# Organic and Biological Chemistry

## The Pentalenylcycloocta-1,5-dienerhodium Anion and Hydropentalenyl Complexes of Thallium, Platinum, and Rhodium

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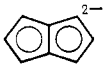
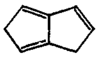
*Contribution from the Department of Chemistry, Columbia University, New York, New York 10027.* *Received September 21, 1966*

**Abstract:** A synthesis of metallocene derivatives of pentalene and hydropentalene is described. Reaction of dihydropentalene (II) with thallous sulfate in aqueous alkali yields thallium hydropentalenide (VI), a yellow solid that decomposes only slowly in air. This substance reacts with ferrous chloride to give the known compound bis(hydropentalenyl)iron (III), with cycloocta-1,5-dienerhodium chloride to give hydropentalenylcycloocta-1,5-dienerhodium (VIIa), and with trimethylplatinum iodide to give hydropentalenyltrimethylplatinum (IX). The rhodium complex in tetrahydrofuran is lithiated by *n*-butyllithium in *n*-hexane to the lithium salt of the pentalenylcycloocta-1,5-dienerhodium anion (VIII), which was identified by its reaction with deuterium oxide to give VIIb, specifically deuterated at the hydropentalene methylene group, and by its reaction with benzophenone to give an alcohol, VIIc. The mass spectra of the hydropentalenyl metal complexes, III, VI, VIIa, and IX, and of dihydropentalene are described. Peaks attributable to $C_8H_6Fe^+$ and $C_8H_6Rh^+$ are prominent. The iron complex shows a prominent peak attributable to $C_8H_6^+$ (presumably pentalene cation radical), while the platinum complex shows as its base peak one attributable to $C_8H_7^+$. A peak attributable to $C_8H_6^{2+}$ (presumably pentalene dication) is observed in some of the spectra. The thallium complex shows as its base peak $^{205}Tl^+$. Thallium isodicyclopentadienide is also prepared. It reacts with ferrous chloride to give a known ferrocene, shown to be either *exo,exo*- (XI) or *endo,endo*-bis(isodicyclopentadienyl)iron (XII). Lithium isodicyclopentadienide in tetrahydrofuran reacts with ferrous chloride to give the same ferrocene, but a small amount of the isomeric ferrocene, XIII, *exo, endo*-bis(isodicyclopentadienyl)iron, could also be isolated.

Derivatives of unsubstituted[2] pentalene anticipated to be sufficiently stable for easy preparation are the pentalenyl dianion (I)[3] and metallocenes related to this anion as ferrocene[4] and similar complexes of other transition metals[5] are related to the cyclopentadienyl anion. The pentalenyl dianion is formed when dihydropentalene (II) is treated in tetrahydrofuran (THF)


I


II

with *n*-butyllithium.[3] If metallocene derivatives of this hydrocarbon are stable, like those of other unsaturated hydrocarbons such as cyclobutadiene,[6] analogy with the preparation of the pentalenyl dianion suggests that these metallocenes be made by the sequence of reactions shown in Scheme I.[7] But other analogies suggest that this scheme might fail. Thus, bis(indenyl)iron, isoelectronic with V, unlike ferrocene decomposes when its solutions are exposed to air,[10] and methylferrocenes are not metalated by *n*-butyllithium[11] or *n*-amylsodium or -potassium[12] in the side chain, but in the ferrocene ring.[13] However, experiment indicates that the reactions in Scheme I do take place as shown.[14] In order to determine whether other metallocene derivatives of pentalene could be prepared and to study their chemistry, the research described below was performed.

### Results

**Thallium Hydropentalenide.** When cyclopentadiene is stirred with thallous sulfate in aqueous potassium

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(1) National Science Foundation Cooperative Fellow, 1961–1962; National Institutes of Health Predoctoral Fellow, 1963–1965.

(2) Ring-substituted pentalenes that have been prepared are (a) dibenzopentalene [C. T. Blood and R. P. Linstead, *J. Chem. Soc.*, 2263 (1952)] and (b) hexaphenylpentalene [E. LeGoff, *J. Am. Chem. Soc.*, **84**, 3975 (1962)].

(3) (a) T. J. Katz and M. Rosenberger, *ibid.*, **84**, 865 (1962); (b) T. J. Katz, M. Rosenberger, and R. K. O'Hara, *ibid.*, **86**, 249 (1964).

(4) M. Rosenblum, "Chemistry of the Iron Group Metallocenes," Interscience Publishers, Inc., New York, N. Y., 1965.

(5) (a) G. Wilkinson and F. A. Cotton, *Progr. Inorg. Chem.*, **1**, 1 (1959); (b) J. M. Birmingham, *Advan. Organometal. Chem.*, **2**, 365 (1964).

(6) (a) R. Criegee and G. Schröder, *Angew. Chem.*, **71**, 70 (1959); (b) G. F. Emerson, L. Watts, and R. Pettit, *J. Am. Chem. Soc.*, **87**, 131 (1965); (c) W. Hübel and E. H. Braye, *J. Inorg. Nucl. Chem.*, **10**, 250 (1959); (d) H. H. Freedman, *J. Am. Chem. Soc.*, **83**, 2194 (1961); (e) P. M. Maitless and A. Efratz, *J. Organometal. Chem.* (Amsterdam), **4**, 172, 175 (1965).

(7) Another scheme for preparing metallocene derivatives of pentalene has been devised by Cais (M. Cais in "The Chemistry of the Alkenes," S. Patai, Ed., Interscience Publishers, Inc., New York, N. Y., 1964), who suggested a synthesis of the pentaleniummanganese tricarbonyl cation. The details of this synthesis have not yet been published; a related scheme for preparing the π-cyclopentadienyl-π-benzpentaleniumiron cation gave instead a dimer.[8] A synthesis of hydropentalenylmanganese tricarbonyl from acetylene and dimanganese decacarbonyl is remarkable.[9]

(8) M. Cais, A. Modiano, and A. Raveh, *J. Am. Chem. Soc.*, **87**, 5607 (1965).

(9) T. H. Coffield, K. G. Ihrman, and W. Burns, *ibid.*, **82**, 4209 (1960).

(10) J. H. Osiecki, C. J. Hoffman, and D. P. Hollis, *J. Organometal. Chem.* (Amsterdam), **3**, 107 (1965).

