# X-ray Crystal Structure and Theoretical Study of Tris(2,3-dimethyl-1,3-butadiene)molybdenum(0)

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*Summary:* Tris(2,3-dimethyl-1,3-butadiene)molybdenum(0), $(C_8H_{10})_3Mo$, crystallizes in the triclinic space group $P\bar{1}$ with $a$ = 9.554 (2) Å, $b$ = 12.312 (2) Å, $c$ = 7.060 (2) Å, $\alpha$ = 97.66 (2)°, $\beta$ = 90.38 (2)°, $\gamma$ = 99.07 (1)°, $V$ = 812.5 Å$^3$, $Z$ = 2, $D_x$ = 1.375 g cm$^{-3}$, $F(000)$ = 359.91, $\lambda$(Mo K$\alpha$) = 0.71073 Å, $\mu$ = 7.50 cm$^{-1}$, and $T$ = 291 K. Final $R$ = 0.0226 for 2873 unique observed $[F_o > 2\sigma(F_o)]$ X-ray diffractometer data. The molybdenum atom is surrounded by the six equidistant terminal carbon atoms of three 2,3-dimethyl-1,3-butadiene ligands in a trigonal-prismatic geometry. The ligands are all cisoid. The internal C–C bond lengths are slightly shorter than the terminal C–C bond lengths of the ligands in the complex. The bonding and structure of the complex were confirmed by extended Hükel molecular orbital calculations.

The homoleptic transition-metal butadiene complex tris(1,3-butadiene)molybdenum(0) (1) was first synthesized by cocondensation of the metal atom with 1,3-butadiene at 77 K.[2] The ligand in complex 1 adopts the s-cis conformation and $\eta^4$-coordination mode. Although the preliminary results of the X-ray crystal structure of 1 showed it to be trigonal prismatic rather than octahedral,[3,4] the full details of the structural data have never been reported. The C–C bond lengths in 1 determined by X-ray crystalllgraphy showed unusually large internal C–C bond lengths compared to the terminal C–C bonds.[3,4] This is a trend opposite to that of the theoretical prediction based on extended Hükel molecular calculations.[4] It was suggested that the unusual C–C bond lengths determined for 1 may be due to the fact that the thermal parameters associated with the butadiene carbon atoms in the complex are large and anisotropic.[4]

Recently, we have synthesized tris(2,3-dimethyl-1,3-butadiene)molybdenum(0) (2), analogous to the 1,3-butadiene complex, and found that 2 is remarkably more stable than 1.[5] Complex 2 is stable in air for periods up to 3 months at room temperature. This stability of 2 has made it possible to determine the crystal structure of a tris(butadiene) type complex very accurately. In this note we report the details of the X-ray crystal structure and extended Hükel calculations on 2. As far as we know, this is the first full report on the crystal structure of the homoleptic tris(butadiene) transition-metal complex.

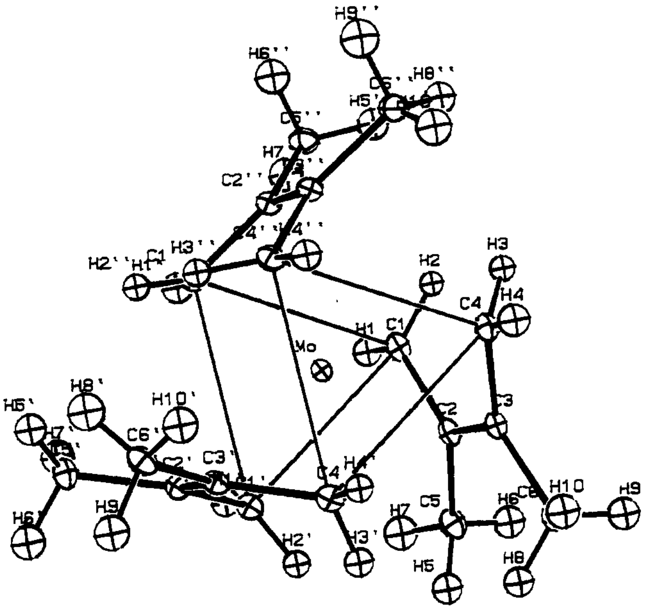

Figure 1. Perspective view of complex 2 with the numbering scheme. The $\bar{6}$-fold axis passing through the Mo atom is almost normal to the paper.

