the case, the salt $FcCH_2NMe_2H^+PF_6^-$ was oxidized and its spectrum recorded. A band was observed in this case at 627 nm, and there were less intense bands at 465 and 545 nm; no bands were observed in the near infrared.

The band seen at 752 nm for **3** with L = $AsPh_3$ was observed in all such complexes (and the dimer **2**) after oxidation of the ferrocenyl group (Table I). The band is assigned as an intervalent transfer band involving the Pd(II) and Fe(III) centers for the following reasons:

(1) Neither complex **1** nor $[1,2\text{-}FcCH_2NMe_2(PPh_2)]PdCl_2$ (**5**)[17] has Pd(II) directly bonded to the ferrocenyl group. No near-infrared band is seen after oxidation of the ferrocenyl group. This is in agreement with Colbran et al., who have found that IT transitions "are only found in mixed valence ferrocene compounds when the redox sites are directly fused or bridged by electron-conducting π groups".[4]

(2) The band is sensitive to a change in solvent medium. A shift in the band maximum of 9 nm to higher energy is observed for **3** (L = PPh_3) when the solvent is changed from CH_2Cl_2 to a 1:1 mixture of CH_2Cl_2 and CH_3CN. Such shifts are expected for a mixed-valence compound of class II.

(3) According to the Hush theory of mixed-valence compounds with weakly interacting centers, the bandwidth at half-height ($\Delta\nu_{1/2}$) for an unsymmetrical ion can be determined from the expression

$$\nu_{op} - \nu_0 = (\Delta\nu_{1/2})^2/2310 \text{ cm}^{-1}$$

where ν_{op} is the energy of the IT transition and ν_0 is the internal energy difference between the two oxidation state isomers

$$\text{Fe(III)–Pd(II)} \rightarrow \text{Fe(II)–Pd(III)}$$

While ν_0 cannot be obtained directly, it has been argued that an upper limit to its value can be obtained[5,6] from the difference between the reduction potentials for

$$[\text{FcCNPdClL}]^{2+} + e^- \rightarrow [\text{FcCNPdClL}]^+$$

and

$$[\text{FcCNPdClL}]^+ + e^- \rightarrow \text{FcCNPdClL}$$

For all of the compounds of type **3**, this difference is approximately 1.5 V or 12 000 cm^{-1}. This means that the bandwidth at half height should be about 1700 cm^{-1}. In fact, the half-height bandwidths are usually slightly larger than this estimate (Table I), a common observation in most mixed-valence ions.[4-7]

As seen in Table I compounds of type **3** with L as a phosphine or arsine exhibited a band in the near infrared at about 750 nm. The parent dimer **2** also gave rise to a band at 730 nm after two-electron oxidation, while **3** with L as a less basic phosphite ligand has a near infrared band nearer 700 nm. It would appear that more basic ligands L cause the intervalent transfer band to move to lower energies, a shift which may be due to stabilization of the Fe(II)–Pd(III) valence isomer. On the other hand, the cationic complex **4** (bidentate ligand = $Ph_2PC_2H_4PPh_2$) has a more energetic IT band; formation of the Fe(II)–Pd(III) valence isomer for the cationic complex is energetically unfavorable.[18]

Since the halide ligand is thought to be trans to the ferrocenyl group,[19] it is anticipated that this ligand will affect the Pd–ferrocenyl bond (owing to the so-called trans influence effect[21]) more than the cis ligand L. Thus, it is not surprising that a relatively large IT band shift is observed on changing the halide ligand from Cl to I to S-bonded SCN (when L = PPh_3).[12]

The significance of the results described is threefold. First, we have observed an intervalent transfer band for a variety of organometallic compounds having a Pd(II) center bound to an Fe(III)-containing ferrocenyl group. Thus, this series of complexes represents only the fourth class of organometallic compounds wherein intervalent transfer has been observed between two *different* metal sites. Second, the major advantage to this series of complexes is that it is capable of being greatly expanded.[22] And finally, Robin and Day in their extensive review of mixed-valence compounds noted that little was known in general about heterometal systems.[23] This series of Fe(III)–Pd(II) compounds begins to rectify that deficiency.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work. We also thank Mr. Wei Lee for preparing compound **5** and Professor Kenneth Karlin and the Department of Chemistry, SUNY—Albany, for use of their NMR facilities.