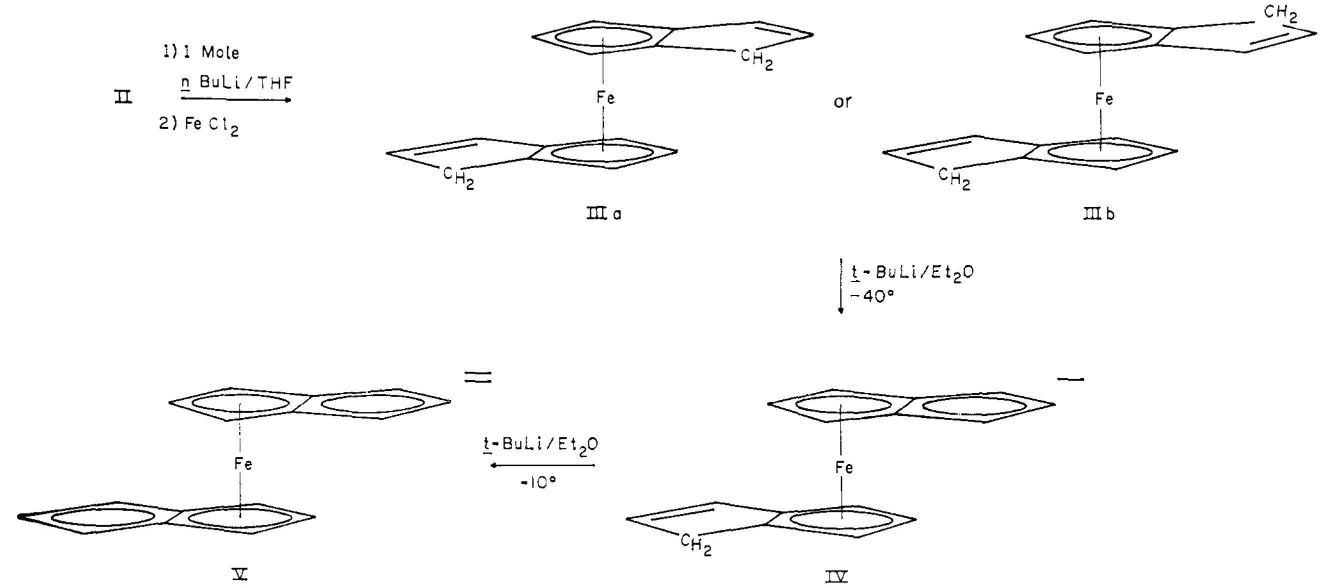
(11) L. Westman and K. L. Rinehart, *Acta Chem. Scand.*, **16**, 1199 (1962).

(12) (a) R. A. Benkeser and J. L. Bach, *J. Am. Chem. Soc.*, **86**, 890 (1964); (b) A. N. Nesmeyanov, E. G. Perevalova, Z. A. Beinoravichute, and I. L. Malygina, *Dokl. Akad. Nauk SSSR*, **120**, 1263 (1958); *cf.* A. N. Nesmeyanov, E. G. Perevalova, and Yu. A. Ustynuk, *ibid.*, **133**, 1105 (1960).

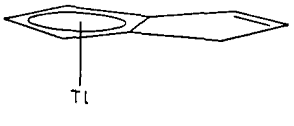
(13) Reference 4, p 124.

(14) T. J. Katz and M. Rosenberger, *J. Am. Chem. Soc.*, **85**, 2030 (1963).

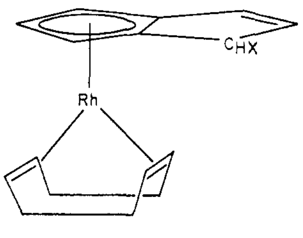
**Scheme I**



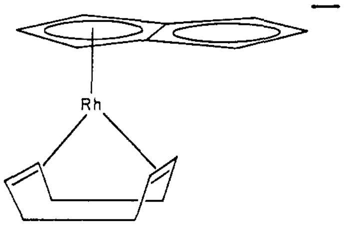
hydroxide, thallium cyclopentadienide, $C_5H_5Tl$, precipitates in nearly quantitative yield.[15] The facility of the preparation, the stability of the product upon brief exposure to air,[16] and the ease with which it reacts in THF with a variety of transition metal halides to give ferrocene[16] and related substances[17] suggested that an analogous substance might be preparable from dihydropentalene (II) as an intermediate in the synthesis of metallocene derivatives of pentalene. When dihydropentalene is shaken with thallous sulfate in aqueous sodium hydroxide, thallium hydropentalenide (VI), a bright yellow solid, mp 87–89° dec, precipitates in nearly quantitative yield. The substance can be sublimed at 80° ( 5 × $10^{-6}$ mm) although some of it decomposes in the process.[18] It is sufficiently stable in air to be handled with no special precautions, but it turns brown after prolonged exposure. The compound was identified by its analysis, by its mass spectrum, which exhibits parent peaks at $m/e$ 308 and 306 of relative intensity 2.39:1 as expected for $C_8H_7{}^{205}Tl$ and $C_8H_7{}^{203}Tl$,[19] by its infrared spectrum, similar to that of the metallocenes described below, and by its reaction in THF with ferrous chloride to give bis(hydropentalenyl)iron[14] (IIIa or IIIb) in 49% yield.[21]



VI



VII a: X = H
b: X = D
c: X = $(C_6H_5)_2COH$



VIII

**Pentalenylcycloocta-1,5-dienerhodium Anion.** Cycloocta-1,5-dienerhodium chloride, (1,5-COD-RhCl)$_2$, reacts with thallium hydropentalenide (VI)[2] to give hydropentalenylcycloocta-1,5-dienerhodium (VIIa), as it reacts with sodium cyclopentadienide to give cyclopentadienylcycloocta-1,5-dienerhodium.[22] The product formed in good yield is a yellow crystalline material easily sublimed and soluble in benzene or hexane. The compound was identified by its analysis, its mass spectrum, and its nmr spectrum, shown in Figure 1. In the nmr spectrum, the olefinic protons exhibit an AB quartet at $\tau$ 3.76 and 4.12. Each line of the pattern is split into a triplet because of the coupling of olefinic and allylic protons in the hydropentalene system,[23] and these latter protons in turn give rise to triplets ($J$ = 2 cps) at $\tau$ 7.45 and 7.63. The allylic protons of the hydropentalene ring are chemically shifted because of

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(15) (a) E. O. Fischer, *Angew. Chem.*, 69, 207 (1957); (b) H. Meister, *ibid.*, 69, 533 (1957).

(16) F. A. Cotton and L. T. Reynolds, *J. Am. Chem. Soc.*, **80**, 269 (1958).

(17) (a) A. N. Nesmeyanov, R. B. Materikova, and N. S. Kochetkova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1334 (1963); *Chem. Abstr.*, 59, 12841*d* (1963); (b) A. N. Nesmeyanov, K. N. Anisimov, and N. E. Kolobova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2220 (1964); *Chem. Abstr.*, 62, 7788*b* (1965).

(18) The infrared spectra of material that precipitated from the reaction mixture and the material that had been sublimed were identical, suggesting that the product formed initially is not grossly impure and that sublimation may not be a desirable purification procedure.

(19) The intensity ratio required, from the known[20] relative abundance of the thallium isotopes, is 2.39.

(20) "Handbook of Chemistry and Physics," 45th ed, The Chemical Rubber Co., Cleveland, Ohio, 1964, p B75.

(21) In ref 14 the compound was called dihydrodipentalenyliron; it was suggested, perhaps incorrectly, to be a mixture of the two isomers.

(22) (a) J. Chatt and L. M. Venanzi, *Nature*, 177, 852 (1956); (b) J. Chatt and L. M. Venanzi, *J. Chem. Soc.*, 4735 (1957).

(23) The lines appear to be further split by a small long-range coupling. The pattern is similar to that shown by related substances, indene,[24] and 3H-pyrrolizine.[25]

(24) D. D. Elleman and S. L. Manatt, *J. Chem. Phys.*, 36, 2346 (1962).