**Table I. Selected Interatomic Distances (Å) and Angles (deg) for $(C_8H_{10})_3Mo$ with Estimated Standard Deviations in Parentheses**

| | | | |
|---|---|---|---|
| | Distances | | |
| Mo–C(1) | 2.249 (3) | C(2)–C(5) | 1.505 (4) |
| Mo–C(4) | 2.247 (3) | C(3)–C(6) | 1.506 (5) |
| Mo–C(2) | 2.393 (3) | C(1)–H(1) | 0.887 (32) |
| Mo–C(3) | 2.396 (3) | C(1)–H(2) | 0.976 (26) |
| Mo–H(1) | 2.829 | C(4)–H(3) | 0.960 (26) |
| Mo–H(2) | 2.691 | C(4)–H(4) | 0.931 (32) |
| Mo–H(3) | 2.691 | C(5)–H(5) | 1.005 (31) |
| Mo–H(4) | 2.858 | C(5)–H(6) | 0.895 (34) |
| C(1)–C(4) | 2.719 (4) | C(5)–H(7) | 0.911 (38) |
| C(1)–C(2) | 1.433 (4) | C(6)–H(8) | 0.970 (29) |
| C(2)–C(3) | 1.400 (4) | C(6)–H(9) | 0.938 (33) |
| C(3)–C(4) | 1.436 (4) | C(6)–H(10) | 0.910 (33) |
| | Angles | | |
| C(1)–Mo–C(4) | 74.4 (1) | H(3)–C(4)–H(4) | 111.6 (2.5) |
| C(2)–Mo–C(3) | 34.0 (1) | C(2)–C(5)–H(5) | 115.9 (1.9) |
| C(1)–C(2)–C(3) | 117.5 (3) | C(2)–C(5)–H(6) | 106.8 (2.1) |
| C(2)–C(3)–C(4) | 117.3 (3) | C(2)–C(5)–H(7) | 114.6 (2.3) |
| C(1)–C(2)–C(5) | 120.5 (3) | H(5)–C(5)–H(6) | 109.1 (2.9) |
| C(4)–C(3)–C(6) | 121.4 (3) | H(5)–C(5)–H(7) | 95.5 (2.8) |
| C(2)–C(3)–C(6) | 121.4 (3) | H(6)–C(5)–H(7) | 114.8 (3.1) |
| C(3)–C(2)–C(5) | 122.0 (3) | C(3)–C(6)–H(8) | 111.3 (2.2) |
| C(2)–C(1)–H(1) | 117.7 (1.8) | C(3)–C(6)–H(9) | 114.0 (2.0) |
| C(2)–C(1)–H(2) | 119.9 (2.0) | C(3)–C(6)–H(10) | 109.0 (1.9) |
| H(1)–C(1)–H(2) | 109.2 (2.5) | H(8)–C(6)–H(9) | 102.2 (2.6) |
| C(3)–C(4)–H(3) | 115.0 (1.7) | H(8)–C(6)–H(10) | 103.8 (2.9) |
| C(3)–C(4)–H(4) | 118.9 (2.0) | H(9)–C(6)–H(10) | 115.8 (2.7) |

## Results and Discussion

**Crystal Structure of Complex 2.** The molecular structure and atom-labeling scheme for 2 are shown in Figure 1. The bond lengths and angles for 2 are given in Table I. The molybdenum atom is surrounded by the six equidistant terminal carbon atoms of three 2,3-dimethyl-1,3-butadiene ligands in a trigonal-prismatic coordination. As shown in a perspective drawing of the coordination geometry (Figure 1), complex 2 possesses an

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[2] Skell, P. S.; Van Dam, E. M.; Silvon, M. P. *J. Am. Chem. Soc.* 1974, *96*, 626.

