A), 112548-95-5; **2b** (isomer B), 112548-96-6; **2b** (isomer C), 112652-65-0; **3a**, 112548-92-2; **3b**, 112548-93-3; **4**, 112548-94-4; **5**, 112574-99-9; Os, 7440-04-2; Pt, 7440-06-4.

Supplementary Material Available: Stereoviews (Figures 4 and 6) of **3a** and **5** and tables of anisotropic thermal parameters and calculated hydrogen atom positional parameters and complete listings of bond length and angles (13 pages); listings of calculated and observed structure factors (52 pages). Ordering information is given on any current masthead page.

Synthesis, Characterization, and Reactivity of Molybdenum–Dienyl Complexes

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The reaction between $CpMo(CO)_3Na$ and 1-chloropenta-2,4-diene or 1-chlorohexa-2,4-diene yields $CpMo(CO)_3(\eta^1$-2,4-pentadien-1-yl) (**1**) or $CpMo(CO)_3(\eta^1$-2,4-hexadien-1-yl) (**2**), respectively. These η^1 complexes readily undergo an $\eta^1 \rightarrow$ syn-$\eta^3 \rightarrow \eta^5$ transformation by chemical or photolytic activation, and the resulting products are characterized by appropriate physical methods. Photolysis of $CpMo(CO)_2$-(*syn*-η^3-2,4-hexadien-1-yl) (**10**) gives rise to $CpMo(CO)_2$(*syn*-η^3-1-methyl-2,4-pentadien-1-yl) (**11**) in addition to the two isomeric η^5 forms $CpMo(CO)(\eta^5$-2,4-hexadien-1-yl) (**15**) and $CpMo(CO)(\eta^5$-1-methyl-2,4-pentadien-1-yl) (**16**). Preparation and characterization of the corresponding phosphine derivatives in η^1 and syn-η^3 configurations are described. At ambient temperatures, **1** readily undergoes [4 + 2] cycloaddition with dienophiles such as tetracyanoethylene and maleic anhydride.

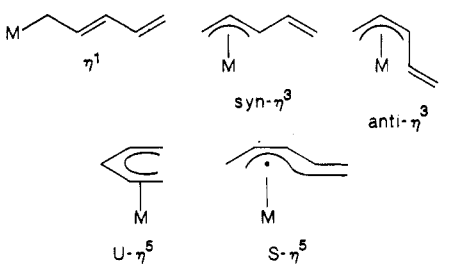
Introduction

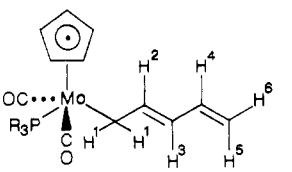
Transition-metal–allyl complexes have been the subject of intensive studies for many years because of their remarkable activity in reaction chemistry. Notable examples are η^1- and η^3-allyls of iron[1] and molybdenum[2] complexes that have proven to be very useful reagents in synthetic chemistry. In recent years, there has been a growing interest in the preparation of transition-metal–pentadienyl complexes.[3] In comparison with their allyl analogues, the chemistry of metal–pentadienyl complexes should in principle be more intriguing because of the various geometries possible for the pentadienyl ligand bound to the metal center as depicted in Chart I. One may reasonably anticipate a wide range of chemical versatility for these complexes. In this paper,[4] we describe the synthesis of a family of molybdenum–pentadienyl complexes in the η^1, syn-η^3, and *S*-η^5 configurations as well as their phosphine derivatives. The reaction chemistry of $CpMo(CO)_3(\eta^1$-pentadienyl) (**1**) with the dienophiles tetracyanoethylene and maleic anhydride is also described.

Results and Discussion

The reaction between $CpMo(CO)_3Na$ and *trans*-1-chloropenta-2,4-diene at −78 °C for 6 h gave a yellow crystalline solid of $CpMo(CO)_3(\eta^1$-pentadienyl) (**1**) in good yield after workup. Preparation of the 2,4-hexadien-1-yl analogue $CpMo(CO)_3(\eta^1$-2,4-hexadien-1-yl) (**2**) is easily achieved through stirring of a tetrahydrofuran solution of $CpMo(CO)_3Na$ and *trans*-1-chloro-2,4-hexadiene; the yield is 57%. These η^1 complexes readily undergo ligand substitution with the phosphines PMe_2Ph and PEt_3. Stirring of **1** with PMe_2Ph or PEt_3 at 23 °C gave high yields of $CpMo(CO)_2(PMe_2Ph)(\eta^1$-pentadienyl) (**3**) or $CpMo(CO)_2(PEt_3)(\eta^1$-pentadienyl) (**4**), respectively. Purification of these compounds by column chromatography gave analytically pure yellow oils. Attempts to obtain the trimethylphosphine analogues were not successful in similar reactions. For **3** and **4**, the ^{13}C NMR spectra reveal that the phosphine ligand is trans to the pentadienyl group. The resonances of the two CO ligands are equivalent and show a single doublet with $J_{PC} \simeq 22$ Hz. The facile CO

Chart I





3, P = PMe_2Ph
4, P = PEt_3

(1) (a) William, J. P.; Wojcicki, A. *Inorg. Chem.* **1977**, *16*, 3116. (b) Cutler, A.; Ehnolt, 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.

(2) (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) Pearson, A. J.; Khetani, V. d. *J. Chem. Soc., Chem. Commun.* **1986**, 1772. (d) Adams, R. D.; Chodosh, D. f.; Faller, J. W.; Rosan, A. M. *J. Am. Chem. Soc.* **1979**, *101*, 1570.

(3) For examples, see: (a) Ernst, R. D. *Acc. Chem. Res.* **1985**, *18*, 56. (b) Yasuda, H.; Nakamura, A. *J. Organomet. Chem.* **1985**, *285*, 15. (c) Bleeke, J. R.; Kotyk, J. J.; Moore, D. A.; Rauscher, D. J. *J. Am. Chem. Soc.* **1987**, *109*, 417 and references therein.

(4) Part of this paper has appeared in an earlier communication: Lee, G.-H.; Peng, S.-M.; Lee, T.-W.; Liu, R.-S. *Organometallics* **1986**, *5*, 2378.

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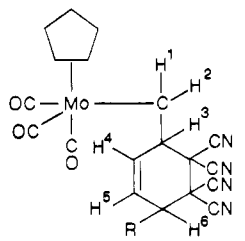
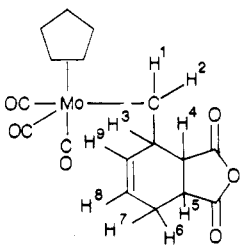
substitution here sharply contrasts with the phosphine-promoted CO insertion that has been a common process for numerous metal–alkyl complexes.[5,6] We have no explanation for this difference in reactivity at the present stage.

