parallel to the surface. We have quantified this approach for **1c** using a theoretical treatment previously described.[24] The differences between the calculated isotropic and experimental monolayer spectra are interpreted in terms of a model structure having a tilt of the aromatic-NO_2 axis of 57° from the surface normal with the ring plane perpendicular to the surface plane and is consistent with the wetting angle and ellipsometry data.

While the absorption of disulfides on many transition metals is well-known, there are important differences that distinguish their closest-packed adsorption on Au. First, "clean", zerovalent gold surfaces are easy to prepare by vacuum evaporation. Second, these surfaces only slowly become contaminated under laboratory ambient conditions and do not form oxides. This feature is particularly significant as we have observed that adsorption of **2** on evaporated Ag shows evidence, by IR, of bonding at both the disulfide and carboxylate ends of the molecule (the latter presumably at oxide sites). Related to this point is the observation[25] that both C–S and S–S bond cleavage occurs in disulfide adsorption on silver. It is expected that other clean transition-metal surfaces will also cleave the C–S bond. Our data give no evidence for such cleavages on Au. At present, the bonding involved in disulfide adsorption on gold is unknown. It can be speculated that S–S dissociative chemisorption occurs similar to the case of silver,[25] but no definitive evidence exists.[26]

We conclude that gold surfaces can be easily functionalized by disulfide adsorption. We will report in greater detail about the preparation and characterization of these monolayers and on their application in model interface studies in subsequent publications.

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[26] X-ray photoelectron emission measurements and surface-enhanced Raman scattering have not shown definitive evidence of a dissociated S–S bond or formation of an Au–S bond.

Approach to Stereochemically Defined Cycloheptadiene Derivatives Using Organoiron Chemistry[1]

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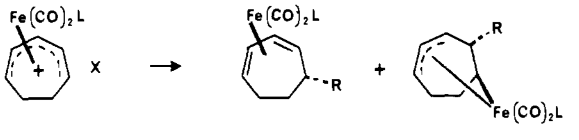
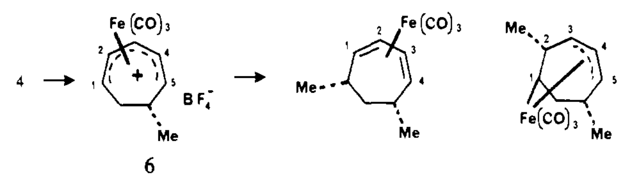
Received March 7, 1983

The attachment of a transition-metal moiety to an olefinic ligand offers a unique means of attaining stereospecificity during a variety of chemical transformations and C–C bond-forming processes.[2,3] The cycloheptadienylmetal system is ideally suited for 1,3-stereocontrol, but inspection of the literature reveals that the reactivity of cycloheptadienyl-$Fe(CO)_3$ complexes, e.g., **1a**,

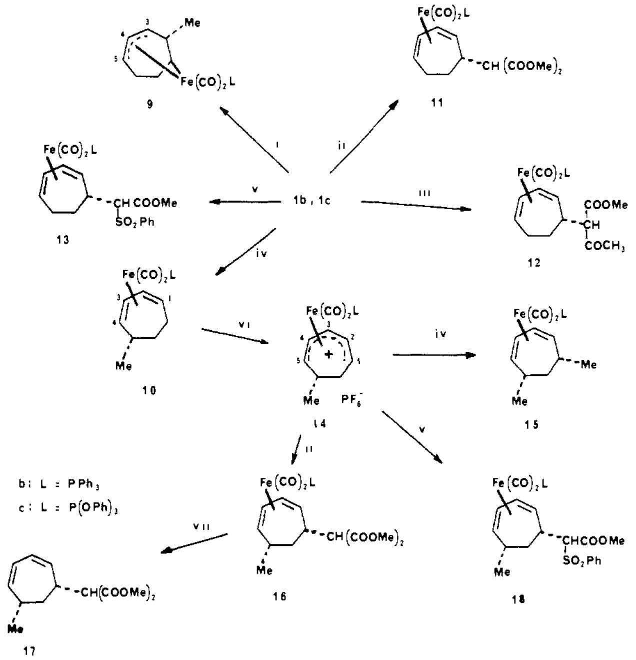


1a, L = CO; X = BF_4^- — **2a**, L = CO — **3a**, L = CO
b, L = Ph_3P, X = PF_6^- — **b**, L = PPh_3; R = H — **b**, L = PPh_3; R = H
c, L = $(PhO)_3P$, X = PF_6^- — **4**, L = CO; R = Me

