Asymmetric Migratory Insertion Reactions of the Chiral [(Binaphthyldiyldimethylene)cyclopentadienyl]iron Complex (BpDMCp)Fe$(CO)_2CH_3$

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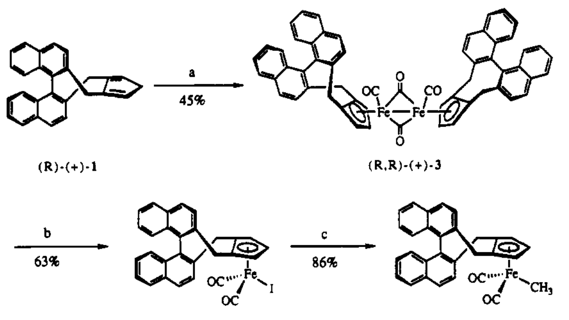
Summary: **The migratory insertion reaction of a (cyclopentadienyl)methyliron dicarbonyl 2 containing the chiral (binaphthyldiyldimethylene)cyclopentadienyl ligand 1 in the presence of triphenylphosphine can proceed with modest diastereoselectivity. The resulting acyliron complexes 5 are separable and are configurationally stable under oxidative conditions.**

Synthetic applications of chiral cyclopentadienyl(triphenylphosphine)acyliron complexes are becoming established,[1] yet little is known about their asymmetric preparation or their configurational stability upon which potential enantioselective reactions of acyliron species depend.[2] In order to investigate the diastereoselective generation of stereogenic iron centers in chiral cyclopentadienyliron complexes and to determine their configurational stability, we undertook a study of cyclopentadienyldicarbonylmethyliron complexes containing our recently developed binaphthyldiyldimethylene-annulated cyclopentadienyl ligand BpDMCp (1).[3] Due to its inherent homotopic π-faces, performing metalations with our C_2-symmetric (binaphthyldiyldimethylene)cyclopentadienyl ligand prevents the formation of diastereomeric metal complexes and eliminates any need for resolution of enantiomeric metal complexes via derivatization. We report here our results in the thermal triphenylphosphine-induced and oxidation-promoted asymmetric migratory insertions of (BpDMCp)Fe$(CO)_2CH_3$ (2).

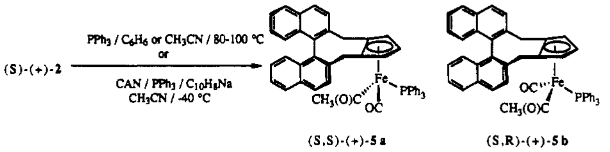
If one starts with BpDMCp (1), enantiomerically enriched 2 can be synthesized in three steps as outlined in the literature.[3b] Heating a mixture of (*R*)-(+)-BpDMCp (1), excess norbornene, and $Fe(CO)_5$[4] (Scheme I) produced a single C_2-symmetric isomer of (*R*,*R*)-(+)-[(BpDMCp)Fe$(CO)_2]_2$ (3), a result consist with the rapid rate of cis/trans isomerism of cyclopentadienyliron dicarbonyl dimer in solution.[5] When racemic BpDMCp (1) was used, the ratio of C_2- to C_s-symmetric isomers 3 was 72:28, respectively. Attempted conversion of dimer 3 to (BpDMCp)Fe$(CO)_2CH_3$ (2) by standard reduction of the iron–iron bond with sodium (shot and sand), sodium amalgam (2% and 6%), or sodium naphthalide followed by methylation with dimethyl sulfate or methyl iodide failed,[2a,6] producing in each case methylated BpDMCp. However, dimer (*R*,*R*)-(+)-3 could be initially cleaved with iodine[7] to yield (*R*)-(+)-(BpDMCp)Fe$(CO)_2$I (4), which was then successfully reduced with 2% Na–Hg and trapped with dimethyl sulfate to produce the desired (*R*)-(−)-(BpDMCp)Fe$(CO)_2CH_3$ (2) as a yellow powder. This compound classically demonstrates the electron-donating character of the new binaphthyldiyldimethylene-substituted cyclopentadiene 1 when the FT-IR ν_{CO} shifts of the parent $CpFe(CO)_2CH_3$, ν_{CO} (cm^{-1}) 2006 and 1944, are compared with those for (BpDMCp)Fe$(CO)_2CH_3$ (2), ν_{CO} (cm^{-1}) 1995 and 1934. The shift of carbonyl stretching frequencies to lower wavenumber is in accordance with the increase of electron density on the iron atom in 2.