[3] Skell, P. S.; McGlinchey, M. J. *Angew. Chem., Int. Ed. Engl.* 1975, *14*, 195.

[4] Green, J. C.; Kelly, M. R.; Grebenik, P. D.; Briant, C. E.; McEvoy, N. A.; Mingos, D. M. P. *J. Organomet. Chem.* 1982, *228*, 239.

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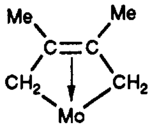
exact $\bar{6}$-fold ($C_{3h}$) symmetry. Therefore, the basic molecular coordination geometry is very similar to those of complex 1,[3] tris(methyl vinyl ketone)tungsten,[6] and tris(*o*-xylidene)tungsten.[7] It is defined by a trigonal prism of base 3.100 Å and height 2.712 Å with six terminal C atoms [C(1), C(4), C(1′), C(4′), C(1″), C(4″)] and six internal C atoms [C(2), C(3), C(2′), C(3′), C(2″), C(3″)] in this complex. The three 2,3-dimethyl-1,3-butadiene ligands themselves are virtually planar to within 0.015 Å and make an average angle of 60° with the rectangular faces of the trigonal prism. The average dimensions of the prism are slightly longer than those found for tris(methyl vinyl ketone)tungsten.[6]

The distances of the central Mo atom to the terminal C atoms range from 2.232 (3) to 2.249 (3) Å with an average of 2.243 Å. The average bond distance from the Mo atom to the terminal C atoms is 0.15 Å shorter than the average of 2.394 Å of the bond distances from the Mo atom to the internal C atoms, which are in the range 2.389 (3)–2.397 (3) Å. The bond distances and angles in the three 2,3-dimethyl-1,3-butadiene ligands are in excellent agreement one another. The distances C(1)–C(2) and C(3)–C(4) vary from 1.421 (4) to 1.436 (4) Å with an average distance of 1.431 Å, and the distances C(2)–C(3) vary from 1.397 (4) to 1.400 (4) Å with an average distance of 1.399 Å. That the internal C(2)–C(3) bond length is slightly shorter than the terminal C(1)–C(2) (or C(3)–C(4)) bond length is consistent with the results of the theoretical calculation, which will be discussed later. It is noted that the C–C bond lengths are alternated long–short–long along the coordinated C(1)–C(2)–C(3)–C(4) backbone. This variation of the C–C bond lengths in 2 is opposite to that in 1[3,4] which is short–long–short. The trends of the variations in the Mo–C, and C–C bond lengths would suggest that the bonding mode between the Mo atom and the ligands is better described by I rather than II, as in the structure of tris(methyl vinyl ketone)tungsten.[6] The average of the C(1)–Mo–C(4) bond angles is 74.4°. The dihedral angle of 90° between the trigonal plane of C(1)–Mo–C(4) and the diene plane of C(1)–C(2)–C(3)–C(4) is larger than that of 1, suggesting that the bonding mode I is more favorable for 2 than for 1.



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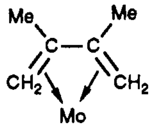

II

All intermolecular contacts appear normal. The molybdenum atoms are well separated, with nearest neighbors being 7.0600 (3) Å apart. The closest intermolecular approach is 2.567 Å for H(5)–H(6″) (1 + *x*, *y*, *z*) and that between non-H atoms is 3.748 Å for C(6)–C(6″) (1 + *x*, 1 − *y*, −*z*). This means that the molecules are held in the crystal by the weak van der Waals forces.

