t, *J* = 148, CH_2C(3)), 56.4 (d, *J* = 138, C(1)), 49.2 (d, *J* = 140, C(5)), 20.9 (q, *J* = 129, CH_3CO). MS (70 eV; *m/e* (relative intensity)): 232 (1.3, $M^{\bullet+}$), 173 (14), 172 (100), 157 (8), 144 (33), 143 (37), 141 (12), 130 (11), 129 (67), 128 (69), 127 (17), 115 (34), 91 (34), 77 (21), 51 (21).

(1*RS*,2*RS*,5*SR*)-3,4,6,7-Tetramethylidene-8-oxobicyclo[3.2.1]oct-2-yl Acetate (6). The solution of **9** obtained above after FC was concentrated below 0 °C to ca. 5%; then $CHCl_3$ was added, diluting **9** to ca. 2%, and evaporation was continued to a concentration of ca. 5%. $CHCl_3$ was added again, and this cycle was repeated until Et_2O was completely eliminated. A solution of 5 mL containing ca. 800 mg (3 mmol) of **9** was then made up, to which CH_2Cl_2 (60 mL) and pyridinium chlorochromate (3 g, 14 mmol) were added successively. After it was stirred at 20 °C for ca. 12 h (control of the end of the reaction by SiO_2 TLC, CH_2Cl_2/Et_2O 9:1), the mixture was filtered through a short column of silica gel (10 g) and the residue rinsed with CH_2Cl_2/Et_2O (9:1). The solution of **6** so obtained cannot be concentrated without polymerization. Spectral data of **6** were obtained by exchanging the solvent through repeated dilution/evaporation procedures, as above. UV (isooctane): λ_{max} 207 (ε 28800), 215 (5500), 253 (6000), 263 nm (4900). UV (CH_3CN): 206 (32200), 243 (5400), 253 (6000), 264 nm (4500). The ε values given here are approximate; the yield was approximated by evaporating the solution and weighing the polymer formed. ^1H NMR (360 MHz, $CDCl_3$): δ 5.66 (s, 1 H), 5.58 (d, 1 H), 5.54 (br s, 2 H), 5.33 (s, 1 H), 5.20 (s, 1 H), 5.11 (s, 1 H), 5.06 (s, 1 H), 4.95 (s, 1 H), 3.62 (br s, 1 H), 3.31 (br d, 1 H), 2.05 (s, 3 H). MS (70 eV; *m/e* (relative intensity)): 230 (0.3, $M^{\bullet+}$), 188 (1), 128 (1), 115 (1), 101 (1), 91 (1), 87 (1), 77 (1), 75 (2), 74 (4), 73 (15), 70 (1), 63 (2), 62 (1), 61 (15), 60 (28), 45 (100).

(1*RS*,2*SR*,5*RS*,8*SR*)-3,4,6,7-Tetramethylidene-2-[(*tert*-butyldimethylsilyl)oxy]bicyclo[3.2.1]octan-8-ol (11) and (1*RS*,2*SR*,5*RS*,8*SR*)-3,4,6,7-Tetramethylidene-8-[(*tert*-butyldimethylsilyl)oxy]bicyclo[3.2.1]octan-2-ol (12). Imidazole (80 mg, 1.2 mmol) and then (tBu)Me_2SiCl (88 mg, 0.58 mmol) were added to a solution of **7** (110 mg, 0.58 mmol) in DMF (3 mL). The mixture was heated to 50 °C for 14 h and then purified by column chromatography on silica gel (10 g, Et_2O/CH_2Cl_2 1:9). The first fraction yielded 60 mg (34%) of a 1:2 mixture of **11**/**12** (by 360 MHz ^1H NMR). The second fraction yielded 70 mg (64%) of unreacted **7**.

μ-Carbonylbis(η⁵-indenyl)[(1*RS*,2*RS*,5*SR*,6*SR*,7*RS*)-*C*,6,7,*C*-η-(3,4,6,7-tetramethylidene-8-oxobicyclo[3.2.1]oct-2-yl acetate)]dirhodium(I)(*Rh*-*Rh*) (13). A solution of **6** (466 mg, 2.02 mmol) in CH_2Cl_2/Et_2O was concentrated and diluted with toluene until complete disappearance of Et_2O and CH_2Cl_2. The final solution was diluted to ca. 70 mL with toluene, and then tris(μ₂-carbonyl)tris(η⁵-indenyl)-*triangulo*-trirhodium (1.6 g, 2.17 mmol) was added and the mixture heated to 50 °C for 15 h (control of the disappearance of **6** by SiO_2 TLC). The solution was filtered through a column of silica gel (height 20 cm, diameter 7 cm), with Et_2O/CH_2Cl_2/petroleum ether (1:9:10) as eluent. The first fraction (yellow) contains a product of degradation of the Rh cluster, the second fraction (green) contains the unreacted trirhodium cluster,

