Organometallics 1986, 5, 2378-2380

Synthesis and Characterization of Molybdenum-Pentadienyl Complexes. The Molecular Structure of $(C_5H_5)Mo(CO)_2$(*syn*-η^3-pentadienyl)

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Received May 23, 1986

Summary: The reaction between $CpMo(CO)_3Na$ and *trans*-1-chloropenta-2,4-diene in tetrahydrofuran at -78 °C gives $CpMo(CO)_3$(η^1-pentadienyl) (**1**). In photolytic reaction, **1** undergoes $\eta^1 \rightarrow$ syn-$\eta^3 \rightarrow \eta^5$ conversion and yields $CpMo(CO)_2$(*syn*-η^3-pentadienyl) (**2**) and CpMo(CO)(η^5-pentadienyl) (**3**). In solution, **2** exists in two stereoisomers characterized as the endo-syn-η^3 and exo-syn-η^3 forms. Its solid structure is the exo form which crystallized in the monoclinic space group $P2_1/n$ with a = 12.647 (5) Å, b = 6.703 (2) Å, c = 13.817 (3) Å, β = 102.59 (3)°, V = 1143.11 Å^3, and Z = 4. For **3**, the pentadienyl configuration is unsymmetric η^5-S-shaped as inferred from its ^{1}H and ^{13}C NMR spectra.

The pentadienyl-alkali-metal salts C_5H_7M and $[2,4\text{-}(CH_3)_2C_5H_5]M$ (M = Na, K) have been extensively used in the synthesis[2,3] of transition-metal-pentadienyl complexes. One of the notable examples is the presence of "open metallocenes" prepared by Ernst and co-workers.[3] These alkali-metal salts nevertheless seldom yield the η^1-pentadienyl compounds which potentially are versatile reagents in many organic reactions.[4] Recently we have prepared acyclic pentadienyl complexes of iron,[5] manganese,[6] and cobalt[7] from 1-halopenta-2,4-diene. 1-Halopenta-2,4-diene seems to be a very intriguing reagent in synthesis because it reacts with metal carbonyl anions, e.g., $CpFe(CO)_2^-$ (Cp = C_5H_5),[5] $Mn(CO)_5^-$,[6] and $Co(CO)_4^-$ [7] to give η^1, syn-η^3, and η^5 compounds in a controllable pathway shown in Scheme I.

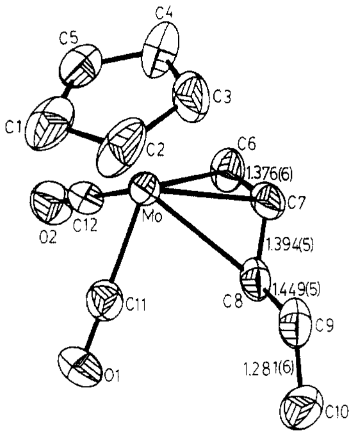


Figure 1. ORTEP drawing of *exo*-$(C_5H_5)Mo(CO)_2$(*syn*-η^3-pentadienyl). Ellipsoids are scaled to represent the 50% probability surface.

Scheme I

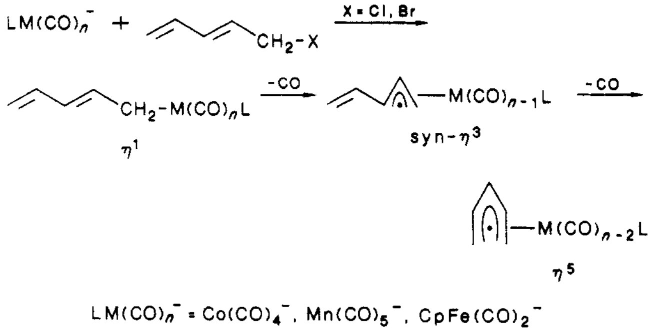
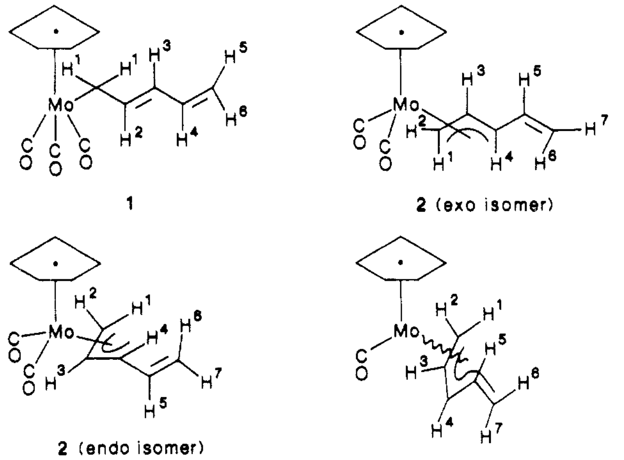