Scheme I



Scheme II[a]



[a] Reagents: (i) MeLi, CH_2Cl_2, −78 °C; (ii) $NaCH(CO_2Me)_2$, THF, 20 °C; (iii) $NaCH(CO_2Me)COCH_3$, THF, 20 °C; (iv) Me_2CuLi, Et_2O, 0 °C; (v) $NaCH(SO_2Ph)CO_2Me$, THF, 20 °C; (vi) $Ph_3C^+PF_6^-$, CH_2Cl_2; (vii) Me_3NO, CH_3CONMe_2, 55 °C, 36 h.

bears little resemblance to that of the well-behaved six-membered ring counterparts. In general, addition of nucleophiles to **1a** results in a mixture of products of type **2a** and **3a**, often in poor yield.[4] Since these complexes offer a unique means of synthesizing cycloheptadiene derivatives, we decided to investigate the possibility of controlling the reactivity of the cycloheptadienyliron system, with gratifying results.

We commence by describing some preliminary, less successful experiments performed on the tricarbonyliron complex **1a**, which will be seen to contrast with the triphenylphosphine and triphenylphosphite derivatives **1b** and **1c**.[5] Treatment of **1a** with methyllithium (CH_2Cl_2, −78 °C)[6] *or* lithium dimethylcuprate

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[5] Preparation of **1b** and **1c** was as follows: Cycloheptadiene-$Fe(CO)_3$ was obtained in 88% yield from the reaction of cycloheptadiene and $Fe(CO)_5$ in Bu_2O (reflux under N_2 42h). This was converted to the desired complexes. **1b**: Treatment of cycloheptadiene-$Fe(CO)_3$ with Ph_3P (1.2 equiv) in Bu_2O (reflux, 24 h) to give crystalline cycloheptadiene-$Fe(CO)_2PPh_3$ (46% yield). Treatment of this product with $Ph_3C^+PF_6^-$ (1.2 equiv, CH_2Cl_2, 20 °C, 2 h) followed by precipitation with wet ether gave **1b** (91%). **1c**: Treatment of cycloheptadiene-$Fe(CO)_3$ with $P(OPh)_3$ (1.1 equiv, Bu_2O, Ar balloon, reflux 17 h) gave cycloheptadiene-$Fe(CO)_2P(OPh)_3$ as an oil that could not be separated from small amounts of residual $P(OPh)_3$. Reaction of the crude complex with $Ph_3C^+PF_6^-$ (1.2 equiv, CH_2Cl_2, 20 °C, 45 min) gave **1c** (80% *overall* from cycloheptadiene-$Fe(CO)_3$).

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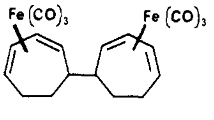
(Et_2O, 0 °C)[7] resulted in a low yield (20–25%) of product **4** of terminal methylation,[8] together with ca. 25% yield of the dimeric species **5**, the latter being indicative of electron-transfer processes.



5

Hydride abstraction from **4** ($Ph_3C^+PF_6^-$, CH_2Cl_2, 20 °C, 45 min) proceeded in high yield to give the substituted dienyl complex **6**.[8]

Reaction of **6** with lithium dimethylcuprate gave a 3:1 mixture of complexes **7** and **8** (NMR), while reaction with methyllithium gave only **8**, both reactions being accompanied by dimer formation and proceeding in low overall yield (20%;[8] Scheme I). Despite the low yields, formation of **7** does indicate the potential for attaining 1,3-stereocontrol by using a seven-membered ring. Surprisingly, reaction of **1a** with dimethyl malonate anion gave low yields of multiple products.[9]