and the third fraction (red) contains 580 mg of two compounds. The fourth fraction (red) yielded 762 mg of **13**. The third fraction was separated by FC (Lobar, column C, Et_2O/CH_2Cl_2/petroleum ether 1:9:10), giving 39 mg of a unknown complex and 541 mg of pure **13**: total yield of **13** 1303 mg (92%); orange crystals; mp 137–138 °C. UV (isooctane): λ_{max} 220 (ϵ 40 200), 255 (shoulder, 23 200), 290 (21 600), 375 nm (24 400). UV (CH_3CN): 220 (36 000), 255 (sh, 21 600), 287 (18 600), 369 nm (21 300). IR (KBr): 3280, 3060, 1795, 1765, 1735, 1625, 1475, 1370, 1325, 1230, 1205, 1175, 1160, 1150, 1020, 970, 955, 915, 900, 855, 820, 800, 740, 605 cm^{-1}. ^1H NMR (360 MHz, $CDCl_3$): δ 7.54 (m, 2 H), 7.34–7.19 (m, 4 H), 7.02 (m, 2 H, H_{arom} of the two indenyl groups), 6.29 (m, 2 H), 5.75 (m, 2 H), 5.71 (m, 1 H), 5.60 (m, 1 H, HC(1′), HC(2′), HC(3′) of the two indenyl groups), 5.44 (d, J_{gem} = 1.5 Hz, H of H_2C=C(3) cis to C(4)), 5.21 (d, J(HC(1),HC(2)) = 5, HC(2)), 5.20 (br s, H of H_2C=C(3) trans to C(4)), 4.95 (d, J_{gem} = 1.5, H of H_2C=C(4) cis to C(3)), 4.56 (br s, H of H_2C=C(4) trans to C(3)), 2.58 (dd, J_{gem} = 2, $J(^1H,^{103}Rh)$ = 2.1, H of H_2C=C(7) trans to C(6)), 2.26 (dd, J_{gem} = 2, J(H,Rh) = 2.1, H of H_2C=C(6) trans to C(7)), 2.15 (d, J(HC(1),HC(5)) = 1, HC(5)), 2.12 (dd, J(HC(1),CH(2)) = 5, J(HC(1),HC(5) = 1, HC(1)), 1.98 (s, Ac), 0.46 (dd, J_{gem} = 2, J(H,Rh) = 2.1, H of H_2C=C(7) cis to C(6)), 0.37 (dd, J_{gem} = 2, J(H,Rh) = 2.1, H of H_2C=C(6) cis to C(7)). ^{13}C NMR (90.55 MHz, $CDCl_3$): δ 226 (t, $J(^{13}C,Rh)$ = 50 Hz, μ-CO(*Rh–Rh*)), 204.8 (s, C(8)), 170.0 (s, COO), 148.2 and 140.0 (2 s, C(3), C(4)), 126.1, 125.7, 124.8, and 124.6 (4 dd, ^1J(C,H) = 160, ^3J(C,H) = 8, 4 C of C(4′), C(5′), C(6′), C(7′) of the two indenyl groups), 122.0 (t, J = 160, H_2C=C), 120.8, 120.5, 119.7, and 119.3 (4 dd, ^1J(C,H) = 160, ^3J(C,H) = 8, 4 C of C(4′), C(5′), C(6′), C(7′) of the two indenyl groups), 115.8, 115.7, 113.4, and 113.2 (4 s, quaternary C of indenyls), 110.4 (t, J = 160, H_2C=C), 96.4 and 96.0 (2 dd, J = 117, 5) and 81.7 (d, J = 177, C(1′), C(2′), C(3′) of the indenyl groups), 80.2 (d, J = 138, C(2)), 78.6, 78.0, and 77.2 (3 d, J = 177, C(1′), C(2′), C(3′) of indenyl groups), 75.3 and 71.4 (2 d, ^1J(C,Rh) = 9, C(6), C(7)), 62.9 (d, J = 148, C(1)), 57.3 (d, J = 149, C(5)), 24.4 and 23.2 (2 td, ^1J(C,H) = 159, ^1J(C,Rh) = 15, H_2C=C(6), H_2C=(7)), 21.0 (q, J = 130, CH_3). MS (70 eV; *m/e* (relative intensity)): 695 (10), 694 ($M^{\bullet+}$, 14), 436 (4), 333 (6), 218 (18), 117 (17), 116 (100), 115 (89), 89 (10), 87 (10), 63 (36), 62 (25), 57 (18), 51 (34), 50 (31), 45 (17). Anal. Calcd. for $C_{33}H_{28}O_4Rh_2$ (694.399) C 57.08, H 4.06. Found: C 57.00, H 4.07.