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[17] Hayashi, T.; Konishi, M.; Fukushima, M.; Mise, T.; Kagotani, M.; Tajika, M.; Kumada, M. *J. Am. Chem. Soc.* **1982**, *104*, 180.

[18] Note that the IT band moves to lower energy as the ligand L in **3** is changed from $P(OPh)_3$ to $P(OMe)_3$ to $P(OEt)_3$, that is, to more and more basic phosphites.

[19] When L = phosphine or phosphite, proton NMR spectra of complexes of type **3** show that each of the pair of lines assigned to the conformationally different $N\text{–}CH_3$ groups is split into a doublet, presumably owing to coupling with ^{31}P. No such splitting is observed in the spectrum of the complex when L is not a phosphine or phosphite. Since it is likely that the $^{31}P\text{–}H$ coupling constant is larger when the atoms are in the trans position than cis to one another,[20] it is believed that the ligand L is trans to the NMe_2 group, whereas X is trans to the ferrocenyl ring.

[20] As an example see: Collman, J. P.; Sears, C. T., Jr. *Inorg. Chem.* **1968**, *7*, 27.

[21] Appleton, T. G.; Clark, H. C.; Manzer, L. E. *Coord. Chem. Rev.* **1962**, *4*, 381.

[22] Approximately 20 complexes of the type described herein have been prepared, and all display the intervalent transfer band in the Fe(II)–Pd(II) state. These complexes will be reported in a forthcoming paper.

[23] Robin, M. B.; Day, P. *Adv. Inorg. Chem. Radiochem.* **1967**, *10*, 248.

Generation of Dicarbonyl(η^5-cyclopentadienyl)(*trans*-2,3-dimethylcyclopropylidene)iron Trifluoromethanesulfonate and Stereochemistry of Opening to the π-Complex of 1,3-Dimethylallene

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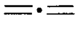
Summary: Compound **11** has been prepared as a potential precursor to the corresponding cyclopropylidene complex **12**. Methoxy abstraction by trimethylsilyl trifluoromethanesulfonate (Me_3SOTf) at −78 °C gave the expected (by analogy with free cyclopropylidenes) ring-opened allene complex. The cyclopropylidene complex **12** could not be trapped with cyclohexene. Resolution of the intermediate carboxylic acid **9** permitted preparation of nearly optically pure **11**, which in turn gave, within experimental error, racemic allene complex **13**. This is consistent with theory that predicts the racemic allyl cation to lie between the chiral complexed carbene and its chiral allene valence isomer.

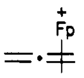
The characteristic unimolecular reaction of monocyclic cyclopropylidenes is ring opening to allenes. The mechanism of this reorganization has been extensively discussed[1] and is somewhat controversial because by analogy with cyclopropyl cations, the ring opening would be expected to be disrotatory but the product requires a net con (or mono) rotation. To accommodate this dichotomy, it has been suggested that the opening begins disrotatorily but before attaining a planar zwitterionic structure (**3**) rotation about one of the carbon–carbon bonds reverses direction to give the perpendicular allene.[2] This mechanism is attractive because it bypasses the achiral zwitterion (**3**), a condition that is required by observed retention of optical activity during the ring opening of optically active carbenes.[3] This further suggests that of the three valence isomers **1**, **2**, and **3**, **3** is probably of the highest energy.[4]


1

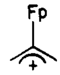

2


3

We have recently carried out EHMO calculations on dicarbonyl(η^5-cyclopentadienyl)iron (Fp) complexes of these molecules, i.e., **4**, **5**, and **6**, and have found that these calculations predict the allyl cation complex **6** to be of lower energy than the cyclopropylidene complex **5** but higher than the allene complex **4**.[5] This ordering provides two interesting predictions: (1) the cyclopropylidene complex **5** should readily collapse to **4**[6] and (2) unlike **2**, chirality may not be retained during the ring-opening process since achiral **6** could be on the energy surface between **5** and **4**.


