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Communications

Electrocyclic Reactions of Open Metallocenes: Carbon–Carbon Bond Formation during Thermolysis of Bis(2,4-dimethyl-1,3-pentadienyl)ruthenium and -osmium

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Summary: Gas-phase pyrolysis of $(\eta^5\text{-}2,4\text{-}Me_2C_5H_5)_2Ru$ at 450 °C results in disrotatory, electrocyclic closure and subsequent dehydrogenation of one of the pentadienyl ligands to a 1,3-dimethylcyclopentadienyl ligand in ~80% yield, >95% conversion. Similar chemistry was observed for $(\eta^5\text{-}2,4\text{-}Me_2C_5H_5)_2Os$ at 500 °C, while $(\eta^5\text{-}2,4\text{-}Me_2C_5H_5)_2Fe$ decomposes above 250 °C. The mixed-ligand complex $(\eta^5\text{-}2,4\text{-}Me_2C_5H_5)Ru(\eta^5\text{-}1,3\text{-}Me_2C_5H_3)$ reacts further at 500 °C to produce $(\eta^5\text{-}1,3\text{-}Me_2C_5H_3)_2Ru$.

Metallocenes, $(\eta^5\text{-}C_5H_5)_2M$ (where M is a transitional metal), rank among the most fundamental compounds in transition-metal organometallic chemistry and have been applied to the organometallic chemical vapor deposition (OMCVD) of transition-metal films.[1,2] Multilayer structures based on Ru–B_4C thin films, in particular, have been proposed for X-ray optical applications.[3] Organometallic chemical vapor deposition of iron and ruthenium films from Cp_2M (M = Fe, Ru) required high temperatures (>550 and 595 °C, for M = Fe, Ru, respectively) and, in some cases, hydrogen gas (M = Ru) to prepare carbon-free films.[4,5] In the past decade, the synthesis of η^5-pentadienyl and substituted pentadienyl complexes ("open metallocenes") of many metals has been realized.[6] The reactivity of open metallocenes was observed to mimic both η^5-cyclopentadienyl compounds as well as η^3-allyl complexes. OMCVD of Rh, Ir, Pd, and Pt from allyl transition-metal complexes has been demonstrated at temperatures between 120 and 250 °C, significantly below the temperatures required for decomposition of ferrocene and ruthenocene.[2,7] These results suggested that the open metallocenes might lower growth temperatures, prompting the present study of the thermolysis of bis(η^5-2,4-dimethylpentadienyl) derivatives of iron (1), ruthenium (2), and osmium (3) as potential precursors for OMCVD of the iron group metals.[8,9]

Sublimation of 2 under dynamic vacuum (80 °C/5 × 10^{-2} Torr) through a 1- × 14-in. (OD) Pyrex tube seated in a Lindbergh tube furnace at 450 °C deposited a pale yellow, air-stable solid on the walls of the reaction tube at the exit from the oven. Isolation and characterization of this material by NMR and mass spectroscopy indicated formation of the mixed sandwich compound (η^5-1,3-dimethylcyclopentadienyl)(η^5-2,4-dimethyl-1,3-pentadie-

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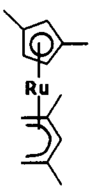
nyl)ruthenium (4) along with small amounts of bis(η^5-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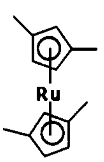
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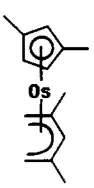
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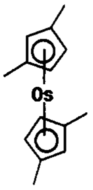
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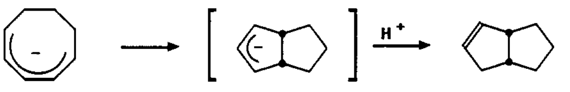
1,3-dimethylcyclopentadienyl)ruthenium (5) (>95:5 ratio of 4:5).[10,11] Mixtures of 2 and 4 were observed at 350 °C (>95:5) and 400 °C (55:45). Only a trace deposit was observed on the walls of the tube inside the furnace or on Pyrex substrates placed in the tube. When a sample of 4 was passed through a 500 °C oven, pure 5 was isolated. At this temperature, a dark film was observed on the walls of the reactor indicating that some decomposition or 4 and/or 5 had occurred at this temperature. On the basis of a residence time of ~10 s, the conversion of 2 to 4 and 5 may be limited more by the length of the hot zone than the temperature; i.e., conversion of 2 to 4 may be complete at 400 °C if a longer tube furnace used for the pyrolysis.