[*cis*-μ-[(1*RS*,2*RS*,3*SR*,4*RS*,5*SR*,6*SR*,7*RS*)-*C*,3,4,*C*-η-(*Rh*):*C*,6,7,*C*-η(*Rh–Rh*)-(3,4,6,7-Tetramethylidene-8-oxobicyclo[3.2.1]oct-2-yl acetate)]μ-carbonyl(*Rh–Rh*)bis(η^5-indenyl)dirhodium(I)(*Rh–Rh*)](indenylrhodium) (16). A solution of **13** (49 mg, 0.07 mmol) and (indenyl)$_3Rh_3(CO)_3$ (50 mg, 0.07 mmol) was heated in toluene to 55 °C for 10 days. The mixture was purified by FC. Elution with CH_2Cl_2 gave a green fraction containing the unreacted (indenyl)$_3Rh_3(CO)_3$. Elution then with CH_2Cl_2/Et_2O (9:1) gave a red fraction containing **13** and **16**. This fraction was separated by FC (Lobar, column B, Et_2O/CH_2Cl_2/petroleum ether 2:9:10). The first fraction yielded 35 mg (55%) of **16** and the second fraction 10 mg (20%) of unreacted **13**. Characteristics of **16**: red crystals; mp 221 °C dec. UV (CH_3CN): λ_{max} 225 (sh, ϵ 56 500), 275 (37 800), 370 nm (27 900). IR (KBr): 3100, 3060, 3000, 2940, 2870, 1770, 1745, 1610, 1480, 1450, 1400, 1375, 1335, 1240, 1215, 1185, 1155, 1030, 990, 945, 915, 865, 815, 800, 755, 630 cm^{-1}. ^1H NMR (360 MHz, $CDCl_3$): δ 7.57 and 7.43 (2 m, 4 H), 7.30 and 7.05 (2 m, 8 H, HC(4′), HC(5′), HC(6′), HC(7′) of the three indenyl groups), 6.35, 6.24, 5.81, 5.71, 5.62, 5.61, 5.53, 5.42, 5.41, and 5.34 (9 m, 9 H, HC(1′), HC(2′), HC(3′) of the three indenyl groups and HC(2)), 2.87 and 2.38 (2 t, J(RhH) = 2.5, J_{gem} = 2.5 Hz, H of H_2C=C(6) trans to C(7), H of H_2C=C(7) trans to C(6)), 2.29 and 2.08 (2 d, J_{gem} = 1, H of H_2C=C(3) trans to C(4), H of H_2C=C(4) trans to C(3)), 2.22 (s, Ac), 1.85 and 1.81 (2 br s, HC(1), HC(5)), 0.66 and 0.34 (2 t, J(Rh,H) = J_{gem} = 2.5, H of H_2C=C(6) cis to C(7), H of H_2C=C(7) cis to C(6)), −0.10 (m, 2 H, H of H_2C=C(3) cis to C(4), H of H_2C=C(4) cis to C(3)). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 226.3 (t, ^1J(Rh,C) = 50 Hz, μ-CO(*Rh–Rh*)), 204.0 (s, C(8)), 170.2 (s, COO), 125.8, 125.7, 124.8, 124.6, 123.5, 123.1, 121.8, 121.4., 120.7, 120.3, 119.6, and 119.5 (12 dd, ^1J(C,H) = 168, ^3J(C,H) = 7, C(4′), C(5′), C(6′), C(7′) of the three indenyl groups), 116.1, 115.0, 113.8, 112.5, 107.9, and 106.5 (6 s, C(3′a), C(7′a) of the three indenyl groups), 103.3 (d, ^1J(Rh,C) = 7, C(3) or C(4)), 96.6, 95.9, and 91.8 (3 dd, ^1J(C,H) = 177, ^1J(Rh,C) = 5, C(2′) of the three indenyl groups), 88.6 (d, ^1J(Rh,C) = 9, C(4) or C(3)), 82.0, 80.7, 78.8, and 78.5 (4 dd, ^1J(C,H) = 174, ^1J(Rh,C) = 5, C(1′), C(3′) of two indenyl groups), 77.7 (d, ^1J(C,H) = 152, C(2)), 76.3 (d, ^1J(Rh,C) = 9, C(6) or C(7)), 73.8 and 72.7 (2 dd, ^1J(C,H) = 177, ^1J(Rh,C) = 5, C(1′), C(3′) of an indenyl group), 73.2 (d, ^1J(Rh,C) = 9, C(7) or C(6)), 59.8 and 56.9 (2 d, ^1J(C,H) = 180, C(1),C(5)), 34.6, 32.2, 24.0, and 23.3 (4 dt, ^1J(C,H) = 170, ^1J(Rh,C) = 15, 4 CH_2=C), 21.0 (q, ^1J(C,H) = 130, CH_3). MS (70 eV; *m/e* (relative intensity)): 912 ($M^{\bullet+}$, 11), 437 (11), 436 (92), 333 (51), 231 (6), 230 (7), 218 (33), 191 (12), 149 (45), 116 (53), 115 (71), 106 (12), 105 (17), 95 (12), 92 (11), 91 (44), 89 (14), 85 (21), 83 (10), 81 (14), 77 (11), 73 (17), 71 (37), 70 (16), 69 (26), 65 (12), 60 (18), 58 (100), 57 (63), 56 (16), 45 (35). Anal. Calcd for $C_{42}H_{35}O_4Rh_3$ (M_r 912.46): C, 55.29; H, 3.87. Found: C, 55.38; H, 3.96.

[*trans*-μ-[(1*RS*,2*RS*,4*RS*,5*RS*,6*SR*,7*RS*)-*C*,4-η^2(*Fe*):*C*,6,7*C*-η(*Rh–Rh*)-(3,4,6,7-Tetramethylidene-8-oxobicyclo[3.2.1]oct-2-yl acetate)]μ-carbonyl(*Rh–Rh*)bis(η^5-indenyl)dirhodium(I)(*Rh–Rh*)](tetracarbonyliron) (17). Ar was bubbled through a solution of **13** (97 mg, 0.14 mmol) and $Fe_2(CO)_9$ (70 mg, 0.19 mmol) in benzene at 20 °C for 10 h. After filtration through Florisil (4 g), the mixture was purified by FC (Lobar, column B, Et_2O/CH_2Cl_2/petroleum ether 2:9:10). The first fraction gave 3 mg (2%) of **18**, the second fraction gave 75 mg (63%) of **17**, and a third fraction gave 20 mg (21%) of unreacted **13**. Complex **17** is unstable in most solvents at 20 °C, giving **13** and iron compounds. IR (KBr): 3450, 3050, 2920, 2080, 2005, 1975, 1780, 1740, 1475, 1365, 1230, 1210, 1170, 1135, 1015, 970, 860, 810, 745, 630 cm^{-1}. ^1H NMR (360 MHz, $CDCl_3$): δ 7.59, 7.53, 7.12, 6.96 (4 dm, 4 H, ^3J = 8 Hz), and 7.30–7.18 (m, 4 H, HC(4′), HC(5′), HC(6′), HC(7′) of two indenyl groups), 6.26, 6.14, 5.87, 5.68, and 5.52 (6 m, 6 H, HC(1′), HC(2′), HC(3′) of two indenyl groups), 5.31 (d, J(HC(1),HC(2)) = 4.5, HC(2)), 5.01 and 4.94 (2 s, H_2C=C(3)), 2.75 (d, J_{gem} = 3, H of H_2C=C(4) cis to C(3)), 2.69 (dd, ^2J(Rh,H) = 2.5, J_{gem} = 2.4, H of H_2C=C(7) trans to C(6)), 2.46 (dd, ^2J(Rh,H) = 2.5, J_{gem} = 2.4, H of H_2C=C(6) trans to C(7)), 2.16 (dd, J(HC(1),HC(2)) = 4.5, ^4J(HC(1),HC(5)) = 1.2, HC(1)), 2.12 (s, Ac), 2.06 (d, J_{gem} = 3, H of H_2C=C(4) trans to C(3)), 1.82 (d, ^4J(HC(1),HC(5)) = 1.2, HC(5)), 0.50 (dd, J(Rh,H) = 2.5, J_{gem} = 2.4, H of H_2C=C(7) cis to C(6)), 0.40 (dd, J(Rh,H) = 2.5, J_{gem} = 2.4, H of H_2C=C(6) cis to C(7)). ^{13}C NMR (62.9 MHz, C_6D_6, [relative Yb(thd)$_3$-induced δ_C]): δ 223.3 (t, ^1J(Rh,C) = 50 Hz, μ-CO(Rh–Rh)), 210.2 (s, $Fe(CO)_4$ [5.4]), 204.7 (s, C(8) [11.4]), 169.6 (s, COO [100]), 143.7 (s, C(3) [15.3]), 126.4, 126.2, 125.0, 125.0, 120.6, 120.3, 119.9 and 119.0 (8 dd, C(4′), C(5′), C(6′), C(7′) of two indenyl groups), 116.4, 115.7, 113.6, and 113.3 (4 s, C(3′a), C(7′a) of two indenyl groups), 114.1 (t, H_2C=C(3) [11.4]), 96.3, 95.9, 81.4, 81.3, 79.4 and 79.2 (6 dd, C(1′), C(2′), C(3′) of two indenyl groups), 83.1 (d, C(2) [33.5]), 78.5 (d, J(Rh,C) = 10, C(6 or 7) [8.0]), 71.7 (d, J(Rh,C) = 10, C(7 or 6) [8.0]), 68.0 (d, C(5) [8.2]), 58.1 (d, C(1) [21.1]), 31.9 (s, C(4)), 30.2 (t, H_2C=C(4) [5.4]), 23.8 (dt, J(Rh,C) = 15, CH_2=C(6 or 7)), 23.2 (dt, J(Rh,C) = 15, CH_2=C(7 or 6)), 20.8 (q, CH_3 [37.5]). Anal. Calcd for $C_{37}H_{28}O_8FeRh_2$ (M_r 862.288): C, 51.54; H, 3.27. Found: C, 51.46; H, 3.32.