Scheme I[a]



[a] Reagents: (a) $Fe(CO)_5$ (12 equiv), norbornene (12 equiv), 0.02 M in toluene, −78 °C to 111 °C, 40 h; (b) I_2 (1.4 equiv), 0.10 M in $CHCl_3$, 62 °C, 30 min; (c) 2% Na–Hg (2.2 equiv), 0.06 M in THF, 23 °C, 25 min, Me_2SO_4 (2 equiv), 23 °C, 15 min.

Scheme II



We initially established the ability of our BpDMCp ligand 1 to induce asymmetry in a thermal reaction of 2 with triphenylphosphine under thermodynamic but not kinetic control. Heating a mixture of methyliron (*S*)-(+)-2 and PPh_3 at 80 °C for 24–67 h in C_6H_6 (34% yield of pure **5a**/**5b** mixture) or CH_3CN (53% yield of pure **5a**/**5b** mixture) (Scheme II)[8] produced a crude mixture of (BpDMCp)Fe(CO)$PPh_3(COCH_3)$ diastereomers (*S*,*S*)-(+)-**5a** and (*S*,*R*)-(+)-**5b** in a 50:50 ratio.[9] We established that this ratio reflected kinetic control by resubjecting the separated acyliron diastereomers **5a** and **5b** to the reaction

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[9] All ratios were obtained by ^1H NMR spectroscopy of unpurified reaction products. Isomer **5a** was found to be less robust than isomer **5b**: crystalline **5a** decomposed over several days under nitrogen at 23 °C in the presence of light while **5b** was unaffected. Both isomers of **5** decompose within hours in unneutralized $CDCl_3$.

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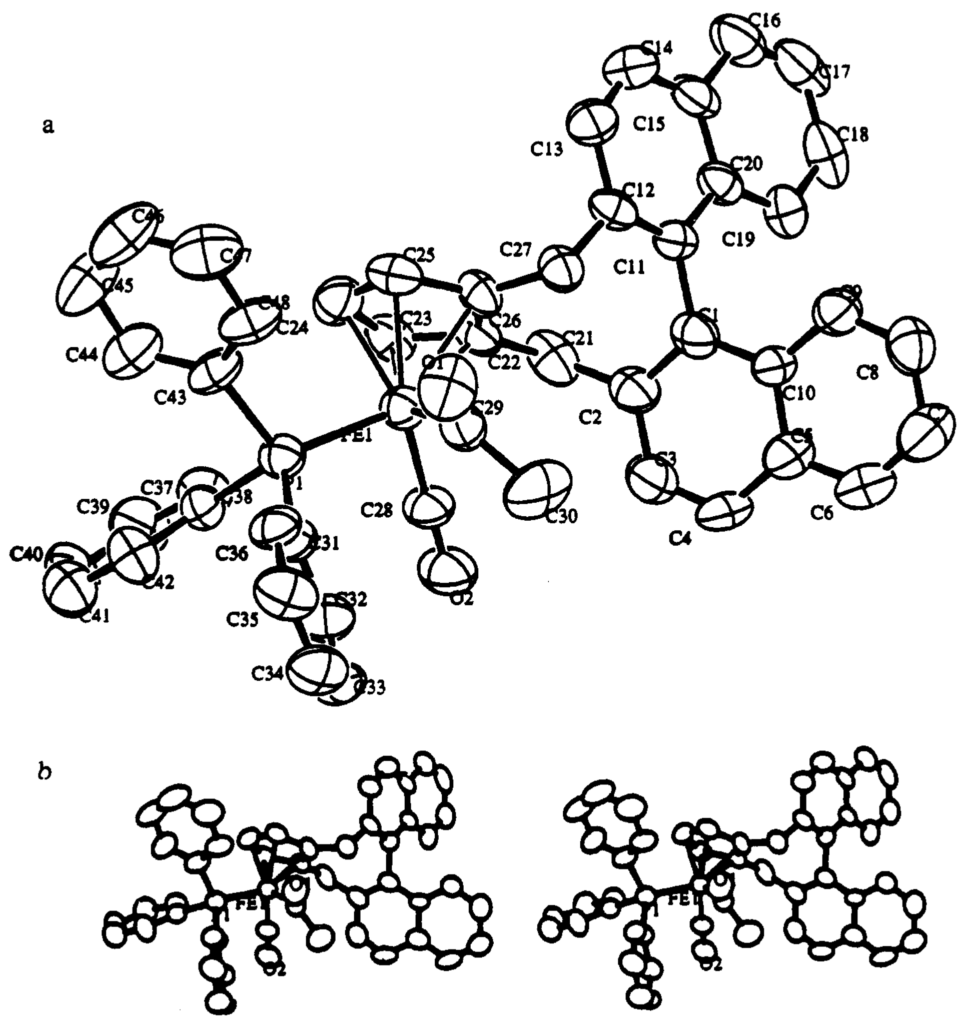

