Organometallics 1983, *2*, 1229–1234

Synthesis and Characterization of Bis(pentadienyl)ruthenium Compounds

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Received October 4, 1982

The syntheses of bis(2,4-dimethylpentadienyl)ruthenium and bis(2,3,4-trimethylpentadienyl)ruthenium are reported. Characterization was achieved by using infrared, ^{1}H NMR, ^{13}C NMR, and mass spectroscopy, as well as elemental analysis. In both cases, variable-temperature ^{1}H NMR data reveals an unsymmetric ground state with respective barriers to ligand oscillation of 9.73 and 10.16 kcal/mol. A single-crystal X-ray diffraction study of Ru(2,3,4-C_8H_{13})$_2$ has also been undertaken. The space group is C_i^1—$P\bar{1}$ (No. 2) with a = 9.213 (4) Å, b = 11.486 (4) Å, c = 7.811 (4) Å, α = 101.20 (4)°, β = 114.97 (3)°, γ = 91.89 (3)°, Z = 2, and D_{calcd} = 1.46 g/cm^3. The final R factor was 0.059 for the 2158 independent observed reflections. Despite the fact that two nearly eclipsing $CH_3 \cdots CH_3$ interactions result, the complex still adopts the gauche-eclipsed conformation in preference to the anti conformation. The complex is characterized by average Ru–C and C–C bond distances of 2.188 (3) and 1.428 (5) Å, respectively. A number of comparisons are made between these structural data and that of ruthenocene as well as other metal pentadienyl and bis(cyclo-η^5-dienyl)metal complexes.

We have recently reported (generally methylated) bis(pentadienyl)metal complexes, or "open metallocenes", for titanium, vanadium, chromium, manganese, and iron.[1] It is now becoming clear that these compounds possess reasonable thermal stabilities while still maintaining substantial and novel chemical reactivities, and therefore these complexes are certainly ideal candidates for extensive physical and chemical studies.[2,3] In view of the detailed data already gathered for the "open ferrocene" complexes,[1a,2-4] it became of clear interest to extend our studies to ruthenium, which is the only second-row transition metal to form a stable, divalent metallocene complex.[5] The information gathered in this study has indeed provided a great deal of further information pertaining to metal–pentadienyl systems in general, and these results are reported herein.

Experimental Section

All operations involving organometallics were carried out under a nitrogen atmosphere in prepurified Schlenk apparatus or in a glovebox. Nonaqueous solvents were thorougly dried and deoxygenated in a manner appropriate to each and were distilled immediately before use. Elemental analyses were performed by Micanal Laboratories. 2,4-dimethyl-1,3-pentadiene was either purchased commercially or prepared according to a reported method.[6] 2,3,4-Trimethyl-1,3-pentadiene was prepared according to a recently developed method.[7] Ruthenium trichloride hydrate was obtained commercially. Activation by the method reported by Arthur and Stephenson[8] did not appear to increase product yields.

Spectroscopic Studies. Infrared spectra were recorded with a Perkin-Elmer 298 spectrophotometer. Mulls were prepared in a glovebox with dry, degassed Nujol. All such spectra were calibrated with polystyrene. ^{1}H and ^{13}C nuclear magnetic resonance spectra were recorded on Varian FT-80 and SC-300 spectrometers. ^{1}H NMR spectra are reported relative to Me_4Si using C_6D_5H (δ 7.27) as internal standard while ^{13}C NMR spectra were similarly referenced (C_6D_6 = 128 ppm vs. Me_4Si). Mass spectra were performed on a Varian MAT 112 spectrometer at 70 eV. Except for the parent fragment, peaks are only quoted if their relative intensities are at least 10% of the intensity of the strongest peak.

Bis(2,3,4-trimethylpentadienyl)ruthenium, Ru(2,3,4-C_8H_{13})$_2$. Approximately 1 g of ruthenium trichloride hydrate is added to 20 mL of ethanol under nitrogen with stirring, after which 8 g of 2,3,4-trimethyl-1,3-pentadiene are added. A 4-g sample of zinc dust is then added, resulting in the generation of substantial heat if not reflux. The solution is allowed to stir at room temperature for about an hour, and then the mixture is refluxed about 2 h. The solvent is then removed in vacuo and the crude product extracted with several small portions of pentane. While some product can be isolated by concentrating this solution and cooling to −78 °C for several days, better yields are obtained if the crude solution is first subjected to column chromatography.[9] The yellow, air-stable crystalline product thus obtained is finally purified by sublimation. Complete infrared data (Nujol mull): 3073 (m), 3060 (sh), 1262 (m), 1151 (m), 1106 (w), 1031 (s), 1021 (ms), 1001 (s), 980 (w), 966 (w), 945 (m), 840 (m), 808 (m), 752 (m), 730 (ms), 682 (ms) cm^{-1}. ^{1}H NMR: δ 2.84 (d, 2 H, J = 2 Hz), 1.66 (s, 6 H), 1.59 (s, 3 H), 0.96 (d, 2 H, J = 2 Hz). ^{13}C NMR: δ 105.3 (s, 1 C), 95.5 (s, 2 C), 48.4 (t, J = 155 Hz), 24.7 (q, 2 C, J = 125 Hz), 15.9 (q, 1 C, J = 125 Hz). Mass spectrum: m/e (relative intensity) 55 (15), 67 (11), 139 (12), 140 (13), 141 (19), 142 (11), 143 (10), 158 (13), 165 (10), 166 (12), 167 (23), 169 (13), 177 (10), 178 (12), 179 (13), 180 (14), 190 (10), 191 (14), 192 (11), 193 (14), 200 (11), 201 (19), 202 (30), 203 (50), 204 (69), 205 (53), 207 (56), 208 (44),

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(1) (a)Wilson, D. R.; DiLullo, A. A.; Ernst, R. D. *J. Am. Chem. Soc.* **1980**, *102*, 5928. (b) Wilson, D. R.; Liu, J.-Z.; Ernst, R. D. *Ibid.* **1982**, *104*, 1120. (c) Liu, J.-Z.; Ernst, R. D. *Ibid.* **1982**, *104*, 3737.