Thermolysis of (η^5-2,4-$Me_2C_5H_5$)$_2$Os (3)[12] at 500 °C and 5 × 10^{-2} Torr yielded the mixed cyclopentadienyl-pentadienylosmium complex 6 and the bis(cyclopentadienyl)osmium derivative 7 in a 9:1 ratio by ^{1}H NMR spectroscopy.[13] When (η^5-2,4-$Me_2C_5H_5$)$_2$Fe[9] was sublimed into the furnace above 250 °C, deposition of a metallic, highly reflective iron-containing coating was observed on the walls of the tube and on substrates (Pyrex, aluminum) placed in the tube.[14]

The gas-phase formation of 4–7 in nearly quantitative yield requires the formation of a C–C bond and the loss of hydrogen. The formation of (η^5-C_5H_5)RuCl(PPh_3)$_2$ upon refluxing (η^5-C_5H_7)RuCl(PPh_3)$_2$ in acetone is the only other reported example of the conversion of an transition-metal-bound η^5-pentadienyl ligand to an η^5-Cp ring.[15] We believe that the most likely pathway for conversion of 2 to 4 involves disrotatory C–C bond formation followed by ruthenium-assisted dehydrogenation of an η^3-1,3-$Me_2C_5H_5$ ligand (Figure 1); however, pathways involving activation of one or two C–H bonds prior to ring closure and loss of hydrogen cannot be ruled out.[16] Disrotatory cyclization of pentadienyl anions is thermally allowed on the basis of predictions from Woodward–Hoffman rules (reaction 1)[17]



(1)

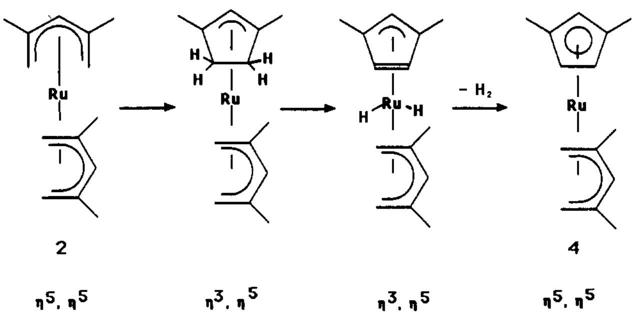


Figure 1. Possible pathways for conversion of 2 to 4.

and was observed for the cyclization of cyclooctadienyllithium to bicyclo[3.3.]cyclooctenyllithium (cis fused rings). Similar electrocyclic reactions of related cyclic systems and heterocyclic anions are known; however, alkali-metal pentadienyls do not appear to undergo thermal cyclization reactions.[18,19] The dehydration step in Figure 1 is consistent with the recently proposed mechanism for the dehydrogenation of cycloalkenes by Cp*Ru$^+$ fragments yielding (η^6-arene)RuCp$^+$ complexes.[20] A series of steps involving coordination of the cycloalkene, repetitive C–H activation, and reductive elimination of hydrogen was proposed in the latter reaction.