Figure 1. (a) ORTEP view of acyl diastereomer **5a** with 50% thermal probability levels. (b) Stereoview of **5a**.

conditions. These equilibration studies were conducted in C_6D_6, since the use of CD_3CN as solvent resulted in a heterogeneous reaction mixture. After ca. 88 h at 80 °C the ratio of each pure diastereomeric sample remained unchanged. This result supports Brunner's observation of configurational stability of iron complexes at moderate temperature.[2c] When the migratory insertion was carried out at a higher temperature of 100 °C for ca. 48 h in C_6H_6 (64% yield of pure **5a**/**5b** mixture) or CH_3CN (89% yield of pure **5a**/**5b** mixture), the formation of a 70:30 ratio of diastereomers **5a** and **5b** was observed, respectively. This ratio reflected thermodynamic control, since the separated diastereomers both converted to this same ratio when resubjected to the same reaction conditions of 100 °C for ca. 55 h. The configuration of the thermodynamically major isomer **5a** was obtained by X-ray diffraction and is shown in Figure 1.[10] In this conformation with the BpDMCp ligand rotated back, the triphenylphosphine group is anti to the large chiral binaphthyldiyl substituent on the cyclopentadienyl ring and the acyl group resides in a sterically unhindered area, whereas the smallest group, the carbonyl, extends toward a naphthyl ring.

Although the electrochemical oxidation-promoted migratory insertion reactions of iron methyl complexes in the presence of electron-donating ligands have been investigated by Giering[11] and others,[12] the chemical oxidation-promoted migratory insertion reaction of the dicarbonyl system $Cp(CO)_2FeCH_3$[13] has not been established nor has the configurational stability of $CpFe(CO)PPh_3(COCH_3)$ under oxidative conditions been reported. We have found that preparative-scale oxidation-promoted migratory insertion reactions of **2** were exceedingly rapid and also gave modest levels of asymmetric induction. Oxidation of (*S*)-(+)-**2** (Scheme II) with ceric ammonium nitrate (CAN) in CH_3CN at −40 °C for 10 min produced the expected dark green cation solution. Addition of triphenylphosphine and 10 min later reduction with sodium naphthalide[14] in THF at −40 °C immediately produced a dark orange so-