**Molecular Orbital Analysis of Complex 2.** Extended Hückel calculations[8] were carried out on complex 2, in $C_{3h}$ symmetry, where Mo–C and C–C bond lengths have been averaged from the experimental structure. Our approach in developing the molecular orbitals of this complex is to allow the linear combinations of the important π orbitals of 2,3-dimethylbutadiene to interact with metal orbitals. Figure 2 shows the orbital interaction diagram for complex 2. A similar diagram for complex 1 has been derived elsewhere.[4] Therefore, we shall only briefly note the salient features of the analysis. The orbitals of the $(C_6H_{10})_3$ fragment are formed by the linear combinations of π orbitals in 2,3-dimethyl-1,3-butadiene, which are shown on the left side of Figure 2. We have labeled them in terms of $C_{3h}$ molecular symmetry. The 1e″ fragment orbitals on the ligand overlap with metal $d_{yz}$ and $d_{xz}$ orbitals (the coordinate system is shown at the top of Figure 2). This produces the stabilized 1e″ set. The more important interactions are the following. The empty 2e′ set on the ligand interacts with metal $d_{xy}$ and $d_{x^2-y^2}$ orbitals to form the 2e′ molecular set. The 2e′ MO is delocalized with 60% ligand and 32% metal character. The lower 2a′ MO is also produced by the metal $d_{z^2}$ and ligand 2a′ fragment orbitals. A total of 0.79 electrons are transferred from metal to ligand by this interaction. The above two interactions involve back-donation of electron density from the filled metal orbitals to empty ligand orbitals. Consequently a large amount of electron density is transferred from the metal to the ligand. This is reflected in the charge of +1.89 calculated for Mo metal.

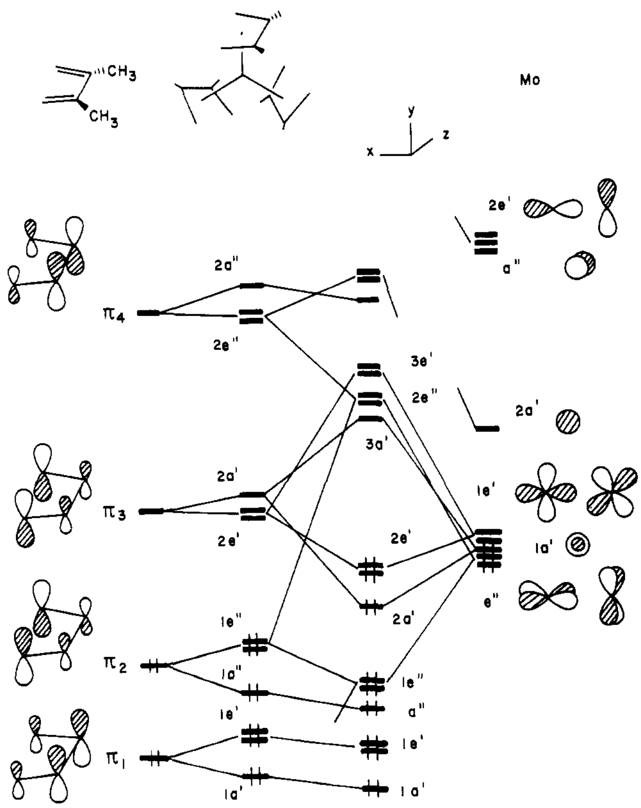

**Figure 2.** Orbital interaction diagram for complex 2.

**Table II. Overlap Populations of Selected Bonds**

| | overlap populations | | | overlap populations | |
|---|---|---|---|---|---|
| bonds | free ligands | complex 2 | bonds | free ligands | complex 2 |
| C(1)–C(2) | 1.1812 | 1.0011 | Mo–C(1) | | 0.1687 |
| C(2)–C(3) | 0.9536 | 1.0510 | Mo–C(2) | | 0.1007 |

In order to investigate the bonding between the Mo atom and the 2,3-dimethyl-1,3-butadiene ligands in more detail, we performed an overlap population analysis. Table II gives the overlap populations of the selected bonds. The computed overlap population for the terminal C–C bond [C(1)–C(2) or C(3)–C(4)] in free 2,3-dimethyl-1,3-butadiene

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[6] Moriarty, R. E.; Richard, D. E.; Bau, R. *J. Chem. Soc., Chem. Commun.* **1972**, 1242.