Transition-metal–η^1-allyl complexes have been used extensively in many organic reactions. The most prominent examples are the [3 + 2] cycloaddition with many electrophiles.[1] One aim of our syntheses of transition-metal–η^1-pentadienyl complexes is to explore their potential in organic reactions because of their structural resemblance to η^1-allyl complexes. The reactions with the electrophiles tetracyanoethylene and maleic anhydride have thus been carried out. Stirring a benzene solution of **1** with tetracyanoethylene at 23 °C for 1 h gave the [4 + 2] cycloadduct **5** in good yields after workup. Similarly, the reaction of **2** with tetracyanoethylene gave **6** but in low yield (8%). The reaction of **1** with maleic anhydride gave **7** in high yields. For **5**, **6**, and **7**, all complexes exist in one



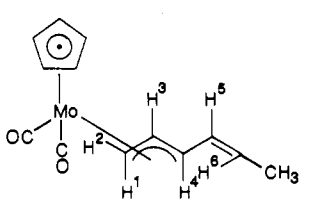
5, R = H
6, R = CH_3



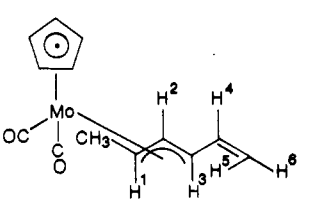
7

stereoisomer as shown from spectroscopic data. The confirmations of the proposed structures derive from the ^{1}H NMR spectra that show the resonances of two olefinic protons at δ 5.60–5.90 and H^1 and H^2 as a AB quartet at δ 1.40–2.20, further split by H^3. The IR spectra that contain the absorptions ν(C=C) at 1652–1658 cm^{-1}, ν(C≡N) at ~2230 cm^{-1}, and ν(C(O)–O–C(O)) at 1775 cm^{-1} are consistent with the structures.

Photolysis of **1** in ether at −20 °C gave a mixture of $CpMo(CO)_2$(*syn*-η^3-pentadienyl) (**8**) and $CpMo(CO)$(η^5-pentadienyl) (**9**) and $Cp_2Mo_2(CO)_6$. All products were isolated by alumina column chromatography under argon. The isolated yields of **8** and **9** were 62% and 12%, respectively. Stirring of anhydrous trimethylamine oxide with **1** in CH_2Cl_2 for 6 h gave only **8** in better yield. For **2**, the best synthesis of the η^3 complex $CpMo(CO)_2$(*syn*-η^3-2,4-hexadien-1-yl) (**10**) was to stir the η^1 complex with Me_3NO in CH_2Cl_2. On irradiation, **2** underwent cleavage of the metal–dienyl bond and gave mainly $Cp_2Mo_2(CO)_6$ and dodecatetraene. The combined yields of the η^3 complexes **10** and $CpMo(CO)_2$(*syn*-η^3-1-methyl-2,4-pentadien-1-yl) (**11**) after irradiation of **2** were only 5–6%. The

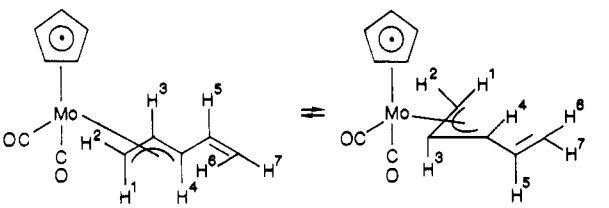


10



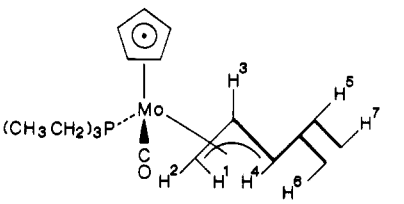
11

molar ratio **11**/**10** depended on the time of irradiation. If the samples were irradiated for a prolonged period (~48 h), the isolated η^3 complexes consisted mainly of **11**. Later experiments confirmed that **11** was produced by photolytic isomerization of **10**. For **8** and **10**, the IR and ^{1}H NMR spectra (−60 °C, toluene-d_8) reveal that the compounds exist in two stereoisomers, i.e. the exo-syn-η^3 and endo-syn-η^3 forms. The exo isomer is characterized by a greater shielding of the two anti protons (e.g. H^1 and H^4 for **10**) than the endo isomer.[7] The assignment of the syn configuration was based on the proton coupling constants, J_{34} (complex **10**) ≃ J_{23}(**11**) ≃ 10.5 Hz. The exo/endo molar ratio in thermal equilibrium at −60 °C was 9.0 and 8.5 for **8** and **10**, respectively. The structure of the exo isomer of **8** has previously been determined by an X-ray diffraction study.[4] The exo–endo isomerization occurred at a rate

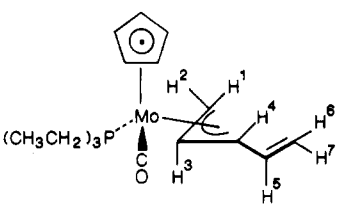


exo isomer endo isomer

within the time scale of NMR spectroscopy. At elevated temperatures, the site exchanges $H_1 \rightleftharpoons H_1'$, $H_2 \rightleftharpoons H_2'$, $H_3 \rightleftharpoons H_3'$, ..., and $H_7 \rightleftharpoons H_7'$ were observed. This dynamic process appears to involve pseudorotation about the metal–allyl axis as in the parent complex $CpMo(CO)_2$(η^3-allyl).[8] The free energies of activation for this process are 18.2 ± 0.3 and 19.8 ± 0.3 kcal/mol for **8** and **10**, respectively. During this dynamic process, no site exchanges within the pentadienyl ligand, $C_1 \rightleftharpoons C_5$, $C_2 \rightleftharpoons C_4$, and $C_3 \rightleftharpoons C_3$, were observed, even at 110 °C in toluene-d_8. For **3** and **4**, the CO ligand was prone to dissociate on irradiation; that process gave $CpMo(CO)(PMe_2Ph)$(*syn*-η^3-pentadienyl) (**12**) and $CpMo(CO)(PEt_3)$(*syn*-η^3-pentadienyl) (**13**) in yields of 36% and 52%, respectively. The formation of **13** was so slow that the endo isomer was obtained



13 (exo isomer)



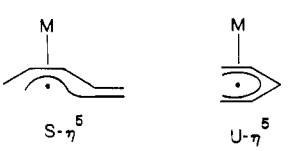
13 (endo isomer)

together with the exo isomer. Similarly, the exo isomer is characterized by a greater shielding of the two anti protons H^1 and H^4 than the endo isomer. At ambient temperature, the endo isomer slowly isomerized to the exo isomer. If an NMR sample (exo/endo = 1:1) was allowed to warm to 45 °C, less than 1% of endo isomer remained in the solution after 4 h. This endo–exo isomerization follows π–σ–π rearrangement rather than pseudorotation

(5) Carbonyl insertion for organomolybdenum complexes has been shown to be promoted by phosphine ligands, see: (a) Webb, S. L.; Gianodomenico, C. M.; Halpern, J. *J. Am. Chem. Soc.* **1986**, *108*, 345. (b) Wax, M. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 7028.
(6) Cotton, J. D.; Kimlin, H. A. *J. Organomet. Chem.* **1985**, *294*, 213.
(7) Fish, R. W.; Giering, W. P.; Marten, D.; Rosenblum, M. J. *J. Organomet. Chem.* **1976**, *105*, 101.
(8) (a) Faller, J. W.; Incorvia, M. J. *Inorg. Chem.* **1968**, *7*, 840. (b) Faller, J. W.; Jakubowski, A. *J. Organomet. Chem.* **1971**, *31*, C75.