(2) Böhm, M. C.; Eckert-Maksić, M.; Ernst, R. D.; Wilson, D. R.; Gleiter, R. *J. Am. Chem. Soc.* **1982**, *104*, 2699.

(3) Cymbaluk, T. H.; Wilson, D. R.; Severson, S.; Higashi, J.; Ernst, R. D.; Parry, R. W., experiments in progress.

(4) (a) Wilson, D. R.; Ernst, R. D.; Cymbaluk, T. H., preceding paper in this issue. (b) Ernst, R. D.; Wilson, D. R.; Herber, R. H., submitted for publication.

(5) (a) Wilkinson, G. *J. Am. Chem. Soc.* **1952**, *74*, 6146. (b) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed.; Interscience: New York, 1980.

(6) (a) Jitkow, O. N.; Bogert, M. T. *J. Am. Chem. Soc.* **1941**, *63*, 1979. (b) Replacement of the methyl Grignard reagent by methyllithium seems to improve the product purity somewhat.

(7) (a) The method of procedure[7b] first involved the Reformatsky reaction of acetone with $CH_3CH(Br)CO_2C_2H_5$ to yield the expected hydroxy ester. Dehydration with methanesulfonyl chloride produced a mixture of the expected conjugated and unconjugated olefin esters, which were equilibrated with KOC_2H_5 in ethanol to yield the conjugated isomer. Treatment of this isomer with 2 equiv of methyllithium yielded 2,3,4-trimethyl-2-penten-4-ol ("pentamethylallyl alcohol"), which produced 2,3,4-trimethyl-1,3-pentadiene on distillation from a small amount of I_2 and glass wool. The overall yield was 35% and the purity was 99% by gc using only vacuum transfers or atmospheric distillations for purification. (b) Wilson, D. R.; Ernst, R. D., unpublished results.

(8) Arthur, T.; Stephenson, T. A. *J. Organomet. Chem.* **1981**, *208*, 369.

(9) Müller, J.; Fischer, E. O. *J. Organomet. Chem.* **1966**, *5*, 275.

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209 (21), 210 (12), 173 (18), 274 (16), 276 (11), 287 (11), 295 (18), 297 (16), 298 (51), 299 (64), 300 (72), 301 (100), 302 (27), 303 (67), 304 (16), 310 (14), 311 (11), 312 (18), 313 (44), 314 (48), 315 (60), 316 (80), 317 (45), 318 (68), 319 (41), 320 (54), 322 (33). Anal. Calcd for $C_{16}H_{26}Ru$: C, 60.17; H, 8.20. Found: C, 60.16; H, 8.48.

Bis(2,4-dimethylpentadienyl)ruthenium, $Ru(2,4\text{-}C_7H_{11})_2$. This air-stable yellow crystalline compound is isolated in an analogous manner as described for $Ru(2,3,4\text{-}C_8H_{13})_2$, substituting 2,4-dimethyl-1,3-pentadiene for 2,3,4-trimethyl-1,3-pentadiene. Complete infrared data (Nujol mull): 3058 (m), 1480 (sh), 1425 (m), 1345 (m), 1275 (m), 1028 (s), 1006 (m), 987 (ms), 936 (s), 925 (w), 915 (m), 900 (m), 891 (w), 878 (w), 860 (sh), 850 (s), 840 (sh), 730 (m), 720 (sh) cm^{-1}. ^1H NMR: δ 4.72 (s, 1 H), 2.81 (d, 2 H, J = 2 Hz), 1.83 (s, 6 H), 0.94 (d, 2 H, J = 2 Hz). ^{13}C NMR: δ 100.1 (s), 97.8 (d, J = 154 Hz), 46.5 (t, J = 154 Hz), 26.2 (q, J = 125 Hz). Mass spectrum: m/e (relative intensity) 55 (16), 102 (14), 114 (15), 116 (12), 127 (11), 128 (13), 139 (14), 140 (13), 141 (16), 142 (10), 152 (13), 153 (12), 154 (12), 165 (11), 166 (10), 167 (13), 178 (10), 179 (11), 188 (15), 189 (17), 190 (27), 191 (44), 192 (43), 193 (50), 194 (43), 195 (30), 196 (15), 267 (16), 270 (28), 271 (32), 272 (42), 273 (80), 274 (20), 275 (52), 276 (13), 281 (11), 282 (13), 284 (27), 285 (58), 286 (75), 287 (100), 288 (86), 289 (72), 290 (80), 291 (41), 292 (70), 293 (12), 294 (38). Anal. Calcd for $C_{14}H_{22}Ru$: C, 57.72; H, 7.61. Found: C, 58.03; H, 7.81.

X-ray Diffraction Study of $Ru(2,3,4\text{-}C_8H_{13})_2$. Single crystals of this compound were isolated by slowly cooling a concentrated solution in pentane. Unit cell data were determined from a combination of oscillation photographs and standard Nicolet P$\bar{1}$ software programs and confirmed by cell reduction. Accurate cell constants and their standard deviations were derived from a least-squares refinement of 15 centered reflections for which 23° < 2θ < 28°, using the Mo K$\bar{\alpha}$ peak at 0.710 730 Å. The unit cell parameters are a = 9.213 (4) Å, b = 11.486 (4) Å, c = 7.811 (4) Å, α = 101.20 (4)°, β = 114.97 (3)°, γ = 91.89 (3)°, V = 728.8 (5) $Å^3$, Z = 2. The space group is C_i^1—$P\bar{1}$ (No. 2).