(25) W. Okamura, Dissertation, Columbia University, 1966.

their different environments, but although geminal, their coupling is not detectable.[26] The multiplets at $\tau$ 4.58 and 4.82 and the triplet ($J$ = 2.4 cps) at 5.60 can be ascribed to the metallocene protons.[27] Some of the fine structure of these peaks presumably results from splitting by the $^{103}$Rh nucleus.[28] The broad peaks at $\tau$ 6.62 and 7.9 are ascribed to the olefinic and nonolefinic protons of the cyclooctadiene ring.[28c,d]

This compound (VIIa) in THF solution is lithiated by $n$-butyllithium in $n$-hexane. The solution's turning red implies a change in the system of conjugated electrons and suggests that the product is the lithium salt of the pentalenylcycloocta-1,5-dienerhodium anion (VIII). That lithiation occurred was shown by quenching the solution with deuterium oxide, which gave after purification a 58% yield of recovered hydropentalenylcycloocta-1,5-dienerhodium (VIIb) shown by mass spectral analysis to be 89% monodeuterated. That the lithiation occurred almost exclusively in the allylic position is indicated by the appearance in the nmr spectrum (Figure 1) of the olefin proton resonances as an AB quartet ($J$ = 5.5 cps) with each peak split into doublets ($J$ = 2 cps) (not triplets as in the undeuterated derivative VIIa) because of coupling with only one allylic proton.[29] Thus one of the allylic protons in each molecule has been replaced by deuterium. This is also indicated in the infrared spectrum of the monodeuterated derivative by the disappearance of a peak present in the undeuterated sample at 1415 cm$^{-1}$, and due presumably to a $CH_2$ bending vibration.[30]

Reaction of lithium cycloocta-1,5-dienerhodiumpentalenide (VIII) in ether with benzophenone gives in 38% yield, after recrystallization from hexane, the alcohol VIIc, identified by its analysis and its infrared spectrum, which exhibits absorptions at 3561 (OH) and 1558 cm$^{-1}$ (C=C stretch), but none between 1400 and 1415 cm$^{-1}$ (hydropentalene $CH_2$).[31]

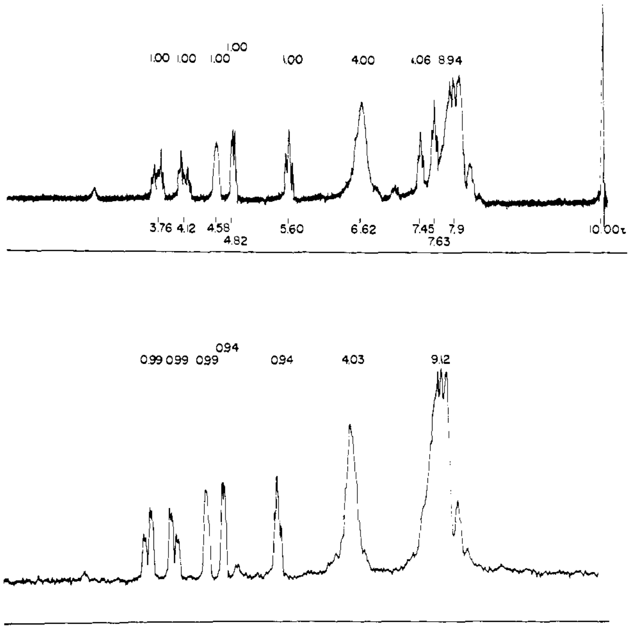
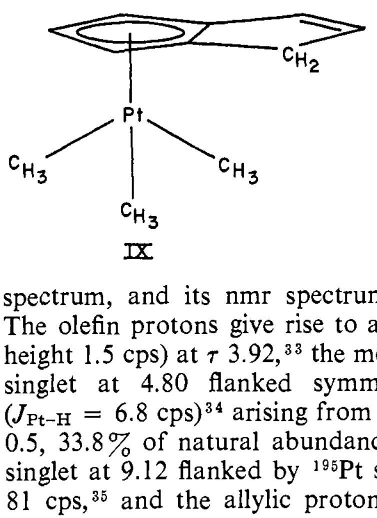
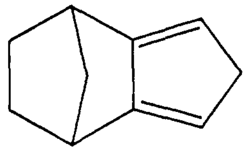


Figure 1. Nmr spectrum (60 Mc/sec) of (top) hydropentalenylcycloocta-1,5-dienerhodium (VIIa) and (bottom) its deuterated derivative, VIIb. The solvent is $C_6D_6$, and TMS ($\tau$10) is the internal standard. Intensities are recorded above the peaks.

**Hydropentalenyltrimethylplatinum.** Thallium hydropentalenide (VI) in THF reacts with trimethylplatinum iodide to give in 43% yield hydropentalenyltrimethylplatinum (IX), a pale yellow, viscous liquid stable to heat—it can be purified by vapor phase chromatography—and exposure to air. The preparation is modeled after that of cyclopentadienyltrimethylplatinum from sodium cyclopentadienide and trimethylplatinum iodide, which proceeds in 32% yield.[32] The compound IX was identified by its analysis, its mass spectrum, and its nmr spectrum, shown in Figure 2. The olefin protons give rise to a singlet (width at half-height 1.5 cps) at $\tau$ 3.92,[33] the metallocene protons to a singlet at 4.80 flanked symmetrically by satellites ($J_{Pt-H}$ = 6.8 cps)[34] arising from splitting by $^{195}$Pt (spin 0.5, 33.8% of natural abundance),[20] the methyls to a singlet at 9.12 flanked by $^{195}$Pt satellites with $J_{Pt-H}$ = 81 cps,[35] and the allylic protons to two singlets at $\tau$ 7.68 (half-width 1.5 cps) and 7.80 (half-width 2 cps).[36]



IX



X

**Metallocene Derivatives of Isodicyclopentadiene.** The ease with which thallium hydropentalenide was prepared and used to make other complexes was somewhat surprising, for thallium methylcyclopentadienide, the only other thallium cyclopentadienide derivative known, is reported to be pyrophoric in air.[16,37] Since the precursor of dihydropentalene (II), isodicyclopentadiene (X), was also a cyclopentadiene and readily

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(26) A few compounds are known that show only small geminal coupling constants: A. A. Bothner-By, "Advances in Magnetic Resonance," Vol. 1, J. S. Waugh, Ed., Academic Press Inc., New York, N. Y., 1965, pp 217, 223.

(27) The chemical shifts of the cyclopentadienyl proton resonances in $\pi$-cyclopentadienyl-diolefinrhodium complexes are between $\tau$ 4.85 and 5.19.[28]

(28) (a) G. N. Schrauzer and K. C. Dewhirst, *J. Am. Chem. Soc.*, 86, 3265 (1964); (b) K. S. Brenner, E. O. Fisher, H. P. Fritz, and C. G. Kreiter, *Chem. Ber.*, 96, 2632 (1963); (c) A. Davison, W. McFarlane, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 4821 (1962); (d) M. L. H. Green, L. Pratt, and G. Wilkinson, *ibid.*, 3753 (1959); (e) R. B. King, *Inorg. Chem.*, 2, 528 (1963).

(29) The intensity of the absorption due to the allylic protons is diminished as expected. It is possible that these resonances could not be resolved in the deuterated sample because deuteration is not stereospecific and would diminish the intensity of both peaks.

(30) K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, Inc., San Francisco, Calif., 1962.

(31) Its nmr spectrum is also in accord with the structure VIIc. In $CDCl_3$ the following peaks were observed: a ten-proton multiplet at $\tau$ 2.6 (phenyl protons); an AB quartet at 3.55 and 4.25 ($J_{AB}$ = 5.8 cps), with each line split further into a doublet, $J$ = 2 cps (olefin protons split by the allylic proton); single-proton multiplets at 4.77, 5.34, 5.54, and 6.06 (metallocene protons and one hydropentalene allylic proton); a four-proton multiplet at 6.6, and a nine-proton multiplet at 7.9 (cyclooctadiene and hydroxyl protons).