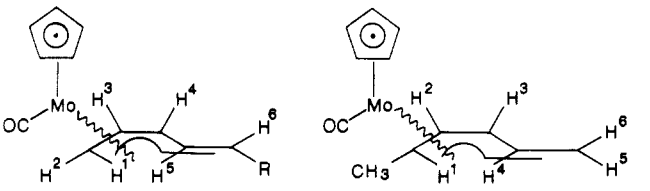
of the metal–allyl axis from consideration of the structures. The proposed structures depicted above were elucidated from the ^1H and ^{13}C NMR spectra. The observed ^1H and ^{13}C NMR coupling constants $J_{PH^1} \simeq 11$ Hz, $J_{PH^2} \simeq 4$ Hz, and $J_{PC_\alpha} \simeq 14$ Hz for the exo isomer and $J_{PH^1} \simeq 13$ Hz and $J_{PC_\alpha} \simeq 8$ Hz for the endo isomer suggest that both vinyl ends lie away from the bulky phosphine group in order to minimize steric hinderance. From comparison of its ^1H NMR data of **12** with those of **13**, the exo isomer of **12** has a similar structure. The basis for such a structural assignment stems from the stereochemistry of the closely related five-coordinate complex $Co(CO)_2(PPh_3)$-(*syn*-η^3-pentadienyl)[9] as well as comparison of their NMR patterns. Although **12** and **13** are present as oils, some structural information was derived from NMR spectra. For **12**, the ^1H and ^{13}C NMR resonances of the two phosphine methyls are nonequivalent, indicative of the absence of a symmetry plane across the Mo–P bond. For the two isomers of **13**, the methylene protons are found to be diastereotopic in the ^1H NMR spectrum.

The CO ligands of **8** and **10** were found to be labile upon irradiation. Irradiation of **8** in the presence of PMe_3, PMe_2Ph, and PEt_3 gave the phosphine-substituted derivatives $CpMo(CO)(PMe_3)$(*syn*-η^3-pentadienyl) (**14**), **12**, and **13**. Likewise, the endo isomer of **13** was isolated together with exo isomer during irradiation. For **14** and **12**, only the exo isomer was obtained. The exo isomer of **14** has a structure similar to those of **12** and **13** as shown from ^1H and ^{13}C NMR resonances. In the absence of the phosphine ligand, irradiation of **8** in ether at −20 °C gave **9** in 32% yield after workup. The successive loss of the CO ligand of **8** to give an uncharacterized red precipitate accounted for the low yield. This syn-$\eta^3 \rightarrow \eta^5$ conversion is not operable in the thermolysis of **8** in toluene even under reflux for 10 h. The ν(CO) band of **9** is observed at 1924 (s) cm^{-1}, significantly higher than the band at 1868 (s) cm^{-1} for $Cp_2Mo(CO)$.[10] The ^1H and ^{13}C NMR spectra reveal that **9** contains a η^5-pentadienyl group but in an unsymmetric environment. Despite vigorous efforts to crystallize **9**, an X-ray diffraction study was hampered by its poor crystallinity. Of the two possible structures, S-η^5 and U-η^5 configurations, the former is assigned to **9** from



the comparison of the ^1H NMR chemical shifts with those of (η^5-*trans*-pentadienyl)$Fe(CO)_3^+$ and related cations.[11] In particular, the resonances of H^1 (δ 1.22) and H^5 (δ 1.55), which lie upfield more than other proton resonances, are characteristic of the two anti protons on the butadiene "mouth" of the ligand. In addition, all reported unsymmetric U-η^5-type complexes[12] are prone to undergo rotation of the pentadienyl ligand at elevated temperatures. Such a process, however, was not observed in ^1H NMR studies of **9**, even up to 110 °C in toluene-d_8. Ernst and coworkers[13] have recently reported the structures of the related complexes $[2,4\text{-}(CH_3)_2C_5H_5]_2M(PEt_3)$ (M = Mo, Nb, Zr). For the molybdenum complex, the two pentadienyl groups exist, respectively, in S-η^5 and unsymmetric U-η^5 forms; and for the niobium and zirconium analogues, both ligands have symmetric U-η^5 structures. The metal sizes and electronic influences of molybdenum are thought to be the key factors in its adoption of the unusual "S" configuration.[13]

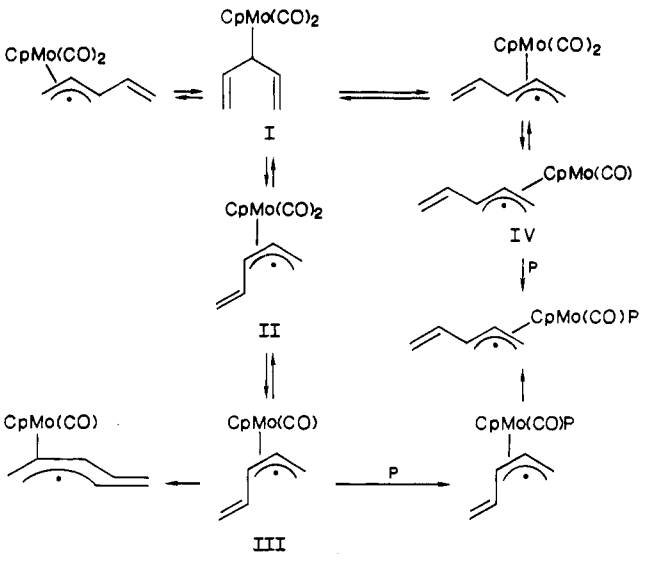
In order to understand further the nature of this syn-$\eta^3 \rightarrow \eta^5$-S transformation, we investigated the photolytic chemistry of **10**. Irradiation of **10** in ether at −20 °C gave mainly **11** and minor amounts of $CpMo(CO)(\eta^5$-2,4-hexadien-1-yl) (**15**) and $CpMo(CO)(\eta^5$-1-methyl-2,4-pentadien-1-yl) (**16**). The structures of **15** and **16** were assigned



below from the comparison of the ^1H NMR resonances with those of **9**. The combined yields of **15** and **16** were exceptionally small—in most cases less than 0.5%. Complexes **15** and **16** were generated by irradiation of **10** since prolonged photolysis of **11** did not produce the η^5 complexes. For **11**, the photochemical inertness of the CO ligand could be attributed to the stronger M–CO bonds (ν(CO) = 1953, 1885 cm^{-1}) than those of **10** (ν(CO) = 1962, 1890 cm^{-1}) and **8** (ν(CO) = 1960, 1890 cm^{-1}). Only one isomer was detected spectroscopically for **11**, and the exo isomer was assigned on the basis of the H^3 chemical shift (δ 2.00). The δ values of H^3 for the endo isomer are expected to be within δ 2.60–2.80. The coupling constant, $J_{12} \simeq 10$ Hz, reveals that H^1 is trans to H^2. Photolysis of **10** in a CO-saturated atmosphere gave only **11**. Thermolysis of **10** in toluene at reflux for 12 h did not give **11**, **15**, or **16**. In photolytic conversion of **8** to **15** and **16**, the molar ratio **15**/**16** lies within the range 0.35–0.50. These values appear to have no correlation with the length of irradiation. Like **9**, further irradiation of a mixture of **15** and **16** in ether at −20 °C gave rise to an uncharacterized red precipitate. These two geometric isomers did not undergo mutual interconversion at elevated temperatures. Thermolysis of **15**/**16** mixtures having different compositions in toluene-d_8 at 110 °C for 0.5 h gave no changes in their relative ^1H NMR intensities. The photolytic conversion of **10** to **11**, **15**, and **16** enables one to investigate the nature of a *syn*-η^3-pentadienyl ligand on photoexcitation. As depicted in Scheme I, on irradiation, complexes **8** and **11** undergo dissociation of the π-allyl ligand to give the η^1-intermediate **I**. This process is accompanied by the site exchanges $C_1 \rightleftharpoons C_5$, $C_2 \rightleftharpoons C_4$, and $C_3 \rightleftharpoons C_3$ if the two ends of the pentadienyl ligand are equivalent. For an η^3-pentadienyl group with two inequivalent ends, photoisomerization to the more thermally stable isomer occurs in this mechanism. Particularly notable is that this process is not operable under thermal activation. We propose that during irradiation, some intermediates exist in the *anti*-