[7] Lappert, M. F.; Raston, C. L.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Chem. Commun.* **1981**, 485.

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**Table III. Crystal Data and Summary of Data Collection Parameters for $(C_6H_{10})_3Mo$**

| | |
|---|---|
| formula | $C_{18}H_{24}Mo$ |
| fw | 336.33 |
| *a*, Å | 9.544 |
| *b*, Å | 12.312 |
| *c*, Å | 7.060 |
| α, deg | 97.66 (2) |
| β, deg | 90.38 (2) |
| γ, deg | 99.07 (1) |
| *V*, Å$^3$ | 812.5 |
| *Z* | 2 |
| space group | $P\bar{1}$ |
| density, g cm$^{-3}$ | 1.375 |
| cryst shape dimens, mm | 0.2 × 0.25 × 0.3 |
| radiation (λ, Å) | Mo Kα (0.71073) from graphite monochromator |
| temp, K | 291 |
| μ, cm$^{-1}$ | 7.5 |
| scan range, deg | $0.8 + 0.14 \tan\theta$ |
| scan mode | $\omega$–$2\theta$ |
| $2\theta$ limits, deg | 3.0–50.0 |
| no. of unique data measd | 2963 |
| no. of unique data used $[F_o > 2\sigma(F_o)]$ | 2873 |
| *h*,*k*,*l* | $-11 \le h \le 11$, $0 \le k \le 14$, $-8 \le l \le 8$ |
| intensity check reflcn | $\bar{2}34$ |
| $R = (\sum\lvert F_o - F_c\rvert)/\sum F_o$ | 0.023 |
| $R_w = (\sum\lvert F_o - F_c\rvert^2/\sum F_o^2)^{1/2}$ | 0.026 |
| tot. no. of params refined | 202 |

**Table IV. Fractional Atomic Coordinates (×10$^4$) and Equivalent Isotropic Thermal Parameters $U_{eq}$ (Å$^2$ × 10$^4$)[a] for $(C_6H_{10})_3Mo$ with Estimated Standard Deviations in Parentheses**