(32) (a) S. D. Robinson and B. L. Shaw, *Z. Naturforsch.*, **18b**, 507 (1963); (b) S. D. Robinson and B. L. Shaw, *J. Chem. Soc.*, 1529 (1965).

(33) This is exactly where these protons appear in the spectrum of III.[14]

(34) In cyclopentadienyltrimethylplatinum a similar pattern is formed at $\tau$ 4.39 with $J_{Pt-H}$ = 5.8 cps.[32b]

(35) The methyls in cyclopentadienyltrimethylplatinum give rise to a resonance at $\tau$ 9.12 with $J_{Pt-H}$ = 82.5 cps.

(36) As in VIIa the geminal coupling constant appears to be zero.[26]

(37) L. T. Reynolds and G. Wilkinson, *J. Inorg. Nucl. Chem.*, 9, 86 (1959).

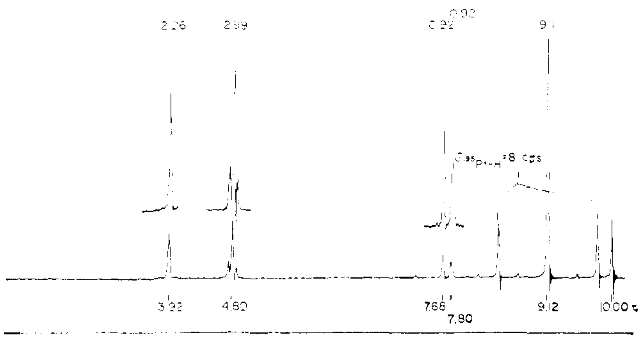


Figure 2. Nmr spectrum (60 Mc/sec) of hydropentalenyltrimethylplatinum (IX) in $C_6D_6$. Some lines are also shown amplified. Intensities are recorded above the peaks. TMS is the internal standard (τ10).

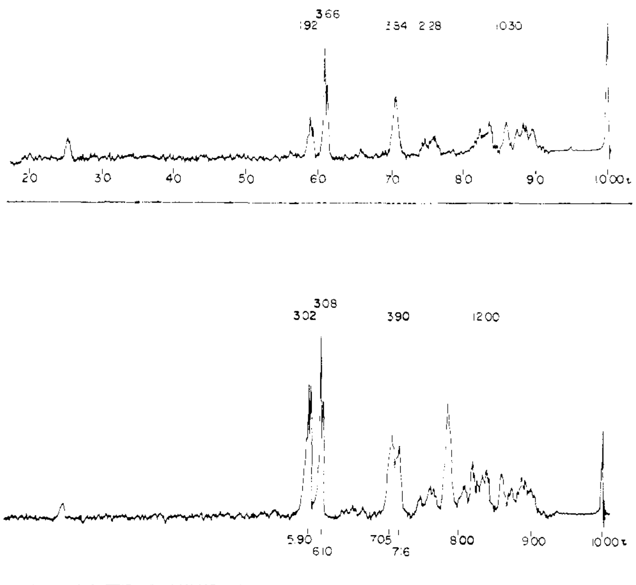
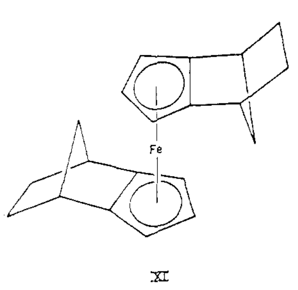


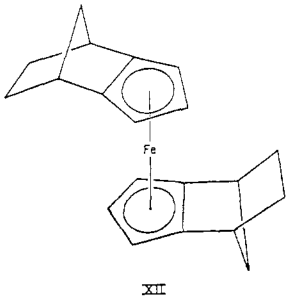
Figure 3. Nmr spectrum (60 Mc/sec) of (top) *exo,exo-* or *endo,endo-*bis(isodicyclopentadienyl)iron (XI or XII) and (bottom) the *exo,endo* isomer XIII. The solvent is $C_6D_6$, and TMS is the internal standard (τ10). Intensities are recorded above the peaks.

available, an attempt was made to prepare and examine the properties of its thallous derivative. The substance forms when isodicyclopentadiene is combined with thallous sulfate in aqueous alkali. Thallium isodicyclopentadienide is a yellow solid that can be sublimed at 80° (5 × $10^{-6}$ mm); it rapidly turns brown in air, but does not spontaneously ignite. Because of its sensitivity, the material was not subjected to the usual analyses; it was identified by its reaction in THF with ferrous chloride, which gave a 20% yield of a yellow-brown ferrocene derivative, $C_{20}H_{22}Fe$, melting at 168.5–169.5°.

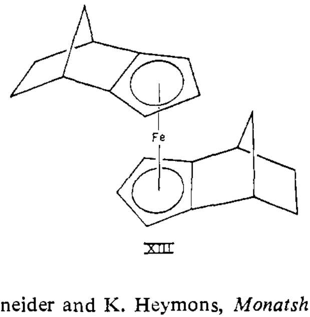
The properties of this ferrocene are similar to those reported for the product of the reaction of isodicyclopentadiene with ethylmagnesium bromide and then with iron acetylacetonate.[38] The substance had also been made previously in our laboratory[39] by treating isodicyclopentadiene in THF with *n*-butyllithium and then with ferrous chloride. Repetition of this preparation to furnish a sample of the ferrocene for comparison with that formed using the thallium derivative gave two isomers, the predominant one (28% yield) identical with that described above, and the minor one (8% yield) a red crystalline solid melting at 68–69°. The nmr spectrum (Figure 3) of the predominant isomer indicates that it is either the *exo,exo* (XI) or the *endo,endo* (XII) derivative. Thus the observation of only one peak at τ 7.07 (4 hydrogens), undoubtedly due to the bridgehead protons,[40] and only one simple $A_2B$ pattern at 6.10 and 5.88 ($J$ = 2 cps) similar to that of other 1,2-disubstituted metallocenes,[41] implies that the two ligands are bonded to the metal in the same way. The nmr spectrum of the minor isomer (Figure 3) suggests that it is the *exo,endo* derivative XIII. The spectrum shows two peaks attributable to dissimilar bridgehead protons, at τ 7.05 and 7.16, and two three-proton multiplets at τ 5.90 and 6.10, which may be two $A_2B$ patterns superimposed.



XI



XII



XIII

## Discussion

The lithiation of hydropentalenylcycloocta-1,5-dienerhodium (VIIa) in the side chain contrasts with the lithiation of simple methylferrocenes in the metallocene ring,[11-13] and shows that metallocene derivatives of pentalene can be prepared. The formation of the alcohol VIIc by the reaction of the pentalenylcycloocta-1,5-dienerhodium anion (VIII) with benzophenone indicates that such compounds may have use in organic synthesis.

The ease with which thallium hydropentalenide can be handled in air was unanticipated because thallium methylcyclopentadienide, unlike thallium cyclopentadienide, is pyrophoric in air.[16,37] The instability of thallium methylcyclopentadienide compared to thallium cyclopentadienide has been suggested[42] to be a consequence of a difference in their crystal lattice energies resulting from their different molecular symmetries, but the stability of thallium hydropentalenide cannot thus be accounted for in an obvious way. The assumption that these substances are ionic[16] has been

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(38) R. Riemschneider and K. Heymons, *Monatsh.*, 92, 1080 (1961).

