The procedure for the reeaction of benzaldehyde with *B*-(*Z*)-3-methyl-1-butenyl-9-BBN follows that for the *E* isomer.[2b] 4-Methyl-1-phenylpent-2-en-1-ol was obtained in 60% yield: bp 108–110 °C (1.0 torr); $n^{22}{}_D$ 1.5170; ^{1}H NMR ($CDCl_3$) δ 7.4 (s, 5 H), 5.4–5.8 (m, 3 H), 2.6–3.0 (m, 1 H), 2.0 (br s, 1 H), 1.0 (two overlapping doublets, J = 6 Hz, 6 H); ^{13}C NMR ($CDCl_3$) δ 22.90, 23.20, 27.0, 69.80, 126.0, 127.30, 128.40, 129.70, 139.10, 144.0; IR (meat) $\bar{\nu}$ 3346 (OH), 1685 cm^{-1} (C=C); MS, *m/e* 176 (M^+); GLC analysis on a 50-M methyl silicone glass capillary column showed >99% isomeric purity.

The procedure for the reaction of methyl vinyl ketone with *B*-(*Z*)-1-hexenyl-9-BBN follows that for the *E* isomer.[2a] (*Z*)-5-Decen-2-one was obtained in 67% yield: bp 70–72 °C (2.50 torr); $n^{20}{}_D$ 1.4433; ^{1}H NMR ($CDCl_3$) δ 5.6–5.3 (m, 2 H), 2.6–2.4 (m, 6 H), 2.20 (s, 3 H), 1.6–1.0 (m, 7 H); ^{13}C NMR ($CDCl_3$) δ 13.75, 21.60, 22.20, 26.74, 29.60, 31.72, 43.41, 127.62, 130.98, 204.51; IR (neat) $\bar{\nu}$ 1715 (>C=O), 1658 cm^{-1} (C=C); MS, *m/e* 154 (M^+); GLC analysis on 50-M methyl silicone capillary glass column showed >98% isomeric purity.

Registry No. *B*-(*Z*)-1-Hexenyl-9-BBN, 67826-85-1; *B*-(*Z*)-1-heptenyl-9-BBN, 100839-97-2; *B*-(*Z*)-3-methyl-1-butenyl-9-BBN, 100839-98-3; *B*-(*Z*)-2-cyclohexylethenyl-9-BBN, 100839-99-4; *B*-(*Z*)-3,3-dimethyl-1-butenyl-9-BBN, 100840-00-4; (*Z*)-4-methyl-1-phenylpent-2-en-1-ol, 100840-01-5; (*Z*)-5-decen-2-one, 100840-02-6; (*Z*)-1-iodo-1-hexene, 16538-47-9; (*Z*)-1-iodo-1-heptene, 63318-29-6; (*Z*)-1-iodo-3-methyl-1-butene, 64245-25-6; (*Z*)-2-cyclohexyl-1-iodo-1-ethene, 67404-69-7; (*Z*)-3,3-dimethyl-1-iodo-1-butene, 64245-24-5; *B*-methoxy-9-BBN, 38050-71-4.

Synthesis and Carbon Monoxide Insertion Reactions of (η^5-Cycloheptadienyl)Fe(CO)L(CH_3) (L = CO, P($OPh)_3$)

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Summary: The first pentadienyl analogues of CpFe(CO)LCH_3 have been prepared from (η^5-C_7H_9)FeL(CO)I (L = CO, P($OPh)_3$). The structure of (η^5-C_7H_9)Fe(CO)(P($OPh)_3$)CH_3 is presented. The reactions of (η^5-C_7H_9)Fe($CO)_2CH_3$ with CO and PPh_3 are described. These insertion reactions occur much more readily than do those of the isoelectronic analogue (C_5H_5)Fe($CO)_2CH_3$. The difference in reactivity is ascribed to a facile η^5–η^3 ring slip for the pentadienyl complex.

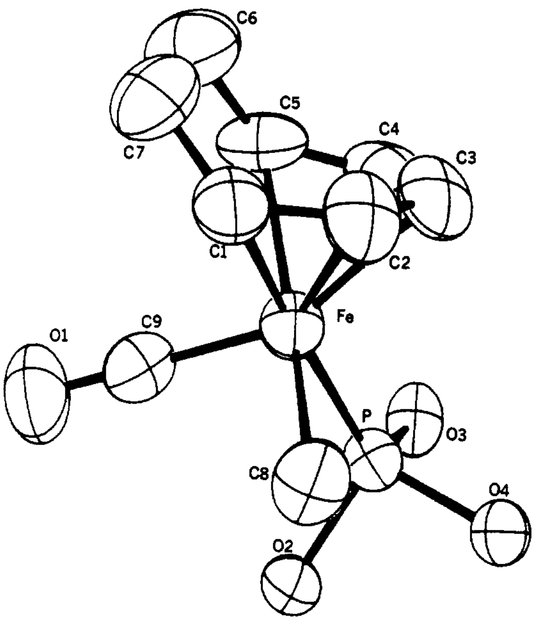
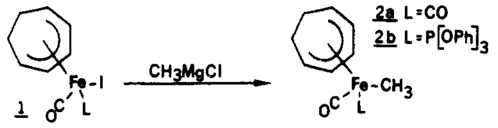


