Preparation of Molybdenum–η^3-Pentadienyl Complexes: Structural Characterization of a Delocalized Pentadienyl Ligand in Anti-η^3 Geometry

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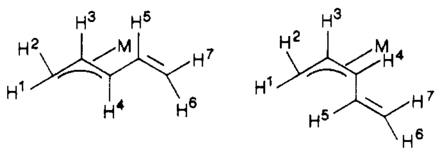
Oxidative addition of 1-halopenta-2,4-diene to $Mo(CO)_3(CH_3CN)_3$ gives $Mo(CO)_2(CH_3CN)_2(\eta^3\text{-}C_5H_7)X$ (X = Cl (**1**), Br (**2**)). Addition of bis(diphenylphosphino)ethane (dppe) and bis(dimethylphosphino)ethane (dmpe) to **1** and **2** gives $Mo(dppe)(CO)_2(\eta^3\text{-}C_5H_7)X$ (X = Cl (**3**); Br (**4**)) and $Mo(dmpe)(CO)_2(\eta^3\text{-}C_5H_7)X$ (X = Cl (**5**), Br (**6**)), respectively, in high yields. The pentadienyl ligands of **3**, **5**, and **6** exist in syn-η^3 geometries whereas those of **4** exist in the anti-η^3 form exclusively. The vinyl bond length in the anti-η^3 isomer is remarkably long, 1.378 (14) Å. Factors affecting the dienyl ligand structures are discussed on the basis of crystallographic data for **3** and **4**. Reaction of **1** and **2** with alkaline-metal salts of cyclopentadienide, indenide, and fluorenide (LiC_5H_5, LiC_9H_7, and $NaC_{13}H_9$) gave compounds of the type $Mo(CO)_2(\eta^3\text{-}C_5H_7)(\eta^5\text{-}Cp')$ (Cp' = C_5H_5 (**7**), C_9H_7 (**8**), $C_{13}H_9$ (**9**)) in good yields. Molecular structures of **2**, **3**, and **4** were determined. Crystallographic data for **2**: space group $P2_12_12_1$, $a = 7.0481$ (1) Å, $b = 12.612$ (2) Å, $c = 16.028$ (2) Å, $Z = 4$, $R_F = 2.4\%$, $R_w = 2.6\%$. For **3**: space group $P\bar{1}$, $a = 10.194$ (1) Å, $b = 11.139$ (2) Å, $c = 16.176$ (2) Å, $\alpha = 93.77$ (1)°, $\beta = 98.10$ (1)°, $\gamma = 106.33$ (1)°, $Z = 2$, $R_F = 3.0\%$, $R_w = 3.0\%$. For **4**: space group $C2/c$, $a = 20.804$ (7) Å, $b = 9.418$ (3) Å, $c = 31.035$ (6) Å, $\beta = 91.54$ (2)°, $Z = 8$, $R_F = 3.9\%$, $R_w = 4.4\%$.

Introduction

The chemistry of pentadienyl–transition-metal complexes has attracted considerable attention in recent years.[1-4] The presence of appropriate reagents such as the pentadienyltin compound $(C_5H_7)Sn(CH_3)_3$[5] and pentadienyl–alkaline-metal salts $[2,4\text{-}(CH_3)_2C_5H_7]M$ (M = Na, K)[6] has promoted the rapid development of this field. In our laboratory, we have used 1-halopenta-2,4-diene for the preparation of these compounds. The 1-halopenta-2,4-diene is an interesting reagent because it can be oxidatively added to low-valent metal complexes. In our previous papers,[7] we have reported the preparation of metal–pentadienyl complexes from the reaction between metal carbonyl anions and 1-halopenta-2,4-diene. In a continuing effort to expand the use of these halides as synthetic reagents, we report here the synthesis and structural chemistry of molybdenum–η^3-pentadienyl compounds derived from oxidative addition of 1-halopentadiene to low-valent molybdenum complexes.

Chart I



syn-η^3 anti-η^3

Table I. Bond Distances (Å) and Angles (deg) for 2

Mo-Br	2.6263 (10)	C(2)-C(3)	1.394 (12)
Mo-C(1)	2.335 (7)	C(3)-C(4)	1.447 (11)
Mo-C(2)	2.221 (7)	C(4)-C(5)	1.293 (12)
Mo-C(3)	2.422 (8)	C(6)-O(1)	1.150 (10)
Mo-C(6)	1.955 (8)	C(7)-O(2)	1.166 (10)
Mo-C(7)	1.946 (8)	C(8)-C(9)	1.432 (10)
Mo-N(1)	2.239 (6)	C(8)-N(1)	1.128 (10)
Mo-N(2)	2.238 (6)	C(10)-C(11)	1.450 (11)
C(1)-C(2)	1.406 (12)	C(10)-N(2)	1.114 (10)
Br-Mo-C(1)	150.95 (21)	N(1)-Mo-N(2)	76.89 (23)
Br-Mo-C(2)	163.63 (21)	C(6)-Mo-C(7)	79.7 (3)
Br-Mo-C(3)	148.50 (19)	C(6)-Mo-N(1)	170.7 (3)
Br-Mo-C(6)	89.02 (22)	C(6)-Mo-N(2)	99.9 (3)
Br-Mo-C(7)	87.47 (22)	C(7)-Mo-N(1)	102.0 (3)
Br-Mo-N(1)	81.91 (15)	C(7)-Mo-N(2)	170.5 (3)
Br-Mo-N(2)	83.01 (16)	C(1)-C(2)-C(3)	117.2 (7)
C(2)-C(3)-C(4)	122.9 (7)	C(3)-C(4)-C(5)	124.6 (8)
Mo-C(6)-O(1)	176.7 (7)	Mo-C(7)-O(2)	176.0 (6)

Recent structural studies[8,9] have shown that a η^3-pentadienyl ligand can bond to the metal in two geometries, i.e. syn-η^3 and anti-η^3 configurations. In a few cases, syn-η^3

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(1) For recent reviews of transition-metal acyclic pentadienyl complexes, see: (a) R. D. Ernst, R. D. *Acc. Chem.* Res. **1985**, *15*, 56. (b) Yasuda, H.; Nakamura, A. *J. Organomet. Chem.* **1985**, *285*, 15. (c) Powell, P. *Adv. Organomet. Chem.* **1986**, *26*, 125.

(2) (a) Kralik, M. S.; Rheingold, A. L.; Ernst, R. D. *Organometallics* **1987**, *6*, 2612. (b) Stahl, L.; Hutchinson, J. P.; Wilson, R. D.; Ernst, R. D. *J. Am. Chem. Soc.* **1985**, *107*, 5016. (c) Kralik, M. S.; Hutchinson, J. P.; Ernst, R. D. *Ibid.* **1985**, *107*, 8296.

(3) (a) Bleeke, J. R.; Rauscher, D. L.; Moore, D. A. *Organometallics* **1987**, *6*, 2614. (b) Bleeke, J. R.; Peng, W.-J. *Ibid.* **1987**, *6*, 1576. (c) Bleeke, J. R.; Hays, M. K., *Ibid.* **1987**, *6*, 486. (d) Bleeke, J. R.; Peng, W.-J. *Ibid* **1987**, *6*, 1576.