4


5


6

Fp = Fe(CO)$_2$Cp

We therefore undertook to develop a method to unambiguously generate cyclopropylidene complexes of transition metals, a method that would be both general and amenable to the chirality studies suggested by our calculations. At this time we report the synthesis of **11** by a procedure that should be useful for preparing precursors to a wide range of cyclopropylidene complexes.[7] We also report that not only does **11** react instantaneously with Me$_3$SiOTf to give **13** quantitatively, but the same reaction with optically active **11** gives racemic allene complex **13**. Preparation of **11** is detailed in Scheme I. Synthesis of the intermediate carboxylic acid **9** was modeled after Cohen's elegant prepartion of (2-methyl-1-methoxycyclopropyl)lithium.[8] In this sequence preparation of **7** was achieved by addition of (thiophenyl)carbene to *trans*-2-butene under phase-transfer conditions (PTC)[9] followed by α-chlorination with trichloroisocyanuric acid (TCIA).[10] Replacement of chlorine by methoxy led to a mixture of **8** and its ring-opened isomer. The most favorable ratio of these isomers (4:1 favoring cyclopropane) was obtained at 0 °C. These were cleanly separated by flash chromatography.[11] Reduction of **8** with lithium naphthalenide followed Cohen's procedure with the exception that, before addition of CO$_2$, the reduction solution was permitted to warm to −10 to −20 °C for an additional 30 min at which time the green-black solution became orange-red. Carboxylation of the recooled (−78 °C) solution gave **9** in 85% yield. The acid was converted to the acyl cmplex **10**[12] in 35% yield from **9**. Decarbonylation to the σ-complex **11**[13] was cleanly effected (60% isolated yield) with [(PPh$_3$)$_2$RhCl]$_2$[14] (photolysis could not be stopped at the σ complex[15]). Treatment of **11** with Me$_3$SiOTf in CH$_2$Cl$_2$ at −78 °C followed by precipitation with ether gave the allene complex **13**[16] in essentially quantitative yield. Attempts to detect or trap the presumed cyclopropylidene complex failed. These included a low-temperature (−78 °C) NMR experiment which gave a broadened spectrum but showed quite clearly immediate allene formation and low-temperature (−78 °C) reactions in the presence of both cyclohexene and styrene. In both cases, only the allene complex was formed.

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(1) Cf. Jones, W. M.; Brinker, U. "Pericyclic Reactions"; Marchand, A. P., Lehr, R. E., Eds.; Academic Press: New York, 1977; Vol. 1, Chapter 3.

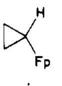
(2) Dillon, P. W.; Underwood, G. R. *J. Am. Chem. Soc.* **1977**, *99*, 2435.

(3) Walbrick, J. M.; Wilson, J. W.; Jones, W. M. *J. Am. Chem. Soc.* **1968**, *90*, 2895.

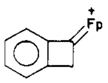
(4) The diradical form of **3** probably lies between **1** and **2**, but for symmetry reasons would not be accessible for the rearrangement.

(5) Winchester, W. R., unpublished results. EHMO calculations also put **3** between **1** and **2**, but this ordering is suspect because EHMO does not take into account charge separation in **3**, a difficulty that would not come into play in **6**.

(6) The literature supports this prediction in that Giering[7] has found that treatment of **i** with **ii** gave **4**, a reaction that was suggested to have proceeded through carbene complex **5**. To our knowledge, this is the only previously reported reaction believed to involve a complex of a carbocyclic cyclopropylidene.



i



ii

(7) Cohen, L.; Kennedy, D.; Magatti, C. V.; Sanders, A.; Giering, W. P. *J Organomet. Chem.* **1974**, *65*, C57.

(8) Mura, A. J.; Bennet, D. A.; Cohen, T. *Tetrahedron Lett.* **1975**, *4433*. See also: Cohen, T.; Bhupathy, M.; Matz, J. R. *J. Am. Chem. Soc.* **1983**, *105*, 520 and references cited therein.