(9) Lee, G.-H.; Peng, S.-M. Liao, M.-Y.; Liu, R.-S. *J. Organomet. Chem.* **1986**, *312*, 113.
(10) (a) Tang Wong, K. L.; Thomas, J. L.; Brintzinger, H. H. *J. Am. Chem. Soc.* **1974**, *96*, 3694. (b) Thomas, J. L. *J. Am. Chem. Soc.* **1973**, *95*, 1838.
(11) (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.
(12) For examples, see: (a) Liu, J.-Z.; Ernst, R. D. *J. Am. Chem. Soc.* **1982**, *104*, 3737. (b) Wilson, D. R.; Dilullo, A. A.; Ernst, R. D. *Ibid.* **1980**, *102*, 5929. (c) Bleeke, J. R.; Stanley, G. G.; Kotyk, J. J. *Organometallics* **1986**, *5*, 1642. (d) Williams, G. M.; Fisher R. A.; Heyn, R. H. *Ibid.* **1986**, *5*, 818.
(13) (a) Stahl, L.; Hutchinson, J. P.; Wilson, D. R.; Ernst, R. D. *J. Am. Chem. Soc.* **1985**, *107*, 5016. (b) A similar complex $CpCr(CO)(\eta^5$-pentadienyl) has been recently prepared by Ernst's group, see: Ernst, R. D.; Freeman, J. W., unpublished results.

Scheme I



η^3-pentadienyl form II, which subsequently loses one molecule of CO to give the 16e anti-η^3 fragment III. In the presence of phosphines, III combines with the ligands to give the phosphine-substituted η^3 complexes. Similarly, on photoexcitation, these anti-η^3 species are converted to the more energetically stable syn-η^3 isomer in a $\pi-\sigma-\pi$ rearrangement. Alternatively, the latter can also be produced by the coordination of phosphines to the 16e syn-η^3 fragment IV, generated by the photodissociation of CO from the dicarbonyl complex. In the absence of phosphines, the anti-η^3 fragment III acquires the vinyl end to give the S-η^5 complex. Following this proposed mechanism, two isomeric S-η^5 complexes are obtainable if the pentadienyl group is not symmetric. This satisfactorily accounts for our results. Although numerous papers[14] have shown a variety of fluxional modes for metal–η^3 allyl complexes, a thermally formidable but photolytically achievable $\pi-\sigma-\pi$ rearrangement, to our best knowledge, has not been cited. This process is of mechanistic interest because the vacant site created by the $\eta^3 \rightarrow \eta^1$ transformation could give rise to novel chemistry through coordination with suitable substrates.[15] Faller[16] and coworkers have recently reported the photolytic CO substitution from the related complex $CpMo(CO)_2(\eta^3$-allyl) by trialkylphosphines; however, little is mentioned about the nature of such a Mo–η^3-allyl ligand on photoexcitation.

Experimental Section

All operations were carried out under argon in a Schlenk apparatus or in a glovebox. The solvents benzene, diethyl ether, tetrahydrofuran, and pentane were dried with sodium/benzophenone and distilled before use. Dichloromethane and chloroform were dried over P_2O_5 and distilled. Anhydrous trimethylamine oxide was prepared by subliming the dihydrate (Fluka) at 100 °C (1.2×10^{-2} Torr). Trimethylphosphine, dimethylphenylphosphine, and triethylphosphine were obtained from Strem Chemicals and used without further purification, $[CpMo(CO)_3]_2$, $CpMo(CO)_3Na$,[17] and (*E*,*E*)-1-chloro-2,4-hexadiene[18] were prepared according to the procedures in the literature. The preparation of **1**, **8**, and **9** were described in an earlier communication.[4]

All ^1H and ^{13}C NMR spectra were obtained on a Bruker AM-400 spectrometer. The δ values were referenced to tetramethylsilane. Infrared spectra were recorded on a Perkin-Elmer 781 spectrophotometer. Microanalyses were carried out in the microanalytical laboratory at National Taiwan University. Mass spectra were obtained on a JEOL JMS-D100 instrument.

Variable-temperature ^1H NMR spectra of **2** and **10** were recorded from −96 to 110 °C in toluene-d_8. Probe temperatures were calibrated by using the temperature dependence of the difference in chemical shift between the ^1H resonances of the methyl and hydroxyl groups of methanol (below ambient temperatures) and between the ^1H resonances of the methylene and hydroxyl groups of ethylene glycol (above ambient temperatures).

The exchange rate constants, k_c, at the coalescence temperature were calculated according to the formula

$$k_c = \pi(\Delta\nu)/2^{1/2}$$

in which $\Delta\nu$ is the difference in frequencies between the two exchanging sites in the stopped-exchange limit.[19] These rate constants were used to determine the free energy of activation ΔG^* at the coalescence temperature, T_c, from the Eyring equation

$$k_c = (k'/\hbar)T_c e^{-\Delta G^*/RT_c}$$

in which k' = Boltzmann's constant, $\hbar$ = Planck's constant, and R = ideal gas constant.

(a) Synthesis of $CpMo(CO)_3(\eta^1$-2,4-hexadien-1-yl) (2). (*E*,*E*)-1-Chlorohexa-2,4-diene (1.3 g, 11.2 mmol) was added dropwise to 50 mL of tetrahydrofuran solution containing $CpMo(CO)_3Na$ (1.5 g, 5.59 mmol) at −78 °C and stirred for 3 h. After the insoluble sodium chloride was filtered off at −78 °C, the solution was warmed to 0 °C and evaporated to dryness to give a yellow residue. The residue was extracted twice with 20 mL of pentane, filtered, and evaporated to dryness. By means of pentane as the eluting solvent, the residue was chromatographed through a neutral alumina column at 23 °C. In addition to the immobile band of $Cp_2Mo_2(CO)_6$, a yellow band was eluted rapidly and collected. After the solvent was removed, followed by crystallization from pentane, yellow needlelike crystals of **2** (1.06 g, 3.24 mmol) were obtained. Anal. Calcd for $C_{14}H_{14}MoO_3$: C, 51.54; H, 4.29. Found: C, 51.76; H, 4.40. Mass spectrum (12 eV, ^{98}Mo 23.78%, *m/e*): 300 (M^+ − CO), 272 (M^+ − 2CO), 244 (M^+ − 3CO), 247 ($M^+ - C_6H_9$), 219 ($M^+ - C_6H_9$ − CO), 191 ($M^+ - C_6H_9$ − 2CO), 163 ($M^+ - C_6H_9$ − 3CO). IR (pentane): ν(CO) 2015 (s), 1962 (s), 1942 (s) cm^{-1}; ν(C=C) 1620 (w) cm^{-1}. ^1H NMR (400.1 MHz, benzene-d_6): δ 1.64 (d, 3 H, CH_3), 2.38 (d, 2 H, H^1), 5.50 (m, 1 H, H^5), 5.90–6.10 (complex, 3 H, $H^2 + H^3 + H^4$), $J_{5\text{-}CH_3}$ = 6.4 Hz, J_{12} = 8.4 Hz, J_{45} = 16.4 Hz.