Mo K$\bar{\alpha}$ radiation was monochromatized by using the 002 face of mosaic graphite. θ–2θ scans were employed from 1.2° below to 0.8° above the peak center using a varable scan rate of from 1.0 to 8.0 deg/min. A 1.0-mm diameter collimator was used as the crystal edges varied from 0.16 to 0.37 mm. Data were collected in two concentric shells of 2θ, 0–50° and 50°–52° with background time equal to half the total scan time. The intensities of five standard reflections were monitored for every 95 reflections and showed during data collection an average 5% loss in intensity for which a correction was applied. All data were processed using the X-RAY 70 Program package.[10] An absorption correction was applied for the data crystal using a modification of the Ibers program AGNOST.[11] The transmission coefficients ranged from 0.728 to 0.861. The crystal faces were indexed as (001), (00$\bar{1}$), (110), ($\bar{1}\bar{1}$0), (11$\bar{1}$), ($\bar{1}\bar{1}$1), (1$\bar{1}$0), and ($\bar{1}$10). A total of 3052 reflections were processed, yielding 2897 unique reflections of which 2158 had intensities judged to be above background ($I > 3\sigma(I)$). These were used in subsequent calculations. The function minimized was $\sum w(|F_o| - |F_c|)^2$, with empirical weights assigned by the method of Cruikshank in the latter stages.[12] The atomic scattering factors were taken from a recent tabulation, as were the anomalous dispersion terms for ruthenium.[13]

The position of the single unique ruthenium atom was readily determined from a Patterson map. All carbon atoms were located on a subsequent difference Fourier map. Least-squares refinement led to an anisotropic agreement index ($R = \sum||F_o| - |F_c||/\sum|F_o|$) of 0.069 and a weighted index ($R_w = (\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)^{1/2}$) of 0.096. A series of difference Fourier maps and least-square refinements led sequentially to the location of the hydrogen atoms, although several were poorly defined. To better define these atom locations, the hydrogen atom positions were refined, which resulted in substantially improved locations for these atoms as well as a reduction in the agreement indices. These new hydrogen atom locations were then idealized, which involved adjusting the C–H bond distances to 0.95 Å and, in the case of the methyl groups, also applying a least-squares fit to a tetrahedral geometry (these fits were considerably closer to tetrahedral when the refined hydrogen atom positions were used rather than the positions from the earlier difference Fourier map). Hydrogen atoms were assigned isotropic thermal parameters equal to 1.0 plus the equivalent isotropic parameter for the carbon atom to which they were attached. Final refinement led to agreement indices of R = 0.059 and R_w = 0.082. A final difference Fourier map revealed no peaks greater than 0.62 e/$Å^3$. The standard deviation of the map was 0.12 e/$Å^3$. The final positional and thermal parameters obtained from the last cycle of least-squares refinement are presented in Tables I and II, respectively, along with their estimated standard deviations. The idealized hydrogen atom parameters are contained in Table III. The final values of $10|F_o|$ and $10|F_c|$ in electrons are available as supplementary material. Other than those mentioned later, intermolecular contacts are normal.

Table I. Positional Parameters for the Non-hydrogen Atoms of $Ru(2,3,4\text{-}C_8H_{13})_2$

atom	x	y	z
Ru	0.35008 (8)	0.30389 (6)	0.10983 (10)
C(1)	0.6050 (11)	0.29192 (86)	0.2533 (16)
C(2)	0.5166 (10)	0.18372 (78)	0.2536 (13)
C(3)	0.3961 (11)	0.11086 (73)	0.0838 (13)
C(4)	0.3278 (11)	0.14325 (79)	−0.1038 (13)
C(5)	0.4072 (13)	0.24271 (88)	−0.1326 (15)
C(6)	0.5458 (15)	0.1571 (12)	0.4473 (16)
C(7)	0.3118 (13)	−0.00202 (87)	0.0964 (16)
C(8)	0.1732 (15)	0.0762 (10)	−0.2621 (14)
C(9)	0.3410 (12)	0.48822 (83)	0.0945 (18)
C(10)	0.1862 (13)	0.42678 (82)	−0.0318 (16)
C(11)	0.0972 (11)	0.35102 (76)	0.0288 (13)
C(12)	0.1677 (11)	0.32493 (88)	0.2146 (14)
C(13)	0.3150 (12)	0.38172 (96)	0.3643 (15)
C(14)	0.1138 (19)	0.4264 (13)	−0.2475 (21)
C(15)	−0.0697 (12)	0.2898 (11)	−0.1178 (16)
C(16)	0.0830 (14)	0.2221 (11)	0.2515 (19)

Synthetic and Spectroscopic Results and Discussion

The reaction of ruthenium trichloride hydrate with zinc dust and an excess of various methylated 1,3-pentadienes leads to the formation of the appropriate bis(pentadienyl)ruthenium complexes, which may subsequently be isolated as yellow crystalline solids, reasonably air stable for several days in the solid state. These compounds are sublimable and readily soluble in organic solvents. The method of preparation employed here is similar to that used for synthesizing various bis(cyclo-η^5-dienyl)ruthenium compounds,[14] although the yields (generally 30%, but occasionally in excess of 60%) are somewhat lower. Attempts to prepare complexes with fewer methyl groups leads to similar yellow solutions; however, the compounds have been thus far isolated in only very small quantities, perhaps due to the formation of polymeric byproducts.