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(5) Seyferth, D.; Goldman, E. W.; Pornet, J. J. *J. Organomet. Chem.* **1981**, *208*, 189. (b) Paz-Sandoual, M. A.; Powell, P. *Ibid.* **1981**, *219*, 81. (c) Paz-Sandoual, M. A.; Powell, P. *Ibid* **1983**, *252*, 205.

(6) Yasuda, H.; Yamauchi, M.; Nakamura, A.; Sei, T.; Kai, Y.; Yasuda, N.; Kasai, N. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1089.

(7) Lee, G.-H.; Peng, S.-M.; Lush, S.-F.; Liao, M.-Y.; Liu, R.-S. *Organometallics* **1987**, *6*, 2094. (b) Lee, T.-W.; Liu, R.-S. *Ibid* **1988**, *7*, 878. (c) Lee, G.-H.; Peng, S.-M.; Lush, S.-F.; Liao, M.-Y.; Liu, R.-S. *Ibid.* **1986**, *5*, 2378. (d) Lush, S.-F.; Liu, R.-S. *Ibid.* **1986**, *5*, 1908.

(8) For syn-η^3 compounds, for example, see: (a) Bleeke, J. R.; Kotyr, J. J. *Organometallics* **1985**, *4*, 194. (b) Bleeke, J. R.; Hays, M. K. *Ibid.* **1984**, *3*, 506. (c) Cheng, C.-C.; Liu, R.-S. *J. Organomet. Chem.* **1986**, *308*, 237. (d) Lee, G.-H.; Peng, S.-M.; Liao, M.-Y.; Liu, R.-S. *Ibid.* **1986**, *312*, 113.

(9) For structural reports of anti-η^3 pentadienyl complexes, see ref 4a and: (a) Bleeke, J. R.; Peng, W. J. *Organometallics* **1984**, *3*, 1422. (b) Bleeke, J. R.; Donaldson, A. J.; Peng, W.-J. *Ibid.* **1988**, *7*, 33.

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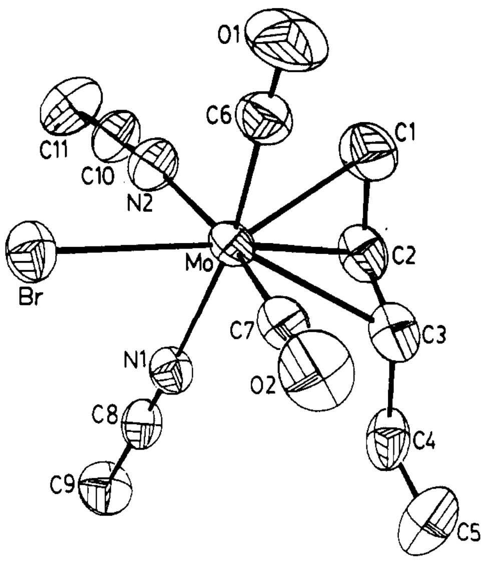

Figure 1. ORTEP drawing of the molecule 2.

and anti-η^3 isomers equilibrate with one another in solution.[8d,9] Studies have shown that the natures of the ligand and the metal determine the configurations of the dienyl ligands.[10] Nevertheless, up to the present, it is still unclear what factors control the ligand configuration. The molecular structures of $Mo(dppe)(CO)_2(\eta^3-C_5H_7)Cl$ (3) and $Mo(dppe)(CO)_2(\eta^3-C_5H_7)Br$ (4) in which the $\eta^3-C_5H_7$ ligands are in syn-η^3 and anti-η^3 geometries, respectively, provide a rare opportunity to investigate the nature of the metal–η^3-pentadienyl bonding. The ionic radii[11] of Cl^- (1.67 Å) and Br^- (1.82 Å) anions are comparable, so variation in metal coordination geometries can be minimized.

Results and Discussion

In a recent review on acyclic pentadienyl–metal complexes, Powell[1c] reported that 1-bromo and 1-chloro-2,4-hexadiene reacted with $Mo(CO)_3(CH_3CN)_3$ to give $Mo(CO)_2(CH_3CN)_2(\eta^3$-2,4-hexadien-1-yl)X (X = Cl, Br). Following this preparation, we obtained a high yield of $Mo(CO)_2(CH_3CN)_2(\eta^3$-pentadien-1-yl)X (X Cl = (1), Br (2)), from the reaction between $Mo(CO)_3(CH_3CN)_3$ and 1-halopenta-2,4-diene. The compounds were obtained in red rodlike crystals after recrystallization from a saturated CH_3CN solution. ^1H NMR spectra in CD_3CN show that the pentadienyl ligands of these two compounds assume a syn-η^3 configuration as revealed by the following coupling constants $J_{13} = J_{34} \simeq 10$ Hz and $J_{23} = 6$–7 Hz. Since no crystallographic data were available for this class of compounds including the parent allyl complex, we have performed an X-ray diffraction study of 2.

An ORTEP drawing of the molecular structure is shown in Figure 1, and the bond distances and angles are shown in Table I. The coordination geometry about the molybdenum atom is approximately an octahedron with two carbonyls, two CH_3CN ligands, an allyl ligand, and a bromide atom occupying the six coordination sites. The two carbonyls and two CH_3CN ligands form an equatorial plane (Mo, N(1), N(2), C(6), and C(7); maximum deviation of 0.205 (9) Å). The bromide atom and allyl group are mutually trans in axial positions. Because of the steric effect of the large allyl group, the two CH_3CN molecules tilt toward the bromide atom with the bond angles N(1)–Mo–Br = 81.9 (15)° and N(2)–Mo–Br = 83.01 (17)°. The pentadienyl group is planar with a dihedral angles between the vinylic plane (C(3), C(4), C(5)) and the allylic plane (C(1), C(2), C(3)) of 9.5 (13)°. The carbon atoms C(1), C(2), C(3), and C(4) of the pentadienyl ligand, however, do form a least-squares plane with a deviation about 0.016 (11) Å while the C(5) atom lies out of this plane at a distance of 0.129 (17) Å. The pentadienyl ligand has a staggered orientation with respect to the Br–C(6)–C(7) face; i.e., the mouth of the allyl group faces the two carbonyl ligands. The molybdenum atom bonds asymmetrically to the allylic moiety with Mo–C(1) (2.335 (7) Å), Mo–C(2) (2.221 (7) Å), and Mo–C(3) (2.422 (8) Å). The bond lengths C(8)–N(1) (1.128 (10) Å) and C(10)–N(2) (1.114 (11) Å) are characteristic of a normal C≡N triple bond (1.16 Å).[11] The Mo–N(2) (2.238 (6) Å) and Mo–N(1) (2.239 (6) Å) bond distances are slightly longer than those (average 2.198 Å) of the $Mo(CH_3CN)_2(CO)_2(\eta^3-C_3H_5)^+$ cation.[12]