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[10] Crystal data for **5a** ($C_{48}H_{37}FePO_2\cdot CH_2Cl_2$) are as follows: Single crystals grown from CH_2Cl_2 by slow diffusion of hexane under static vacuum; M_r = 817.56 at 297 K; monoclinic space group $C2/c$ (No. 15), a = 32.629 (7) Å, b = 10.680 (3) Å, c = 25.787 (8) Å, β = 121.70 (2)°, V = 7645 (4) Å^3, d(calc) = 1.417 g cm^{-3}, Z = 8, μ(Cu Kα) = 52.01 cm^{-1}. The structure was solved by Patterson methods and refined by least squares with a p factor of 0.03 to R = 0.066% and R_w = 0.070 for 2702 unique reflections ($>3\sigma$) using the program TEXSAN-TEXRAY Structure Analysis Package, Molecular Structure Corp. (1985). Full details are given in the Supplementary Material.

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[13] Oxidation of *parent* $Cp(CO)_2FeCH_3$ with 1.1 equiv of ceric ammonium nitrate, addition of 1.1 equiv of PPh_3, and reduction with 1.1 equiv of sodium naphthalide (−40 °C isothermal, 8 mM CH_3CN) produced $CpFe(CO)PPh_3(COCH_3)$ in 90 s, 60% yield.

[14] Reduction of *parent* $[CpFe(CO)PPh_3(COCH_3)]^+$ with heterogeneous reagents such as zinc powder (−40 °C to 23 °C, 1 h or 10 h) instead of $C_{10}H_8Na$ (−40 °C, 30 s) resulted in lower yields (40%) of the parent acyl. A 40% yield of $CpFe(CO)PPh_3(COCH_3)$ was also obtained when the reductant was excluded, quenching the acyl cation at −40 °C after 5 min.

lution. A 60:40 ratio of acyliron diastereomers (*S*,*S*)-(+)-**5a** and (*S*,*R*)-(+)-**5b**, similar to the thermal product, was isolated respectively (41% yield of pure **5a**/**5b** mixture). Conducting this reaction as quickly as 30 s to 1 min for each step and with a greater excess of oxidant and reductant both resulted in lower chemical yields. In order to determine the configurational stability of **5** under oxidative conditions, the pure acyliron isomers were separately subjected to oxidations with ceric ammonium nitrate in CH_3CN at -40 °C (or 0 °C to room temperature) for 10 min followed by reduction with sodium naphthalide solution in THF at -40 °C (or 0 °C to room temperature). The same reactions were run on each isomer with 2.1 or 10 molar equiv of triphenylphosphine added after the oxidation step. In each case the reaction mixture turned green upon addition of the oxidant, indicating the formation of a 17-electron intermediate, then orange upon reduction. In each case the clean crude product contained only one diastereomer with **5a** or **5b** recovered unchanged. In general a 90–100% recovery of the starting diastereomer via alumina(I) was accomplished for these studies. Thus the 17-electron $[(BpDMCp)Fe(CO)PPh_3(COCH_3)]^+$ (**5**) diastereomer with or without the addition of PPh_3 is configurationally stable,[15] and the 60:40 ratio of isomers reflects kinetic product formation. The very rapid conversion of methyiron **2** to the acyliron diastereomers **5** under these oxidation, reduction conditions (<1 h) constitutes a dramatic synthetic improvement over the much longer, thermal conditions (>48 h).

The above results demonstrate that our chiral BpDMCp ligand **1** can induce asymmetry upon the migratory insertion reaction of $CpFe(CO)_2CH_3$ with PPh_3 under thermodynamic ($\Delta G° = 0.7$ kcal/mol) or kinetic ($\Delta\Delta G^{\ddagger} = 0.2$ kcal/mol) control. We have shown that the thermally driven migratory insertion reaction of chiral methyliron complex **2** in the presence of triphenylphosphine is irreversible at 80 °C but reversible at 100 °C. The oxidation-promoted insertion is exceedingly rapid at -40 °C, and the 17-electron complex of acyliron **5** is configurationally stable. The facile separation of the diastereomeric (BpDMCp)acyliron complexes should enable future applications of these chiral complexes in enantioselective synthesis.