| atom | *x* | *y* | *z* | $U_{eq}$ |
|---|---|---|---|---|
| Mo | 3318 (0) | 2303 (0) | 2431 (0) | 280 (1) |
| C(1) | 3682 (3) | 3489 (2) | 5166 (4) | 434 (16) |
| C(2) | 2438 (3) | 3785 (2) | 4359 (4) | 419 (16) |
| C(3) | 2511 (3) | 4054 (2) | 2493 (4) | 406 (15) |
| C(4) | 3825 (3) | 4003 (2) | 1536 (4) | 432 (16) |
| C(5) | 1108 (4) | 3789 (3) | 5488 (4) | 565 (19) |
| C(6) | 1252 (4) | 4361 (3) | 1514 (4) | 543 (19) |
| C(1′) | 1450 (3) | 1420 (2) | 3804 (4) | 409 (15) |
| C(2′) | 1755 (3) | 575 (2) | 2339 (4) | 388 (15) |
| C(3′) | 1817 (3) | 832 (2) | 470 (4) | 375 (14) |
| C(4′) | 1582 (3) | 1925 (2) | 197 (4) | 417 (15) |
| C(5′) | 1976 (3) | −544 (2) | 2802 (4) | 521 (18) |
| C(6′) | 2133 (3) | 13 (3) | −1192 (4) | 470 (17) |
| C(1″) | 4663 (3) | 1246 (2) | 3750 (4) | 434 (15) |
| C(2″) | 5682 (3) | 2158 (2) | 3369 (4) | 403 (15) |
| C(3″) | 5739 (3) | 2417 (2) | 1498 (4) | 407 (15) |
| C(4″) | 4754 (3) | 1751 (2) | 117 (4) | 411 (15) |
| C(5″) | 6668 (3) | 2823 (3) | 4932 (5) | 540 (18) |
| C(6″) | 6773 (3) | 3362 (3) | 927 (5) | 546 (19) |
| H(1) | 3655 (32) | 3264 (26) | 6311 (43) | 585 (92) |
| H(2) | 4585 (28) | 3967 (23) | 5045 (40) | 409 (80) |
| H(3) | 4654 (29) | 4381 (23) | 2261 (39) | 429 (81) |
| H(4) | 3875 (32) | 4117 (26) | 258 (44) | 629 (95) |
| H(5) | 193 (34) | 3507 (27) | 4746 (46) | 663 (95) |
| H(6) | 1106 (34) | 4492 (29) | 6017 (46) | 741 (103) |
| H(7) | 977 (36) | 3280 (30) | 6322 (49) | 848 (110) |
| H(8) | 362 (31) | 3889 (25) | 1691 (42) | 558 (88) |
| H(9) | 1257 (32) | 5127 (27) | 1817 (43) | 651 (93) |
| H(10) | 1328 (34) | 4261 (28) | 221 (47) | 692 (100) |
| H(1′) | 1501 (31) | 1267 (25) | 4975 (41) | 547 (88) |
| H(2′) | 636 (29) | 1789 (24) | 3571 (39) | 477 (82) |
| H(3′) | 713 (30) | 2157 (25) | 709 (41) | 522 (86) |
| H(4′) | 1712 (29) | 2110 (23) | −970 (39) | 449 (79) |
| H(5′) | 2592 (33) | −858 (26) | 2092 (45) | 629 (94) |
| H(6′) | 1049 (35) | −1066 (28) | 2619 (47) | 768 (105) |
| H(7′) | 2214 (35) | −531 (28) | 3966 (48) | 740 (102) |
| H(8′) | 2782 (36) | −429 (29) | −892 (48) | 792 (107) |
| H(9′) | 1229 (33) | −438 (27) | −1695 (44) | 685 (96) |
| H(10′) | 2571 (34) | 378 (28) | −2098 (45) | 695 (100) |
| H(1″) | 4593 (32) | 1156 (27) | 4964 (46) | 664 (98) |
| H(2″) | 4528 (28) | 556 (23) | 2911 (39) | 449 (79) |
| H(3″) | 4578 (28) | 978 (23) | 44 (39) | 444 (78) |
| H(4″) | 4727 (30) | 1983 (25) | −1072 (40) | 534 (87) |
| H(5″) | 6885 (33) | 3603 (28) | 4845 (45) | 677 (99) |
| H(6″) | 7594 (36) | 2596 (30) | 4886 (48) | 819 (109) |
| H(7″) | 6267 (35) | 2678 (29) | 6065 (47) | 820 (106) |
| H(8″) | 6984 (32) | 3988 (27) | 1901 (45) | 633 (96) |
| H(9″) | 7681 (37) | 3104 (30) | 646 (49) | 905 (114) |
| H(10″) | 6423 (35) | 3596 (29) | −130 (48) | 790 (107) |

[a] $U_{eq} = {}^1/_3\sum_{ii}U_{ii}$. The thermal parameters for the hydrogen atoms are isotropic.

is larger than that for the central C(2)–C(3) bond. However, the values for complex **2** display the opposite trend, i.e. 1.0011 and 1.0510 for the terminal C(1)–C(2) and central C(2)–C(3) bonds, respectively. This is consistent with the experimental structure, where the terminal C–C bond length of 1.431 Å is longer than the central C–C distance of 1.399 Å, as already mentioned. Our structural data are different from the structural data for complex **1** reported previously, where the terminal C–C bond is shorter than the central C–C bond by about 0.22 Å.[3,4] We can easily rationalize our results by the fact that the ligand orbitals 2a′ and 2e′ receive substantial electron density via back-donation. These fragment orbitals are linear combinations of the $\pi_3$ orbital, shown on the left side of Figure 2. Notice that the terminal C–C bond is antibonding between the p orbitals on carbon atoms, while the central bond is bonding. Therefore, occupation of this orbital by back-donation reinforces the central bond and weakens the terminal bonds.