The infrared, ^1H NMR, and ^{13}C NMR spectra are quite similar to those reported for the bis(pentadienyl)iron complexes,[1a,4a] and the mass spectra and analytical data (see Experimental Section) provide further confirmation for the formulation of these complexes as "open sandwiches", i.e., I and II. The depiction of I and II in

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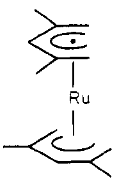
(10) Stewart, J. A.; Kundell, F. A.; Baldwin, J. C. "The X-ray System of Crystallographic Programs"; Computer Science Center, University of Maryland: College Park, Md., 1970.

(11) Ernst, R. D.; Marks, T. J.; Ibers, J. A. *J. Am. Chem. Soc.* **1977**, *99*, 2090.

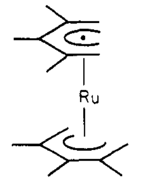
(12) (a) Cruikshank, D. W. J. In "Crystallographic Computing"; Ahmed, F. R., Ed.; Munksgaard: Copenhagen, 1970; pp 187–196. (b) The function used was $w = (200 + |F_o| + 0.10|F_o|^2 + 0.005|F_o|^3)^{-1}$.

(13) Cromer, D. T.; Waber, J. T. In "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, Tables 2.2A and 2.3.1.

(14) Pertici, P.; Vitalli, G.; Paci, M.; Porri, L. *J. Chem. Soc., Dalton Trans.* 1980, 1961.

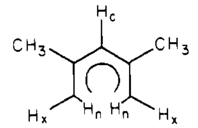


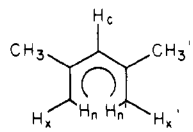
I



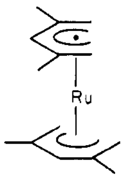
II

the gauche-eclipsed conformation above follows from the conclusions reached in the iron system, as well as X-ray and variable-temperature ^1H NMR studies of $Ru(2,4\text{-}C_7H_{11})_2$ and $Ru(2,3,4\text{-}C_8H_{13})_2$ (vide infra). The variable-temperature ^1H NMR spectra for $Ru(2,4\text{-}C_7H_{11})_2$ can be seen in Figure 1. At room temperature, four resonances are observed at 4.72, 2.81, 1.83, and 0.94 ppm downfield from Me_4Si, attributable to the H_c, H_x, CH_3, and H_n protons, respectively. However, as the temperature is lowered, broadening of these peaks occurs, with the exception of H_c resonance, so that a seven-line pattern is ultimately frozen out. The seven-line pattern may be attributed to the adoption of the unsymmetric gauche-eclipsed conformation, wherein the idealized perpendicular mirror plane of symmetry is destroyed, i.e.

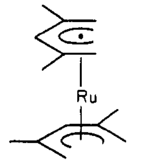




Since there is only one H_c resonance expected at low or high temperature, no broadening of this resonance would be expected, and indeed none is observed. The two rotational isomers IIIa and IIIb which are thereby frozen out are mirror images of one another and thus demonstrate equivalent seven line spectra. $\Delta G^\ddagger$ for this process is determined to be 9.73 kcal/mol with a maximum error of less than 0.1 kcal/mol.[15] This value is higher than the value of ca. 9 kcal/mol observed for related iron complexes.[4a]



IIIa



IIIb

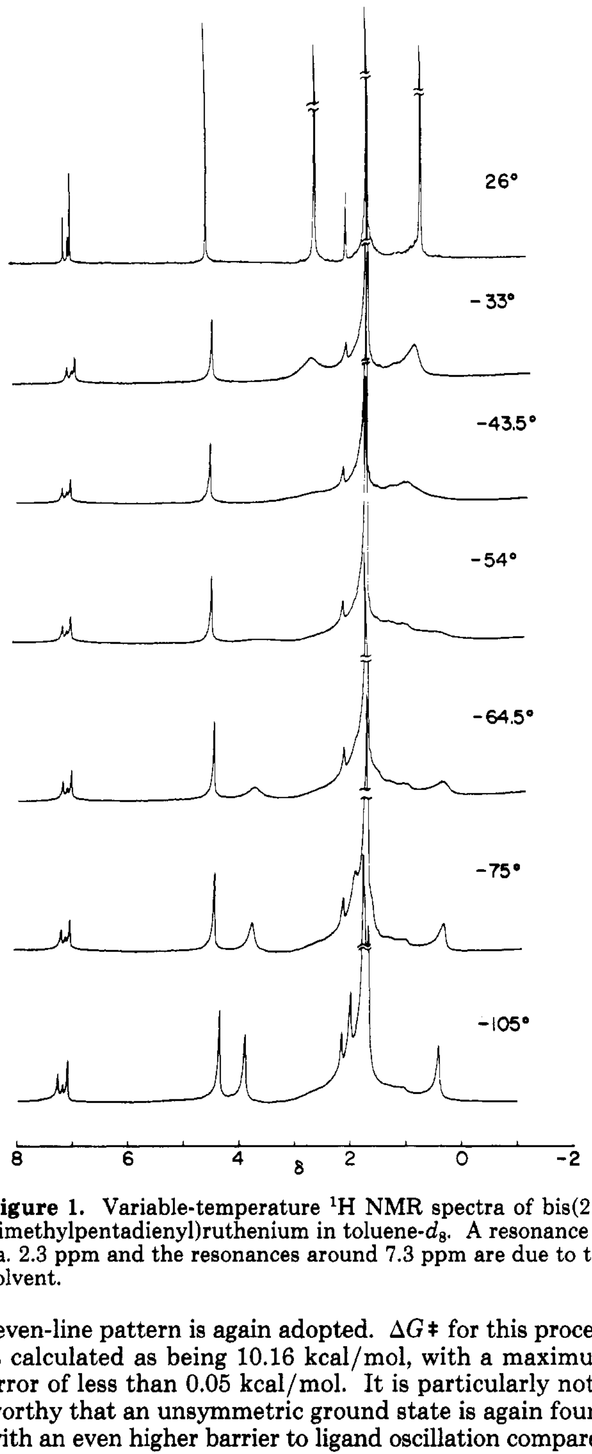
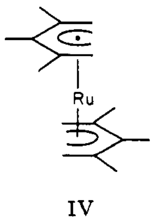


Figure 1. Variable-temperature ^1H NMR spectra of bis(2,4-dimethylpentadienyl)ruthenium in toluene-d_8. A resonance at ca. 2.3 ppm and the resonances around 7.3 ppm are due to the solvent.