Chart I



1

2 (exo isomer)

2 (endo isomer)

3

In the past, $CpMo(CO)_2$(allyl)[8] and $Cp_2Mo(CO)$[9] have been the subject of extensive studies in organic and organometallic reactions. These two compounds constitute a wide scope of chemistry which enables one to look into the functionality of a η^3-allyl ligand and the 16e short-lived species "Cp_2Mo", respectively. In a continuing search for transition-metal-pentadienyl complexes of versatile reactivity, we have therefore prepared $CpMo(CO)_3$(η^1-pentadienyl) (**1**), $CpMo(CO)_2$(*syn*-η^3-pentadienyl) (**2**), and CpMo(CO)(η^5-pentadienyl) (**3**) according to scheme I.

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[1] Yasuda, H.; Ohnuma, Y.; Yamauchi, M.; Tani, H.; Nakamura, A. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 2036.

[2] For examples see: (a) Bleeke, J. R.; Peng, W.-J. *Organometallics* **1984**, *3*, 1422. (b) Bleeke, J. R.; Hays, M. K. *Ibid.* **1984**, *3*, 506. (c) Bleeke, J. R.; Kotyk, J. J. *Ibid.* **1985**, *4*, 194. (d) Stahl, L.; Hutchinson, J. P.; Wilson, D. R.; Ernst, R. D. *J. Am. Chem. Soc.* **1985**, *107*, 5016.

[3] For open metallocenes, see the recent review paper: Ernst, R. D. *Acc. Chem. Res.* **1985**, *18*, 56 and references therein.

[4] The transition-metal η^1-allyl complexes are notable for their [3 + 2] cycloaddition with a variety of electrophiles, see: (a) Williams, J. P.; Wojcicki, A. *Inorg. Chem.* **1977**, *16*, 3116. (b) Cutler, A.; Ehntholt, D.; Gierinin, W. P.; Lennon, P.; Raghu, S.; Rosan, A.; Rosenblum, M.; Tancrede, J.; Wells, D. *J. Am. Chem. Soc.* **1976**, *98*, 3495. (c) Wright, M. E. *Organometallics* **1983**, *2*, 558. (d) Genco, N.; Marten, D.; Raghu, S.; Rosenblum, M. *J. Am. Chem. Soc.* **1976**, *98*, 848.

[5] Lush, S.-F.; Liu, R.-S. *Organometallics*, in press.

[6] Lee, T.-W.; Liu, R.-S., submitted for publication in *J. Organomet. Chem.*

[7] Lee, G.-H.; Peng, S.-M.; Liao, M.-Y.; Liu, R.-S. *J. Organomet. Chem.*, in press.

[8] $CpMo(CO)_2$(η^3-*anti*-crotyl) and its homologues undergo hydride abstraction to form $CpMo(CO)_2$(η^4-butadiene)$^+$ which is subject to nucleophilic additions. Its nitrosonium cation CpMo(NO)(CO)(allyl)$^+$, derived from $CpMo(CO)_2$(allyl), displays similar reactivity, see: (a) Faller, J. W.; Rosan, A. M. *J. Am. Chem. Soc.* **1977**, *99*, 4858. (b) Faller, J. W.; Rosan, A. M. *Ann. N. Y. Acad. Sci.* **1977**, *295*, 186. (c) Faller, J. W.; Chodosh, D. F.; Katahira, D. *J. Organomet. Chem.* **1980**, *187*, 227. (d) Adams, R. D.; Chodosh, D. F.; Faller, J. W.; Rosan, A. M. *J. Am. Chem. Soc.* **1979**, *101*, 1570.