[*cis*-μ-[(1*RS*,2*RS*,3*SR*,4*RS*,5*RS*,6*SR*,7*RS*)-*C*,3,4,*C*-η-(*Fe*):*C*,6,7,*C*-η(*Rh–Rh*)-(3,4,6,7-Tetramethylidene-8-oxobicyclo[3.2.1]oct-2-yl acetate)]μ-carbonyl(*Rh–Rh*)bis(η^5-indenyl)dirhodium(I)(*Rh–Rh*)(tricarbonyliron) (18). $Fe_2(CO)_9$ (210 mg, 0.58 mmol) was added to a benzene (20 mL) solution of **13** (198 mg, 0.29 mmol) degassed with Ar. The mixture was stirred at 40 °C for 24 h. More $Fe_2(CO)_9$ (ca. 50 mg) was added after 12 and 18 h (control by SiO_2 TLC). The mixture was purified by FC. Elution with CH_2Cl_2/petroleum ether (3:2) gave $Fe_3(CO)_{12}$. Then elution with CH_2Cl_2/Et_2O (9:1) afforded a red fraction, which was separated by FC (Lobar, column B, Et_2O/CH_2Cl_2/petroleum ether 2:9:10). The first fraction yielded 187 mg (79%) of **18**. The second fraction gave 6 mg (3%) of **13**. Characteristics of **18**: orange crystals; mp 198 °C dec. UV (isooctane): λ_{max} 204 (ϵ 54 000), 292 (21 000), 379 nm (22 500). UV (CH_3CN): 200 (62 000), 290 (20 700), 373 nm (21 000). IR (KBr): 3070, 3000, 2930, 2055, 1980, 1790, 1470, 1440, 1370, 1325, 1220, 1200, 1175, 1025, 910, 860, 810, 745, 610 cm^{-1}. ^1H NMR (360 MHz, $CDCl_3$): δ 7.58, 7.51 (2 m, 2 H), 7.31–7.14 (m, 4 H) and 6.92 (m, 2 H, HC(4′), HC(5′), HC(6′), HC(7′) of two indenyl groups), 6.47, 6.42, 5.86, 5.74 (4 m, 4 H), and 5.82 (m, 2 H, HC(1′), HC(2′), HC(3′) of two indenyl groups), 5.55 (d, J(HC(1),HC(2)) = 2 Hz, HC(2)), 2.95 (dd, J_{gem} = 2, J(Rh,H) = 2.1, H of H_2C=C(7) trans to C(6)), 2.43

(dd, J_{gem} = 2, J(Rh,H) = 2.1 H of H_2C=C(6) trans to C(7)), 2.06 (s Ac), 1.68 (m, HC(1)), 1.47 (br s, HC(5)), 1.37 (br d, J_{gem} = 3, H of H_2C=C(3) trans to C(4)), 1.28 (d, J_{gem} = 2.5, H of H_2C=C(4) trans to C(3)), 0.72 (dd, J_{gem} = 2, J(Rh,H) = 2.1, H of H_2C=C(7) cis to C(6)), 0.48 (dd, J_{gem} = 2, J(Rh,H) = 2.1, H of H_2C=C(6) cis to C(7)), 0.02 (d, J_{gem} = 2.5, H of H_2C=C(4) cis to C(3)), -0.10 (br d, J_{gem} = 3, H of H_2C=C(3) cis to C(4)). ^{13}C NMR (90.55 MHz, $CDCl_3$): δ 225.7 (t, ^1J(Rh,C) = 50 Hz, μ-CO(*Rh-Rh*)), 208.0 (br s, $Fe(CO)_3$), 203.9 (s, C(8)), 170.1 (s, COO), 126.6, 126.1, 125.0, 124.9, 121.4, 120.9, 119.4 and 119.0 (8 dd, ^1J(CH) = 160, ^3J(C,H) = 8, C(4′), C(5′), C(6′), C(7′) of two indenyl groups), 116.2, 115.2, 114.1 and 113.2 (4 s, C(3′a), C(7′a) of two indenyl groups), 110.8 and 97.8 (2 s, C(3), C(4)), 96.5, 96.2, 77.3, and 77.2 (4 dd, ^1J(C,H) = 178, ^1J(Rh,C) = 5, C(1′), C(3′) of two indenyl groups), 83.2 and 82.2 (2 d, ^1J(C,H) = 177, C(2′) of two indenyl groups), 78.0 (d, ^1J(C,H) = 152, C(2)), 75.4 and 72.1 (2 d, J(Rh,C) = 8, C(6), C(7)), 58.1 and 56.4 (2 d, ^1J(C,H) = 152, C(1), C(5)), 37.8 and 33.4 (2 t, ^1J(C,H) = 160, CH_2=C(3), CH_2=C(4)), 24.5 and 22.6 (2 dt, ^1J(C,H) = 160, J(Rh,C) = 15, CH_2=C(6), CH_2=C(7)), 20.1 (q, ^1J(C,H) = 129, CH_3). MS (70 eV; *m/e* (relative intensity)) 836 ($M^{\bullet+}$ + 2, 9), 835 ($M^{\bullet+}$ + 1, 29), 834 ($M^{\bullet+}$, 74), 833 (32), 806 (6), 751 (6), 750 (7), 692 (6), 679 (8), 663 (13), 662 (47), 649 (8), 648 (29), 647 (38), 607 (12), 579 (18), 492 (10), 436 (13), 333 (51), 274 (16), 273 (10), 232 (10), 226 (15), 218 (100), 216 (13), 141 (12), 131 (13), 115 (65), 112 (22), 103 (34), 91 (10), 85 (13), 84 (13), 77 (15), 73 (10), 69 (12), 63 (81), 57 (88), 56 (40), 55 (41), 54 (16), 53 (21). Anal. Calcd for $C_{36}H_{28}O_7FeRh_2$ (M_r 834.277): C, 51.83; H, 3.38. Found: C, 51.85; H, 3.47. Solutions of **18** are stable only if thoroughly degassed. Otherwise, partial loss of $Fe(CO)_3$ is observed.