The two CH_3CN molecules of 1 and 2 are readily displaced by bidentate phosphine ligands. Addition of bis(diphenylphosphino)ethane (dppe) and bis(dimethylphosphino)ethane (dmpe) to 1 and 2 afforded (in 75%–85% yield) $Mo(dppe)(CO)_2(\eta^3$-pentadienyl)X (X = Cl (3), Br (4)) and $Mo(dmpe)(CO)_2(\eta^3$-pentadienyl)X (X = Cl (5), Br (6)), respectively. All were obtained as red block crystals after crystallization from a $CHCl_3$/ether solution. Crystals of 4 contain 1 equiv of chloroform as shown by elemental analyses and an X-ray diffraction study (vide infra). In solution, only one isomer was detectable for 3, 5, and 6; two isomers in a 72:28 molar ratio were found for 4 by ^1H NMR spectra. A *syn*-η^3-pentadienyl structure is assignable to 3, 5, and 6 as well as the minor isomer of 4 based on the coupling constants $J_{13} \simeq J_{34} \simeq 10.0$ Hz and $J_{23} = 6.4$ Hz. An anti-η^3 configuration is assignable to the major isomer of 4 based on the following coupling constants $J_{23} \simeq J_{34} = 7.2$ Hz and $J_{13} = 10.1$ Hz. For all compounds, the solution IR spectra show two carbonyl absorption bands in equal intensity; this indicates that the two carbonyls are mutually cis.[13] ^{31}P NMR spectra show an AB quartet even at elevated temperatures ($CDCl_3$, 70 °C), unlike its parent complex, $Mo(dppe)(CO)_2(\eta^3$-allyl)X, which shows mutual phosphine exchanges at ambient temperatures.[13] For the anti isomer of 4, the proton NMR resonances of vinylic hydrogens and ν(C=C) band are unusual. The resonances of H^5 lie at δ 4.78 even more upfield than those of H^6 (δ 4.98), H^7 (δ 5.10), and H^4 (δ 5.18). This feature is uncommon for a vinyl group. In addition, a very low ν(C=C) stretching band is found at 1459 (w) cm^{-1}. In contrast, for the syn-η^3 isomer of 4, the ^1H NMR resonances and the ν(C=C) stretching frequency are normal. The spectroscopic data for the anti isomer of 4 could be explained once its structure had been determined.

X-ray diffraction studies of 3 and 4 were undertaken. Complex 4 contains one solvent molecule ($CHCl_3$). The ORTEP drawings of the molecular structures are given in Figures 2 and 3, and the bond distances and angles are given in Tables II and III. For these two molecules, the coordination geometry around the molybdenum atom can

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[10] For examples, the major isomer of $Co(\eta^3-2,4-(CH_3)_2(C_5H_5)-(PEt_3)_3$[9a] assumes an anti-$\eta^3$ form whereas the major isomer of $Co(P(C_6H_5)_3)(CO)_2(\eta^3-C_5H_7)$ has a syn-η^3 geometry.[8d]

[11] Huheey, J. E. *Inorganic Chemistry, Principles of Structures and Reactivity*, 3rd ed.; Harper and Row: New York, 1983.

[12] Drew, M. G. B.; Brisdon, B. J.; Cartwright, M. *Inorg. Chim. Acta* **1979**, *36*, 127.

[13] For complexes of the type $Mo(P\frown P)(CO)_2X(\eta^3$-allyl), the chloride complexes usually have lower ν(CO) frequencies than their bromide analogues. See: (a) Brisdon, B. J. *J. Organomet. Chem.* **1977**, *125*, 225. (b) Hayta, R. G. *J. Organomet. Chem.* **1968**, *13*, 1. (c) Dieck, H. Tom.; Friedel, H. *Ibid.* **1968**, *14*, 375. (d) Faller, J. W.; Haitko, D. A.; Adams, R. D.; Chodosh, D. F. *J. Am. Chem. Soc.* **1979**, *101*, 865.

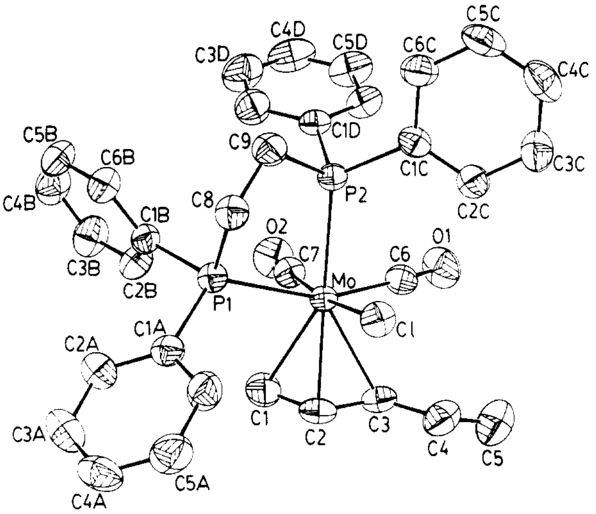


Figure 2. ORTEP drawing of the molecule 3.

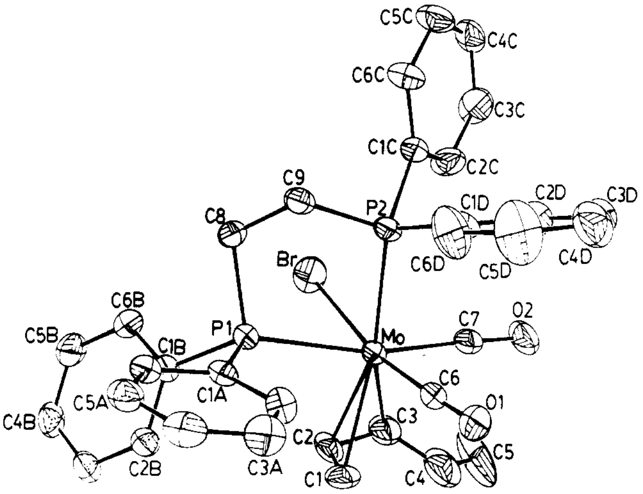


Figure 3. ORTEP drawing of the molecule 4.

be described as pseudooctahedral if the allyl group occupies one coordination site. The molybdenum atom is coordinated to the six ligands including two carbonyls, a halide atom, allyl and bidentate diphos groups. An equatorial plane can be defined to include the two carbon atoms of carbonyls, the halogen, and one phosphorus atom (P(1)) with a maximum deviation of 0.029 (1) Å for 3 and 0.391 (7) Å for 4. The allyl moiety and the second phosphorus atom (P(2)) lie trans to each other occupying the axial position. The remaining two carbonyl groups are cis to one another, consistent with the structure in solution. The angles P(1)-Mo-P(2) are 75.53 (3)° (3) and 76.52 (5)° (4) which indicate distortion from an ideal octahedral structure.

The most notable difference between these two compounds is the configuration of the pentadienyl ligand. In compound 3, it adopts a W-shaped syn-η^3 configuration, whereas in 4 it adopts an anti-η^3 structure, consistent with prediction from their ^{1}H NMR spectra. The allylic moieties are oriented similarly; i.e., their mouths face the two carbonyl groups C(6)-O(1) and C(7)-O(2). The molybdenum-allyl bond distances are asymmetric and nearly equal: Mo-C(1), 2.360 (3) Å (3), 2.327 (6) Å (4); Mo-C(2), 2.250 (3) Å (3), 2.235 (5) Å (4); Mo-C(3), 2.429 (3) Å (3), 2.464 (7) Å (4). The pentadienyl ligands of 3 and 4 are not as planar as that of 2. The dihedral angles between the vinylic plane (C(3), C(4), C(5)) and the allylic plane (C(1), C(2), C(3)) are 18.8° and 32.3° for 3 and 4, respectively. The vinyl end of the anti-η^3 ligand points away from the bromide atom while the vinyl end of the syn-η^3 form points toward the chloride atom and lies away from the bulky phosphine group. The Mo-Br bond and the Mo-C(6)-O(1) bond are essentially parallel to the C(3)-C(4) bond of the ligand. Interligand steric hindrance appears to cause the nonplanarity of the dienyl ligand. The Br atom and the C(6)-O(1) bond of 4 exert a steric effect on the C(4) carbon atom of the pentadienyl ligand and force the C(4)-C(5) double bond to twist away from the C(1)-C(2)-C(3) allylic plane as well as away from the metal center.