Similar features are observed in the variable-temperature ^1H NMR spectra of $Ru(2,3,4\text{-}C_8H_{13})_2$. While a four-line pattern is again observed at room temperature (see Experimental Section), on cooling broadening of all but the 3-CH_3 resonance is observed, so that by −70 °C a seven-line pattern is again adopted. $\Delta G^\ddagger$ for this process is calculated as being 10.16 kcal/mol, with a maximum error of less than 0.05 kcal/mol. It is particularly noteworthy that an unsymmetric ground state is again found with an even higher barrier to ligand oscillation compared to $Ru(2,4\text{-}C_7H_{11})_2$. With methyl groups in the 2-, 3-, and 4-positions, $Ru(2,3,4\text{-}C_8H_{13})_2$ in a gauche-eclipsed conformation (II) would have two $CH_3 \cdots CH_3$ eclipsing interactions present, whereas the anti conformation, IV, would be free of such interactions. Thus, one would expect that



IV

if the anti conformation were at all close in energy elec-

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[15] (a) The rate constant $k = (k_bT/h)\exp(-\Delta G^\ddagger/RT)$; at the coalescence temperature $k = k_c = \pi\Delta\nu/(2)^{1/2}$.[15b] (b) Kessler, H. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 219. (c) For each of the seven-line spectra, both H_{endo} resonances appear to higher field than the H_{exo} resonances. For $Ru(2,4\text{-}C_7H_{11})_2$, one of the H_{endo} resonances appears under a methyl resonance. The assignments for this compound at −105 °C are (toward low field) H_{endo}, CH_3, (CH_3 + H_{endo}), H_{exo}, H_{tol}, H_{exo}, and H_3. For Ru-$(2,3,4\text{-}C_8H_{13})_2$, the low-temperature assignments are similarly H_{endo}, CH_3(2 or 4), CH_3(3), H_{endo}, CH_3(2 or 4), H_{exo}, H_{tol}, and H_{exo}.

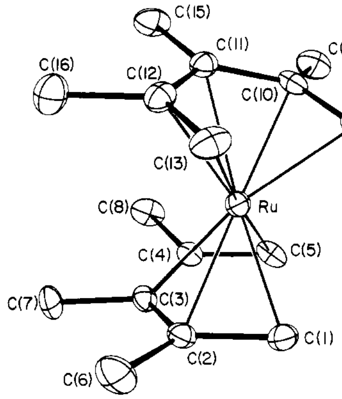

Figure 2. Perspective view and numbering scheme for bis(2,3,4-trimethylpentadienyl)ruthenium. The 20% probability ellipsoids are shown.

tronically to that of the gauche-eclipsed conformation, the complex would be sterically forced into the symmetric anti ligand orientation. Since this does not occur, one must conclude that there is a substantial electronic influence providing stabilization of the gauche-eclipsed conformation. The presence of a higher barrier to ligand oscillation for II compared to I might be most readily traced to the greater number of methyl groups in the former, although electronic effects operative on the ground-state gauche-eclipsed conformation might also be considered.[16] In this regard, the fact that the ruthenium complexes demonstrate a higher barrier to ligand oscillation as compared to the iron analogues strongly indicates the importance of electronic factors, since a greater interligand (and hence intermethyl) separation is present in the ruthenium complexes. In any case, the dominance of the gauche-eclipsed conformation in these systems is again underscored.

Crystallographic Results and Discussion

The result of the $Ru(2,3,4-C_8H_{13})_2$ structural investigation can be seen in Figure 2, along with the atom numbering scheme. According to the numbering scheme, a given C(*n*) atom (*n* = 1–8) is related by an approximate C_2 axis to the C(*n* + 8) atom. The hydrogen atoms have been numbered sequentially (H(1)–H(26)) but have been deleted for clarity. It can be readily observed from Figure 2 that a nearly gauche-eclipsed conformation has been adopted in this structure, similar to that observed in $Fe(2,4-C_7H_{11})_2$. Thus, the complex has adopted the gauche-eclipsed conformation despite the fact that close interligand $CH_3\cdots CH_3$ contacts have resulted (C(7)–C(16) = 3.72 (2) Å, C(8)–C(15) = 3.70 (2) Å), rather than adopting what would appear to be a less-crowded anti-eclipsed conformation.[17] In fact, this complex was specifically targeted for study on the assumption that if the anti- and gauche-eclipsed conformations were at all close energetically, the complex would be preferentially forced into the anti conformation. To best understand the conformation, one can define a plane for each of the C_8H_{13} ligands. These planes are composed of the Ru atom, the appropriate carbon atom in position 3 (i.e., C(3) or C(11)), and the midpoint between either C(1) and C(5) or C(9) and C(13). The angle between these two planes will define the conformation, where a cis-eclipsed complex will be considered as having a conformation angle of 0°. Ideally the gauche-eclipsed conformation will be characterized by an angle of 60°. In fact, in $Fe(2,4-C_7H_{11})_2$ this angle was 59.7°, even though interligand $C\cdots C$ contacts could have been reduced by ligand twisting. However, here an angle of 52.5° is found, whose larger deviation from 60° could very possibly be ascribed to the two eclipsing methyl interactions above. Thus, the complex has actually undergone a 7.5° rotation from the gauche-eclipsed conformation toward the cis-eclipsed conformation (or 25% of the way to the intermediate staggered conformation).