During the above study we consistently observed the formation of considerable amounts of polar material (TLC), which was too unstable for characterization. This might arise from nucleophile attack at a CO ligand[10] and might be effectively overcome by increasing the electron density at the metal. We therefore examined reactions of complexes **1b** and **1c**, summarized in Scheme II. Treatment of **1b** with MeLi (CH_2Cl_2, −78 °C) gave the product **9b** of methylation at C-2 of the dienyl ligand, while reaction of **1b** or **1c** with Me_2CuLi (Et_2O, 0 °C) gave the product **10** of terminal methylation,[8] in 85–90% yield. Reaction of **1b** or **1c** with dimethyl sodiomalonate (THF, 20 °C) gave **11**; reaction with methyl sodioacetoacetate gave an equimolar mixture of diastereomers **12** and with methyl phenylsulfonylsodioacetate gave **13**, all reactions occurring in 90–100% yield and at the dienyl terminus, as shown conclusively by NMR spectra of the products.[8] Hydride abstraction ($Ph_3C^+PF_6^-$, CH_2Cl_2, 20 °C, 45 min) from the methyl-substituted complex **10** proceeded in excellent yield to give **14**, which upon treatment with Me_2CuLi, gave a single crystalline product in 83% yield, readily identified as **15** from its *symmetrical* 200-MHz ^1H NMR spectrum.[8] (Addition of the second methyl group *syn* to the metal would have given a compound showing widely differing CH_3 chemical shifts.) Reaction of **14** with dimethyl sodiomalonate occurred with equal regio- and stereospecificity to give **16** in essentially quantitative yield.[8] Decomplexation of **16c** (Me_3NO, dimethylacetamide, 55 °C, 36 h) afforded the stereochemically defined cycloheptadiene derivative **17**[8] in 80% yield. Finally, treatment of the methylated dienyl complex **14** with methyl phenylsulfonylsodioacetate gave the diene complex **18** as a mixture of distereomers in 90% yield after preparative TLC.

In conclusion, we have now demonstrated that (a) alteration of the electronic character of the metal in cycloheptadienyl-Fe-$(CO)_2L$ complexes has a profound effect on the reactivity of these molecules toward a range of synthetically useful nucleophiles, (b) changes in the nature of the nucleophile have a profound effect on regioselectivity of the reaction, and (c) the metal can be successfully removed in high yield in the presence of functional groups. Thus, it is possible to synthesize stereochemically defined substituted cycloheptadiene derivatives via iron complexes. We are currently studying functionalization of the diene unit of compounds related to **17**.

Acknowledgment. 200-MHz NMR spectra were recorded on a Varian XL-200, purchased with the aid of a grant from the National Science Foundation.