Another interesting point we have investigated is the unequal Mo–C bond lengths. In the experimental structure presented in the previous section, the Mo–C(1) (terminal) distance of 2.243 Å is shorter than the Mo–C(2) (central) distance of 2.394 Å. The unequal bond distances between central metal and carbon atoms have been also observed and discussed in other butadiene complexes.[9] Our calculations on complex **2** show the Mo–C(1) (terminal) overlap population of 0.1687 to be much larger than the Mo–C(2) (central) one of 0.1007 (see Table II). The major orbitals that participate in the interactions between metal and ligand fragments are of the $\pi_2$ and $\pi_3$ types. In these orbitals the contribution of the p atomic orbitals on terminal C atoms is larger than that on central C atoms. This feature is shown on the left side of Figure 2 by orbital size. This polarization in $\pi_2$ and $\pi_3$ creates the larger overlap with the corresponding metal orbitals and results in shorter bond distances.

## Experimental Section

Metal atom cocondensation with the organic substrate[2] was employed to synthesize complex **2**. The cocondensation of Mo metal vapor with 2,3-dimethyl-1,3-butadiene at 77 K produces a yellow matrix.[5] After the condensate was warmed to room temperature and the excess organic substrate was removed, the brown solid residual was collected in the nitrogen atmosphere. Yellow crystals of **2** were obtained by sublimation (10$^{-4}$ Torr and 70–100 °C) and then by recrystallization of the residue from *n*-hexane. The yield is about 60% based on the amount of deposited Mo atoms. Elemental analysis and spectral (IR and $^1$H NMR) data of the product agreed well with those reported previously for **2**.[5] Elemental analysis was performed by the Analytical Laboratory of the Korea Institute of Chemical Technology, Taejon, Korea.

**Crystallographic Analysis of Complex 2.** Preliminary cell constants and space group $P\bar{1}$ for this crystal were determined

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[9] (a) Erker, G.; Wicher, J.; Engel, K.; Rosenfeldt, F.; Dietrich, W.; Krüger, C. *J. Am. Chem. Soc.* **1980**, *102*, 6346. (b) Yasuda, H.; Tatsumi, K.; Okamoto, T.; Mashima, K.; Lee, K.; Nakamura, A.; Kai, Y.; Kanehisa, N.; Kasai, N. *J. Am. Chem. Soc.* **1985**, *107*, 2410. (c) Yamamoto, H.; Yasuda, H.; Tatsumi, K.; Lee, K.; Nakamura, A.; Chen, J.; Kai, Y.; Kasai, N. *Organometallics* **1989**, *8*, 105.

from the X-ray photographic method using Weissenberg and precession cameras, where a quick adjustment method for the crystal orientation was used.[10] A crystal of 2 was mounted on a computer-controlled Enraf-Nonius CAD-4 X-ray diffractometer with graphite-monochromated Mo K$\alpha$ radiation. The cell dimensions and the orientation matrix were determined by least-squares calculations based on the setting angles of 25 reflections with $6.67 < \theta < 14.30°$. The crystallographic parameters are summarized in Table III. The intensities were collected at room temperature up to $\theta = 25°$ corresponding to $(\sin\theta)/\lambda = 0.59$ Å$^{-1}$ with $\omega$–$2\theta$ scan mode and $\omega$ scan width $(0.8 + 0.14 \tan\theta)°$. One standard reflection ($\bar{2}34$) was monitored after every $1^1/_2$ h of exposure and showed no apparent variation during data collection. The orientation matrix was checked every 100 reflections.