(39) The reaction was investigated by Dr. Michael Rosenberger.

(40) The bridgehead protons in norbornene appear at τ 7.15 [P. Laszlo and P. von R. Schleyer, *J. Am. Chem. Soc.*, 86, 1171 (1964)].

(41) (a) R. B. King and M. B. Bisnette, *Inorg. Chem.*, 3, 796 (1964); (b) J. H. Osiecki, C. J. Hoffman, and D. P. Hollis, *J. Organometal. Chem.* (Amsterdam), 3, 107 (1965); (c) K. L. Rinehart, Jr., D. E. Bublitz, and D. H. Gustafson, *J. Am. Chem. Soc.*, 85, 970 (1963).

(42) Reference 5a, p 10.

Table I. Mass Spect ra (75 ev) of Hydropentalene Derivatives[a]

| *m/e* | R.A.[b] | *m/e* | R.A. | *m/e* | R.A. |
|---|---|---|---|---|---|
| | | Bis(hydropentalenyl)iron | | | |
| 50 | 5 | 103 | 60 | 158 | 68 |
| 51 | 11 | 104 | 10 | 159 | 12 |
| 56 | 52 | 105 | 9 | 202 | 6 |
| 57 | 6 | 107 | 7 | 203 | 5 |
| 63 | 5 | 121 | 7 | 260 | 20 |
| 76 | 8 | 131 | 17 | 261 | 13 |
| 77 | 29 | 132 | 7 | 262 | 300 |
| 78 | 6 | 133 | 9 | 263 | 38 |
| 81 | 23 | 134 | 12 | 264 | 5 |
| 102 | 100 | 156 | 6 | | |
| | | Thallium hydropentalenide | | | |
| 50 | 8 | 76 | 9 | 203 | 42 |
| 51 | 59 | 77 | 32 | 205 | 100 |
| 51.5 | 2 | 78 | 13 | 262 | 2 |
| 52 | 4 | 101 | 2 | 306 | 23 |
| 62 | 2 | 102 | 40 | 307 | 2 |
| 63 | 5 | 103 | 53 | 308 | 55 |
| 74 | 6 | 104 | 28 | 309 | 5 |
| 75 | 2 | 105 | 5 | | |
| | | Hydropentalenylcycloocta-1,5-dienerhodium | | | |
| 50 | 4 | 141 | 3 | 209 | 3 |
| 51 | 9 | 142 | 5 | 218 | 5 |
| 52 | 3 | 152 | 3 | 260 | 7 |
| 53 | 5 | 153 | 5 | 271 | 10 |
| 54 | 3 | 154 | 11 | 273 | 6 |
| 63 | 3 | 155 | 5 | 284 | 20 |
| 65 | 3 | 156 | 3 | 285 | 26 |
| 76 | 3 | 157 | 5 | 286 | 12 |
| 77 | 13 | 168 | 9 | 287 | 3 |
| 78 | 4 | 178 | 5 | 297 | 8 |
| 79 | 5 | 179 | 8 | 299 | 11 |
| 92 | 3 | 180 | 15 | 309 | 4 |
| 102 | 5 | 181 | 9 | 310 | 4 |
| 103 | 37 | 182 | 11 | 311 | 21 |
| 104 | 3 | 204 | 23 | 312 | 9 |
| 105 | 4 | 205 | 62 | 313 | 20 |
| 115 | 5 | 206 | 100 | 314 | 100 |
| 129 | 5 | 207 | 15 | 315 | 18 |
| 130 | 4 | 208 | 16 | | |
| | | Dihydropentalene | | | |
| 50 | 13 | 65 | 2 | 79 | 4 |
| 51 | 23 | 66 | 2 | 89 | 2 |
| 51.5 | 1 | 73 | 1 | 98 | 1 |
| 52 | 9 | 74 | 7 | 101 | 1 |
| 53 | 2 | 75 | 5 | 102 | 13 |
| 61 | 2 | 76 | 6 | 103 | 65 |
| 62 | 4 | 77 | 23 | 104 | 100 |
| 63 | 8 | 78 | 34 | 105 | 9 |
| 64 | 1 | | | | |
| | | Hydropentalenyltrimethylplatinum | | | |
| 50 | 36 | 116 | 8 | 283 | 5 |
| 51 | 74 | 117 | 11 | 284 | 5 |
| 51.5 | <1 | 118 | 7 | 285 | 4 |
| 52 | 24 | 133 | 12 | 295 | 17 |
| 53 | 7 | 134 | 13 | 296 | 44 |
| 57 | 6 | 135 | 4 | 297 | 62 |
| 62 | 9 | 208 | 5 | 298 | 46 |
| 63 | 28 | 209 | 6 | 299 | 22 |
| 64 | 3 | 210 | 4 | 300 | 8 |
| 65 | 10 | 211 | 7 | 301 | 5 |
| 74 | 14 | 212 | 14 | 307 | 5 |
| 75 | 15 | 221 | 8 | 308 | 6 |
| 76 | 30 | 222 | 7 | 309 | 29 |
| 77 | 96 | 223 | 7 | 310 | 29 |
| 78 | 50 | 224 | 4 | 311 | 37 |
| 79 | 5 | 225 | 4 | 312 | 44 |
| 89 | 7 | 233 | 3 | 313 | 46 |
| 91 | 17 | 239 | 6 | 314 | 24 |
| 101 | 4 | 240 | 7 | 315 | 5 |
| 102 | 76 | 241 | 5 | 316 | 6 |
| 103 | 100 | 244 | 4 | 325 | 6 |
| 104 | 51 | 245 | 5 | 326 | 5 |
| 105 | 6 | 246 | 4 | 327 | 6 |
| 107 | 11 | 269 | 6 | 328 | 3 |
| 108 | 20 | 270 | 13 | 329 | 3 |
| 109 | 3 | 271 | 15 | 342 | 10 |
| 115 | 28 | 272 | 10 | 343 | 12 |
| | | | | 344 | 9 |

[a] Metastable peaks and peaks with half-integral *m/e* values other than 51.5 are not listed. [b] R.A. = relative abundance.

questioned.[43] The effect of a methyl group in facilitating the oxidation of thallium cyclopentadienide is likely to be related to the similar effect (presumably inductive) it has on the oxidation potentials of ferrocenes,[44] and the stability of thallium hydropentalenide (VI) to air oxidation is then possibly a consequence of the cancellation of the opposing effects of a vinyl and an alkyl group.[44]

**Mass Spectra.** The intense peaks in the mass spectra of dihydropentalene (II) and its organometallic derivatives III, VI, VIIa, and IX are recorded in Table I.

In the ferrocene III the molecular ion, $C_{16}H_{14}{}^{56}Fe$, gives rise to the base peak. ($^{56}Fe$ constitutes 92% of natural iron.) Interestingly, the next most intense peak, although only one-third the size of the base, is at *m/e* 102, where the pentalene cation radical $C_8H_6{}^+$ should be found, and the next at 158, where $C_8H_6{}^{56}Fe$ should be. The latter is analogous to the $C_5H_5Fe$ fragment observed in the spectra of ferrocene[45] and the $C_4H_4Fe$ fragment in cyclobutadieneiron tricarbonyl.[46]

It is noteworthy in the fragmentation occurring in the mass spectrometer that it is the pentalene cation, $C_8H_6{}^+$, not a protonated pentalene, $C_8H_7{}^+$, that is observed. The loss of a hydrogen atom appears particularly facile in the fragmentation of the iron compound, for while all the others do give a large peak at 102, it is less intense that the one at 103.