(b) Synthesis of $CpMo(CO)_2(PMe_2Ph)(\eta^1$-pentadienyl) (3). PMe_2Ph (0.3 mL, 0.28 g, 1.95 mmol) was added to **1** (0.47 g, 1.50 mmol) in ether and the mixture stirred at 23 °C for 4 h. The solution was evaporated to dryness, and the residue was chromatographed through a neutral alumina column with pentane as the eluting solvent. A yellow band was developed and collected. After removal of the solvent, an analytically pure yellow-green oil of **3** (0.52 g, 1.23 mmol) was obtained. Anal. Calcd for $C_{20}H_{23}MoO_2P$: C, 56.88; H, 5.45. Found: C, 57.12; H, 5.55. Mass spectra (12 eV, ^{98}Mo 23.78% *m/e*): 424 (M^+), 396 (M^+ − CO), 368 (M^+ − 2CO), 286 ($M^+ - PMe_2Ph$), 258 ($M^+ - PMe_2Ph$ − CO), 230 ($M^+ - PMe_2Ph$ − 2CO). IR (Nujol): ν(C=C) 1622 (w) cm^{-1}; ν(CO) 1938 (s), 1845 (s) cm^{-1}. ^1H NMR (400.1 MHz, benzene-d_6): δ 1.37 (d, 6 H, PCH_3), 2.53 (dd, 2 H, H^1), 4.35 (s, 5 H, C_5H_5), 4.88 (dd, 1 H, H^6), 5.12 (dd, 1 H, H^5), 6.15 (dd, 1 H, H^3), 6.48–6.56 (complex m, 2 H, $H^2 + H^4$), 7.01 and 7.28 (complex m, 5 H, PC_6H_5), J_{P-1} = 3.2 Hz, J_{12} = 8.2 Hz, J_{23} = 15.2 Hz, J_{34} = 10.2 Hz, J_{45} = 17.3 Hz, J_{46} = 10.2 Hz, J_{56} = 1.8 Hz, $J_{P\text{-}CH_3}$ = 8.8 Hz. $^{13}C\{^1H\}$ NMR (100.6 MHz, chloroform-d_1): δ 5.6 (d, CH^1, J_{PC} = 9 Hz), 20.3 (d, PCH_3, J_{PC} = 32 Hz), 91.2 (s, C_5H_5), 111.6 (s, CH^5H^6), 129.2, 130.4,

(14) (a) Vrieze, K. In *Dynamic Nuclear Magnetic Resonances Spectroscopy*; Jackman, L. M., Cotton, F. A., Eds.; Academic: New York, 1975. (b) Faller, J. W. *Adv. Organomet. Chem.* **1978**, *16*, 211.

(15) For metal–pentadienyl complexes, a thermal interconversion between the bonding modes $\eta^5-\eta^3$ has been described in several papers, see: (a) Knowalcski, R. M.; Basolo, F.; Trogler, W. C.; Ernst, R. D. *J. Am. Chem. Soc.* **1986**, *108*, 6046. (b) Paz-Sandoval, M. d. l. A.; Powell, P.; Drew, M. G. B.; Perutz, R. *Organometallics* **1984**, *3*, 1026.

(16) Ma, Y.; Faller, J. W. *Organometallics* **1986**, *5*, 1949.

(17) Eisch, J. J., King, R. B., Eds. *Organometallics Synthesis*; Academic: New York, 1965; Vol. 1, pp 114–116.

(18) Prevost, C.; Miginiac, P.; Miginiac-Groizeleau, L. *Bull. Soc. Chim. Fr.* **1964**, 2485.

(19) Pople, J. A.; Schneider, W. G.; Bernstein, H. J. *High Resolution Nuclear Magnetic Resonance*; McGraw-Hill: New York, 1959; p 223.

130.9 (C_6H_5), 236.8 (d, CO, J_{PC} = 23 Hz).

(c) Synthesis of $CpMo(CO)_2[P(C_2H_5)_3](\eta^1$-pentadienyl) (4). This complex was prepared similarly from the reaction between **1** and triethylphosphine; the yield was 91%. Anal. Calcd for $C_{18}H_{27}MoO_2P$: C, 53.74; H, 6.71. Found: C, 53.87; H, 6.92. Mass spectrum (12 eV, ^{98}Mo 23.78%, *m/e*): 404 (M^+), 376 (M^+ - CO), 348 (M^+ - 2CO), 286 (M^+ - PEt_3), 258 (M^+ - PEt_3 - CO). IR (pentane): ν(CO) 1930 (s), 1949 (s) cm^{-1}; ν(C=C) 1617 cm^{-1}. ^{1}H NMR (400.1 MHz, benzene-d_6): δ 0.73 (m, 9 H, PCH_2CH_3), 1.22 (m, 6 H, PCH_2), 2.49 (d, 2 H, H^1), 4.48 (s, 5 H, C_5H_5), 4.90 (dd, 1 H, H^6), 5.15 (dd, 1 H, H^5), 6.21 (dd, 1 H, H^3), 6.58 (complex m, 2 H, H^2 + H^4), J_{12} = 7.6 Hz, J_{23} = 16.0 Hz, J_{34} = 10.4 Hz, J_{45} = 17.4 Hz, J_{46} = 10.4 Hz, J_{56} = 1.5 Hz. ^{13}C{^{1}H} NMR (100.6 MHz, benzene-d_6): δ 6.1 (d, CH^1, J_{PC} = 9.6 Hz), 7.9 (d, CH_3, J_{PC} = 8 Hz), 22.7 (d, CH_2, J_{PC} = 26 Hz), 91.9 (s, C_5H_5), 110.7 (s, CH^5H_6), 123.2, 137.4 (s, s, CH^2 + CH^3), 146.8 (s, CH^4), 238.4 (d, CO, J_{PC} = 24 Hz).

(d) Reaction of 1 with Tetracyanoethylene. Tetracyanoethylene (0.25 g, 1.98 mmol) and **1** (0.48 g, 1.51 mmol) were dissolved in 20 mL of benzene and stirred at 23 °C for 2 h. After removal of the solvent under reduced pressure, the residues were extracted twice with 20 mL of chloroform, filtered, and evaporated to dryness. Further recrystallization from dichloromethane–hexane gave yellow crystalline **5** (0.44 g, 1.00 mmol). Anal. Calcd for $C_{19}H_{12}MoO_3N_4$: C, 51.82; H, 2.27. Found: C, 51.94; H, 2.52. IR (Nujol): ν(C≡N) 2232 (w); ν(CO) 2010 (s), 1950 (s), 1920 (s) cm^{-1}; ν(C=C) 1656 cm^{-1}. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ 1.40 (dd, 1 H, H^1), 2.00 (dd, 1 H, H^2), 3.3–3.0 (complex m, 3 H, H^3 + H^6 + H^7), 5.41 (s, 5 H, C_5H_5), 5.75 (m, 1 H, H^5), 5.79 (m, 1 H, H^4), J_{12} = 10.4 Hz, J_{13} = 12.0 Hz, J_{23} = 3.2 Hz, J_{45} = 10.4 Hz, J_{67} = 19.2 Hz.

(e) Reaction of 2 with Tetracyanoethylene. This reaction was conducted in a similar way to preparation of **5**; the yield of **6** was 8%. Anal. Calcd for $C_{20}H_{14}MoO_3N_4$: C, 52.48; H, 3.08. Found: C, 52.64; H, 3.34. IR (KBr): ν(C≡N) 2230 (w) cm^{-1}; ν(CO) 2010 (s), 1948 (s), 1923 (s) cm^{-1}; ν(C=C) 1654 (w) cm^{-1}. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ 1.52 (d 3 H, CH_3), 1.71 (dd, 1 H, H^1), 2.01 (dd, 1 H, H^2), 3.12 (complex m, 2 H, H^3 + H^6), 5.42 (s, 5 H, C_5H_5), 5.62 (dd, 1 H, H^5), 5.85 (dd, 1 H, H^4), J_{12} = 10.0 Hz, J_{13} = 10.4 Hz, J_{23} = 4.4 Hz, J_{45} = 9.8 Hz, J_{34} = 5.2 Hz, J_{56} = 3.3 Hz, $J_{6\text{-}CH_3}$ = 6.8 Hz.