Figure 1. ORTEP illustration of (η^5-C_7H_9)Fe(CO)(P($OPh)_3$)CH_3 (**2b**). Phenyl rings are omitted for clarity.

The η^5-pentadienyl ligand has received significant attention in recent years because of its potential as a substrate for carbon–carbon bond-forming reactions[1] and because multiple coordination modes for the pentadienyl ligand make its complexes attractive candidates for new homogeneous catalysts.[2] The versatility of the dienyl ligand coupled with the wealth of chemistry known for complexes of its isoelectronic counterpart, cyclopentadienyl (Cp), prompted us to initiate studies of the chemical reactivity patterns of (η^5-dienyl)metal complexes. In this paper we report the synthesis of (η^5-C_7H_9)FeL(CO)CH_3 (L = CO, P($OPh)_3$), the first examples of pentadienyl iron alkyl complexes that have direct cyclopentadienyl counterparts.[3] We also discuss the CO insertion reactions of the dicarbonyl species; acetyl-substituted (diene)Fe($CO)_2$L complexes are produced.

Each of the iron methyl complexes can be prepared by treating the corresponding iodoiron dienyl 1[4] with CH_3MgCl (eq 1). In contrast with its Cp counterpart, **2a** is



(1)

a very sensitive compound. It must be removed from reaction byproducts by filtration through silica gel at low temperature. Removal of solvent (−30 °C) and sublimation (25 °C (10^{-5} torr)) provides **2a** as a waxy yellow-orange solid in 95% yield. Once purified, **2a** can be stored for several days under an inert atmosphere at −25 °C with only minor decomposition. Consistent with the known chemistry of the Cp series, substitution of P($OPh)_3$ for CO results in increased stability of the complex. Hence, **2b** is an orange crystalline solid which may be handled briefly in air.

Complex **2b** was characterized by X-ray crystallography; the ORTEP is shown in Figure 1. The pentadienyl fragment is distorted from planarity to a somewhat larger degree than is commonly observed for this ligand.[2,5] Thus, C4 is 0.069 Å below the least-squares plane of the five dienyl

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[3] The only other known (pentadienyl)M(alkyl) is an iron species isolated from the reaction of (cycloheptatriene)Fe($CO)_3$ with dimethyl maleate. Davis, R. E.; Dodds, T. A.; Hseu, T.-H.; Wagnon, J. C.; Devon, T.; Tancrede, J.; McKennis, J. S.; Pettit, R. *J. Am. Chem. Soc.* **1974**, *96*, 7562.

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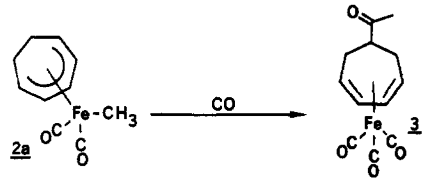
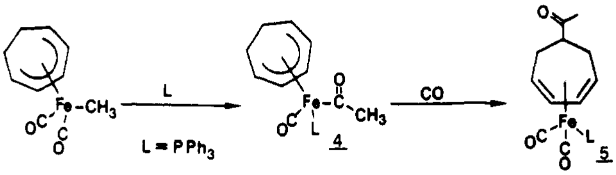
carbons. Other bond lengths and angles are as expected. The angle between the least-squares planes containing C1–C5 and C1, C5, C6, and C7 is 47.1°.[6] The iron–methyl bond length is 2.113 Å. All other data support the suggested structure.[7]

Characterization of **2a** rests on spectroscopic data. At −70 °C, each of the five dienyl protons appears as a distinct multiplet in the ^{1}H NMR (δ 5.14, 4.42, 4.13, 3.85, 3.25). Upon warming, the multiplets at δ 4.42 and 4.13 (H2,4) merge to a doublet of doublets (δ 4.42). Coalescence of H1 and H5 (δ 3.86, 3.25) occurs at −4 °C (δ 3.71; $\Delta G^{\ddagger} = 13.1$ kcal mol^{-1}).[8] These data are consistent with a rotation of the cycloheptadienyl ligand.[9] At the low-temperature limit, the methyl group must be situated beneath the pentadienyl fragment (approximately aligned with C2 as is found for **2b**). The NMR data can be explained by rotation through either of two possible C_{2v} isomers; however, we can conclude that neither of these conformers reaches an appreciable population since the central pentadienyl proton, as well as the methyl group, remain well resolved at temperatures from 25 °C to −70 °C.