[9] $Cp_2Mo(CO)$ is a convenient reagent to form the short-lived species "Cp_2Mo", see: (a) Tang Wong, K. L.; Thomas, J. L.; Brintzinger, H. H. *J. Am. Chem. Soc.* **1974**, *96*, 3694. The chemistry of the "Cp_2Mo", see 9a. (b) Thomas, J. L. *J. Am. Chem. Soc.* **1973**, *95*, 1838. (c) Geoffroy, G. L.; Bradley, M. G. *Inorg. Chem.* **1978**, *17*, 2410. (d) Gremenik, P.; Downs, A. J.; Green, M. L. H.; Perutz, R. N. *J. Chem. Soc., Chem. Commun.* **1979**, 742.

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Table I. Selected Bond Distances (Å) and Angles (deg) with Estimated Standard Deviations in Parentheses

		Bond Distances			
Mo–C_7	2.197 (4)	Mo–C_6	2.320 (4)	C_7–C_8	1.394 (5)
Mo–C_8	2.389 (4)	C_9–C_{10}	1.281 (6)	C_8–C_9	1.449 (5)
C_6–C_7	1.376 (6)				
		Bond Angles			
C_6–Mo–C_8	62.1 (1)	C_7–Mo–C_8	35.1 (1)	Mo–C_8–C_7	64.9 (2)
C_6–Mo–C_{12}	74.9 (1)	C_8–Mo–C_{12}	108.0 (1)	C_8–C_9–C_{10}	126.5 (4)
C_8–Mo–C_{11}	70.7 (1)	Mo–C_6–C_7	67.5 (2)	C_6–C_7–C_8	122.5 (4)
C_{11}–Mo–C_{12}	79.9 (1)	Mo–C_7–C_6	77.2 (2)	C_7–C_8–C_9	124.7 (3)

Stirring a tetrahydrofuran solution of CpMo(CO)$_3$Na[10a] with *trans*-1-chloropenta-2,4-diene[10b] at −78 °C for 6 h gave a yellow crystalline solid of CpMo(CO)$_3$(η^1-pentadienyl) (1) in good yields (72%) after workup.[11] The compound was stored at 0 °C to obtain satisfactory analytical data[12] and to avoid slow decomposition at room temperature. On the basis of its mass, IR, and NMR spectroscopic data,[12] the structure of 1 was assigned as shown in Chart I.

Photolysis of 1 in ether at −20 °C for 6 h gave a mixture of 2 and 3. After separation of the mixture by column chromatograph, pale yellow crystals of **2** were obtained in good yields (65%) after workup.[13] The elemental analysis and mass spectrum[14] are consistent with the formula $(C_5H_5)Mo(CO)_2(C_5H_7)$. The IR and ^{1}H NMR spectra (−60 °C, toluene-d_8)[15] reveal that **2** forms two stereoisomers, i.e., the exo-syn-η^3 and endo-syn-η^3 forms (Chart I).[16] Both isomers have *syn*-pentadienyl ligands as shown by their coupling constants $J_{13} \simeq J_{34} \simeq 10$ Hz and $J_{23} \simeq 7$ Hz. The assignment of the observed spectroscopic data to the two isomers follows that of CpFe(CO)(η^5-*syn*-pentadienyl).[5] The exo–endo isomerization occurs at a rate within the time scale of NMR spectroscopy. In its variable-temperature ^{1}H NMR study, the ratio of exo/endo at −60 °C is about 9, and with increasing temperatures, the two sets of well-defined resonances of the two isomers broaden and eventually coalesce at 100 °C[17] ($\Delta G^{\ddagger} = 18.2 \pm 0.3$ kcal/mol). The solid-state structure of **2** for clarity was determined by an X-ray diffraction study.[18] An ORTEP drawing of the molecular structure is shown in Figure 1, and the selected bond distances and angles are given in Table I. Compound **2** crystallizes in exo-syn-η^3 form;[19] i.e., the mouth of the allyl moiety lies away from the Cp group. The coordination geometry about the molybdenum atom approximates a distorted tetrahedron with two carbonyl, an allyl, and a Cp group occupying the four coordination sites.[20] The structure of the pentadienyl ligand of **2** closely resembles that of (*syn*-η^3-pentadienyl)Co(CO)$_2$(PPh$_3$),[7] (syn-η^3-2,4-hexadien-1-yl)Fe(CO)(C$_5$H$_5$),[21] *syn,syn*-bis(η^3-2,4-pentadienyl)Fe[P(CH$_3$)$_3$]$_2$,[2c] and (*syn*-η^3-pentadienyl)Mn(dmpe)$_2$.[2b] The pentadienyl ligand is bonded to the molybdenum atom in an unsymmetric fashion with Mo–C6 = 2.320 (4), Mo–C7 = 2.197 (4), and Mo–C8 = 2.389 (4) Å. The vinyl group of the pentadienyl ligand points away from the rest of the complex minimizing the steric hinderance, and the dihedral angle between vinylic plane (C8, C9, C10) and allylic plane (C6, C7, C8) is 21.4°. Alternatively, carbon atoms C6, C7, C8, and C9 of the pentadienyl ligand are coplanar to within 0.026 Å, while C10 lies out of the plane away from the molybdenum by 0.29 Å.