Table II. Bond Distances (Å) and Angles (deg) for 3

Mo-Cl	2.5855 (8)	Mo-P(1)	2.5840 (8)
Mo-P(2)	2.5236 (8)	Mo-C(1)	2.360 (3)
Mo-C(2)	2.250 (3)	Mo-C(3)	2.429 (3)
Mo-C(6)	1.973 (3)	Mo-C(7)	1.935 (3)
O(1)-C(6)	1.146 (3)	O(2)-C(7)	1.159 (3)
C(1)-C(2)	1.380 (5)	C(2)-C(3)	1.398 (4)
C(3)-C(4)	1.444 (5)	C(4)-C(5)	1.319 (5)
Cl-Mo-P(1)	82.86 (3)	C(6)-Mo-C(7)	77.92 (12)
Cl-Mo-P(2)	81.25 (3)	C(1)-C(2)-C(3)	119.6 (3)
Cl-Mo-C(1)	112.15 (9)	C(2)-C(3)-C(4)	124.5 (3)
Cl-Mo-C(2)	83.59 (8)	C(3)-C(4)-C(5)	124.0 (3)
Cl-Mo-C(3)	84.91 (7)	Mo-C(6)-O(1)	174.0 (3)
Cl-Mo-C(6)	100.17 (9)	Mo-C(7)-O(2)	176.8 (3)
Cl-Mo-C(7)	171.98 (8)	P(1)-Mo-P(2)	75.53 (3)
P(1)-Mo-C(1)	81.53 (8)	P(1)-Mo-C(2)	97.08 (8)
P(1)-Mo-C(3)	131.19 (7)	P(1)-Mo-C(6)	159.71 (8)
P(1)-Mo-C(7)	96.27 (9)	P(2)-Mo-C(1)	151.82 (8)
P(2)-Mo-C(2)	163.83 (8)	P(2)-Mo-C(3)	147.92 (7)
P(2)-Mo-C(6)	85.05 (8)	P(2)-Mo-C(7)	90.81 (8)
C(1)-Mo-C(2)	34.74 (11)	C(1)-Mo-C(3)	60.15 (11)
C(1)-Mo-C(6)	115.03 (11)	C(1)-Mo-C(7)	75.49 (12)
C(2)-Mo-C(3)	34.50 (11)	C(2)-Mo-C(6)	103.19 (11)
C(2)-Mo-C(7)	104.42 (11)	C(3)-Mo-C(6)	69.08 (11)
C(3)-Mo-C(7)	101.48 (11)		

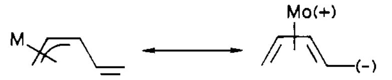
Table III. Bond Distances (Å) and Angles (deg) of 4

Mo-Br	2.6759 (10)	Mo-P(1)	2.5844 (16)
Mo-P(2)	2.5454 (16)	Mo-C(1)	2.327 (6)
Mo-C(2)	2.235 (5)	Mo-C(3)	2.464 (7)
Mo-C(6)	1.909 (7)	Mo-C(7)	1.955 (6)
C(1)-C(2)	1.402 (10)	C(2)-C(3)	1.427 (10)
C(3)-C(4)	1.351 (12)	C(4)-C(5)	1.378 (14)
C(6)-O(1)	1.165 (8)	C(7)-O(2)	1.150 (7)
Br-Mo-P(1)	79.62 (4)	Br-Mo-P(2)	84.35 (5)
Br-Mo-C(1)	119.46 (18)	Br-Mo-C(2)	86.55 (19)
Br-Mo-C(3)	80.42 (19)	Br-Mo-C(6)	169.10 (16)
Br-Mo-C(7)	95.73 (20)	Mo-C(6)-O(1)	176.9 (5)
P(1)-Mo-P(2)	76.52 (5)	Mo-C(7)-O(2)	175.2 (6)
P(1)-Mo-C(1)	81.23 (16)	P(1)-Mo-C(2)	87.56 (16)
P(1)-Mo-C(3)	119.67 (17)	P(1)-Mo-C(6)	102.82 (18)
P(1)-Mo-C(7)	166.93 (16)	P(2)-Mo-C(1)	143.69 (17)
P(2)-Mo-C(2)	162.84 (16)	P(2)-Mo-C(3)	154.87 (18)
P(2)-Mo-C(6)	85.91 (17)	P(2)-Mo-C(7)	90.93 (17)
C(1)-Mo-C(2)	35.7 (3)	C(1)-Mo-C(3)	61.31 (24)
C(1)-Mo-C(6)	71.43 (24)	C(1)-Mo-C(7)	111.51 (22)
C(2)-Mo-C(3)	34.92 (23)	C(2)-Mo-C(6)	104.09 (25)
C(2)-Mo-C(7)	104.45 (23)	C(3)-Mo-C(6)	106.9 (3)
C(3)-Mo-C(7)	70.98 (24)	C(6)-Mo-C(7)	79.5 (3)
C(1)-C(2)-C(3)	119.7 (6)	C(2)-C(3)-C(4)	126.3 (8)
C(3)-C(4)-C(5)	119.6 (10)		

The bond length of the pentadienyl moiety of 3 appears to be normal in comparison with those of other reported syn-η^3 compounds. The bond lengths C(3)—C(4) (1.444 (5) Å) and C(4)=C(5) (1.319 (5) Å) represent single and double bonds, respectively. In the pentadienyl ligand of the anti isomer (4), the bond lengths are very surprising. The most striking feature is the short C(3)-C(4) bond distance (1.351 (12) Å) and a remarkable long C(4)-C(5) bond (1.378 (14) Å). These bond lengths are consistent with the high-field chemical shift of H^5 as well as the very low ν(C=C) stretching IR frequency (vide ante). The

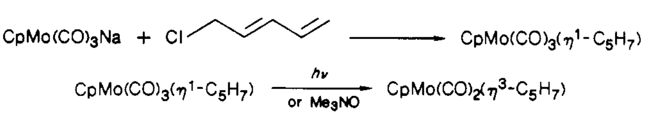
C(3)–C(4) and C(4)–C(5) bond lengths herein are unprecedented in the structural chemistry of metal anti-η^3 pentadienyl compounds. The reported anti-η^3 complexes including Co[η^3-2,4-$(CH_3)_2(C_5H_5)$]$(PEt_3)_3$,[9a] $Mn(CO)_3(PEt_3)(\eta^3\text{-}C_5H_7)$,[4a] and Rh[$\eta^3$-2,4-$(CH_3)_2(C_5H_5)$](pinacop)[9b] have the following bond lengths C(3)–C(4), 1.41–1.47 Å; C(4)–C(5), 1.28–1.37 Å; much more characteristic of a vinylic group. The short C(3)–C(4) and long C(4)–C(5) bond lengths suggest a significant overlap of the p–π orbitals between the allylic and vinylic moiety. Together with the C(1)–C(2) (1.402 (10) Å) and C(2)–C(3) (1.427 (10) Å), the pattern in bond length of the dienyl ligand closely resemble to the η^5 sickle-shaped ligand of the complex Mo[2,4$(CH_3)_2(C_5H_5)$]$_2$PEt$_3$[14] (C(1)–C(2), 1.37 (2) Å; C(2)–C(3), 1.48 (2) Å, C(3)–C(4), 1.33 (3) Å, C(4)–C(5), 1.38 (2) Å). In this manner, this acyclic five carbon chain can be truly described as *a delocalized η^3-pentadienyl ligand.* Although one might reasonably expect that the anti isomer is energetically favorable because it brings the p_z orbital of the C(4) carbon close to the metal center, the Mo–C(4) bond distance of 4 is very long, 3.346 (9) Å owing to the very nonplanarity of the dienyl moiety. This value is comparable to that of 2 (3.349 (4) Å) and 3 (3.385 (3) Å) and therefore does not suggest any support for any significant Mo···C(4) interaction.