[*cis*-μ-[(1*RS*,2*RS*,3*SR*,4*RS*,5*SR*,6*SR*,7*RS*)-*C*,3,4,*C*-η-(*Rh*):*C*,6,7,*C*-η(*Rh*-*Rh*)-(3,4,6,7-Tetramethylidene-8-oxobicyclo[3.2.1]octan-2-ol)]μ-carbonyl(*Rh*-*Rh*)bis(η^5-indenyl)dirhodium(I)(*Rh*-*Rh*)](indenylrhodium) (20). A solution of **16** (17 mg, 0.019 mmol) in CH_2Cl_2 (2 mL) was added to a solution of anhydrous K_2CO_3 (50 mg, 0.36 mmol) in anhydrous MeOH (8 mL). After it was stirred at 20 °C for 90 min, the mixture was filtered through a short column of Florisil (4 g) and purified by FC (Lobar, column A, Et_2O/CH_2Cl_2/petroleum ether 2:9:10). The first fraction yielded 5 mg (30%) of **20**. A second fraction afforded a mixture of compounds. Characteristics of **20**: orange oil. ^1H NMR (250 MHz, $CDCl_3$): δ 7.57 (m, 2 H), 7.30 (m, 6 H), 7.08 (m, 6 H), 6.23 (m, 1 H), 6.20 (m, 1 H), 5.88 (m 1 H), 5.78 (m, 1 H), 5.70 (m, 2 H), 5.66 (m, 1 H), 5.58 (m, 1 H), and 5.53 (m, 1 H) (three indenyl groups), 4.11 (br d, J(OH,HC(2)) = 12 Hz, HC(2)), 2.69 (t, J(Rh,H) = J_{gem} = 2.5, H of H_2C=C(7) trans to C(6)), 2.57 (br s, H of H_2C=C(3) trans to C(4)), 2.32 (t, J(Rh,H) = J_{gem} = 2.5, H of H_2C=C(6) trans to C(7)), 2.17 (br s, H of H_2C=C(4) trans to C(3)), 2.02 (br s, HC(1)), 1.66 (br s, HC(5)), 0.68 (d, J(OH,HC(2)) = 12, OH), 0.55 (t, J(Rh,H) = J_{gem} = 2.5, H of H_2C=C(7) cis to C(6)), 0.34 (t, J(Rh,H) = J_{gem} = 2.5, H of H_2C=C(6) cis to C(7)), 0.27 (m, H of H_2C=C(3) cis to C(4), H of H_2C=C(4) cis to C(3)).