The average[18] delocalized C–C bond distance in the complex is 1.428 (5) Å. No distinction can be made regarding the relative lengths of the "internal" vs. "external" C–C bonds.[19] The C–C–C bond angles around the ligand backbone (i.e., not involving methyl groups) all appear about the same, averaging 122.5 (4)°. Thus it appears that contraction of the C–C–C bond angles by methylation has been reasonably comparable whether the 2-, 3-, or 4-carbon atom positions are involved.[20]

The average distances from the ruthenium atom to the C(1), C(2), C(3), C(4), and C(5) atoms (and their equivalent C(*n* + 8) counterparts) are 2.152 (7), 2.195 (7), 2.258 (7), 2.166 (8), and 2.172 (9) Å. (See Table IV.) The average Ru–C bond distance is 2.188 (3) Å, which can be compared to ruthenocene's average Ru–C bond distance of 2.196 (3) Å.[21] While the difference amounts to only ca. two standard deviations, it is quite clear that at the very least these values are more comparable than observed for the iron system where $Fe(2,4-C_7H_{11})_2$ was found to possess an average Fe–C bond distance of 2.089 (1) Å[1a,4a] compared to 2.064 (3) Å for ferrocene.[22] It seems most reasonable to ascribe this greater similarity to the fact that the "open ruthenocene" complex possesses substantially less interligand repulsion than does the "open ferrocene" complex, simply due to the larger size of ruthenium. However, the interligand repulsion in the present case is by no means negligible, so that it is certain that in the absence of these repulsions, the average Ru–C bond distance in the "open ruthenocene" complex would be significantly shorter than the corresponding difference in ruthenocene.[23] It is also

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(16) The molecular orbital calculations indicate that ligand to metal interactions are more important in the gauche-eclipsed conformation, while metal to ligand interactions become more important for the anti conformation.[2] Overall, however, methylation had a net destabilizing effect on the complexes.

(17) (a) The van der Waals radius for a methyl group is 2.0 Å.[17b] (b) Pauling, L. "The Nature of the Chemical Bond", 3rd. ed.; Cornell University Press: Ithaca, N.Y., 1960.

(18) When average values are discussed, the standard deviation of the mean is cited.

(19) (a) The "internal" carbon–carbon bonds are those formed between carbon atom positions 2 and 3 as well as 3 and 4; the "external" carbon–carbon bonds are those formed between carbon atom positions 1 and 2 as well as 4 and 5. In the other transition-metal pentadienyl structures, as well as in $Nd(2,4-C_7H_{11})_3$,[19b] the "external" set appeared to be shorter than the "internal" set. (b) Ernst, R. D.; Cymbaluk, T. H. *Organometallics*, **1982**, *1*, 708.

(20) (a) In the related $Fe(2,4-C_7H_{11})_2$ structure, the angles around the carbon atoms in positions 2 and 4 were noticeably contracted compared to the angles around the 3-positions (124.1 (4)° and 120.7 (3)° vs. 125.5 (3)°), whereas in $Mn_3(3-C_6H_9)_4$, the opposite ordering was observed (125.2 (4)° and 127.5 (3)° vs. 121.1 (4)°). (b) Also of interest are the $C(1)\cdots C(5)$ and $C(9)\cdots C(13)$ intraligand contacts, which are 2.713 (14) and 2.717 (12) Å, respectively (average = 2.715 (9) Å). Because of the ligand contraction induced by three methyl groups, this is the most contracted pentadienyl group we have yet encountered.

(21) (a) Haaland, A.; Nilsson, J. E. *Acta. Chem. Scand.* **1968**, *22*, 2653. (b) Hardgrove, G. L.; Templeton, D. H. *Acta Crystallogr.* **1959**, *12*, 28. (c) The standard deviations reported in these comparisons are based on the assumption that the distances averaged are all part of the same population. Hence these deviations are not reflective of the distribution of values, but should reflect the overall accuracy of the average.

(22) Bohn, R. K.; Haaland, A. *J. Organomet. Chem.* **1966**, *5*, 470.

(23) Interligand contacts which are less than the sum of the appropriate carbon atom (1.7 Å) or methyl group (2.0 Å) radii are $C(2)\cdots C(13)$ = 3.200 (15) Å, $C(5)\cdots C(10)$ = 3.198 (17) Å, $C(1)\cdots C(13)$ = 3.279 (17) Å, $C(5)\cdots C(9)$ = 3.249 (15) Å, $C(5)\cdots C(14)$ = 3.409 (20) Å, and $C(6)\cdots C(13)$ = 3.383 (18) Å. The methyl-methyl contacts are mentioned separately in the text.

Table IV. Selected Bond Distances (Å) and Angles (deg) for $Ru(2,3,4\text{-}C_8H_{13})_2$

Bond Distances

Ru-C(1)	2.157 (9)	Ru-C(9)	2.146 (10)	C(1)-C(2)	1.465 (15)	C(9)-C(10)	1.407 (13)
Ru-C(2)	2.192 (9)	Ru-C(10)	2.199 (10)	C(2)-C(3)	1.398 (10)	C(10)-C(11)	1.447 (17)
Ru-C(3)	2.258 (9)	Ru-C(11)	2.257 (10)	C(3)-C(4)	1.459 (14)	C(11)-C(12)	1.416 (14)
Ru-C(4)	2.172 (9)	Ru-C(12)	2.160 (12)	C(4)-C(5)	1.441 (16)	C(12)-C(13)	1.393 (11)
Ru-C(5)	2.169 (13)	Ru-C(13)	2.174 (12)	C(2)-C(6)	1.515 (17)	C(10)-C(14)	1.527 (19)
				C(3)-C(7)	1.530 (15)	C(11)-C(15)	1.516 (11)
				C(4)-C(8)	1.491 (12)	C(12)-C(16)	1.533 (19)