(f) Reaction of Maleic Anhydride with 1. Maleic anhydride (0.50 g, 5.1 mmol) and compound **1** (0.51 g, 1.60 mmol) were stirred in 20 mL of benzene for 4 h. After removal of the insoluble remaining maleic anhydride, the filtrate was evaporated to dryness. After extraction of the residue twice with chloroform, the extracts were evaporated to dryness under reduced pressure to give an orange solid. Further recrystallization from dichloromethane–hexane gave orange blocks of **7** (0.52 g, 1.26 mmol). Anal. Calcd for $C_{17}H_{14}MoO_6$: C, 49.75; H, 3.41. Found: C, 49.34; H, 3.62. IR (Nujol): ν(CO) 2005 (s), 1935 (s), 1910 (s), 1775 (s) cm^{-1}; ν(C=C) 1650 (w) cm^{-1}. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ 1.65 (dd, 1 H, H^1), 1.92 (dd, 1 H, H^2), 2.25 (complex m, 1 H, H^6), 2.63 (ddd, 1 H, H^7), 2.70 (complex m, 1 H, H^3), 3.30 (dd, 1 H, H^4), 3.38 (ddd, 1 H, H^5), 5.32 (s, 5 H, C_5H_5), 5.85 (complex m, 1 H, H^8), 5.95 (ddd, 1 H, H^9), J_{12} = 10.1 Hz, J_{13} = 10.1 Hz, J_{23} = 4.0 Hz, J_{34} = 5.8 Hz, J_{45} = 9.6 Hz, J_{56} = 8.8 Hz, J_{57} = 2.9 Hz, J_{67} = 16.0 Hz, J_{68} = 4.4 Hz, J_{78} = 5.8 Hz, J_{89} = 9.8 Hz, J_{39} = 3.2 Hz, J_{69} = 2.1 Hz, J_{38} = 1.5 Hz; the value of J_{36} was not determined because of the complex multiplicities of H^3 and H^6. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 2.2 (CH^1H^2), 23.2 (CH^6H^7), 40.6, 40.7, 48.5 (CH^3 + CH^4 + CH^5), 125.9, 136.3 (CH^8 + CH^9), 172.4, 174.8 (CO–O–CO), 228.8, 229.5, 239.2 (CO).

(g) Synthesis of $CpMo(CO)_2(\eta^3$-2,4-hexadien-1-yl) (10). Method A. A 25-mL dichloromethane solution of **2** (0.62 g, 1.89 mmol) was stirred with anhydrous trimethylamine oxide (0.50 g, 6.55 mmol) at 0 °C for 6 h. After the solution was evaporated to dryness, the residues were extracted with 20 mL of ether twice. The extract was then evaporated to dryness, and the residue was chromatographed on neutral alumina by using ether as the eluting solvent. A yellow band was developed and collected. Recrystallization from pentane at −25 °C gave yellow blocks of **10** (0.34 g, 1.13 mmol). Anal. Calcd for $C_{13}H_{14}MoO_2$: C, 52.35; H, 4.69. Found: C, 52.21; H, 4.42. Mass spectrum (12 eV, ^{98}Mo, 23.78%): 300 (M^+), 272 (M^+ - CO), 244 (M^+ - 2CO). IR (pentane): exo isomer, ν(CO), 1962 (s), 1890 (s) cm^{-1}; endo isomer, 1970 (s), 1905 (s) cm^{-1}; ν(C=C) 1623 (w) cm^{-1}. ^{1}H NMR (400.1 MHz, toluene-d_8): exo isomer, δ 0.74 (dd, 1 H, H^1), 1.58 (d, 3 H, CH_3), 2.16 (t, 1 H, H^4), 2.27 (dd, 1 H, H^2), 3.55 (td, 1 H, H^3), 4.55 (s, 5 H, C_5H_5), 5.21 (dd, 1 H, H^5), 5.72 (m, 1 H, H^6), J_{12} = 1.8 Hz, J_{13} = 10.8 Hz, J_{23} = 6.4 Hz, J_{34} = J_{45} = 10.4 Hz, J_{56} = 15.8 Hz, $J_{6\text{-}CH_3}$ = 6.4 Hz; endo isomer, δ 0.82 (d, 1 H, H^1), 1.83 (d, 3 H, CH_3), 2.35 (d, 1 H, H^2), 3.01 (t, 1 H, H^4), 3.52 (td, 1 H, H^3), 4.55 (s, 5 H, C_5H_5), 5.45 (m, 1 H, H^6), 5.83 (dd, 1 H, H^5), J_{13} = 10.8 Hz, J_{23} = 6.6 Hz, J_{34} = J_{45} = 10.5 Hz, J_{56} = 16.2 Hz. ^{13}C{^{1}H} NMR (100.6 MHz, benzene-d_6): exo isomer, δ 18.2 (CH_3), 33.7 (CH^1H^2), 67.8, 68.4 (CH^3 + CH^4), 91.6 (C_5H_5), 123.9 (CH^6), 132.9 (CH^5).

Method B. A 25-mL ether solution of **2** (0.42 g, 1.28 mmol) in a vacuum-sealed tube was irradiated by a 400-W mercury lamp at −20 °C for 4 h. After removal of ether in vacuo (2.5 × 10^{-1} Torr, 0 °C), the remaining red semisolid was further distilled (3.2 × 10^{-4} Torr, 23 °C) into a −35 °C cold trap and gave an oil analyzed as $C_{12}H_{18}$ from its mass spectrum. The nonvolatile residues were then eluted through a neutral alumina column using pentane as the solvent. In addition to an immobile purple band, a yellow band was developed, collected, and evaporated to dryness. Further crystallization from pentane gave a mixture of **10** and **11** (30 mg, 0.10 mmol, molar ratio of **7**/**8** = 3:7) in a yellow crystalline solid. The top purple band was identified as $Cp_2Mo(CO)_6$ after elution with dichloromethane.