As a first step in contrasting the chemistry of η^5-dienyl metal complexes and their Cp counterparts, we have examined the insertion reactions of **2a** with CO and PPh_3. Solutions of **2a** react with CO (1 atm, THF, 25 °C, 48 h) to give the endo-acylated iron diene complex **3** in 60% yield (eq 2). Presumably CO insertion to give an (η^1-acyl)iron intermediate precedes reductive migration to the bottom face of the η^5-dienyl ligand. Subsequent isomerization and coordination of CO gives **3**. This reaction supports our suggested mechanism for the formation of **3** from a dienyliron anion and acetyl chloride.[10] Although we have no direct evidence for the (η^1-acyl)iron intermediate, treatment of **2a** with excess PPh_3 (THF-d_8, 25 °C, 30 min) provides a new species whose ^{1}H NMR spectrum is consistent with the η^1-acyl **4** (eq 3).[7,11] This compound exhibits five multiplets for the pentadienyl fragment, one of which is strongly coupled to phosphorus (12.0 Hz); the coupling pattern is similar to that of **2b**. The η^1-acetyl group appears as a singlet at δ 2.31. When generated in situ from solutions of **2a**, **4** reacts with CO to provide the endo-substituted iron diene complex **5** (THF, 48 h, 1 atm of CO, 85%).[7]



(2)



(3)

The CO insertion reactions of **2a** occur much more readily than do those of their isoelectronic counterpart $CpFe(CO)_2CH_3$.[12] The latter require elevated temperature and/or pressure. We attribute this significant difference in reactivity to a facile η^5–η^3 ring slip in the dienyl system; insertion will be promoted by creation of a vacant site for the incoming ligand.[13] Similar η^5–η^3 slippage is known for Cp complexes;[14] however, this process is not common since the aromatic character of the Cp ligand is lost (or at least diminished) in the η^3 form.

Reactivity studies of pentadienyl complexes are currently limited to a few accounts of η^5–η^3 ligand slip induced by neutral donor ligands. The insertion reactions of **2a** suggest that fundamental organometallic reactions requiring a vacant coordination site will occur more readily for η^5-pentadienyl complexes than for their Cp counterparts. Further studies on the reactivity patterns of these and other pentadienyl complexes are in progress.

Acknowledgment. Supported by an Atlantic Richfield Foundation Grant of the Research Corp. We thank Professor Robert J. Doedens and Dr. Tim Hanusa for assistance with the crystal structure.

Supplementary Material Available: Tables of crystallographic data, interatomic distances, bond angles, positional parameters, and temperature factors for **2b** as well as tables of spectroscopic data for **2a**, **2b**, **4**, and **5** (10 pages). Ordering information is given on any current masthead page.

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(7) Microanalytical data or high-resolution MS, NMR (^{1}H, ^{13}C, ^{31}P) and IR for new compounds are given in the supplementary material.

(8) The two exo protons and the two endo protons on the sp^3 carbons also become equivalent.

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(11) Mixtures of **2a** and **4** are produced by added phosphine. For example, 4 equiv of Ph_3P gives $4/2a \approx 2$. A large excess of PPh_3 is required for complete formation of **4**. We have not isolated analytically pure samples of **4**; this species is very unstable in the absence of excess ligand.

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Preparation of Molybdenum Pentacarbonyl Complexes of the Ph_2PNSO and $Ph_2PNSNPPh_2$ Ligands: X-ray Crystal Structure and Fluxional Behavior of $(CO)_5MoP(Ph)_2NSN(Ph)_2PMo(CO)_5$

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Summary: The reactions of $(CO)_5Mo(Ph_2PCl)$ with KNSO or K_2SN_2 in acetonitrile produce $(CO)_5Mo(Ph_2PNSO)$ (**3a**) or $(CO)_5MoP(Ph)_2NSN(Ph)_2PMo(CO)_5$ (**4a**), respectively. An X-ray crystal structure determination of **4a** shows that the $Ph_2PNSNPPh_2$ ligand adopts a cis,trans conformation. A variable-temperature ^{31}P NMR spectroscopic study of **4a** provides evidence for a cis,trans → trans,cis interconversion ($\Delta G^{\ddagger}_{213} = 9.4 \pm 0.2$ kcal mol^{-1}) in solution.

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