The rhodium complex VIIa shows its parent ion as the base peak ($^{103}Rh$ = 100% natural abundance), but equally intense is a peak attributable to $C_8H_7Rh$ at 206, while that attributable to $C_8H_6Rh$ at 205 is only slightly weaker.

The base peak shown by the platinum complex IX is the one attributable to protonated pentalene, at 103. The molecule thus appears to fragment easily. The thallium complex also fragments easily; it shows $^{205}Tl^+$ as its base peak. In this regard it resembles the presumably ionic biscyclopentadienyls of Mn and Mg, which exhibit much less intense parent ion peaks than the covalent biscyclopentadienyls of V, Cr, Fe, Ni, Co, and Ru.[47]

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(43) S. Shibata, L. S. Bartell, and R. M. Gavin, Jr., *J. Chem. Phys.*, **41**, 717 (1964), and references therein.

(44) (a) Reference 4, p 50 ff; (b) A. N. Nesmeyanov and E. G. Perevalova, *Ann. N. Y. Acad. Sci.*, **125**, 67 (1965).

(45) F. W. McLafferty, *Anal. Chem.*, **28**, 306 (1956); A. Mandelbaum and M. Cais, *Tetrahedron Letters*, 3847 (1964).

(46) G. F. Emerson, L. Watts, and R. Pettit, *J. Am. Chem. Soc.*, **87**, 131 (1965).

(47) L. Friedman, A. P. Irsa, and G. Wilkinson, *ibid.*, **77**, 3689 (1955). See also R. E. Winters and R. W. Kiser, *J. Organometal. Chem.* (Amsterdam), **4**, 190 (1965).

Dihydropentalene (II), the thallium complex VI, and the platinum complex IX all exhibit large peaks at m/e 51. It is likely that at least in part these are due to $C_8H_6^{2+}$ (presumably pentalene dication), for a small peak is also observed at m/e 51.5.[48,49] In the case of the ferrocene III, the peak at 51 is weak and none was observed at 51.5, but in the deuterated derivative formed from the anions IV and V and deuterium oxide, the peak at 51.5 is clearly shown.[48] The observation of a peak attributable to pentalene dication has some analogy in the observation of an intense peak attributable to tetraphenylcyclobutadiene dication in the mass spectrum of tetraphenylcyclobutadienepalladium dichloride.[50]

**Infrared Spectra.** The infrared spectra of the hydropentalenyl metal complexes II, VI, VII, and IX are recorded in the Experimental Section. All show an absorption between 1540 and 1558 cm$^{-1}$, probably due to a C=C stretching vibration, and absorption between 710 and 726 cm$^{-1}$, presumably an olefinic C–H out-of-plane vibration. All having an allylic $CH_2$ group show a peak between 1409 and 1415 cm$^{-1}$, attributable to a symmetric $CH_2$ deformation,[51] absent in the deuterated derivatives formed when the anions V and VIII are quenched with deuterium oxide.

## Experimental Section

**Thallium Hydropentalenide (VI).** A solution of sodium hydroxide (1.00 g, 25 mmoles) and thallous sulfate (2.02 g, 4 mmoles) in water (10 ml, degassed by boiling while purging with nitrogen) was prepared in a 50-ml centrifuge tube. The tube was sealed with a serum bottle cap and repeatedly evacuated and filled with argon through a syringe needle. Dihydropentalene[3] (0.20 g, 1.9 mmoles) was then added by syringe, and the mixture was shaken at room temperature. After 4 hr the yellow precipitate was centrifuged and the supernatant liquid removed with a syringe. The solid was washed three times with degassed water using the syringe technique and dried overnight under vacuum in a desiccator over Drierite. The yield was 0.59 g (quantitative). At 5 × $10^{-6}$ mm the product sublimed with decomposition at 80°, giving 0.34 g (58%) of bright yellow solid, mp 87–89° dec (evacuated capillary), molecular weight (mass spectrum): 308 ($C_8H_7{}^{205}Tl$).

*Anal.* Calcd for $C_8H_7Tl$: C, 31.22; H, 2.28; Tl, 66.50. Found: C, 31.42; H, 2.28; Tl, 67.10.

Thallium hydropentalenide is insoluble in water, hexane, benzene, tetrahydrofuran, and diethyl ether. It is sufficiently stable to be handled in air, but turns brown after prolonged exposure.

The infrared spectrum (Nujol mull) showed: 3055 (w), 3035 (w), 2980–2860 (Nujol), 1540 (m), 1460 (Nujol), 1410 (m), 1370 (Nujol), 1345 (m), 1305 (m), 1263 (w), 1228 (m), 1110 (m), 1015 (s), 970 (m), 920 (s), 901 (s), 825 (s), 726 (vs), 698 (s), 661 (m), and 639 (vs) cm$^{-1}$.

**Bis(hydropentalenyl)iron from Thallium Hydropentalenide (III).** Sublimed thallium hydropentalenide (0.243 g, 0.79 mmole) and anhydrous ferrous chloride (0.150 g, 1.2 mmoles) were placed in a dry glass tube attached to a ground-glass joint. The tube was connected to a vacuum manifold, and 5 ml of dry tetrahydrofuran was distilled in. The tube was sealed and shaken for 44 hr at room temperature. The solution turned red-orange and a gray solid precipitated. The tube was opened, and the solid was filtered and washed with ether. THF and ether were removed from the filtrate under vacuum giving an orange-brown crystalline residue from which the complex was sublimed [50° (5 × $10^{-6}$ mm)] as an orange solid (0.51 g, 49% yield).

The nmr spectrum, infrared spectrum, and melting point (95–99°) of this complex were identical with those of bis(hydropentalenyl)iron obtained from lithium hydropentalenide and ferrous chloride.[14] The base peak in the mass spectrum is observed at m/e 262, as expected for $C_{16}H_{14}{}^{56}Fe$.

The infrared spectrum (Nujol mull) showed: 3110 (vw), 3095 (w), 3055 (w), 2990–2810 (Nujol), 1556 (m), 1460 (Nujol), 1424 (m), 1410 (s), 1375 (Nujol), 1354 (sh), 1312 (s), 1264 (s), 1233 (s), 1168 (w), 1130 (w), 1118 (m), 1013 (s), 995 (w), 920 (s), 902 (m), 876 (w), 849 (m), 825 (w), 792 (s), 725 (m), 710 (vs), 695 (s), 660 (s), and 640 (vs) cm$^{-1}$.

**Thallium Isodicyclopentadienide.** The procedure was the same as that used for the preparation of thallium hydropentalenide. Substitution of isodicyclopentadiene[3b,52] for dihydropentalene gave the complex as a yellow-brown solid. It was transferred[53] under argon to a sublimation apparatus and sublimed [80° (5 × $10^{-6}$ mm)] as a pale yellow solid.

Thallium isodicyclopentadienide rapidly turns brown when exposed to air, but it not pyrophoric. Because of its sensitivity to air no attempt was made to characterize the compound using the usual analytical and spectral methods.