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[8] Structural types **2** and **3** show significant differences in their ^1H NMR spectra, and our data agree with published spectra of similar compounds.[2,4] Spectral data of representative compounds follow. **4**: IR ν_{max} ($CHCl_3$) 2039, 1964 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.28 (2 H, m, 2-H, 3-H), 3.07, 2.86 (1 H, m, each, 1-H, 4-H), 1.97 (3 H, br m), 1.43 (1 H, m), 1.28 (1 H, m), 0.95 (3 H, d, J = 6 Hz). **6**: IR ν_{max} (CH_3CN) 2103, 2056 cm^{-1}; ^1H NMR (CD_3CN) δ 7.12 (1 H, t, J = 7 Hz, 3-H), 6.20 (1 H, dd, J = 8, 6 Hz), 5.80 (1 H, dd, J = 10, 7 Hz), 4.85 (2 H, m, 1-H, 5-H), 3.4 (1 H, m, 6-H), 2.4 (1 H, m, endo-7-H), 0.93 (3 H, d, J = 7 Hz), 0.9 (1 H, m, obscured, exo-7-H). **7**: IR ν_{max} ($CHCl_3$) 2040, 1970 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.18 (2 H, m, 2-H, 3-H), 2.79 (2 H, m, 1-H, 4-H), 1.98 (2 H, m), 1.19 (2 H, m) 0.86 (6 H, d, J = 7 Hz). **8**: IR ν_{max} ($CHCl_3$) 2045, 1975 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.59 (1 H, t, J = 8 Hz, 4-H), 4.3 (2 H, m, 3-H, 5-H), 2.79 (1 H, m, 2-H), 2.35 (2 H, m), 1.68 (1 H, m), 1.39 (1 H, d, J = 8.8 Hz), 0.86 (3 H, d, J = 7.2 Hz), 0.85 (3 H, d, J = 6.3 Hz). **9**: IR ν_{max} ($CHCl_3$) 1972, 1911, cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.3 (15 H, m), 3.94 (1 H, t, J = 8 Hz, 4-H), 3.58 (2 H, m, 3-H, 5-H) 2.85 (1 H, m, 2-H), 2.13 (1 H, m, 1-H), 1.88 (2 H, m), 1.50 (2 H, m), 0.60 (3 H, d, J = 7.1 Hz). **10b**: IR ν_{max} ($CHCl_3$) 1968, 1907 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.33 (15 H, m), 4.57 (2 H, m, 2-H, 3-H), 2.28 (2 H, m, 1-H, 4-H), 1.83 (3 H, m), 1.10 (1 H, m), 0.77 (3 H, d, J = 6 Hz). **11b**: IR ν_{max} (CCl_4) 1980, 1923, 1760, 1740 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.4 (15 H), 4.4 (2 H, m, 2-H, 3-H), 3.64 (3 H, s), 3.60 (3 H, s), 3.12 (1 H, d, J = 6.3 Hz, malonate CH), 2.8–1.9 (5 H, m), 1.25 (2 H, m). **12b**: IR ν_{max} (CCl_4) 1977, 1923, 1738, 1715 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.33 (15 H), 4.63 (2 H, m, 2-H, 3-H), 3.60 and 3.56 (3 H, two s), 3.0 (1 H, s), 2.05 (2 H, m, 1-H, 4-H), 2.06 and 2.02 (3 H, two s), 1.95 (3 H, m), 1.15 (2 H, m). **14**: IR ν_{max} (CH_3CN) 2042, 2002 cm^{-1}; ^1H NMR (CD_3CN) δ 7.06 (15 H), 6.09 (1 H, m, 3-H), 5.36 (2 H, m, 2-H, 4-H), 4.4 (1 H, m, 1-H or 5-H), 3.74 (1 H, m, 5-H or 1-H), 3.31 (1 H, m), 2.2 (1 H, m), 0.84 (3 H, d, J = 6 Hz, and 1 H, m). **15**: IR ν_{max} ($CHCl_3$) 1968, 1908 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.36 (15 H), 4.59 (2 H, m, 2-H, 3-H), 2.20 (4 H, m, 1-H, 4-H, 5-H, 7-H), 1.48 (1 H), 0.98 (1 H), 0.79 (6 H, d, J = 6.5 Hz). **16**: IR ν_{max} ($CHCl_3$) 1976, 1917, 1758, 1734 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.32 (15 H), 4.53 (2 H, m, 2-H, 3-H), 3.57 (3 H, s), 3.53 (3 H, s), 3.0 (1 H, d, J = 7 Hz, malonate CH), 2.2 (2 H, m, 1-H, 4-H), 1.8 (2 H, m), 1.2–0.8 (2 H, m), 0.8 (3 H, d, J = 6.5 Hz). **17**: IR ν_{max} ($CHCl_3$) 1750, 1733 cm^{-1}; ^1H NMR (CCl_4) δ 5.58 (4 H, s, olefinic), 3.75 (6 H, s), 3.36 (1 H, d, J = 7 Hz), 2.8–2.5 (2 H, m), 1.9–1.5 (2 H, m), 1.12 (3 H, d, J = 7 Hz).

[9] Contrast with the following: Genco, N.; Marten, D.; Raghu, S.; Rosenblum, M. *J. Am. Chem. Soc.* **1976**, *98*, 848.

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2-Indanol Formation from Photocyclization of α-Arylacetophenones

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Received March 7, 1983

Part of the elegance of Paquette's dodecahedrane synthesis[1] was his anticipation of efficient δ-hydrogen abstraction by photoexcited ketones of restricted conformational mobility. There had been a few examples[2-5] of efficient photocyclization due to triplet state δ-hydrogen abstraction in ketones in which the only reactive C–H bonds are situated δ to the carbonyl, but the controlling conformational factors were not explicitly considered. We report an apparently overlooked example of a very efficient δ-hydrogen transfer process that leads cleanly to 2-indanols and that provides unique information about a rotational equilibrium.

We have studied a group of α-(o-tolyl)acetophenones, which undergo quantitative photocyclizations to 2-phenyl-2-indanols. Table I lists several of the compounds together with excited-state kinetics data. All starting ketones were synthesized by standard methods; product structures were determined by isolation and standard spectroscopic analysis. In all cases, the yield of indanol was within experimental error of 100% for 313-nm irradiation of 0.1 M ketone solutions. Quantum efficiencies are quite high,

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