(9) Boche, G.; Scheider, D. R. *Tetrahedron Lett.* **1975**, 4247.

(10) Thioether **7** has been previously prepared by a more classical method: Masuda, T.; Furukawa, N.; Oae, S. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 2659.

(11) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

(12) Dicarbonyl(η^5-cyclopentadienyl)(1-methoxy-*trans*-2,3-dimethylcyclopropyl-1-carbonyl)iron (**10**): mp 61.0–62.0 °C; IR (CDCl$_3$) ν(CO) 2000 (vs), 1950 (vs), 1650 (s) cm^{-1}; ^{1}H NMR (300 MHz, benzene-d_6) δ 0.903 (p, 1 H), 1.001 (d, 3 H), 1.076 d, 3 H), 1.433 (p, 1 H), 3.161 (s, 3 H), 4.374 (s, 5 H); ^{13}C NMR (25 MHz, benzene-d_6) δ 12.803 (CH$_3$), 13.680 (CH$_3$), 26.929 (cyclopropyl C) 30.827 (cyclopropyl C), 57.535 (OCH$_3$), 86.577 (Cp), 88.528 (cyclopropyl C$_1$), 215.524 (C=O), 216.011 (C=O), 255.875 (C=O); mass spectrum, *m/e* 276 (M$^+$ − CO), 248 (M$^+$ − 2CO), 205 (FpCO$^+$), 99 (M$^+$ − FpCO). Anal. Calcd for C$_{14}$H$_{16}$O$_4$Fe: C, 55.29; H, 5.30. Found: C, 55.41; H, 5.35.

(13) Dicarbonyl(η^5-cyclopentadienyl)(1-methoxy-*trans*-2,3-dimethylcyclopropan-1-yl)iron (**11**): IR (neat) ν(CO) 2000 (vs), 1940 (vs) cm^{-1}; ^{1}H NMR (300 MHz, benzene-d_6) δ 0.192 (p, 1 H), 0.268 (p, 1 H), 1.005 (d, 3 H), 1.053 (d, 3 H), 2.812 (s, 3 H), 4.061 (s, 5 H); ^{13}C NMR (25 MHz, CD$_2$Cl$_2$) δ 14.376 (CH$_3$), 18.275 (CH$_3$), 29.287 (cyclopropyl C) 35.818 (cyclopropyl C) 56.431 (OCH$_3$), 77.581 (cyclopropyl C$_1$), 87.328 (Cp), 218.127 (C=O), 218.517 (C=O); mass spectrum, *m/e* 276 (M$^+$).

(14) Kuhlman, E. J.; Alexander, J. J. *J. Organomet. Chem.* **1979**, *174*, 81.

(15) The photochemistry of the σ complex will be reported in a forthcoming paper: Lisko, J. R.; Jones, W. M., submitted for publication.

(16) Complex **13** has previously been isolated as the tetrafluoroborate salt: Rosenblum, M.; Foxman, B.; Marten, D.; Rosan, A.; Raghu, S. *J. Am. Chem. Soc.* **1977**, *99*, 2160. Physical data for the triflate salt is as follows. (η^2-1,3-Dimethylallene)dicarbonyl(η^5-cyclopentadienyl)iron trifluoromethanesulfonate (**13**): mp 87.0–88.0 °C; IR (Nujol mull) ν(CO) 2070 (s), 2020 (s) cm^{-1}; ^{1}H NMR (300 MHz, CD$_2$Cl$_2$) major (*anti*-3-methyl) isomer δ 1.633 (d, 3 H), 2.078 (d of d, 3 H), 4.371 (m, 1 H), 4.371 (m, 1 H), 5.634 (s, 5 H), 6.157 (m, 1 H), minor (*syn*-3-methyl) isomer δ 1.590 (d, 3 H), 2.226 (d of d, 3 H), 4.351 (m, 1 H), 5.699 (s, 5 H), 6.755 (m, 1 H); ^{13}C NMR (25 MHz, CD$_2$Cl$_2$) major (*anti*-3-methyl) isomer δ 19.862 (CH$_3$), 20.934 (CH$_3$), 44.183 (allene C$_1$), 92.237 (Cp), 129.000 (allene C$_3$), 151.356 (allene C$_2$) 209.876 (C=O), minor (*syn*-3-methyl) isomer δ 18.157 (CH$_3$), 42.100 (allene C$_1$), 92.042 (Cp), 113.828 (allene C$_3$), 152.526 (allene C$_2$), 209.876 (C=O). Anal. Calcd for C$_{13}$H$_{13}$O$_5$F$_3$FeS: C, 39.62; H, 3.32. Found: C, 39.52; H, 3.33.