μ-Carbonylbis(η^5-indenyl)[(1*RS*,5*RS*,6*SR*,7*RS*)-*C*,6,7,*C*-η-(4-methyl-6,7-dimethylidene-8-oxobicyclo[3.2.1]oct-2-ene-3-carbaldehyde)]dirhodium(I)(*Rh*-*Rh*) (24). A solution of **13** (60 mg. 0.086 mmol) in CH_2Cl_2 (20 mL) was added to a solution of K_2CO_3 (105 mg, 0.76 mmol) in MeOH (35 mL). After the mixture was stirred at 20 °C for 3 h, the solvent was evaporated and the residue purified by FC (CH_2Cl_2/Et_2O 9:1): yield 54 mg (90%); orange crystals; mp 175 °C dec; insoluble in isooctane. UV (CH_3CN): λ_{max} 222 (ε 36 000), 255 (sh, 27 000), 290 (sh, 23 000), 367 nm (22 700). IR (KBr): 3450, 3080, 3040, 2930, 2900, 2860, 1775, 1655, 1620, 1485, 1475, 1445, 1430, 1370, 1345, 1325, 1280, 1235, 1210, 1170, 1155, 1125, 1030, 940, 860, 810, 780, 745, 620 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ 9.93 (s, HCO), 7.60 (m, 2 H), 7.30 (m, 4 H), 7.10 (m, 1 H), 7.00 (m, 1 H), 6.33 (m, 2 H), 5.85, 5.72, 5.70, and 5.67 (4 m, 4 H, two indenyl groups), 2.66 (m, H_2C(2)), 2.64 (dd, J(Rh,H) = 2.5, J_{gem} = 2.4 Hz, H of H_2C=C(7) trans to C(6)), 2.41 (dd, J(Rh,H) = 2.5, J_{gem} = 2.4, H of H_2C=C(6) trans to C(7)), 2.08 (br s, CH_3C(4)), 1.84 (br s, HC(1)), 1.82 (s, HC(5)), 0.57 (dd, J(Rh,H) = 2.5, J_{gem} = 2.4, H of H_2C=C(7) cis to C(6)), 0.30 (dd, J(Rh,H) = 2.5, J_{gem} = 2.4, H of H_2C=C(6) cis to C(7)). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 226.1 (t, ^1J(Rh,C) = 50 Hz, μ-CO(*Rh-Rh*)), 207.5 (s, C(8)), 189.8 (d, ^1J(C,H) = 174, HCO), 159.9 (s, C(4)), 129.3 (br s, C(3)), 125.9, 125.8, 124.9, 124.6, 120.9, 120.5, 119.5 and 119.3 (8 dd, ^1J(C,H) = 166, ^3J(C,H) = 7, C(4′), C(5′), C(6′), C(7′) of two indenyl groups), 116.5, 115.0, 114.0 and 112.7 (4 s, C(3′a), C(7′a) of two indenyl groups), 96.5 and 96.1 (2 dd, ^1J(C,H) = 178, ^1J(Rh,C) = 5), 82.2 and 81.1 (2 dd, ^1J(C,H) = 172, ^1J(Rh,C) = 4), 78.4 and 78.0 (2 dd, ^1J(C,H) = 174, ^1J(Rh,C) = 4, C(1′), C(2′), C(3′) of two indenyl groups), 76.9 and 76.7 (2 s, C(6), C(7)), 60.2 and 52.2 (2 d, ^1J(C,H) = 149, C(1), C(5)), 39.2 (t, ^1J(C,H) = 134, C(2)), 24.2 and 20.9 (dt, ^1J(C,H) = 161, ^1J(Rh,C) = 15, H_2C=C(6), H_2C=C(7)), 18.3 (q, ^1J(C,H) = 130, CH_3). MS (70 eV; *m/e* (relative intensity)): 653 ($M^{\bullet+}$ + 1, 6), 652 ($M^{\bullet+}$, 15), 651 (10), 437 (23), 436 (99), 406 (9), 334 (20), 333 (100), 218 (68), 117 (11), 116 (65), 115 (76), 103 (11), 91 (28), 89 (11), 84 (13), 63 (13), 58 (13), 57 (11), 51 (12), 49 (18). Anal. Calcd. for $C_{31}H_{26}O_3Rh_2$ (M_r 652.361): C, 57.08; H, 4.02. Found: C, 57.12; H, 4.08.

[*cis*-μ-[(1*RS*,2*RS*,3*SR*,4*RS*,5*RS*,6*SR*,7*RS*)-*C*,3,4,*C*-η-(*Fe*):*C*,6,7,*C*-η(*Rh*-*Rh*)-(3,4,6,7-Tetramethylidene-8-oxobicyclo[3.2.1]octan-2-ol)]μ-carbonyl(*Rh*-*Rh*)bis(η^5-indenyl)dirhodium(I)(*Rh*-*Rh*)](tricarbonyliron) (25) and [*cis*-μ-[(1*RS*,2*SR*,3*SR*,4*RS*,5*RS*,6*SR*,7*RS*)-*C*,3,4,*C*-η(*Fe*):*C*,6,7,*C*-η(*Rh*-*Rh*)-(3,4,6,7-Tetramethylidene-8-oxobicyclo[3.2.1]octan-2-ol)]μ-carbonyl(*Rh*-*Rh*)bis(η^5-indenyl)dirhodium(I)(*Rh*-*Rh*)](tricarbonyliron) (26). A solution of **18** (90 mg, 0.11 mmol) in CH_2Cl_2 (2 mL) was added to a solution of K_2CO_3 (200 mg, 1.45 mmol) in MeOH (8 mL). After the mixture was stirred at 20 °C for 3 h, the solvent was evaporated and the residue taken up in CH_2Cl_2 (4 mL). The mixture was filtered through Florisil (4 g) and separated by FC (Lobar, column B, Et_2O/CH_2Cl_2/petroleum ether 3:9:10). The first fraction yielded 32 mg (37%) of **25** and the second 42 mg (48%) of **26**. Characteristics of **25**: red crystals; mp 199 °C dec; insoluble in isooctane. UV (CH_3CN): λ_{max} 225 (sh, ε 61 500), 290 (26 800), 370 nm (26 200). IR (KBr): 3500, 3050, 3000, 2930, 2045, 1975, 1790, 1760, 1740, 1600, 1475, 1445, 1380, 1325, 1260, 1235, 1210, 1175, 1155, 1140, 1060, 1035, 1010, 980, 940, 860, 800, 740, 610 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ 7.63 (m, 1 H), 7.54 (m, 1 H), 7.38 (m, 2 H), 7.20 (m, 2 H), 7.05 (m, 1 H), 6.95 (m, 1 H), 6.48, 6.42, 5.90, 5.88, 5.82 and 5.78 (6 m, 6 H, two indenyl groups), 4.61 (d, J(OH,HC(2)) = 9 Hz, HC(2) anti to C(8)), 3.34 (dd, J(Rh,H) = 2.1, J_{gem} = 2, H of H_2C=C(7) trans to C(6)), 2.40 (dd, J(Rh,H) = 2.1, J_{gem} = 2, H of H_2C=C(6) trans to C(7)), 2.07 (d, J = 9, OH) 1.88 (br s, HC(1)), 1.67 (d, J_{gem} = 2.5, H of H_2C=C(3) trans to C(4)), 1.35 (br s, HC(5)), 1.26 (d, J_{gem} = 2, H of H_2C=C(4) trans to C(3)), 0.70 (dd, J(Rh,H) = 2.1, J_{gem} = 2, H of H_2C=C(7) cis to C(6)), 0.52 (dd, J(Rh,H) = 2.1, J_{gem} = 2, H of H_2C=C(6) cis to C(7)), 0.03 (d, J_{gem} = 2.5, H of H_2C=C(3) cis to C(4)), -0.01 (d, J_{gem} = 2, H of H_2C=C(4) cis to C(3)). ^{13}C NMR (90.55 MHz, $CDCl_3$ [relative Yb(thd)$_3$-induced δ_C]): δ 225.9 (t, ^1J(Rh,C) = 50 Hz, μ-CO(*Rh-Rh*) [4]), 209.5 (br s, $Fe(CO)_3$ [25.8]), 205.4 (s, C(8) [30.3]), 126.6, 126.3, 125.0, 124.9, 121.3, 120.9, 119.4 and 118.9 (8 dd, ^1J(C,H) = 162, ^3J(C,H) = 8), 116.2, 115.3, 113.8 and 113.2 (4 s), 110.7 (s, C(4) [25.8]), 103.9 (s, C(3) [49.4]), 96.4, 96.2, 82.6 and 82.2 (4 dd, ^1J(C,H) = 177, ^1J(Rh,H) = 3), 78.2 (d, ^1J(C,H) = 152, C(2) [100]), 77.8 and 76.8 (2 dd, ^1J(C,H) = 177, ^1J(Rh,H) = 3), 75.7 (d, J(Rh,C) = 8, C(6) [13.9]), 72.8 (d, J(Rh,C) = 8, C(7) [20.9]), 61.0 (d, ^1J(C,H) = 148, C(1) [43.4]), 58.0 (d, ^1J(C,H) = 151, C(5) [20.4]), 37.2 (t, ^1J(C,H) = 160, CH_2=C(4) [13.7]), 34.4 (t, ^1J(C,H) = 160, CH_2=C(3) [32.3]), 24.9 (dt, J(Rh,C) = 15, ^1J(C,H) = 160, CH_2=C(7) [7.0]), 22.4 (dt, J(Rh,C) = 15, ^1J(C,H) = 160, CH_2=C(6) [6.5]). MS (70 eV; *m/e* (relative intensity)): 792 ($M^{\bullet+}$, 3), 492 (10), 436 (21), 333 (19), 274 (5), 218 (34), 117 (10), 116 (95), 115 (100), 91 (27), 89 (15), 63 (17), 58 (21), 57 (17). Anal. Calcd for $C_{34}H_{26}O_6FeRh_2$ (M_r 792.24): C, 51.55; H, 3.31. Found: C, 51.65; H, 3.36.