The role of ruthenium in promoting the cyclization of the pentadienyl ligand can be inferred from single-crystal X-ray diffraction studies of the related complex (η^5-2,3,4-C_5H_4)$_2$Ru (8).[10] In the latter open ruthenocene, the endo hydrogens of the terminal CH_2 groups were pointed away from the metal by an average of 42° while the exo hydrogens were pointed toward the metal by an average of 17°. The origin of this twist was postulated to result from improved overlap between ligand p orbitals and ruthenium d orbitals. In the present context, a positioning of the p orbitals in this fashion may promote electrocyclic C–C bond formation, forcing H_{exo} of the terminal CH_2 group even further toward the ruthenium center. Resonances assigned to H_{endo} and H_{exo} observed at 0.26 and 2.68 ppm, respectively, for 1, 0.94 and 2.81 ppm for 2, and 0.94 and 3.01 ppm for 3 are consistent with a twist about the terminal CH=CH_2 axis in solution even though crystallograhic evidence is not available for compound 2.[10] The positions of H_{exo} and H_{endo} in 1 and 3 were not revealed in the published crystallographic data.[9,15]

While thermal and photochemical rearrangements of transition-metal-coordinated cyclic polyolefins are well documented,[21] electrocyclic reactions of acyclic carbanionic ligands in transition-metal chemistry remain largely unexplored.[22] Syntheses of deuterium-labeled derivatives of 2 are in progress to test the disrotatory reaction pathway. We are pursuing studies on the extent of gas-phase pericyclic reactions at transition-metal-coordinated hy-

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(10) 4. ^{1}H NMR (C_6D_6) (δ) 0.39, d, J = 3 Hz, 2 H, *endo*-CH_2; 1.67, s, 6 H, CH_3; 1.83, s, 6 H, CH_3; 2.60 d, 2 H, *exo*-CH_2; 4.34 s, 2 H, CH of Cp ring; 4.45 s, CH of pentadienyl ring; 5.17 s, CH of Cp ring. Satisfactory elemental analyses were obtained for compound 4.

(11) 5. ^{1}H NMR (C_6D_6) (δ): 1.78, s, 6 H, CH_3; 4.34, s, 2 H, CH; 4.37 s, 1 H, CH. Satisfactory elemental analyses were obtained for compound 5.

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(13) 6. ^{1}H NMR (C_6D_6) (δ): 0.455, d, J = 3 Hz, 2 H, *endo*-CH_2; 1.72, s, 6 H, CH_3; 1.93, s, 6 H, CH_3; 3.01, d, J = 3 Hz, 2 H, *exo*-CH_2; 4.55, s, 2 H, CH of Cp ring; 4.62, s, 1 H, CH of pentadienyl ring; 5.56, s, 1 H, CH of Cp ring. 7. ^{1}H NMR (C_6D_6) (δ): 1.87, s, 6 H, CH_3; 4.52, s, 2 H, CH of Cp ring; 5.11, s, 1 H, CH of Cp ring. A trace of the starting material, 3, comprising less than 1% of the product mixture, was detected. ^{1}H NMR (C_6D_6) (δ): 1.79, s, CH_3; see ref 15.

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drocarbon ligands and potential differences between solution- and gas-phase chemistry.

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Supplementary Material Available: Text describing experimental details on the pyrolysis, isolation, and characterization of the new compounds prepared in this work and a figure showing a hot wall reactor (3 pages). Ordering information is given on any current masthead page.

Reversible Thermal and Photochemical Interconversion between Cis and Trans Isomers of the Silylene-Bridged Diiron Complex $Cp'_2Fe_2(CO)_3(\mu\text{-}SiHTol)$ (Cp' = $\eta\text{-}C_5Me_5$, Tol = $p\text{-}CH_3C_6H_4$)

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Summary: Isomerization between *cis*-$Cp'_2Fe_2(CO)_3(\mu\text{-}SiHTol)$ (*cis*-**1**; Cp' = $\eta\text{-}C_5Me_5$, Tol = $p\text{-}CH_3C_6H_4$) and *trans*-**1** was found to occur both thermally and photochemically. The composition in the thermal equilibrium state (*cis*-**1**:*trans*-**1** = 2:98 in cyclohexane-d_{12}) is considerably different from that in the photostationary state (*cis*-**1**:*trans*-**1** = 70:30).