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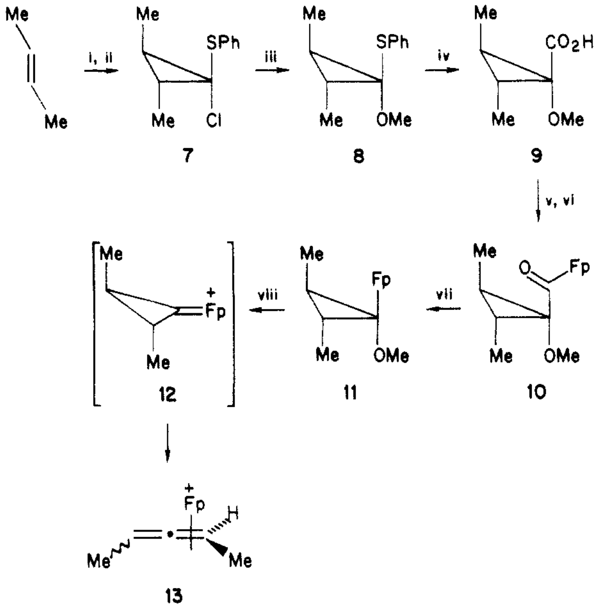
Scheme I



(i) $PhSCH_2Cl$, NaOH, H_2O/CH_2Cl_2, catalyst, 0 °C, 8 h; (ii) TCIA, CCl_4, 0 → 20 °C, 6 h; (iii) $AgBF_4$, $CdCO_3$, MeOH, 0 °C, 4 h; (iv) $LiC_{10}H_8$, THF, CO_2; (v) $SOCl_2$, Et_2O, catalyst, DMF, Δ, 8 h; (vi) $KFe(CO)_2Cp$, THF, -78 → 20 °C, 6 h; (vii) $[(PPh_3)_2RhCl]_2$, CH_3CN, 20 °C, 48 h; (viii) Me_3SiOTf, CH_2Cl_2, -78 °C, 5.0 min.

Optically acitve σ-complex 11 was prepared from active acid 9 ($[\alpha]^{25}{}_D$ -17.46 (*c* 0.24, ethanol)) that had been resolved with quinine. High optical purity (96% by ^1H NMR integration) of the acyl complex prepared from this acid was determined by using 5.0 mol % of the chiral shift reagent (-)-tris[3-[(heptafluoropropyl)hydroxymethylene]-*d*-camphorato]europium, (-)-Eu(hfc)$_3$.

Decarbonylation followed by low-temperature (-78 °C) methoxy abstraction gave the allene complex which was found to have, within experimental error, no optical rotation, i.e., $[\alpha]^{25}{}_D$ 0.2, (*c* 0.013, CH_2Cl_2).[17] From these results we conclude that the Fp^+ complex of *trans*-2,3-dimethylcyclopropylidene does, indeed, rapidly collapse to the allene complex. Further, from lack of rotation in the product from nearly optically pure σ complex it is likely[18] that the reaction proceeds by an allowed disrotatory ring opening to an achiral intermediate[19] (presumably the allyl cation that corresponds to 6) which then rapidly collapses to the allene complex 13.

Acknowledgment. This research was supported by the National Science Foundation to whom the authors are most grateful. The 300-MHz spectra were obtained on a Nicolet NT-300 spectrometer purchased with financial assistance from the Instrument Program, Chemistry Division, National Science Foundation.

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(17) The error in this rotation is large due to light absorption by the complex which forced us to measure rotations on dilute solutions. Attempts to determine optical purity using a chiral shift reagent were not successful.