(h) Synthesis of $CpMo(CO)_2$(*syn*-η^3-1-methyl-2,4-pentadienyl) (11), $CpMo(CO)(\eta^5$-2,4-hexadien-1-yl) (15), and $CpMo(CO)(\eta^5$-1-methyl-2,4-pentadien-1-yl) (16). An 20-mL ether solution of **10** (0.47 g, 1.43 mmol) in a vacuum-sealed NMR tube was irradiated by a 400-W mercury lamp at −20 °C for 18 h. After evaporation of the solvent, the residues were chromatographed through neutral alumina column at 0 °C using pentane as the eluting solvent. A yellow band eluting first from the column was identified as a mixture of **15** and **16** and collected. A second yellow band was collected and evaporated to dryness; further recrystallization of the residue from pentane gave pale yellow crystals of **11** (0.29 g, 0.96 mmol). Anal. Calcd for $C_{13}H_{14}MoO_2$: C, 52.35; H, 4.69. Found: C, 52.47; H, 4.42. Mass spectrum (12 eV, ^{98}Mo, 23.78%, *m/e*): 300 (M^+), 272 (M^+ - CO). IR (pentane): ν(C=C) 1617 (w) cm^{-1}; ν(CO) 1956 (s), 1885 (s) cm^{-1}. ^{1}H NMR (400.1 MHz, toluene-d_8): δ 1.48 (m, 1 H, H^1), 1.42 (d, 3 H, CH_3), 2.00 (t, 1 H, H^3), 3.58 (t, 1 H, H^2), 4.70 (s, 5 H, C_5H_5), 4.80 (dd, 1 H, H^6), 5.23 (dd, 1 H, H^5), 5.55 (dt, 1 H, H^4), $J_{CH_3\text{-}1}$ = 6.8 Hz, J_{12} = J_{23} = 10.4 Hz, J_{34} = 10.5 Hz, J_{45} = 16.8 Hz, J_{46} = 10.4 Hz. ^{13}C{^{1}H} NMR (100.6 MHz, benzene-d_6): δ 20.3 (CH_3), 58.0 (CH^1), 61.0 (CH^3), 71.7 (CH^2), 91.5 (C_5H_5), 110.5 (CH^6H^5), 139.6 (CH^4). Removal of the solvent from the first yellow band in vacuo gave a yellow crystal line solid of **15** and **16** (3.7 mg, 1.1 × 10^{-2} mmol). Mass spectrum (12 eV, ^{98}Mo, 23.78%, *m/e*): 272 (M^+), 244 (M^+ - CO). IR (pentane): ν(CO) 1920 (br, s) cm^{-1}. ^{1}H NMR (400.1 MHz, benzene-d_6): **15**, δ 1.25 (dd, 1 H, H^1), 1.62 (m, 1 H, H^5), 1.62 (d, 1 H, CH_3), 2.42 (m, 1 H, H^6), 2.52 (dd, 1 H, H^2), 2.63 (t, 1 H, H^4), 4.14 (ddd, 1 H, H^3), J_{12} = 2.0 Hz, J_{13} = 9.5 Hz, J_{23} = 6.8 Hz, J_{34} = J_{45} = 5.2 Hz, J_{56} = 5.4 Hz, $J_{6\text{-}CH_3}$ = 8.1 Hz; **16**, δ 1.40 (d, 3 H, CH_3), 1.50 (m, 1 H, H^4), 1.73 (d, 1 H, H^6), 1.90 (m, 1 H, H^1), 2.20 (d, ^{1}H, H^5), 2.63 (t, 1 H, H^3), 4.09 (dd, 1 H, H^2), $J_{1\text{-}CH_3}$ = 7.2 Hz, J_{12} = 10.1 Hz, J_{23} = J_{34} = 5.6 Hz, J_{46} = 8.4 Hz, J_{45} = 5.6 Hz. Attempts to obtain the elemental analyses and 2-D ^{13}C–^{1}H NMR correlation spectrum were not successful owing to the very small sample.

(i) Synthesis of $CpMo(CO)(PMe_2Ph)$(*syn*-η^3-pentadien-yl) (12). Method A. A 20-mL ether solution of **3** (0.35 g, 0.17 mmol) in a vacuum-sealed Pyrex tube was irradiated by a 400-W mercury lamp at −20 °C for 18 h. After removal of the solvent in vacuo, the residue was chromatographed on a neutral alumina column at 0 °C with pentane as eluting solvent. A yellow band eluting first from the column was identified as unreacted **3**. A second yellow band was collected and evaporated to dryness to give an analytically pure oil (0.19 g, 0.47 mmol). Anal. Calcd for $C_{19}H_{23}MoOP$: C, 57.88; H, 5.83. Found: C, 59.11; H, 6.12. Mass spectrum (12 eV, ^{98}Mo, 23.78%, *m/e*): 396 (M^+), 368 (M^+ - CO), 258 (M^+ - PMe_2Ph). IR (Nujol): ν(CO) 1827 (s) cm^{-1}; ν(C=C) 1616 (w) cm^{-1}. ^{1}H NMR (400.1 MHz): δ 0.07 (ddd, 1 H, H^1), 1.34 (d, 3 H, PCH_3), 1.40 (d, 3 H, PCH_3'), 1.92 (ddd, 1 H, H^2), 2.54 (t, 1 H, H^4), 3.92 (td, 1 H, H^3), 4.52 (d, C_5H_5), 4.82 (dd, 1 H, H^7), 5.50 (dd, 1 H, H^6), 5.81 (dt, 1 H, H^5), 7.04, 7.10, 7.45 (complex m, 5 H, PC_6H_5), $J_{P\text{-}CH_3}$ = $J_{P\text{-}CH_3'}$ = 8.1 Hz, $J_{P\text{-}C_5H_5}$ = 1.4 Hz, $J_{P\text{-}1}$

= 11.3 Hz, J_{P-2} = 4.8 Hz, J_{12} = 1.4 Hz, J_{13} = 9.8 Hz, J_{23} = 6.2 Hz, J_{34} = 10.2 Hz, J_{45} = 10.2 Hz, J_{57} = 10.2 Hz, J_{56} = 16.9 Hz, J_{67} = 1.8 Hz. $^{13}C\{^1H\}$ NMR (100.6 MHz, benzene-d_6): δ 20.5 (d, PCH_3, J_{PC} = 31 Hz), 20.8 (d, PCH_3', J_{PC} = 32 Hz), 33.4 (d, CH^1H^2, J_{PC} = 13 Hz), 69.0, 63.1 (s, s, CH^3 + CH^4), 91.6 (s, C_5H_5), 111.4 (s, CH^6H^7), 127.8-131.4 (PC_6H_5, overlapping with benzene-d_6 resonances), 139.4 (s, CH^5), 248.4 (d, CO, J_{PC} = 28 Hz).

Method B. This complex was also prepared by irradiation of **8** and PMe_2Ph in ether at -20 °C for 5 h, followed by purification by column chromatography; the yield was 43%.

(j) Synthesis of CpMo(CO)[P(C_2H_5)$_3$](*syn*-η^3-pentadienyl) (13). Method A. This complex was prepared similarly by irradiation of **4** in ether at -20 °C. The yield is 52%. Anal. Calcd for $C_{17}H_{27}MoOP$: C, 54.55; H, 7.22. Found: C, 54.68; H, 7.54. Mass spectrum (12 eV, ^{98}Mo, 23.78%, *m/e*): 376 (M^+), 348 (M^+ - CO), 258 (M^+-PEt_3). IR (Nujol): exo isomer, ν(CO) 1835 cm^{-1}; endo isomer, 1841 cm^{-1}; ν(C=C) 1617 cm^{-1}. ^1H NMR (400.1 MHz, benzene-d_6): exo isomer, δ -0.04 (ddd, 1 H, H^1), 0.67 (m, 9 H, PCH_2CH_3), 1.12 (m, 3 H, $PCHH'$-CH_3), 1.16 (m, 3 H, $PCHH'$-CH_3), 1.84 (ddd, 1 H, H^2), 2.43 (t, 1 H, H^4), 3.87 (td, 1 H, H^3), 4.64 (d, 5 H, C_5H_5), 4.84 (dd, 1 H, H^7), 5.52 (dd, 1 H, H^6), 5.85 (dt, 1 H, H^5), J_{P-1} = 11.7 Hz, J_{P-2} = 4.4 Hz, $J_{P-C_5H_5}$ = 1.2 Hz, J_{12} = 1.4 Hz, J_{13} = 10.2 Hz, J_{23} = 6.5 Hz, J_{34} = J_{45} = 10.2 Hz, J_{56} = 16.8 Hz, J_{57} = 10.2 Hz, J_{67} = 1.4 Hz; endo isomer, δ 0.79 (m, 9 H, PCH_2CH_3), 1.28 (m, 3 H, $PCHH'$), 1.40 (m, 3 H, $PCHH^1$), 1.53 (dd, 1 H, H^1), 1.65 (d, 1 H, H^2), 2.77 (dd, 1 H, H^4), 3.80 (td, ^1H, H^3), 4.63 (s, 5 H, C_5H_5), 4.80 (dd, 1 H, H^7), 5.00 (dd, 1 H), 6.78 (dt, 1 H, H^5), J_{P1} = 13.5 Hz, J_{23} = 6.0 Hz, J_{13} = 10.7 Hz, J_{34} = 10.7 Hz, J_{45} = 10.3 Hz, J_{56} = 16.8 Hz, J_{57} = 10.2 Hz, J_{67} = 1.0 Hz. $^{13}C\{^1H\}$ NMR (100.1 MHz, benzene-d_6): exo isomer, δ 8.3 (d, PCH_2CH_3, J_{PC} = 18 Hz), 21.26 (d, PCH_2CH_3, J_{PC} = 23 Hz), 30.0 (d, CH^1H^2, J_{PC} = 14 Hz), 63.0, 67.9 (s, s, CH^2 + CH^3), 91.2 (s, C_5H_5), 108.8 (s, CH^6H^7), 141.5 (s, CH^5), 249.7 (d, CO, J_{PC} = 38.2 Hz); endo isomer, δ 8.4 (d, PCH_2CH_3, J_{PC} = 18 Hz), 23.3 (d, PCH_2), 33.5 (d, CH^1H^2, J_{PC} = 8 Hz), 56.2, 82.6 (s, s, CH^3 + CH^4), 89.4 (s, C_5H_5), 105.5 (s, CH^6H^7), 145.6 (s, CH^5), 252.6 (d, CO, J_{PC} = 26 Hz).