**Bis(isodicyclopentadienyl)iron from Thallium Isodicyclopentadienide.** Thallium isodicyclopentadienide was prepared, as described above, from potassium hydroxide (1.00 g, 18 mmoles), thallous sulfate (2.50 g, 5 mmoles), and isodicyclopentadiene (0.45 g, 3.4 mmoles) in 20 ml of degassed water. The dry complex in the centrifuge tube was not sublimed. Instead, anhydrous ferrous chloride (0.39 g, 3.1 mmoles) was quickly added, the tube was sealed with a serum bottle cap, and an argon atmosphere was introduced through a syringe needle. Degassed tetrahydrofuran (15 ml) was injected with a syringe, and the mixture was shaken at room temperature for 7 hr. The reaction was filtered and THF removed from the filtrate under vacuum. The residue was dissolved in pentane and filtered, and the pentane solution was evaporated to dryness under vacuum. Sublimation [100° (5 × $10^{-3}$ mm)] of the residue afforded 0.11 g (20% yield based on isodicyclopentadiene) of the compound as a yellow-brown crystalline solid. Recrystallization from hexane and two recrystallizations from acetone gave yellow-brown rhombic crystals, mp 168.5–169.5° (lit.[38] 172.5–173°). The nmr spectrum, infrared spectrum, and melting point of this compound were identical with those of one of the isomers of bis(isodicyclopentadienyl)iron formed from lithium isodicyclopentadienide and ferrous chloride (see below), molecular weight (mass spectrum): 318 ($C_{20}H_{22}{}^{56}Fe$).

*Anal.* Calcd for $C_{20}H_{22}Fe$: C, 75.49; H, 6.97. Found: C, 75.38; H, 6.95.

For the nmr spectrum, see Figure 3.

**Bis(isodicyclopentadienyl)iron from Lithium Isodicyclopentadienide.**[54] To a solution of isodicyclopentadiene (3.00 g, 23 mmoles) in THF (30 ml) under argon at −78° was added 17 ml of 1.5 *N* *n*-butyllithium in hexane (25.5 moles). The reaction was allowed to warm to room temperature and was then stirred for 30 min. The resulting orange-yellow solution was added by syringe to a suspension of anhydrous ferrous chloride (3.00 g, 23.6 mmoles) in THF (20 ml,) under argon, and the mixture was stirred at room temperature for 2.5 hr. Dilute HCl (100 ml) and then 50 ml of ether were added. The organic layer was separated, the aqueous solution was extracted with an additional 50 ml of ether, the combined ether extracts were washed with water (two 100-ml portions) and dried ($MgSO_4$), and the ether was removed under vacuum. The orange crystalline residue was washed from the flask with acetone (40 ml) and filtered giving a yellow-brown solid and an orange-red acetone solution. The solution was stored in a flask covered with aluminum foil, which allowed the acetone to evaporate slowly.

Crystallization of the yellow-brown solid from acetone yielded 1.02 g (28% yield) of the complex, *exo,exo* (XI) or *endo,endo*-bis(isodicyclopentadienyl)iron (XII), as yellow-brown crystals, mp 167–169°. Another recrystallization raised the melting point to 168.5–169.5°.

For the nmr spectrum, see Figure 3.

After 2 weeks, the orange-red acetone solution had evaporated to a volume of about 5 ml. Well-shaped red crystals formed along

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[48] K. Biemann, "Mass Spectrometry: Organic Chemical Applications," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 157.

[49] The peak is due to the natural occurrence of 1.11% $^{13}C$ in carbon compounds.

[50] J. H. Beynon, R. F. Curtis, and A. E. Williams, *Chem. Commun.*, 237 (1966); J. H. Beynon, R. C. Cookson, R. R. Hill, D. W. Jones, R. A. Saunders, and A. E. Williams, *J. Chem. Soc.*, 7052 (1965).

[51] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Methuen and Co., London, 1958, p 22.

[52] K. Alder, F. H. Flock, and P. Janssen, *Chem. Ber.*, **89**, 2689 (1956).

[53] This transfer was effected in a polyethylene bag manufactured by $I^2R$ Co., Cheltenham, Pa.

[54] We are grateful to James C. Carnahan, Jr., for experimental assistance with this reaction.

with some yellow-brown crystalline solid. After filtering and drying, the red crystals were selected by hand. The yield was 0.29 g (8%). The product, *exo,endo*-bis(isodicyclopentadienyl)iron (XIII), after further purification by crystallization from acetone at −78° melted at 68–69°. The analytical sample was prepared by sublimation [65° (5 × $10^{-3}$ mm)], molecular weight (mass spectrum): 318 ($C_{20}H_{22}{}^{56}Fe$).

*Anal.* Calcd for $C_{20}H_{22}Fe$: C, 75.49; H, 6.97. Found: C, 75.62; H, 6.98.

For the nmr spectrum, see Figure 3.

**Hydropentalenyltrimethylplatinum (IX).** Thallium hydropentalenide was prepared from dihydropentalene (0.47 g, 4.5 mmoles), sodium hydroxide (2.00 g), and thallous sulfate (4.04 g) in 20 ml of degassed water as described above. This gave 1.25 g (4.07 mmoles) of the dry complex, which was not sublimed. It was transferred to a flamed-out flask equipped with a magnetic stirring bar, an opening sealed with a serum bottle cap, and an argon inlet. Trimethylplatinum iodide[55] (1.50 g, 4.1 mmoles) was added, and an argon atmosphere was introduced. Degassed tetrahydrofuran (25 ml) was added with a syringe, and the reaction was stirred at room temperature for 1 day. The yellow solid (thallous iodide) that precipitated was filtered, and the solvent was removed from the filtrate at room temperature under the vacuum of an aspirator. The liquid residue was taken up in 20 ml of hexane and filtered, and the filtrate concentrated to about 2 ml under vacuum. Preparative vapor phase chromatography (5 ft × $^5/_8$ in. column GE SF-96 on 45–60 mesh Chromosorb P at 150° with 0.2-ml injections) gave 0.60 g (43% yield based on thallium hydropentalenide, 39% based on dihydropentalene) of the complex as a pale yellow, viscous liquid; molecular weight (mass spectrum): 343 ($C_{11}H_{16}{}^{195}Pt$).

*Anal.* Calcd for $C_{11}H_{16}Pt$: C, 38.47; H, 4.69; Pt, 56.84. Found: C, 38.71; H, 4.76; Pt, 57.14.

Hydropentalenyltrimethylplatinum crystallizes from methanol at −78° as pale yellow needles that melt on warming to room temperature. It is soluble in organic solvents (extremely soluble in benzene) and exhibits remarkable thermal stability—it can be recovered unchanged from a 20-ft SE-30 vpc column heated at 200°.

For the nmr spectrum, see Figure 2.

The infrared spectrum (neat) showed: 3110 (m), 3055 (m), 2955 (vs), 2890 (vs), 2810 (s), 1556 (m), 1430 (s), 1409 (s), 1370 (w), 1350 (w), 1307 (s), 1251 (vs), 1232 (s), 1210 (vs), 1170 (w), 1109 (m), 1050 (w), 1010 (s), 920 (s), 902 (s), 855 (s), 828 (s), 774 (vs), 710 (s), 688 (m), and 632 (s) $cm^{-1}$.