(18) Enantiomeric excess in allenes from concerted opening of *trans*-2,3-disubstituted cyclopropylidenes or their metal complexes is believed to be steric in origin. In principle it would therefore be possible that 12 could give optically inactive product without going through an achiral intermediate (if steric interactions of methyl vs. β-H exactly cancelled methyl vs. Fp). We have no data that can exclude this possibility.

(19) If the opening is disrotatory to an allyl cation, the intermediate is achiral in only one conformation. This is the conformation that would result from opening of the electronically preferred "upright" conformation of the carbene complex. Even if this conformer were not formed initially, rotation about the Fe–C bond should be fast due to the LUMO node on the central carbon of the allyl cation.

Possible Formation of Rhenabenzene. Lithium–Halogen Exchange Reactions in η^1-4-Bromo-1,4-diphenyl-1,3-butadienyl Ligands To Form Rhenabenzene and Ferrabenzene

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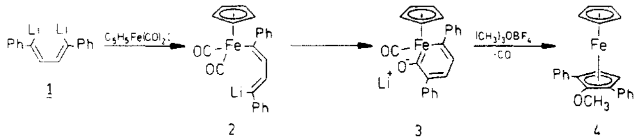
Received October 10, 1984

Summary: Introduction of (*E*,*E*)-1,4-dilithio-1,4-diphenyl-1,3-butadiene (**1**) to $(CO)_4PPh_3ReBr$ followed by protonation or methylation give (1,3-diphenyl-2-hydroxycyclopentadienyl)tricarbonylrhenium (**5a**) and (1,3-diphenyl-2-methoxycyclopentadienyl)tricarbonylrhenium (**5b**), respectively. A mechanism consistent with generation of **5** involves formation of an anionic acyl intermediate followed by alkyl migration to give (η^1-4-lithio-1,4-diphenyl-1,3-butadienyl)rhenium complex **7**. Cyclization by attack on a terminal carbonyl by the alkenyllithium moiety generates rhenabenzene **8** from **7**. Reductive elimination, loss of triphenylphosphine, and protonation or methylation give **5a** or **5b**, respectively. A second synthetic approach to **8** is described. Preparation of (η^1-4-bromo-1,4-diphenyl-1,3-butadienyl)rhenium complex **10** is reported. Lithium–halogen exchange with **10** using *n*-butyllithium gives **7**. Intermediate **7** may convert to **5** as described above. Preparation of (η^1-4-bromo-1,4-diphenyl-1,3-butadienyl)iron complex **11** is also reported. Lithium–halogen exchange and cyclization form an unstable ferrabenzene. Reductive elimination, loss of a terminal carbonyl, and methylation give 1,3-diphenyl-2-methoxyferrocene (**4**).

We recently reported that (*E*,*E*)-1,4-dilithio-1,4-diphenyl-1,3-butadiene (1)[2] reacts with (η^5-C_5H_5)Fe(CO)$_2$I to possibly form metal–alkyl and metal–carbene bonds giving an unstable ferrabenzene intermediate 3 (eq 1).[3]



(1)

We now report [1] reaction of 1 with another transition-metal carbonyl halide, $(CO)_4PPh_3ReBr$, and [2] probable generation of metallabenzenes by lithium–halogen exchange with η^1-4-bromobutadienyl ligands of transition metals containing electrophilic carbonyl ligands. These reactions support the hypothesis[3] that metallabenzenes are intermediates leading to η^5-cyclopentadienyl complexes.

The success of generating 4 from 1 prompted us to test the generality of this method with other transition metals. A solution of 1 in ethyl ether was added to a refluxing

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(1) (a) Department of Chemistry, University of Arkansas. (b) National Center for Toxicological Research.

(2) Barton, T. J.; Nelson, A. J.; Clardy, J. *J. Org. Chem.* **1972**, *37*, 895–901. Atwell, W. H.; Weyenberg, D. R.; Gilman, H. *Ibid.* **1967**, *32*, 885–888.

(3) Ferede, R.; Allison, N. T. *Organometallics* **1983**, *2*, 463–465.

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