For a pentadienyl ligand itself, the W-shaped syn-η^3 form is less sterically hindered than the sickel-shaped anti form because the C(1)–C(2) and C(3)–C(4) bonds are mutually trans in the former. In particular, the anti ligand of 4 interacts sterically with the C(6)–O(1) bond as indicated from the nonplanarity of the pentadienyl ligand. Clearly a powerful driving force is operative here in favor of the anti geometry. In order to study the electronic states of the metal centers, we examined the ν(CO) bands of compounds 3–6. The anti-η^3 isomer of 4 has ν(CO) vibrational frequencies (1943 (s), 1851 (s) cm^{-1}) higher than those of 3 (1935 (s), 1843 (s) cm^{-1}), 5 (1933 (s), 1829 (s) cm^{-1}), and 6 (1936 (s), 1824 (s) cm^{-1}). For the parent complexes, Mo(P⌒P)$(CO)_2(\eta^3\text{-}C_3H_5)$X (X = Cl, Br), the chloride complexes show lower ν(CO) frequencies than the bromide analogue.[13] Although a pπ–dπ(Mo) bonding model can partly account for the higher electron density of 3 than 4 through donation of the lone pair of the chloride atom to the empty d_{xz} (d_{yz}) orbital,[15] we believe that the higher ν(CO) vibration frequencies of 4 are primarily caused by the electronic effects of the anti sickle-shaped ligand. As depicted,



for this delocalized η^3-pentadienyl ligand, some negative charge resides on the C(5) carbon atom and leaves some positive charge character on the metal center. What are the key factors cause such a delocalized configuration? At the present stage, we cannot offer a rational explanation.

The halides of 1 and 2 are readily displaced by cyclopentadienide, indenide, and fluorenide. The fluorenide sodium salt is more effective than its lithium salt. The reaction of these salts with 1 and 2 gave in moderate yield (45%–30%) compounds of the type $Mo(CO)_2(\eta^3$-pentadienyl$)(\eta^5$-Cp′) (Cp′ = C_5H_5 (7), C_9H_7 (8), $C_{13}H_9$ (9)). Previously, we reported the synthesis of 7 from the following reaction.[7b]



However compounds 8 and 9 were obtained in very low yields (0.5%–2%) from the reaction between Cp′Mo$(CO)_3$Na and 1-halopenta-2,4-diene (Cp′ = C_9H_7, $C_{13}H_9$). Two isomers in a 6:1 molar ratio were detectable for 8. The pentadienyl ligands of these two isomers are syn-η^3 according to their coupling constants. The exo isomer is assignable to the major isomer because of the larger vicinal coupling constant (J_{12} = 2.1 Hz). In the $(\eta^5\text{-}C_5H_5)M(\eta^3$-allyl)Ln system,[16] the vicinal coupling constant J_{12} and chemical shifts of the two anti protons H^1 and H^3 were used to assign the exo and endo isomers.[16] In this case, like complex 8 having the η^5-indenyl ligand, the chemical shifts of the two anti protons were not reliable for structural assignment because of the shielding effect of the benzene ring.[17] In particular, for the major isomer of 8, the proton resonances of H^3 lie the most upfield (0.57 ppm). This feature suggests that the allyl ligand lies under the benzene ring of the indenyl group.[17] Likewise, the endo isomer has the same allylic orientation in molecular structure, as indicated from the chemical shifts of the two anti protons H^1 (0.42 ppm) and H^4 (0.65 ppm). In comparison with the endo isomer of $CpMo(CO)_2(\eta^3\text{-}C_5H_7)$,[7b] these chemical shifts are about 2 ppm more upfield, which reflects the shielding effect of the benzene ring. For 9, only one isomer is detectable and the exo-syn-η^3 conformer is assigned on the basis of the proton NMR data: J_{12} = 2.3 Hz, $J_{13} = J_{34}$ = 10.2 Hz, and J_{23} = 6.4 Hz. The proton NMR resonances of the pentadienyl ligand of 9 have chemical shifts similar to those of the exo isomer of $(C_5H_5)Mo(CO)_2(\eta^3\text{-}C_5H_7)$.[7b] The two aromatic rings of the fluorenyl ligand show no shielding effects. This feature suggests that the allyl moiety lies between the two benzene groups of the fluorenyl ligand.

Conclusion

The present studies have shown the structural and reaction chemistry of a family of molybdenum–pentadienyl complexes. Particularly notable are the structures of Mo(dppe)$(CO)_2(\eta^3\text{-}C_5H_7)$X (X = Cl (3), Br (4)), which suggest the effect of the halide atom in the η^3-pentadienyl configuration. Crystallographic data and spectroscopic studies support that the anti isomer has a delocalized η^3-pentadienyl ligand. Expansion of the reaction chemistry of these complexes is currently in progress.

Experimental Section

All operations were carried out under argon in a Schlenk apparatus or in a glovebox. Diethyl ether, tetrahydrofuran, and pentane were dried with sodium/benzophenone and distilled before use. Dichloromethane, chloroform, and acetonitrile were dried over phosphorus pentoxide and distilled. Bis(diphenylphosphino)ethane (dppe), bis(dimethylphosphino)ethane (dmpe), and molybdenum hexacarbonyl were purchased from Strem Chemicals and used without further purification. Lithium cyclopentadienide and indenide were prepared following the literature. Sodium fluorenide was prepared by stirring dispersed sodium with fluorene in THF.

All ^{1}H (100 and 400 MHz), ^{13}C (100 MHz), and ^{31}P (40.2 MHz) NMR spectra were obtained on either a JEOL FX-100 or a Bruker AM-400 spectrometer. The ^{1}H and ^{13}C NMR spectra were referenced to tetramethylsilane. Infrared spectra were recorded on

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a Perkin-Elmer 781 spectrophotometer. Microanalyses were performed by the Microanalytic Laboratory at National Taiwan University.