Method B. This complex was also prepared by irradiation of **8** and $P(CH_2CH_3)_3$ in ether at -20 °C for 5 h, followed by purification through column chromatography; the yield was 46%.

(k) Synthesis of CpMo(CO)(PMe_3)(*syn*-η^3-pentadienyl) (14). This complex was prepared similarly by irradiation of an ether solution of **8** and PMe_3. The yield was 34%. Anal. Calcd for $C_{14}H_{21}MoOP$: C, 50.61; H, 6.32. Found: C, 50.94; H, 6.48. IR (pentane): ν(CO) 1832 cm^{-1}; ν(C=C) 1617 (w) cm^{-1}. Mass (12 eV, ^{98}Mo 23.78%, *m/e*): 334 (M^+), 306 (M^+ - CO), 258 (M^+ - PMe_3). ^1H NMR (400.1 MHz, benzene-d_6): δ -0.04 (ddd, 1 H, H^1), 1.02 (d, 3 H, CH_3), 1.82 (ddd, 1 H, H^2), 2.48 (t, 1 H, H^4), 3.86 (td, 1 H, H^3), 4.58 (d, C_5H_5), 4.81 (dd, 1 H, H^7), 5.48 (dd, 1 H, H^6), 5.83 (dt, 1 H, H^5), J_{P-CH_3} = 8.5 MHz, $J_{P-C_5H_5}$ = 1.4 Hz, J_{P-1} = 12.0 Hz, J_{P-2} = 4.6 Hz, J_{12} = 1.4 Hz, J_{13} = 10.2 Hz, J_{23} = 6.6 Hz, J_{34} = 10.2 Hz, J_{45} = 10.2 Hz, J_{57} = 16.8 Hz, J_{56} = 10.2 Hz, J_{67} = 1.2 Hz. $^{13}C\{^1H\}$ NMR (100.6 MHz, benzene-d_6): δ 21.6 (d, PCH_3, J_{PC} = 29 Hz), 31.1 (d, CH_1H_2, J_{PC} = 14 Hz), 62.8, 68.3 (CH^3 + CH^4), 108.4 (CH^6H^7), 141.6 (CH^5), 248.0 (d, CO, J_{PC} = 22 Hz).

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Registry No. **1**, 104293-11-0; **2**, 112373-46-3; **3**, 112373-48-5; **4**, 112373-49-6; **5**, 112373-50-9; **6**, 112373-51-0; **7**, 112373-47-4; **8**, 104293-12-1; **9**, 104293-13-2; **10** (exo isomer), 112373-52-1; **10** (endo isomer), 112455-87-5; **11**, 112373-53-2; **12**, 112373-54-3; **13** (exo isomer), 112457-41-7; **13** (endo isomer), 112373-58-7; **14**, 112373-55-4; **15**, 112373-56-5; **16**, 112373-57-6; $CpMo(CO)_3Na$, 12107-35-6; PMe_2Ph, 672-66-2; PMe_3, 594-09-2; $P(CH_2CH_3)_3$, 554-70-1; (*E,E*)-1-chlorohexa-2,4-diene, 17100-75-3; tetracyanoethylene, 670-54-2; maleicanhydride, 108-31-6.

Synthesis and Asymmetric Reactivity of Enantiomerically Pure Cyclopentadienylmetal Complexes Derived from the Chiral Pool

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Starting from pulegone, camphor, and tartrate, three chiral cyclopentadienes were prepared efficiently. Metalation with $Co_2(CO)_8$ and $TiCl_3$ resulted in new chiral and enantiomerically pure substituted cyclopentadienyldicarbonylcobalt and -titanocene complexes. The latter were used in the quantitative catalytic asymmetric hydrogenation of 2-phenyl-1-butene in up to 34% optical yield. The former allowed the first asymmetric [2 + 2 + 2] cycloadditions promoted by chiral cyclopentadienylcobalt complexes to be observed.

Introduction

Organometallic compounds containing chiral ligands have recently been regarded with intense interest as potential mediators of enantioselective transformations.[1] Although transition-metal complexes attached to the most common auxiliary, chiral chelating diphosphines,[1,2] have been used successfully in several cases,[1-3] their stereodifferentiating ability can suffer due to their lability as complexing agents. In order for efficient transfer of asymmetry to a substrate to occur, the chiral ligand must be bound to the metal during the stereodifferentiating step. The relatively weak bonding ability of many such ligands is a potential drawback that can limit their applications and invites the use of a more stable system. We chose as an example the η^5-cyclopentadienyl unit because of the superior tenacity with which it attaches itself to transition metals, involving bond strengths as high as 118 kcal mol^{-1}.[4]

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(1) ApSimon, J. W.; Collier, T. L. *Tetrahedron* **1986**, *42*, 5157. Paquette, L. A. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic: New York, 1984; Vol. 3, p 455. Oppolzer, W. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 876. ApSimon, J. W.; Seguin, R. P. *Tetrahedron* **1979**, *35*, 2797. Valentine, D., Jr.; Scott, J. W. *Synthesis* **1978**, 329.

(2) (a) Kagan, H. B. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic: New York, 1984; Vol. 5, p 1. (b) Knowles, W. S. *Acc. Chem. Res.* **1983**, *16*, 106. (c) Kagan, H. B. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: New York, 1982; Vol. 8, p 463.

(3) See also: (a) Koenig, K. E. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic: New York, 1984; Vol. 5, p 71. (b) For a recent reference, see: Takaya, H.; Ohta, T.; Sayo, N.; Kumobayashi, H.; Akutagawa, S.; Inoue, S.; Kasahara, I.; Noyori, R. *J. Am. Chem. Soc.* **1987**, *109*, 1596.

(4) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1985**, *107*, 7399.

0276-7333/88/2307-0883$01.50/0