Experimental Section

General Methods. Reaction, chromatographic, and recrystallizing solvents were purified and/or dried by standard methods.[16] C_6D_6 was distilled from calcium hydride. Triphenylphosphine and ceric ammonium nitrate were dried under vacuum prior to use. Reactions involving air- or moisture-sensitive compounds were performed under nitrogen and manipulated in a Vacuum Atmospheres Dri-Box. Freeze–pump–thaw degassing cycles were conducted under argon on a Schlenk line at <0.001 mmHg. NMR spectra were recorded on a Varian XL-400 or a Jeol JNM GSX-270 instrument. Infrared spectra were obtained on a Perkin-Elmer 1800 FT-IR instrument, and optical rotations were obtained on a Rudolph Research Autopol III polarimeter at 589 nm. Low- and high-resolution mass spectra were recorded on a Finnegan MAT-90 instrument. Melting points were determined in open Pyrex capillary tubes with a Thomas-Hoover Unimelt apparatus and are uncorrected. Combustion analyses were performed by Desert Analytics (Tucson, AZ). Preparative column chromatography was performed on neutral alumina (E. Merck Reagents activated alumina F-20, 80–200 mesh). Preparative thin-layer chromatography was accomplished using 500 μE Merck 60 F-254 silica gel.

Thermodynamic Formation of (*S*,*S*)-(+)-[2,3-(1,1′-Binaphthyl-2,2′-diyldimethylene)cyclopenta-1,3-dienyl]carbonyl(triphenylphosphine)acetyliron (5a) via Thermal Conditions. (*S*)-(+)-(BpDMCp)$Fe(CO)_2CH_3$ (**2**) (20 mg, 0.042 mmol) was combined with triphenylphosphine (45 mg, 0.170 mmol) in C_6H_6 (1 mL) under nitrogen and refluxed at 100 °C for 48 h excluding light. The crude orange reaction mixture was concentrated resulting in a 70:30 diastereomeric mixture by ^1H NMR spectroscopy. The crude mixture of isomers was purified on alumina(I) by elution with hexane and (8:2) hexane/CH_2Cl_2 to remove impurities and then CH_2Cl_2 (or CH_3CN) to afford orange crystalline acyl **5** (20 mg, 64%). The two diastereomers of **5** were separated by preparative thin-layer chromatography (SiO_2, CH_2Cl_2/petroleum ether (7:3), developed 1–2 times). The isolated yields of the pure diastereomers matched the diastereoselectivity ratio obtained by ^1H NMR integration. Less polar acyl diastereomer (*S*,*S*)-(+)-**5a** was characterized as follows: mp 185–188 °C; ^1H NMR (400 MHz, C_6D_6) δ 8.32 (d, $J = 8.5$ Hz, 1 H), 7.92 (d, $J = 8.5$ Hz, 1 H), 7.69 (m, 8 H), 7.33 (d, $J = 8.5$ Hz, 1 H), 7.20 (m, 3 H), 7.11 (ddd, $J = 8.0, 7.0, 1.0$ Hz, 1 H), 7.01 (m, 11 H), 6.87 (ddd, $J = 8.0, 7.0, 1.0$ Hz, 1 H), 4.09 (ddd, $J = 6.0, 2.5, 2.5$ Hz, 1 H), 3.98 (s, 1 H), 3.96 (dd, $J = 2.5, 2.5$ Hz, 1 H), 3.48 (d, $J = 15.0$ Hz, 1 H), 3.32 (s, 2 H), 3.30 (d, $J = 15.0$ Hz, 1 H), 1.90 (s, 3 H); ^{13}C NMR (100 MHz, C_6D_6) δ 272.80 (d, $J = 25.0$ Hz, acyl carbon), 221.94 (d, $J = 31.0$ Hz, CO), 137.48 (d, $J = 6.0$ Hz), 137.09, 136.76, 135.38, 134.86, 133.91 (d, $J = 10.0$ Hz), 133.20, 132.97, 132.68, 130.34, 129.87, 129.25 (d, $J = 7.0$ Hz), 129.00–127.00 (obscurred by solvent), 126.95, 126.70 (d, $J = 7.0$ Hz), 125.81, 125.55, 107.46, 98.62, 87.06, 86.74, 80.66, 48.62 (d, $J = 7.0$ Hz, acyl CH_3), 34.15, 33.64; IR (neat film) 3047, 2963, 1899, 1597, 1432, 1261, 1091, 1067, 1026, 919, 824, 800, 764, 747, 694 cm^{-1}; $[\alpha]^{23}_D$ +29.1° (*c* 0.350, C_6H_6); MS *m*/*z* (CI, NH_3, relative intensity) 749 ($M^+ + NH_3$, 0.05%), 734 ($M^+ + 2$, (0.05), 733 ($M^+ + 1$, 0.13), 732 (M^+, 0.08), 470 (2), 455 (82), 344 (2), 263 (100); HRMS (CI, NH_4^+, 150 eV) *m*/*z* ($M^+ + NH_4^+$) calcd for $C_{48}H_{41}O_2PNFe$ 750.2224, found 750.2323. A diastereomeric mixture of orange crystalline **5** was characterized as a 3:1 acyliron–methylene chloride adduct as seen by ^1H NMR spectroscopy (C_6D_6). Anal. Calcd for $C_{48}H_{37}O_2PFe{\cdot}0.33CH_2Cl_2$: C, 76.31; H, 4.99. Found: C, 76.60; H, 5.05.