Although thermolysis of **2** in toluene at reflux fails to give **3**, the syn-$\eta^3 \rightarrow \eta^5$ conversion is feasible in photolysis of an etherate solution of **2** at −20 °C. Analytic purity of the greenish yellow crystalline solid was only obtained in 35% yields after workup.[22] The successive loss of the CO ligand of **3** to give an uncharacterized red precipitate ac-

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(10) (a) Hayter, R. G. *Inorg. Chem.* **1963**, *2*, 1031. (b) Prevost, C.; Miginiac, P.; Miginiac-Groizeleau, L. *Bull. Soc. Chim. Fr.* **1964**, 2485.

(11) In a typical preparation, *trans*-1-chloropenta-2,4-diene (1.2 g, 11.6 mmol) was added dropwise to 50 mL of tetrahydrofuran solution containing CpMo(CO)$_3$Na (8.2 mmol) at −78 °C and stirred for 6 h. After the insoluble amalgam residues were filtered at −78 °C, the solution was warmed to 0 °C and evaporated to dryness to yield dark red residues. The residues were extracted with 20 mL of pentane three times, filtered, and evaporated to dryness. With use of pentane as the eluting solvent, the residues were chromatographed through alumina column (60 g, Merck) at 0 °C. In addition to an immobile band of Cp$_2$Mo$_2$(CO)$_6$, a gold-yellow band was fast eluted and collected. After removal of the solvent in vacuo at 0 °C, yellow crystalline solid with analytic purity of 1 was obtained (1.67 g, 5.33 mmol).

(12) Anal. Calcd for $C_{13}H_{12}MoO_3$: C, 50.00; H, 3.85. Found: C, 50.41; H, 3.96. Mass spectrum (12 eV, ^{98}Mo 23.78%, *m/e*): 286 ($M^+ - CO$), 258 ($M^+ - 2CO$), 247 ($M^+ - C_5H_7$), 219 ($M^+ - C_5H_7 - CO$), 191 ($M^+ - C_5H_7 - 2CO$), 163 ($M^+ - C_5H_7 - 3CO$). IR spectrum (pentane): ν(CO) 2018 (s), 1960 (s), 1940 (vs) cm^{-1}; ν(C=C) 1620 (w) cm^{-1}. ^{1}H NMR spectrum (400.1 MHz, benzene-d_6): δ 2.30 (d, 2 H, H^1), 4.39 (s, 5 H, C$_5$H$_5$), 4.92 (dd, 1 H, H^6), 5.05 (dd, 1 H, H^5), 6.00–6.05 (complex m, 2 H, H^2 and H^3), 6.25–6.40 (complex m, 1 H, H^4), $J_{12} = 7.2$ Hz, $J_{46} = 9.6$ Hz, $J_{45} = 16.1$ Hz, $J_{56} = 1.2$ Hz.

(13) A 20-mL ether solution of 1 (0.50 g, 1.6 mmol) in a vacuum-sealed Pyrex tube was irradiated by a 400-W mercury lamp at −20 °C for 6 h. After removal of the solvent in vacuo, the residues were chromatographed through neutral alumina column (30 g, Merck) at 0 °C with pentane as the eluting solvent. A yellow band eluted first off the column was identified as a mixture of **1** and **3** and was not collected. A second yellow band off the column was collected, and the solvent was removed under reduced pressure. A dark red band which remained on the top portion of the column was identified as Cp$_2$Mo$_2$(CO)$_6$ and was not collected. Further crystallization of the yellow solid from the second band in pentane gave pale yellow crystals of **2** (0.23 g, 0.8 mmol).