The intensities were corrected for Lorentz–polarization but not for absorption or extinction. Atomic scattering factors $f'$ and $f''$ were taken from ref 11.

The structure was solved by using Patterson and direct methods,[12] which revealed the position of the Mo atom. The remaining heavy atoms and also all hydrogen atoms were located in successive difference Fourier syntheses. All heavy atoms were refined anisotropically, but H atoms were refined isotropically. The structure was refined by using full-matrix least-squares methods with the SHELX program.[13] All calculations were carried out on a MV/10000 computer at the computer center of Chungnam National University. Table IV lists the final atomic parameters and their estimated standard deviations. The drawing of the molecular geometry was made with the ORTEP program.[14]

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**Registry No.** 2, 104083-32-1.

**Supplementary Material Available:** Tables listing complete interatomic distances and angles, anisotropic thermal parameters, isotropic thermal parameters for hydrogen atoms, and least-squares planes and deviations of individual atoms from the planes and a figure showing a unit cell packing diagram as viewed down the *c* axis (8 pages); a table of observed and calculated structure factors (12 pages). Ordering information is given on any current masthead page.

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# Unexpected Synthesis of CpIr($\eta^4$-$C_5H_6$) and a $^1$H and $^{13}$C NMR Comparison with Its Cobalt and Rhodium Congeners

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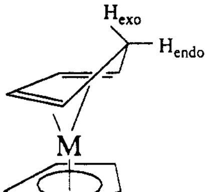
*Summary:* The complex CpIr($\eta^4$-$C_5H_6$) was prepared unexpectedly in up to 37% yield from the reaction of $[(\eta^2\text{-}C_8H_{14})_2IrCl]_2$ and thallium cyclopentadienide. The $^1$H NMR resonance for the exo methylene proton of the coordinated cyclopentadiene ring is shifted well downfield of what is observed for the analogous Co and Rh complexes. Complete proton and carbon NMR assignments for all three complexes were determined by $^1$H–$^{13}$C correlation experiments. The $H_{exo}/H_{endo}$ assignment for CpIr($\eta^4$-$C_5H_6$) was supported by a $^1$H–$^1$H NOE experiment and by the preparation of CpIr($\eta^4$-$C_5H_5D$) from $[Cp_2Ir^+]$.

As part of our recent work involving Ir(I) olefin complexes,[1] we attempted to prepare the cyclooctene complex CpIr($\eta^2$-$C_8H_{14}$)$_2$[2] from the reaction of $[(\eta^2\text{-}C_8H_{14})_2IrCl]_2$ with thallium cyclopentadienide in diethyl ether. However, the isolated product proved to be the cyclopentadiene complex CpIr($\eta^4$-$C_5H_6$), which had been reported by Fischer in 1959.[3] Although the use of $^1$H NMR spectroscopy to characterize the cyclopentadiene complexes CpM($\eta^4$-$C_5H_6$), M = Co, Rh,[4] constituted one of the earliest applications of this technique in organometallic chemistry, the spectrum of CpIr($\eta^4$-$C_5H_6$) has not been previously reported. Coordination of the cyclopentadiene ring to a metal center places the methylene protons into separate "exo" and "endo" positions (see I), and interest in these compounds relates to the differential physical and chemical properties of the C–$H_{exo}$ and C–$H_{endo}$ bonds. For the purposes of comparison we present $^1$H and $^{13}$C NMR data for the entire set of congeneric complexes CpM($\eta^4$-$C_5H_6$), M = Co, Rh, Ir, obtained with modern one- and two-dimensional NMR techniques.



I

## Experimental Section

**General Data.** All synthetic manipulations were conducted under an atmosphere of nitrogen by using standard Schlenk techniques. CpCo($\eta^4$-$C_5H_6$) and CpRh($\eta^4$-$C_5H_6$) were prepared by the method of Green et al.[4] $[(\eta^2\text{-}C_8H_{14})_2IrCl]_2$[5] and thallium

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