Reversibility of *rac*-[2,3-(1,1′-Binaphthyl-2,2′-diyldimethylene)cyclopenta-1,3-dienyl]carbonyl(triphenylphosphine)acetyliron (5a) under Thermal Conditions. Acyliron **5a** (7 mg, 0.0096 mmol) was combined with triphenylphosphine (5 mg, 0.019 mmol) and dissolved in C_6D_6 (300 μL). This orange solution was transferred to an NMR tube, and the system was degassed with three consecutive freeze–pump–thaw cycles. Upon the last cycle the tube was flame-sealed, and the reaction mixture was heated under static vacuum at 80 °C for 88 h excluding light. The presence of acyliron diastereomer **5b** was not detected by ^1H NMR spectroscopy. The system was then heated further for 65 h at 100 °C excluding light. After progression toward the equilibrium mixture was complete, a 70:30 partition of **5a**/**5b** resulted. Likewise acyliron diastereomer **5b** was subjected to the same reaction conditions with no detectable formation of diastereomer **5a** at 80 °C. Heating at 100 °C produced isomers **5a**/**5b** in a 70:30 ratio.

Kinetic Formation of (*S*,*R*)-(+)-[2,3-(1,1′-Binaphthyl-2,2′-diyldimethylene)cyclopenta-1,3-dienyl]carbonyl(triphenylphosphine)acetyliron (5b) via Oxidative Conditions. (*S*)-(+)-(BpDMCp)$Fe(CO)_2CH_3$ (**2**) (11 mg, 0.023 mmol) was dissolved in CH_3CN (1 mL), and the solution was cooled to -40 °C and excluded from light. A yellow solution of $(NH_4)_2Ce(NO_3)_6$ (14.1 mg, 0.026 mmol) in CH_3CN (1 mL) was then introduced via syringe, instantly forming a deep green reaction mixture. After 10 min at -40 °C a solution of triphenylphosphine (6.75 mg, 0.026 mmol) in CH_3CN (1 mL) was added via syringe, and the green solution was stirred again for 10 min at -40 °C. The iron complex was then reduced with a solution of $C_{10}H_8Na$ (0.234 M in THF, 110 μL, 0.026 mmol) at -40 °C and stirred further for 10 min. The light orange reaction mixture was quenched at -40 °C into a separatory funnel and partitioned between water and CH_2Cl_2. The organic extracts were dried over anhydrous Na_2SO_4 and concentrated to a dark orange oil. The crude ^1H NMR spectrum

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[15] In a related system, resolved $CpFe(CO)PPh_3CH_3$ has been shown to racemize when subjected to oxidation via 5% Cp_2FeBF_4 in an atmosphere of carbon monoxide or nitrogen: Mierowitz, R. Ph.D. Dissertation, Boston University, 1983.