(14) Anal. Calcd for $C_{12}H_{12}MoO_2$: C, 50.71; H, 4.23. Found: C, 50.64; H, 4.08. Mass spectrum (12 eV, ^{98}Mo 23.78%, *m/e*): 286 (M$^+$), 258 ($M^+ - CO$).

(15) IR spectrum (pentane): ν(C=C) 1625 (w) cm^{-1}; ν(C=O) 1975, 1905 (s) cm^{-1} (endo isomer) and 1960 (s), 1890 (s) cm^{-1} (exo isomer). ^{1}H NMR (400.1 MHz, −60 °C, toluene-d_8): exo isomer, δ 0.77 (dd, 1 H, H^1), 1.88 (t, 1 H, H^4), 2.20 (dd, 1 H, H^2), 3.35 (td, 1 H, H^3), 4.42 (s, 5 H, C$_5$H$_5$), 4.86 (dd, 1 H, H^7), 5.35 (dd, 1 H, H^6), 5.31 (dt, 1 H, H^5), $J_{13} = J_{34} = 10.0$ Hz, $J_{23} = 7.0$ Hz, $J_{12} = 2$ Hz, $J_{45} = J_{57} = 10.0$ Hz, $J_{56} = 16.2$ Hz, $J_{67} = 1.5$ Hz; endo isomer, δ 1.33 (d, 1 H, H^1), 2.40 (d, 1 H, H^2), 2.90 (t, 1 H, H^4), 3.45 (1 H, H^3, overlapping with H^3 of exo form, irradiation of this resonance turns the triplet at δ 2.90 into a doublet), 4.42 (s, 5 H, C$_5$H$_5$), 4.98 (d, 1 H, H^7), 5.06 (d, 1 H, H^6), 6.25 (dt, 1 H, H^5), $J_{13} = J_{34} = 10.0$ Hz, $J_{23} = 7.0$ Hz, $J_{45} = J_{57} = 10.0$ Hz, $J_{56} = 16.0$ Hz. ^{13}C NMR spectrum (100.6 MHz, 23 °C, benzene-d_6): exo isomer, 34.5 (CH^1H^2), 66.5 (CH^4), 69.2 (CH^3), 91.7 (C_5H_5), 139.2 (CH^5), 111.3 (CH^6H^7), 237, 240 ppm (CO).

(16) The exo and endo conformers are inferred from the stereochemistry of the parent compound (C$_5$H$_5$)Mo(CO)$_2$(allyl), see: Faller, J. W.; Chodosh, D. F.; Katahira, D. *J. Organomet. Chem.* **1980**, *187*, 227.

(17) ^{1}H NMR spectrum (400.1 MHz, 100 °C, toluene-d_8): δ 0.98 (br d, 1 H, H^1), 2.35 (br m, 1 H, H^4), 2.40 (dd, 1 H, H^2), 3.75 (td, 1 H, H^3), 4.70 (d, 1 H, H^6), 4.80 (s, 5 H, C$_5$H$_5$), 5.20 (d, 1 H, H^7), 5.75 (br m, 1 H, H^5), $J_{23} = 7.0$ Hz, $J_{12} = 1.8$ Hz, $J_{13} = J_{34} = 10$ Hz, $J_{56} = 16$ Hz, $J_{57} = 10$ Hz.

(18) Compound **2** crystallizes in the space group $P2_1/n$ with $a = 12.647$ (5) Å, $b = 6.703$ (2) Å, $c = 13.817$ (3) Å, $\beta = 102.59$ (3)°, $V = 1143.11$ Å^3, and $Z = 4$. X-ray diffraction data were collected at room temperature on an Enraf-Nonius CAD-4 diffractometer, using graphite-monochromated Mo Kα radiation. A total of 3589 independent reflections with $0° < 2\theta < 60°$ were collected by using the θ–2θ scanning technique. A total of 2001 reflections with $I > 3\sigma(I)$ were used in the least-squares refinement. The structure were solved by heavy-atom method using the NRCC SDP program library (Gabe, E. J.; Lee, F. L. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr.,* Theor. *Gen. Crystallogr.* **1981**, *A37*, S399). The final values of the agreement indices were $R = 0.036$ and $R_w = 0.024$ with 137 variables.

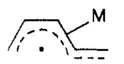
(19) The parent compound CpMo(CO)$_2$(η^3-allyl) similarly crystallized in exo conformer: see the ref 16.