It is well-known that an ER_2 group (E = group 14 (4B) elements; R = alkyl, aryl, hydrogen, halogen) can function as a bridging unit across a metal–metal bond.[1] The group of complexes with formula $Cp_2M_2(CO)_3(\mu\text{-}ER_2)$ is particularly interesting because geometrical isomers are possible for these complexes and, moreover, they are interconvertible. In fact, isomerism and interconversion between these isomers have been reported for $Cp_2M_2(CO)_3(\mu\text{-}CR_2)$ (M = Fe, Ru; R = H, alkyl, alkenyl, Ph, SR, etc.),[2a–i] $Cp_2M_2(CO)_3(\mu\text{-}C{=}CHR)$ (M = Fe, Ru; R = H, alkyl, Ph),[2g,i] $Cp_2Fe_2(CO)_3(\mu\text{-}SiHMe)$,[3] $Cp_2Fe_2(CO)_3(\mu\text{-}SiXBu^t)$ (X = Cl, Br, I, Me),[4] and $Cp_2Fe_2(CO)_3(\mu\text{-}GeMe_2)$.[5]

We previously reported photoinduced direct synthesis of the silylene-bridged dinuclear iron complexes $Cp_2Fe_2(CO)_3(\mu\text{-}SiHR)$ (R = *t*-Bu, $(CMe_2)_2H$) from $CpFe(CO)_2SiMe_3$ and $RSiH_3$.[6] These complexes exist only in the cis form, probably due to the steric interaction between the tertiary alkyl group and the Cp rings. This observation prompted us to synthesize the analogous but bulkier pentamethylcyclopentadienyl derivatives, in an attempt to encourage formation of the less hindered trans isomer.

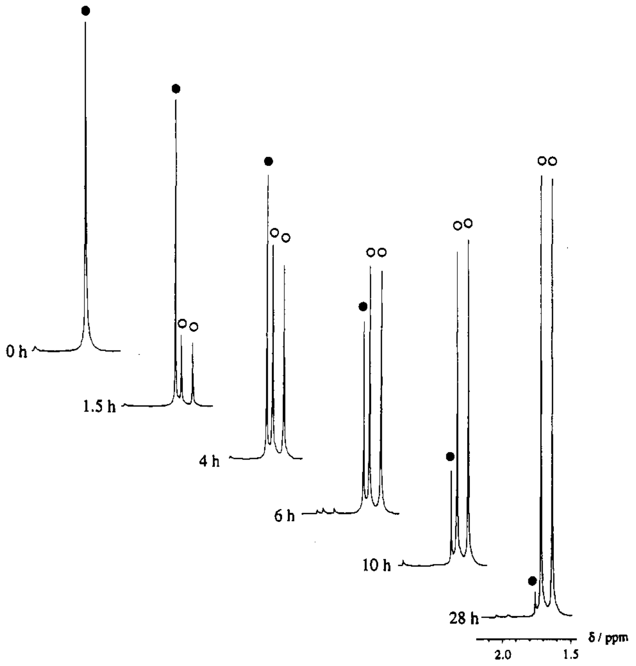

Figure 1. ^1H NMR spectral change of *cis*-**1** in cyclohexane-d_{12} at 40 °C: (●) *cis*-**1**; (○) *trans*-**1**.

Here we report the synthesis of the diiron complex $Cp'_2Fe_2(CO)_3(\mu\text{-}SiHTol)$ (**1**) and the thermal and photochemical interconversion of the cis and trans isomers. In this interconversion, remarkably different cis–trans ratios have been observed between the thermal equilibrium and the photostationary state.

When a mixture of $Cp'Fe(CO)_2SiMe_3$ and *p*-tolylsilane in a 2:1 molar ratio was irradiated in dry pentane using a 450-W medium-pressure mercury lamp, red crystals of the silylene-bridged diiron complex **1** were obtained as the major product. This consists of both cis and trans isomers (eq 1), which can be separated by silica gel flash chromatography. Isolated yields of *cis*- and *trans*-**1** immediately after the photolysis were 41% and 3%, respectively.

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