(A) Synthesis of (η^3-C_5H_7)MoCl(CO)$_2$(CH_3CN)$_2$ (1). Molybdenum hexacarbonyl (10.0 g, 37.8 mmol) was refluxed in 40 mL of CH_3CN under argon for 6 h. The resulting yellow solution was cooled to 0 °C, and 4.6 mL of 1-chloro-2,4-pentadiene[18] (49.6 mmol) was added. The solution was stirred for 4 h during which the solution gradually turned red. The solution was concentrated to 15 mL, and the orange solids were filtered and washed twice with 10 mL of THF. Further recrystallization from slow evaporation of a saturated CH_3CN solution gave red rod crystals (8.9 g, 26.4 mmol). ^{1}H NMR (400 MHz, CD_3CN): δ 1.24 (1 H, d, H^1), 2.04 (3 H, s, CH_3CN), 2.20 (1 H, t, H^4), 2.37 (3 H, s, CH_3CN), 3.26 (1 H, d, H^2), 4.26 (1 H, td, H^3), 5.14 (1 H, dd, H^7), 5.37 (1 H, dd, H^6), 6.50 (1 H, td, H^5), J_{13} = 10.0 Hz, J_{23} = 6.4 Hz, J_{34} = 10.0 Hz, J_{45} = 10.2 Hz, J_{56} = 15.6 Hz, J_{57} = 10.2 Hz. IR spectrum (CH_2Cl_2): ν(C=C) 1605 (w) cm^{-1}; ν(CO) 1919 (s), 1849 (s) cm^{-1}. Anal. Calcd for $C_{11}H_{13}N_2ClMoO_2$: C, 39.23; H, 3.68; N, 8.32. Found: C, 39.41; H, 3.92; N, 8.54.

(B) Synthesis of (η^3-C_5H_7)MoBr(CO)$_2$(CH_3CN)$_2$ (2). This complex was prepared similarly from the reaction between Mo(CO)$_3$(CH_3CN)$_3$ and 1-bromo-2,4-pentadiene; the yield is 70%. ^{1}H NMR (400 MHz, CD_3CN): δ 1.25 (1 H, d, H^1), 2.04 (3 H, s, CH_3CN), 2.24 (1 H, t, H^4), 2.27 (3 H, s, CH_3CN), 3.15 (1 H, d, H^2), 4.31 (1 H, td, H^3), 5.16 (1 H, dd, H^7), 5.38 (1 H, dd, H^6), 6.47 (1 H, td, H^5), J_{13} = 9.9 Hz, J_{23} = 6.2 Hz, J_{34} = 10.4 Hz, J_{45} = 10.4 Hz, J_{56} = 16.9 Hz, J_{57} = 10.2 Hz, J_{67} = 1.4 Hz. IR spectrum (CH_2Cl_2): ν(C=C) 1607 (w) cm^{-1}; ν(CO) 1925 (s), 1844 (s) cm^{-1}. Anal. Calcd for $C_{11}H_{13}N_2BrMoO_2$: C, 34.67; H, 3.44; N, 7.35. Found: C, 34.71; H, 3.40; N, 7.03.

(C) Synthesis of (η^3-C_5H_7)Mo(CO)$_2$(dppe)Cl (3). dppe (1.04 g, 2.63 mmol) in 15 mL of THF was added dropwise to 1 g of 1 (2.75 mmol) dissolved in 30 mL of THF. The solution was stirred for 1 h. After removal of solvent, the residue was chromatographed through silica gel column using dichloromethane as the eluting solvent. An orange band was developed, collected, and evaporated to dryness to give an orange solid. Recrystallization from CH_2Cl_2/ether yielded red block crystals (1.42 g, 2.17 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.82 (1 H, dd, H^1), 2.14–2.39 (2 H, complex m, P–CH_2), 2.84–3.02 (2 H, complex m, P–CH_2), 3.10 (1 H, t, H^4), 3.58 (1 H, dd, H^2), 4.11 (1 H, m, H^3), 5.10 (1 H, d, H^7), 5.33 (1 H, d, H^6), 6.38 (1 H, td, H^5), 7.32–7.40 (20 H, complex m, P–C_6H_5), $J_{p\text{-}1}$ = 2.7 Hz, $J_{p\text{-}2}$ = 4.5 Hz, J_{13} = 10.2 Hz, J_{23} = 16.58 Hz, J_{34} = 10.2 Hz, J_{45} = 10.2 Hz, J_{56} = 17.0 Hz, J_{57} = 10.5 Hz. ^{31}P NMR (40.2 MHz, $CDCl_3$): δ -43.41 (dd), -42.89 (dd), $J_{PP'}$ = 14.5 Hz. IR spectrum (CH_2Cl_2): ν(CO) 1935 (s), 1843 (s) cm^{-1}; ν(C=C) 1615 (w) cm^{-1}. Anal. Calcd for $C_{33}H_{31}MoO_2ClP_2$: C, 60.70; H, 4.78. Found: C, 60.84; H, 4.92.

(D) Synthesis of (η^3-C_5H_7)Mo(CO)$_2$(dppe)Br·$CHCl_3$ (4). This complex was prepared similarly from the reaction between **2** and dppe in THF; the yield is 68%. ^{1}H NMR (400 MHz, $CDCl_3$): anti isomer, δ 2.32 (2 H, m, P–CH_2), 2.47 (1 H, d, H^1), 3.05 (2 H, m, P–CH_2), 3.81 (1 H, dd, H^2), 3.96 (1 H, m, H^3), 4.78 (1 H, td, H^5), 4.98 (1 H, d, H^6), 5.10 (1 H, dd, H^7), 5.18 (1 H, dd, H^4), 7.30–7.70 (20 H, m, P–C_6H_5), J_{13} = 11.0 Hz, J_{23} = 6.0 Hz, J_{34} = 6.5 Hz, J_{45} = 10.0 Hz, J_{56} = 10.2 Hz, J_{57} = 16.4 Hz; syn isomer, δ 1.85 (1 H, dd, H^1), 2.18–2.46 (2 H, m, P–CH_2), 3.10 (1 H, t, H^3), 3.12–3.90 (2 H, m, P–CH_2), 3.46 (1 H, dd, H^2), 5.11 (1 H, d, H^7), 5.32 (1 H, d, H^6), 6.49 (1 H, td, H^5), J_{13} = 10.0 Hz, J_{1p} = 2.2 Hz, J_{23} = 5.5 Hz, J_{34} = 10.1 Hz, J_{45} = 10.4 H, J_{56} = 10.3 Hz, J_{57} = 16.8 Hz. ^{31}P NMR (40.25 MHz, $CDCl_3$): anti isomer, δ -44.4 (dd), -45.3 (dd), $J_{PP'}$ = 14.8 Hz; syn isomer, δ -46.9 (dd), -48.2 (dd), $J_{PP'}$ = 14.6 Hz. IR spectrum (CH_2Cl_2): anti isomer, ν(C=C) 1495 (w) cm^{-1}; syn isomer, ν(C=C) 1610 cm^{-1}; anti isomer, ν(CO) 1943 (s), 1851 (s) cm^{-1}. Anal. Calcd for $C_{34}H_{32}MoO_2BrP_2Cl_3$: C, 49.99; H, 3.92. Found: C, 49.84; H, 3.87.