(20) The allyl and pentadienyl groups are treated as monodentate ligands. The geometry of this complex can be described as a tetrahedron with C$_{11}$, C$_{12}$, and the centroids of the allyl and pentadienyl groups Ca and Cp, respectively, occupying the four coordination sites. The L–Mo–L angles are 79.9°, 122.2°, 96.8°, 121.1°, 96.9°, and 127.8° for C$_{11}$–Mo–C$_{12}$, C$_{11}$–Mo–Cp, C$_{11}$–Mo–Ca, C$_{12}$–Mo–Cp, C$_{12}$–Mo–Ca, and Cp–Mo–Ca, respectively.

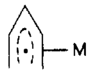
(21) Lee, G.-H.; Peng, S.-M.; Liao, M.-Y.; Liu, R.-S., unpublished results.

(22) In a typical reaction, a 20-mL etherate solution of **2** (0.3 g, 1.05 mmol) was irradiated by a 400-W mercury lamp at −20 °C for 6 h. After removal of the solvent, the residues were chromatographed through neutral alumina column (15 g, Merck) with pentane as the eluting solvent. The first eluted yellow band identified as **3** was collected. A second yellow band off the column identified as unreacted **2** was not collected. After removal of the solvent from the first band, analytically pure greenish yellow solid of **3** (0.11 g, 0.14 mmol) was obtained.

counted for the low yields.[23] Its ^1H and ^{13}C NMR spectra[24] reveal that compound **3** contains a η^5-pentadienyl group but in unsymmetric environments. Despite vigorous efforts in crystallization of **3**, an X-ray diffraction study[25] of **3** was hampered by its poor crystallinity. Of the two possible structures η^5-S and η^5-U shapes, the former is more likely



η^5-S



η^5-U

for **3** from the comparison of its ^1H NMR chemical shifts[26] to those of (η^5-*trans*-pentadienyl)$Fe(CO)_3^+$ and related cations.[27] In particular, the resonances of H^1 (δ 1.22) and H^5 (δ 1.55), which lie more upfield than other proton resonances, are characteristic of the two anti protons on the "butadiene" mouth of the ligand. Moreover, all reported unsymmetric η^5-U-type compounds[28] are prone to undergo rotation of the pentadienyl group at ambient temperatures. Such a process however is not observed for **3** even at 110 °C from the ^1H NMR studies (toluene-d_8). Ernst and co-workers[2d] have recently reported the structures of the related compounds $[2,4\text{-}(CH_3)_2C_5H_5]_2M(PEt_3)$ (M = Mo, Nb, Zr). For molybdenum complex, the two pentadienyl groups exist, respectively, in η^5-S and symmetric η^5-U forms; and for niobium and zirconium analogues, both ligands have the symmetric η^5-U structures. The metal sizes and electronic influences of molybdenum are thought to be the key factors in adoption of the unusual "S" configurations.

The ν(CO) band of **3** is observed at 1924 (s) cm^{-1}, significantly higher than that at 1868 (s) cm^{-1} for $Cp_2Mo(CO)$.[9b] The pentadienyl ligand appears to withdraw more electron density from the molybdenum center than the cyclopentadienyl group. The two compounds however have common aspects in chemical and physical properties. Like $Cp_2Mo(CO)$, **3** is greenish yellow solid extremely soluble in organic solvent and readily sublimes at 40 °C. Upon photolysis, **3** loses the CO group to give a red precipitate of undetermined composition. $Cp_2Mo(CO)$ forms the very reactive species "Cp_2Mo" in photolytic reactions. Experimental evidence to prove the existence of its pentadienyl analogue, the 16e "$(C_5H_5)Mo(C_5H_7)$", is underway.

Acknowledgment. We wish to thank the National Science Council, ROC, for financial support of this work.

Registry No. 1, 104293-11-0; 2 (exo isomer), 104293-12-1; 2 (endo isomer), 104418-74-8; 3, 104293-13-2; $CpMo(CO)_3Na$, 12107-35-6; *trans*-1-chloropenta-2,4-diene, 28070-18-0.

Supplementary Material Available: Tables of bond distances and angles, final fractional coordinates, and thermal parameters (3 pages); a listing of observed and calculated structure (23 pages). Ordering information is given on any current masthead page.