Bond Angles

C(1)-C(2)-C(3)	122.4 (9)	C(3)-C(4)-C(5)	119.8 (7)	C(11)-C(10)-C(14)	116.9 (9)
C(1)-C(2)-C(6)	118.3 (8)	C(3)-C(4)-C(8)	119.9 (10)	C(10)-C(11)-C(15)	118.6 (9)
C(2)-C(3)-C(4)	124.2 (9)	C(5)-C(4)-C(8)	120.3 (9)	C(12)-C(11)-C(15)	119.7 (10)
C(3)-C(2)-C(6)	119.0 (9)	C(9)-C(10)-C(11)	122.6 (11)	C(11)-C(12)-C(13)	124.4 (11)
C(2)-C(3)-C(7)	119.1 (9)	C(9)-C(10)-C(14)	120.0 (13)	C(11)-C(12)-C(16)	118.4 (8)
C(4)-C(3)-C(7)	116.2 (7)	C(10)-C(11)-C(12)	121.5 (8)	C(13)-C(12)-C(16)	117.1 (10)

useful to compare the present results of those found for the complex $Ru(\eta^5\text{-}C_7H_7)(\eta^5\text{-}C_7H_9)$.[24] In this latter complex, essentially the same gauche-eclipsed conformation is observed, and the average Ru–C bond distance was determined to be 2.194 (2) Å. In each of these ruthenium complexes, the Ru–C bonds are longest to the carbon atoms in the 3-positions, although in $Ru(2,3,4\text{-}C_8H_{13})_2$ the terminal carbon atoms seem to be closer to the metal than the atoms in the 2- and 4-positions, while the reverse seems to be the case for $Ru(\eta^5\text{-}C_7H_7)(\eta^5\text{-}C_7H_9)$. Note that in $Fe(2,4\text{-}C_7H_{11})_2$, the longest Fe–C bond distances involved the terminal carbon atoms.[1a,4a]

Also of interest are some of the parameters related to the ligands themselves. The ligands are distorted somewhat from planarity (see Table V), with the C(1,9), C(2,10), C(3,11), C(4,12), and C(5,13) atoms averaging respectively –0.007, –0.015, 0.045, –0.053, and 0.029 Å from the ligand least-squares planes, each defined by the five carbon atoms bound to ruthenium. A positive value here denotes a deviation away from the ruthenium atom. This pattern results in an accommodation of one ligand for the other, as any pair of near eclipsing carbon atoms (one from each ligand) will have one atom bent toward the ruthenium atom and the other bent away. The ruthenium atoms average 1.582 Å from these ligand planes,[25] and there is an angle of 18.2° between the ligand planes themselves.

Somewhat related to the above considerations are various tilting deformations experienced by the substituents attached to the five principle carbon atoms of each ligand. In general, a tilt of the substituents down toward the metal is expected (so as to point the ligand p orbitals toward the metal[27]), and for the $M(2,4\text{-}C_7H_{11})_2$ (M = V, Cr, Fe)[1a,4a,28] complexes this tilt averages ca. 9°, whereas for $Mn_3(3\text{-}C_6H_9)_4$ the tilt is smaller at 3.7°.[1a] These tilts are defined by the angle between the respective $C\text{–}CH_3$ vectors and the least-squares plane defined by the five metal-bound carbon atoms in a given pentadienyl ligand. In ferrocene a tilt of 3.7 (9)° has been observed.[22] Notably, the methyl groups attached to the 2- or 4-positions have tilted down by an average of 9.5°; however, the methyl groups attached to the 3-positions are essentially untilted (0.3° toward the metal). Of course, tilting of the 3-methyl groups would result in further interligand $CH_3\cdots CH_3$ interactions, but it still seems apparent that the 3-methyl groups are more deformable than those attached to the 2- or 4-positions and seemingly have less tendency toward tilting.

A similar trend can be observed for the terminal CH_2 groups. The H_{exo} protons are bent down toward the metal by an average of 17° (the values being 18°, 5°, 23°, and 20°), which may also be attributed to an attempt by the ligand to point it's p orbitals more toward the ruthenium atom.[27] However, the H_{exo} protons are tilted an average of 42° (the values being 45°, 45°, 50°, and 29°) away from the metal so that the bulk of this twist might be ascribed to intraligand $H_{exo}\cdots H_{exo}$ repulsions. Similar trends have been observed in the other metal–pentadienyl complexes.[1a,4,28]

The present results serve to point out several similarities as well as several dramatic differences between the metallocenes and these "open metallocenes". The structural results for the M = Cr, Fe, and Ru complexes demonstrate a close correspondence between the two systems with regard to average metal–carbon bond distances and the so-called electron imbalance relationships.[29] Further, the colors of the 18-electron iron or ruthenium complexes are reasonably similar. However the greater localization of negative charge in a pentadienyl anion as well as it's open nature and the fact that the resulting bis(pentadienyl)-metal complexes have much lower symmetry bring about some dramatic differences as well. Conformationally these complexes are far richer than the metallocenes, and they are chemically and catalytically more reactive.[3] Further, there appears to be greater mixing of metal and ligand orbitals in the resulting molecular orbitals of the complex.[2] Finally, it is now clear that in the cases of titanium and vanadium at least, the adoption of a low-spin configuration can impart even greater stability for the "open metallocenes" compared to the metallocenes themselves.[1c,28] It is clear that much remains to be gained from studying these systems and our efforts are continuing.