Characteristics of **26**: red crystals; mp 182 °C dec; insoluble in isooctane. UV (CH_3CN): λ_{max} 225 (sh, ε 54 600), 290 (24 900), 374 nm (26 200). IR (KBr): 3500, 3050, 3000, 2920, 2045, 1970, 1780, 1760, 1600, 1475, 1440, 1390, 1350, 1325, 1235, 1210, 1180, 1150, 1050, 1010, 980, 940, 850, 810, 750, 625, 605 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ 7.67, 7.54 (2 m, 2 H), 7.38 and 7.17 (2 m, 4 H), 7.10 and 6.93 (2 m, 2 H), 6.56, 6.37, 5.98, 5.88, 5.80 and 5.77 (6 m, 6 H, two indenyl groups), 4.49 (dd, J(OH,HC(2)) = 10.5, J(HC(1),HC(2)) = 6 Hz, HC(2) syn to C(8)), 3.12 (dd, J(Rh,H) = 2.1, J_{gem} = 2, H of H_2C=C(7) trans to C(6)), 2.48 (m, OH, C(1)), 2.35 (dd, J(Rh,H) = 2.1, J_{gem} = 2, H of H_2C=C(6) trans to C(7)), 1.88 (d, J_{gem} = 3, H of H_2C=C(3) trans to C(4)), 1.22 (d, J_{gem} = 2.5, H of H_2C=C(4) trans to C(3)), 1.18 (br s, HC(5)), 0.77 (dd,

J(Rh,H) = 2.1, J_{gem} = 2, H of H_2C=C(7) cis to C(6)), 0.55 (dd, J(Rh,H) = 2.1 J_{gem} = 2, H of H_2C=C(6) cis to C(7)), 0.08 (d, J_{gem} = 3, H of H_2C=C(3) cis to C(4)), -0.08 (d, J_{gem} = 2.5, H of H_2C=C(4) cis to C(3)). ^{13}C NMR (90.55 MHz, $CDCl_3$ [relative Yb(thd)$_3$-induced δ_C]): δ 225.8 (t, J(Rh,C) = 50 Hz, μ-CO(*Rh-Rh*) [8.2]), 208.7 (br s, $Fe(CO)_3$ [5.8]), 201.7 (s, C(8) [21.6]), 126.6, 126.3, 125.2, 124.9, 121.4, 120.8, 119.7 and 118.6 (8 dd, ^1J(C,H) = 170, ^3J(C,H) = 8), 116.0, 115.7, 113.7, 113.5 (4 s), 107.9 (s, C(4) [26.6]), 99.8 (s, C(3) [52.8]), 96.9, 95.8, 82.7, 82.5, 78.3 and 76.5 (6 dd, ^1J(C,H) = 176, J(Rh,C) = 5), 76.2 (d, J(Rh,C) = 8, C(6) [23.2]), 75.1 (d, ^1J(C,H) = 150, C(2) [100]), 70.8 (d, J(Rh,C) = 8, C(7) [38.7]), 60.1 (d, ^1J(C,H) = 150, C(1) [46.9]), 56.9 (d, ^1J(C,H) = 150, C(5) [20.8]), 37.8 (t, ^1J(C,H) = 158, CH_2=C(3) [34.3]), 36.7 (t, ^1J(C,H) = 158, CH_2=C(4) [14.5]), 27.0 (td, ^1J(C,H) = 159, J(Rh,C) = 15, CH_2=C(7) [34.6]), 21.9 (td, ^1J(C,H) = 159, J(Rh,C) = 15, CH_2=C(6) [15.1]). MS (70 eV; m/e (relative intensity)): 792 ($M^{\bullet+}$, 19), 791 (10), 493 (7), 492 (26), 437 (8), 436 (55), 334 (7), 333 (67), 274 (11), 246 (7), 218 (57), 116 (60), 115 (84), 106 (43), 105 (23), 103 (13), 92 (16), 91 (100), 89 (12), 86 (20), 84 (25), 77 (11), 74 (11), 65 (11), 63 (16), 58 (52), 57 (22), 52 (10), 51 (39), 49 (44), 45 (12). Anal. Calcd for $C_{34}H_{26}O_6FeRh_2$ (M_r 792.24): C, 51.55; H, 3.31. Found: C, 51.41; H, 3.41.