(E) Synthesis of (η^3-C_5H_7)Mo(CO)$_2$(dmpe)Cl (5). This complex was prepared similarly from the reaction between (η^3-C_5H_7)Mo(CO)$_2$(CH_3CN)$_2$Cl and dmpe in tetrahydrofuran; the yield is 72%. ^{1}H NMR ($CDCl_3$): δ 0.34 (1 H, d, H^1), 1.62 (3 H, d, P–CH_3), 1.63 (3 H, d, PCH_3), 1.66 (3 H, d, PCH_3), 1.69 (3 H, d, PCH_3), 1.83 (2 H, m, P–CH_2), 2.07 (2 H, m, P–CH_2), 3.73 (2 H, m, H^4 + H^2), 4.88 (1 H, ddd, H^3), 5.15 (1 H, d, H^7), 5.35 (1 H, d, H^6), 6.39 (1 H, td, H^6), J_{13} = 11.6 Hz, J_{23} = 7.0 Hz, J_{34} = 10.2 Hz, J_{45} = 10.1 Hz, J_{56} = 16.1 Hz, J_{57} = 10.1 Hz. ^{31}P NMR (40.2 MHz, $CDCl_3$): δ -35.7 (d), -38.0 (d), $J_{PP'}$ = 40.6 Hz. IR spectrum (CH_2Cl_2): ν(C=C) 1615 (w) cm^{-1}; ν(CO) 1933 (s), 1829 (s) cm^{-1}. Anal. Calcd for $C_{13}H_{23}MoO_2ClP_2$: C, 40.81; H, 5.72. Found: C, 41.80; H, 5.62.

Table IV. Crystal Data for Compounds 2, 3, and 4

	2	3	4
a, Å	7.048 (1)	10.194 (1)	20.804 (7)
b, Å	12.612 (2)	11.139 (2)	9.418 (3)
c, Å	16.028 (2)	16.176 (2)	31.035 (6)
α, deg	90	93.77 (1)	90
β, deg	90	98.70 (1)	91.54 (2)
γ, deg	90	106.33 (1)	90
V, Å^3	1424.67	1730.99	6078.75
space group	$P2_12_12_1$	$P\bar{1}$	$C2/c$
Z	4	2	8
cryst dimens, mm	0.15 × 0.2 × 0.5	0.4 × 0.5 × 0.5	0.3 × 0.4 × 0.45
cryst color	red	red	red
wavelength (Mo)	0.7093	0.7093	0.7093
scan parameter	0.65 + 0.35 tan θ	0.65 + 0.35 tan θ	0.6 + 0.35 tan θ
scan type	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$
2θ range, deg	2.5–50	2.5–50	2.5–50
abs coeff, mm^{-1}	3.67	0.80	1.85
abs correctn	Ψ rotation	Ψ rotation	Ψ rotation
no. of unique reflectns	1467	6077	5338
no. of reflectns ($I > 3\ \sigma(I)$)	1295	5434	3400
final R_F, %	2.4	3.0	3.9
final R_w, %	2.6^a	3.0^a	4.4^b
final E map (max), e Å^3	0.38	0.68	0.64
goodness of s^c	2.81	4.00	1.93

^{a} $w = 1/\sigma^2(F_o)$. ^{b} $w = 1/[\sigma^2(F_o) + (0.01F_c)^2]$. ^{c} $s = [\sum w|F_o - F_c|^2/(N_o - N_v)]^{1/2}$. N_o is the number of observations; N_v is the number of variables.

(F) Synthesis of (η^3-C_5H_7)Mo(CO)$_2$(dmpe)Br (6). This complex was prepared similarly from the reaction between (η^3-C_5H_7)Mo(CO)$_2$(CH_3CN)$_2$Br and dmpe in THF; the yield is 65%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.60 (3 H, d, P–CH_3, J_{PH} = 8.6 Hz), 1.63 (3 H, d, P–CH_3, J_{PH} = 8.4 Hz), 1.70 (3 H, d, P–CH_3, J_{PH} = 9.3 Hz), 1.76 (3 H, d, P–CH_3, J_{PH} = 9.2 Hz), 1.73–2.00 (2 H, m, P–CH_2), 2.03–2.22 (2 H, m, P–CH_2), 2.43 (1 H, d, H^1), 3.63 (1 H, ddd, H^2), 3.79 (1 H, t, H^4), 4.98 (1 H, td, H^3), 5.15 (1 H, dd, H^7), 5.34 (1 H, dd, H^6), 6.36 (1 H, td, H^5), J_{P2} = 6.0 Hz, $J_{P'2}$ = 5.7 Hz, J_{13} = 10.6 Hz, J_{34} = 10.7 Hz, J_{45} = 10.7 Hz, J_{56} = 17.0 Hz, J_{57} = 10.0 Hz, J_{67} = 1.0 Hz. ^{31}P NMR (40.2 MHz, $CDCl_3$): δ -42.82 (dd), -40.69 (dd), $J_{PP'}$ = 39.4 Hz. IR spectrum (CH_2Cl_2): ν(C=C) 1612 (w) cm^{-1}; ν(CO) 1936 (s), 1824 (s) cm^{-1}. Anal. Calcd for $C_{13}H_{23}MoO_2BrP_2$: C, 34.76; H, 5.16. Found: C, 35.02; H, 5.24.

(G) Synthesis of (η^5-C_9H_7)Mo(CO)$_2$(η^3-C_5H_7) (8). Method A. Indene (0.32 mL, 2.62 mmol) was treated with a 1.6-mL hexane solution of butyllithium (1.6 M, 2.60 mmol) at -78 °C. The resulting yellow solution was warmed to room temperature and added dropwise to 1 g of **2** (2.62 mmol) at 0 °C and stirred for 12 h. After removal of solvent, the residues were chromatographed through neutral alumina column. A yellow band was developed, collected, and evaporated to dryness to yield yellow solid. Further recrystallization from ether gave yellow crystals (0.38 g, 1.14 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): exo isomer, δ 0.57 (1 H, td, H^3), 1.12 (1 H, dd, H^1), 2.03 (1 H, dd, H^2), 2.28 (1 H, t, H^4), 4.56 (1 H, dd, H^7), 5.32 (1 H, dd, H^6), 5.68 (1 H, td, H^5), 5.75 (1 H, t), 5.93 (1 H, d), 6.13 (1 H, t), 7.21–7.39 (4 H, m), J_{12} = 2.1 Hz, J_{13} = 10.5 Hz, J_{23} = 6.8 Hz, J_{34} = 10.4 Hz, J_{45} = 10.5 Hz, J_{57} = 10.2 Hz, J_{56} = 16.5 Hz, J_{67} = 1.2 Hz; endo isomer, δ -0.42 (1 H, d, H^1), 0.65 (1 H, t, H^4), 3.41 (1 H, d, H^2), 3.69 (1 H, td, H^3), 4.90 (1 H, dd, H^7), 5.23 (1 H, dd, H^6), 6.33 (1 H, td, H^5), 5.75 (1 H, t), 5.93 (1 H, d), 6.13 (1 H, t), 7.21–7.39 (4 H, m). Mass spectrum (12 eV, ^{98}Mo, 23.78%): m/e 336 (M$^+$), 308 (M$^+$ – CO), 280 (M$^+$ – 2CO). IR spectrum (CH_2Cl_2): ν(C=C) 1610 (w) cm^{-1}; ν(CO) 1940 (s), 1860 (s) cm^{-1}. Anal. Calcd for $C_{16}H_{14}MoO_2$: C,

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[18] Miginiac, P. *Ann. Chim.* **1962**, 445.

57.50; H, 4.22. Found: C, 57.84; H, 4.22.