Acknowledgment. R.D.E. expresses his gratitude for partial support of this research through grants from National Science Foundation (Grant CHE-81-20683), from the University of Utah Research Committee, and from the donors of the Petroleum Research Fund, administered by the American Chemical Society. We would also like to thank Mr. David R. Wilson for supplying some of the 2,3,4-trimethyl-1,3-pentadiene used in this work and to

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(24) Schmid, H.; Ziegler, M. L. *Chem. Ber.* **1976**, *109*, 125.

(25) The distances from the ruthenium atom to the center of masses of the bonded portions of the ligands are 1.641 (5) and 1.649 (5) Å, averaging 1.645 (4) Å.

(26) It is also possible that a downward tilt of the 3-methyl groups is retarded by the closer intraligand $CH_3\cdots CH_3$ contacts that would ensue; however, even in $Mn_3(3\text{-}C_6H_9)_4$ only a relatively small downward tilt of 3.7° was observed.[1b]

(27) (a) The fact that the pentadienyl ligand is larger than cyclopentadienyl would lead to the expectation of greater tilting. Note also that in $Fe(C_5(CH_3)_5)_2$ the methyl groups point away from the metal.[26b] (b) Freyberg, D. P.; Robbins, J. L.; Raymond, K. N.; Smart, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 892.

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Prof. Gary E. Keck for helpful synthetic advice.

Registry No. I, 85908-78-7; II, 85893-68-1; ruthenium trichloride, 10049-08-8; 2,3,4-trimethyl-1,3-pentadiene, 85893-67-0; 2,4-dimethyl-1,3-pentadiene, 1000-86-8.

Supplementary Material Available: A listing of non-hydrogen atom anisotropic thermal parameters (Table II), the hydrogen atom parameters (Table III), least-squares plane data (Table V), and the structure amplitude table (22 pages). Ordering information is given on any current masthead page.

Preparation of 3,3′,4,4′-Tetramethyl-1,1′-biphospholyl and Its Reactions with Iron and Cobalt Carbonyls. Synthesis and X-ray Crystal Structure of a Phospholyl Complex with a Chain of Four Cobalt Atoms

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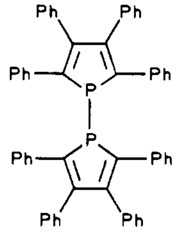
Received January 31, 1983

3,3′,4,4′-Tetramethyl-1,1′-biphospholyl (L–L) has been prepared by reaction of iodine with (3,4-dimethylphospholyl)lithium (L–Li) in the presence of $AlPh_3$. It reacts with $Fe_2(CO)_9$ to yield a mixture of $L_2Fe_2(CO)_6$, $L_2Fe_3(CO)_9$, and $L_2Fe_4(CO)_{12}$. The first compound is a classical phosphido-bridged species in which L acts as a three-electron donor through its phosphorus atom. The η^4 complexation by $Fe(CO)_3$ of the dienic system of one of the phospholyl units in $L_2Fe_2(CO)_6$ produces the second complex. In the third compound, both phospholyls act as (4 + 3)-electron donors. The reaction of L–L with $Co_2(CO)_8$ yields $L_2Co_4(CO)_8$ which has been shown by X-ray crystal structure analysis to contain a chain of four cobalt atoms sandwiched between two phospholyl units again acting as (4 + 3)-electron donors.

1,1′-Biphospholyls are especially interesting molecules for three main reasons: (a) They are convenient sources for a wide range of unknown phospholes with P substituents such as alkoxy, amino, halo, etc.... (b) They offer the opportunity to study a fulvalene-like interaction between two 6π-electron phosphole rings. (c) They can be used as generators of phospholyl radicals through thermal or UV-induced homolytic cleavage of the phosphorus–phosphorus bond. Up to now, only three such species were known **1**–**3**.[2-4] Unfortunately, in all cases, the substitution drastically alters the properties of the phosphole rings since the phenyl groups conjugate with the diene systems and hinder the phosphorus lone pairs. We report hereafter on the synthesis of **4** which is the first discovered fully representative 1,1′-biphospholyl and on its very peculiar coordinating behavior toward iron and cobalt carbonyls.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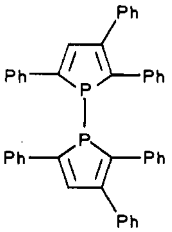
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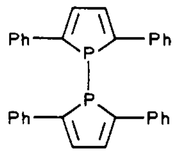
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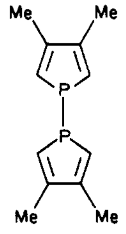
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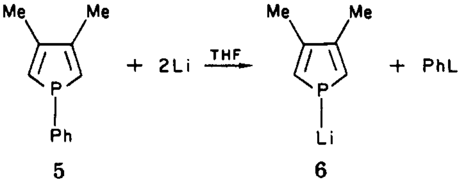
Results and Discussion

Synthesis and Coordination Chemistry of 4. The only easily available starting material for the synthesis of **4** is the 3,4-dimethylphospholyl anion **6** obtained by lithium cleavage of the phosphorus–phenyl bond[5] in 1-phenyl-3,4-dimethylphosphole (eq 1). However, the treatment of the crude mixture of **6** and phenyllithium by phosgene in strict analogy with the successful synthesis of **3**[4] does not produce the expected biphospholyl. Similarly, the reaction of this mixture with iodine produces mainly **5** through cross-coupling of **6** and phenyllithium and yields only minute amounts of **4**. On the other hand, if phenyllithium is first "neutralized" by a stoichiometric amount of aluminum chloride, then the synthesis of **4** succeeds (eq 2). Iodine is the most convenient oxidizing agent for that purpose; however, other positive halogen sources such as bromophenylacetylene, ethyl bromo-



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