[*cis*-μ-[(1*RS*,2*SR*,3*SR*,4*RS*,5*RS*,6*SR*,7*RS*)-*C*,3,4,*C*-η-(*Fe*):*C*,6,7,*C*-η(*Rh-Rh*)-(3,4,6,7-Tetramethylidene-8-oxobicyclo[3.2.1]oct-2-yl acetate)]μ-carbonyl(*Rh-Rh*)bis(η^5-indenyl)dirhodium(I)(*Rh-Rh*)](tricarbonyliron) (28). A mixture of **26** (8 mg, 0.01 mmol), Ac_2O (1 mL), and anhydrous pyridine (1 mL) was stirred at 20 °C for 3 h. After addition of toluene (5 mL) the solvent was evaporated to dryness and the residue purified by FC (Lobar, column A, Et_2O/CH_2Cl_2/petroleum ether 2:9:10): yield 7.5 mg (90%); red crystals; mp 140 °C dec. ^1H NMR (360 MHz, $CDCl_3$): δ 7.63 and 7.54 (2 m, 2 H), 7.39 and 7.17 (2 m, 4 H), 7.11 and 6.92 (2 m, 2 H), 6.56, 6.26, 5.97, 5.84, 5.80 and 5.73 (6 m, 6 H, two indenyl groups), 5.52 (d, J(HC(1),HC(2)) = 6 Hz, HC(2) syn to C(8)), 2.75 (dd, J(HC(1),HC(2)), = 6, ^4J(HC(1),HC(5)) = 1, HC(1)), 2.74 (dd, J_{gem} = 2.5, J(Rh,H) = 2.4, H of H_2C=C(7) trans to C(6)), 2.37 (dd, J_{gem} = 2.5, J(Rh,H) = 2.4, H of H_2C=C(6) trans to C(7)), 2.12 (s, Ac), 1.65 (d, J_{gem} = 3.5, H of H_2C=C(3) trans to C(4)), 1.26 (d, J_{gem} = 2.5, H of H_2C=C(4) trans to C(3)), 1.19 (br s, HC(5)), 0.74 (dd, J(Rh,H) = 2.1, J_{gem} = 2.5, H of H_2C=C(7) cis to C(6)), 0.61 (dd, J(Rh,H) = 2.1, J_{gem} = 2.5, H of H_2C=C(6) cis to C(7)), 0.04 (d, J_{gem} = 3.5, H of H_2C=C(3) cis to C(4)), -0.01 (d, J_{gem} = 2.5, H of H_2C=C(4) cis to C(3)).

Interaction of Rhodium(I) with Cyclopropenones: Decarbonylation and Formation of 1-Rhodacyclopentene-2,5-diones and Cationic Oxygen σ-Bound Cyclopropenone Complexes. X-ray Crystal Structure of *trans*-Carbonylbis(triphenylphosphine)(di-*tert*-butylcyclopropenone)rhodium Trifluoromethanesulfonate

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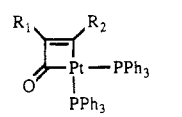
Received April 20, 1990

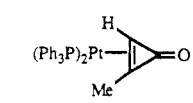
Cyclopropenones **5a,b** react with chlorotris(triphenylphosphine)rhodium to form *trans*-chlorocarbonylbis(triphenylphosphine)rhodium and acetylenes **7a,b**. Reactions of **5a,b** with *trans*-chlorocarbonylbis(triphenylphosphine)rhodium result in the formation of rhodacyclopentenediones **8a,b** through the insertion of both the rhodium and the carbonyl into the three-membered ring. Di-*tert*-butylcyclopropenone, **5c**, in contrast, does not react with chlorotris(triphenylphosphine)rhodium or *trans*-chlorocarbonylbis(triphenylphosphine)rhodium under similar reaction conditions. All three cyclopropenones **5a-c** react with *trans*-carbonylbis(triphenylphosphine)rhodium trifluoromethanesulfonate (triflate) to give the cationic rhodium complexes **10a-c** without ring opening. However, **5a,b** yield the insertion products **12a,b** when the reactions are done in benzene at ca. 60 °C. The X-ray crystal structure of *trans*-carbonylbis(triphenylphosphine)(di-*tert*-butylcyclopropenone)rhodium triflate, **10c**, is reported.

Introduction

There is considerable interest in the organometallic chemistry of organic molecules containing small rings;[1] however, cyclopropenones are less studied. To our knowledge, only a few cyclopropenone complexes have been reported and fully characterized. Thus, $(PPh_3)_4Pt$ or $(PPh_3)_2PtC_2H_4$ reacts with selected cyclopropenones to form metallacyclobutenones **1a,b** through the insertion of platinum into the strained three-membered ring.[2,3] It has been proposed that these reactions go through an intermediate **2** in which platinum is bound to the cyclopropenone in an η^2 fashion. This intermediate has been detected by NMR spectroscopy at low temperature in the case of methylcyclopropenone. When allowed to react with $Pt_3(t\text{-BuNC})_6$, diphenylcyclopropenone gave an interesting



1a R_1=R_2=Ph
1b R_1=Me, R_2=H



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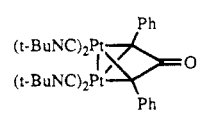

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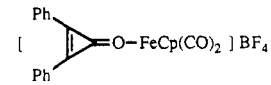

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