[16] Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*, 2nd ed.; Pergamon Press: London, 1980.

showed a 60:40 mixture of diastereomers, which was then purified on alumina(I) as before to afford orange crystalline acyl **5** (7 mg, 41%). After preparative TLC (SiO_2) as before, the more polar acyl diastereomer (*S,R*)-(+)-**5b** was isolated and characterized as follows: mp 186 °C; ^1H NMR (400 MHz, C_6D_6) δ 8.04 (d, J = 8.5 Hz, 1 H), 7.94 (d, J = 8.5 Hz, 1 H), 7.71 (m, 9 H), 7.32 (m, 4 H), 6.97 (m, 12 H), 4.12 (s, 1 H), 4.08 (s, 1 H), 3.89 (d, J = 13.0 Hz, 1 H), 3.80 (m, 1 H), 3.42 (d, J = 15 Hz, 1 H), 3.26 (m, 2 H), 2.60 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 278.20 (d, J = 21.0 Hz, acyl carbon), 219.81 (d, J = 39.0 Hz, CO), 136.65, 136.23, 135.72, 134.80, 134.46, 133.40–133.30, 132.68, 132.40, 132.28, 132.14, 132.03, 131.93, 130.32, 129.61, 128.95, 128.86, 128.54, 128.46, 128.29–127.70, 126.90, 126.79, 126.52, 126.26, 125.87, 125.30, 100.26, 96.68, 94.17, 84.31, 82.48, 52.81 (d, J = 5.5 Hz, acyl CH_3), 33.42, 33.00; IR (neat film) 3055, 2963, 2924, 1910, 1593, 1434, 1261, 1092, 1023, 865, 800, 696 cm^{-1}; $[\alpha]^{23}_D$ +6° (c 0.20, C_6D_6); MS, m/z (CI, NH_3, relative intensity) 749 ($M^+ + NH_3$, 0.05%), 733 (M^+ + 1, 0.15), 732 (M^+, 0.29), 470 (0.69), 454 (100), 344 (2), 263 (56).

Configurational Stability of *rac*-[2,3-(1,1′-Binaphthyl-2,2′-diyldimethylene)cyclopenta-1,3-dienyl]carbonyl(triphenylphosphine)acetyliron (5a) under Oxidative Conditions. Acyliron **5a** (9 mg, 0.012 mmol) was dissolved in CH_3CN (900 μL), and the solution was cooled to −40 °C and excluded from light. A solution of $(NH_4)_2Ce(NO_3)_6$ (7.4 mg, 0.014 mmol) in CH_3CN (600 μL) was then added via syringe, causing a consecutive color change from yellow starting material to brown to red to dark green over a period of 10 min. A solution of $C_{10}H_8Na$ (0.234 M in THF, 58 μL, 0.014 mmol) was then added via syringe at −40 °C, which caused an immediate color change from green to orange. The reaction mixture was allowed to stir at −40 °C for 10 min after which it was quenched in a separatory funnel with CH_2Cl_2 and water. After workup, the crude ^1H NMR spectrum revealed the presence of **5a** with no detection of **5b**. Likewise acyliron diastereomer **5b** was subjected to these reaction conditions, producing the same series of color changes with recovery of **5b** and no detectable trace of diastereomer **5a**. When oxidation of **5a** was performed at 23 °C (15 min), there was no detection of the characteristic green 17-electron acyl cation. Subsequent addition of $C_{10}H_8Na$ at 0 °C (15 min) resulted in no presence of either isomer.