Method B. 1-Chloro-2,4-pentadiene was added dropwise to a tetrahydrofuran solution of $(\eta^5\text{-}C_9H_7)Mo(CO)_3Na$ (2.08 g, 6.65 mmol) at 0 °C and stirred for 3 h. The solution was evaporated to dryness and chromatographed through neutral alumina column using ether as the eluting solvent. A yellow band was developed, collected, and evaporated to dryness to give a yellow solid. Further recrystallization from ether gave yellow crystals (0.042 g, 0.12 mmol).

(H) Synthesis of $(\eta^5\text{-}C_{13}H_9)Mo(CO)_2(\eta^3\text{-}C_5H_7)$ (9). Method A. Sodium fluorenide (0.50 g, 2.62 mmol) was added dropwise to **2** (1 g, 2.62 mmol) in 30 mL of tetrahydrofuran solution and stirred at 0 °C for 16 h. The solution was evaporated to dryness and chromatographed through a neutral alumina column using ether as the eluting solvent. A yellow band was developed, collected, and evaporated to dryness. The residues were heated under vacuum (4.0×10^{-4} Torr) at 60 °C until fluorene solids were completely removed. The residues were chromatographed through a neutral alumina column using ether as the solvent. A yellow band was collected concentrated and cooled to 0 °C to give yellow crystals (0.399 g, 1.04 mmol). ^1H NMR (400 MHz, $CDCl_3$): δ 0.57 (1 H, dd, H^1), 0.85 (1 H, dd, H^2), 1.51 (1 H, t, H^4), 3.17 (1 H, td, H^3), 4.69 (1 H, dd, H^6), 5.05 (1 H, td, H^5), 7.05 (2 H, m), 7.20 (2 H, m), 7.57 (1 H, d), 7.61 (1 H, d), 7.62 (1 H, d), 7.65 (1 H, d), $J_{12} = 2.4$ Hz, $J_{13} = 10.2$ Hz, $J_{23} = 7.1$ Hz, $J_{34} = 10.4$ Hz, $J_{45} = 10.4$ Hz, $J_{56} = 16.4$ Hz, $J_{57} = 10.0$ Hz, $J_{67} = 1.3$ Hz. Mass spectrum (12 eV, ^{98}Mo, 23.78%): m/e 386 (M^+), 358 ($M^+ - CO$), 336 ($M^+ - 2CO$). IR spectrum (CH_2Cl_2): $\nu(C{=}C)$ 1614 cm^{-1}; $\nu(CO)$ 1943 (s), 1864 (s) cm^{-1}. Anal. Calcd for $C_{20}H_{16}MoO_2$: C, 62.51; H, 4.20. Found: C, 62.74; H, 4.34.

Method B. This complex can be also obtained from the reaction between $(\eta^5\text{-}C_{13}H_9)Mo(CO)_3Na$ and 1-chloro-2,4-pentadiene in tetrahydrofuran at 0 °C. The yield is 2–0.5%.

(I) X-ray Diffraction Study of 2, 3, and 4. Data were collected at room temperature on a CAD4 diffractometer, using graphite-monochromated Mo Kα radiation. All data reduction and structure refinement were performed by using the NRCC-SDP-VAX package. Crystal data, details of data collection, and structure analysis are summarized in Table IV. Compound **2** has a noncentric space group and the one presented had the best R factor ($R_f = 2.4\%$; $R_w = 2.6\%$). The other enantiomorphic structures had higher R factor after refinement ($R_F = 4.7\%$; $R_w = 4.6\%$).

The structure of three compounds were solved by Patterson method. All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were added at idealized positions and included in the structure factor calculations.

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Registry No. **1**, 117652-88-7; **2**, 117652-89-8; **3**, 117652-90-1; **4** (anti isomer), 117652-91-2; **4**$\cdot CHCl_3$ (anti isomer), 117708-21-1; **4** (syn isomer), 117708-20-0; **5**, 117652-92-3; **6**, 117652-93-4; **8** (exo isomer), 117652-94-5; **8** (endo isomer), 117708-22-2; **9**, 117652-95-6; $Mo(CO)_6$, 13939-06-5; $Mo(CO)_3(CH_3CN)_3$, 15038-48-9; $(\eta^5\text{-}CaH_7)Mo(CO)_3Na$, 12088-81-2; $NaC_{13}H_9$, 3531-83-7; $(\eta^5\text{-}C_{13}H_9)Mo(CO)_3Na$, 117652-96-7; 1-chloro-2,4-pentadiene, 40596-30-3; 1-bromo-2,4-pentadiene, 1001-93-0; indene, 95-13-6.

Supplementary Material Available: Tables of atomic coordinates, anisotropic thermal parameters, and complete bond distances and bond angles for **2**, **3**, and **4** (9 pages); listings of structure factor amplitdues for **2**, **3**, and **4** (85 pages). Ordering information is given on any current masthead page.

Chemistry of {η^6-Bis(tri-*n*-butylstannyl)benzene}chromium Tricarbonyl Complexes: Versatile Intermediates in the Preparation of Substituted (η^6-Arene)chromium Tricarbonyl Systems

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The {η^6-1,3-bis(tri-*n*-butylstannyl)benzene}- and {η^6-1,4-bis(tri-*n*-butylstannyl)benzene}chromium tricarbonyl complexes, prepared as stable yellow oils, react smoothly with *n*-BuLi at −78 °C in tetrahydrofuran (THF) to produce the (η^6-1,3-dilithiobenzene)- and (η^6-1,4-dilithiobenzene)$Cr(CO)_3$ complexes. The latter react with a variety of reagents to give good to excellent yields of some new (η^6-arene)$Cr(CO)_3$ complexes. The transmetalations were found to proceed most efficiently in THF; almost no reaction took place in ether. The $Cr(CO)_3$ complexation is capable of directing the transmetalation in {η^6-4,4′-bis(tri-*n*-butylstannyl)biphenyl}$Cr(CO)_3$ regioselectively to the coordinated phenyl ring. The palladium-catalyzed cross-coupling of selected aryl halides, $(\eta^6\text{-}C_6H_5Cl)Cr(CO)_3$, and trimethyl(phenylethynyl)stannane was studied. The study indicated that the $Cr(CO)_3$ complexation significantly enhanced the rate of the cross-coupling reaction.

Introduction

(η^6-Arene)$Cr(CO)_3$ complexes have been studied extensively in a wide variety of applications ranging from their use as stoichiometric asymmetric reagents to models for ligand substitution reactions.[1] The widespread use of the complexes is in part due to their robust nature and often simple and high-yield syntheses. The $Cr(CO)_3$ complexation activates the arene ligand in nucleophilic substitution and deprotonaton reactions, and the $Cr(CO)_3$ unit can be easily removed from the arene ligand at the end of the synthetic sequence.

In general, the syntheses of (η^6-arene)$Cr(CO)_3$ complexes in which the arene contains electron-withdrawing groups usually proceed in low conversions and require a large excess of arene present.[2] In cases where the arene is a solid

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[1] Davis. R.; Kane-Maguire, L. A. P. *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Vol. 3, pp 1001–54 and references cited therein.

[2] For examples see: (a) Fischer, E. O.; Öfele, K.; Essler, H.; Frohlich, W.; Mortensen, P.; Semmlinger, W. *Chem. Ber.* **1958**, *91*, 2763. (b) Strohmeier, W.; Hartmann, P. *Z. Naturforsch., B* **1963**, *18*, 506. (c) Klopman, G.; Calderazzo, F. *Inorg. Chem.* **1967**, *6*, 977.

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