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(23) In a blank test, a vacuum-sealed NMR tube containing minor amount (~5 mg) of **3** in toluene-d_8 was irradiated by a 400-W mercury lamp which slowly deposited red insoluble solid during photolysis. The ^1H NMR resonances characteristic of **3** completely vanished after irradiation for 10 h.

(24) Anal. Calcd for $C_{11}H_{12}MoO$: C, 51.57; H, 4.69. Found: C, 51.50; H, 4.65. Mass spectrum (12 eV, ^{98}Mo 23.78%, *m/e*): 258 (M^+). IR spectrum (pentane): ν(CO) 1924 (s) cm^{-1}. ^1H NMR spectrum (400 MHz, benzene-d_6, 23 °C): δ 1.22 (dd, 1 H, H^1), 1.55 (m, 1 H, H^5), 1.76 (d, 1 H, H^7), 2.13 (d, 1 H, H^6), 2.42 (dd, 1 H, H^2), 2.78 (t, 1 H, H^4), 4.15 (m, 1 H, H^3), 4.58 (s, 5 H, C_5H_5), J_{12} = 2.5 Hz, J_{13} = 9.4 Hz, J_{23} = 6.8 Hz, J_{34} = J_{45} = 5.1 Hz, J_{56} = 5.0 Hz, J_{57} = 8.4 Hz, J_{67} = 0 Hz. ^{13}C NMR spectrum (100.6 MHz, 23 °C, benzene-d_6): δ 36.2, 40.1 (CH^1H^2 and CH^6H^7), 69.0, 75.8, 84.8 (CH^3, CH^4, and CH^5), 88.62 (C_5H_5), 239.4 (CO).

(25) Only preliminary data were obtained: space group *Pmma* with a = 10.024 (5) Å, b = 6.58 (2) Å, and c = 17.25 (2) Å. The crystal used for data collection was multiple. A total of 1084 independent reflections with $0° < 2\theta < 50°$ were collected by using the θ–2θ scanning technique; 318 reflections with $I > 2\sigma(I)$ were used. The molybdenum was located at 0.265, 0.356, 0.114 by Patterson synthesis, and the structure factor calculation based on the position of Mo gave R = 33%. The subsequent Fourier map indicated the disorder of the molecule.

(26) For **3**, the value of J_{45} is about 5 Hz, somewhat smaller than the expected value from the trans proton coupling. It is noteworthy that in the related compound $[2,4\text{-}(CH_3)_2C_5H_5]_2Mo(PEt_3)$[2d] the pentadienyl moiety is quite nonplanar. We believe that the distoriton from planarity will lead to a small value of J_{45}.

(27) (a) Sorenson, T. S.; Jablonski, C. R. *J. Organomet. Chem.* **1970**, *25*, C62. (b) Lillya, C. P.; Sahajian, R. A. *Ibid.* **1970**, *25*, C67. (c) Clinton, N. A.; Lillya, C. P. *J. Chem. Soc., Chem. Commun.* **1968**, 579; *J. Am. Chem. Soc.* **1970**, *92*, 3065.

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Multiple Insertion and C–C Coupling of Isocyanides: Reaction of Bis(η^5-methylcyclopentadienyl)zirconium Dihydride with Isocyanides

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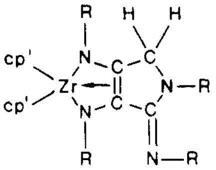
Received May 20, 1986

Summary: Reaction of *tert*-butyl isocyanide and cyclohexyl isocyanide with bis(η^5-methylcyclopentadienyl)zirconium dihydride led to multiple insertions into the Zr–H bond and to simultaneous reductive coupling of isocyanides with the formation of an unusual zirconacycle:



Current interest in the reduction of carbon monoxide has led to studies of the reactivity of CO with various zirconocene hydrides which have resulted in the observation of C–C bond formation.[1a,b] as well as simple CO reduction by these complexes.[1c] Examination of the reactivity of zirconocene hydrides has recently been extended to reactivity with isocyanides, which are isoelectronic with CO.[2] Specifically, interest has focused on the question of whether CO insertion into a Zr–H bond is thermodynamically feasible and, by analogy, whether such a process occurs in the cp_2ZrH_2–isocyanide system.

Another aspect of this chemistry concerns the role that the cp ligand plays. It has been noted that alkyl substituents on the cp ring increase the ligand to metal electronic donation, thereby heightening metal basicity.[3]

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