**Hydropentalenylcycloocta-1,5-dienerhodium (VIIa).** The apparatus consisted of a flamed-out flask equipped with a magnetic stirring bar, an opening sealed with a serum bottle cap, and an argon inlet. Sublimed thallium hydropentalenide (0.22 g, 0.72 mmole) and bis(cycloocta-1,5-diene)-di-μ-chloro-dirhodium[22b] (0.19 g, 0.39 mmole) were placed in the flask, and an atmosphere of argon was introduced. Degassed tetrahydrofuran (8 ml) was added by syringe, and the reaction was stirred at room temperature for 20 hr. Filtration, evaporation of the filtrate under vacuum, and sublimation of the residue [85° (5 × $10^{-3}$ mm)] gave 0.17 g (76% yield) of the complex as a yellow solid, mp 85–86°. The analytical sample was prepared by resublimation (quantitative), molecular weight (mass spectrum): 314 ($C_{16}H_{19}{}^{103}Rh$).

*Anal.* Calcd for $C_{16}H_{19}Rh$: C, 61.16; H, 6.10; Rh, 32.75. Found: C, 61.31; H, 6.28; Rh, 32.14.

For the nmr spectrum, see Figure 1.

The infrared spectrum (Nujol mull) showed: 3095 (vw), 3079 (w), 2990–2810 (Nujol), 1557 (m), 1460 (Nujol), 1430 (m), 1415 (s), 1373 (Nujol), 1325 (s), 1310 (s), 1300 (m), 1235 (m), 1206 (m), 1155 (m), 1115 (m), 1002 (w), 960 (m), 930 (m), 921 (s), 910 (m), 870 (s), 860 (s), 830 (w), 812 (s), 789 (s), 719 (vs), 670 (w), 661 (w), and 640 (vs) $cm^{-1}$.

The complex was also prepared under similar conditions using thallium hydropentalenide that had not been sublimed. Thallium hydropentalenide was prepared from 0.75 g (7.2 mmoles) of dihydropentalene, 3.00 g of sodium hydroxide, and 6.00 g of thallous sulfate in 30 ml of water. The dry product was stirred with 1.38 g of bis(cycloocta-1,5-diene)-di-μ-chloro-dirhodium in 30 ml of degassed tetrahydrofuran for 1 day. Work-up as above furnished 1.48 g of the complex (66% over-all yield based on dihydropentalene).

**The Pentalenylcycloocta-1,5-dienerhodium Anion (VIII) and Its Reaction with $D_2O$.** Hydropentalenylcycloocta-1,5-dienerhodium (VIIa, 0.150 g, 0.48 mmole) was placed in a flamed-out flask equipped with a magnetic stirring bar, an argon inlet, and an opening sealed with a serum bottle cap. An argon atmosphere was introduced, and THF (5 ml, degassed by purging with nitrogen) was added with a syringe. The yellow solution was cooled to −78°, and 0.5 ml of 1.5 *N* *n*-butyllithium in hexane (0.75 mmole) was injected. The reaction was stirred and allowed to warm to room temperature over a period of 2 hr and was then stirred for an additional 0.5 hr. The resulting red solution was cooled to −78°, and 0.1 ml of deuterium oxide was added followed by 30 ml of ether and 30 ml of water. The orange ether layer was separated, washed three times with 30-ml portions of water, dried ($MgSO_4$), and evaporated to dryness under vacuum. Three sublimations of the residue [80° (5 × $10^{-3}$ mm)] gave 0.087 g (58% yield) of the deuterated complex VIIb as yellow crystals, mp 80–83°.

The mass spectrum showed the complex to be 7.7% nondeuterated, 88.7% monodeuterated, 2.9% dideuterated, and 0.1% trideuterated.[56]

For the nmr spectrum, see Figure 1.

The infrared spectrum showed significant absorptions at 2167 (vw) ($\nu_{C-D}$), 1556 (m) ($\nu_{C=C}$), and 718 (vs) $cm^{-1}$ (out-of-plane *cis* olefinic C–H deformation). There was no absorption in the 1400–1415-$cm^{-1}$ region.

The lithium salt of the anion, when prepared in ether, precipitated at −10° as a yellow solid.

**The Reaction of the Pentalenylcycloocta-1,5-dienerhodium Anion with Benzophenone.** To a magnetically stirred solution of hydropentalenylcycloocta-1,5-dienerhodium (0.30 g, 0.96 mmole) in 10 ml of ether under argon at −78° was added 0.7 ml of a 1.5 *N* solution of *n*-butyllithium in hexane (1.05 mmoles). The reaction was allowed to warm slowly to room temperature over a period of 3 hr and was stirred for an additional 0.5 hr at this temperature. The resulting brown solution with yellow precipitate was cooled to −40°, and a solution of benzophenone (0.174 g, 0.96 mmole) in ether (5 ml) was added by syringe. The reaction was stirred overnight at room temperature. To the dark brown reaction mixture was then added 25 ml of a 5% ammonium chloride solution followed by 25 ml of ether. The ether layer was separated, washed twice with water, dried ($MgSO_4$), and evaporated to dryness under vacuum. The residue was dissolved in hot hexane (30 ml), filtered, and cooled overnight at −78°. Filtration and drying gave 0.21 g of the alcohol as a yellow solid. Recrystallization from cold hexane afforded 0.18 g (38% yield) of yellow crystals of VIIc, which darken at 145–155° and melt with decomposition at 155–157°.

*Anal.* Calcd for $C_{29}H_{29}ORh$: C, 70.16; H, 5.88. Found: C, 70.00; H, 5.77.

The infrared spectrum (Nujol mull) showed: 3561 (s) ($\nu_{O-H}$), 1558 (w) ($\nu_{C=C}$), and 701 (vs) $cm^{-1}$ (*cis* olefinic out-of-plane C–H deformation). There was no absorption in the 1400–1415-$cm^{-1}$ region.

**Deuteration of Bis(hydropentalenyl)iron.**[14] To a magnetically stirred solution of bis(hydropentalenyl)iron (III, 0.20 g, 0.76 mmole) in 10 ml of ether under argon at −78° was added 2.5 ml of a 1.5 *N* solution of *n*-butyllithium in hexane (3.75 mmoles). The reaction was allowed to warm slowly to room temperature over a period of 1 hr and was stirred at this temperature for an additional 0.5 hr. The resulting red-brown solution and brown precipitate was cooled to −40°, and 0.5 ml of $D_2O$ was injected. Ether (25 ml) and water (25 ml) were then added. The orange-red ether layer was separated, washed with 25 ml of water, dried ($MgSO_4$), and evaporated to dryness under vacuum. Sublimation [80° (5 × $10^{-3}$ mm)] of this residue gave 0.17 g (85%) of red crystals, mp 95–99°. The mass spectrum of this material showed that it consisted of a mixture of nondeuterated, monodeuterated, and dideuterated complexes. The peak attributable to the dideuterated species ($C_{16}H_{12}D_2{}^{56}Fe$) at *m/e* 264 was the most intense. The spectrum exhibited a small peak at *m/e* 51.5, which was absent in the spectrum of the nondeuterated complex and in the instrument background.

The infrared spectrum (Nujol mull) showed significant absorptions at 2155 (vw) ($\nu_{C-D}$), 1556 (m) ($\nu_{C=C}$), and 710 (vs) $cm^{-1}$ (*cis* olefinic C–H out-of-plane deformation). There was no absorption in the 1400–1430-$cm^{-1}$ region.

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(55) H. Gilman, M. Lichtenwalter, and R. A. Benkeser, *J. Am. Chem. Soc.*, **75**, 2063 (1953).

(56) Reference 48, Chapter 5.