Configurational Stability of *rac*-[5a]$^+$ in the Presence of PPh_3. Acyliron **5a** (13 mg, 0.018 mmol) was dissolved in CH_3CN (1.0 mL), and the solution was cooled to −40 °C and excluded from light. A solution of $(NH_4)_2Ce(NO_3)_6$ (10.7 mg, 0.020 mmol) in CH_3CN (600 μL) was then added via syringe and stirred for 30 min and then warmed to −20 °C (15 min) and 0 °C for 15 min. The green reaction mixture was cooled to −10 °C, and a solution of PPh_3 (9.8 mg, 0.037 mmol) in CH_3CN (600 μL) was added and stirred for 20 min. The green reaction mixture was then cooled further to −40 °C, and a solution of $C_{10}H_8Na$ (0.234 M in THF, 84 μL, 0.020 mmol) was added via syringe, causing an immediate color change from green to orange. The reaction mixture was allowed to stir at −40 °C for 10 min, after which it was quenched and worked up. The crude ^1H NMR spectrum revealed the presence of **5a** with no detection of **5b**. Likewise acyliron diastereomer **5b** was subjected to the same reaction conditions recovering **5b** with no detectable trace of diastereomer **5a**. Conducting this reaction isothermally at 0 °C (15 min each step, 8 mM in CH_3CN) with addition of a homogeneous solution of PPh_3 (36 mg, 0.137 mmol) to **5a** (10 mg, 0.014 mmol) preceding reduction resulted in the recovery of **5a** and the absence of **5b**.

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Registry No. (*S*)-(+)-**2**, 138259-99-1; (*S,S*)-(+)-**5a**, 138259-98-0; *rac*-**5a**, 138332-60-2; (*S,R*)-(+)-**5b**, 138332-59-9.

Supplementary Material Available: Tables of bond lengths and angles, crystallographic data, and thermal and positional parameters for **5a** (9 pages); listings of h,k,l, F_o, F_c, and $\sigma(F_o)$ values for **5a** (16 pages). Ordering information is given on any current masthead page.

Decomposition Kinetics of Methyl- and *n*-Propyldisilane

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Summary: The thermal decomposition kinetics of methyl- and *n*-propyldisilane (MDS and PrDS, respectively) under static reaction conditions are reported. These kinetics, extrapolated via transition-state theory to 298 K, are combined with kinetic data on the reverse reactions to obtain heats of formation of the reactant disilanes and the product silylenes. Thus $\Delta H_f°$(MDS) = 4.7 kcal/mol, $\Delta H_f°$(PrDS) = −2.0 kcal/mol, $\Delta H_f°$(MeSiH) = 49.6 kcal/mol, and $\Delta H_f°$(nPrSiH) = 41.6 kcal/mol.

The only important primary dissociation reactions in the thermal decompositions of disilanes having at least one Si–H bond are 1,2-H shifts[1] forming a monosilane and a silylene as products. For example there are just two primary dissociation channels in the thermal decomposition of methyldisilane (reactions 1 and 2). In neat systems,

$$MeSi_2H_5 \rightarrow MeSiH_3 + SiH_2 \tag{1}$$

$$MeSi_2H_5 \rightarrow MeSiH + SiH_4 \tag{2}$$

primary process silylenes react further to form trisilanes which, being somewhat more reactive than the reactant,[2] decompose to produce additional silane products and other potentially reactive silylenes, as in reactions 3–5. Under

$$SiH_2 + MeSi_2H_5 \rightarrow MeSi_3H_7 \tag{3}$$

$$MeSi_3H_7 \rightarrow SiH_4 + MeSi_2H_3 \tag{4}$$

$$MeSi_3H_7 \rightarrow MeSiH_3 + SiH_3SiH \tag{5}$$

such chain-enhanced conditions, identification of the formation kinetics of any monosilane product with the kinetics of its corresponding primary process reaction could be erroneous, particularly in studies carried to high reactant conversions. Nevertheless, such identifications were routine in most early disilane kinetic studies.[3] We have been concerned in recent years with establishing the thermochemistry of key organosilanes and silylenes, the ultimate objective being the generation of a Benson type group additivity scheme for polysilanes and organosilanes.

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