Coordination Modes

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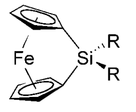
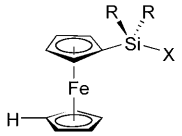
Reversible, Strain-Controlled Haptotropic Shifts of Cyclopentadienyl Ligands in [1]- and [2]Metallocenophanes**

*Makoto Tanabe, Sara C. Bourke, David E. Herbert, Alan J. Lough, and Ian Manners**

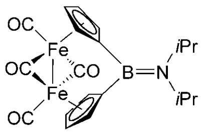
Strained rings containing transition-metal elements are of growing interest as a result of their intriguing structures, enhanced reactivity, and ability to function as precursors to high-molecular-weight metallopolymers through ring-opening polymerization.[1–4] Ring-strained metallocenophanes and their analogues have attracted particular attention in this regard and their ring-opened polymeric derivatives exhibit a variety of interesting properties.[3,4] The appreciable ring tilting (α) of the planes of the cyclopentadienyl ligands in ferrocenophanes relative to ferrocene, where the ligands are parallel ($\alpha = 0°$), has been shown to comprise the major contribution to ring strain.[5] Silicon-bridged [1]ferrocenophanes such as **A** ($\alpha \approx 16$–$21°$) have been most well investigated in this area. The moderate ring strain present in **A** has been shown to lead to enhanced reactivity of the bond between the *ipso* cyclopentadienyl (Cp) carbon and the bridging silicon atom. Stoichiometric reactions of **A** with protic regents, for example, lead to facile Si–Cp bond cleavage and to ring-opened species **B**.[6]



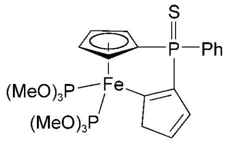
A



B



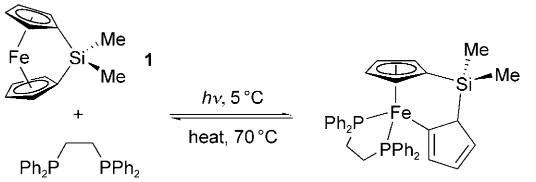
C



D

In contrast, highly strained, boron-bridged [1]ferrocenophanes ($\alpha \approx 31$–$32°$) have been shown to undergo unexpected ring-opening chemistry involving an Fe–Cp bond on reaction with, for example, $[Fe_2(CO)_9]$ to yield bimetallic species **C**.[7] Very recently, Miyoshi and co-workers have shown that UV-photoirradiation of phosphorus-bridged [1]ferrocenophanes in the presence of a phosphine ligand (e.g., $P(OMe)_3$) leads to a haptotropic shift of a Cp ligand (from η^5 to η^1) to yield the ring-slipped product **D**.[8] Herein, we report some of our initial results from comparative studies of the photolytic reactivity of a range of [1]- and [2]metallocenophanes, which demonstrate that either *reversible* or *irreversible* haptotropic rearrangements from η^5- to η^1-Cp are observed depending on the degree of strain present.

UV-photoirradiation of a slight excess of sila[1]ferrocenophane **1** ($\alpha = 20.8(5)°$)[9] in the presence of 1,2-bis(diphenylphosphanyl)ethane (dppe) in THF at 5 °C led to a haptotropic shift of a Cp ligand from η^5 to η^1 and coordination of the bidentate phosphine ligand to afford $[\{Fe(\eta^5\text{-}C_5H_4)SiMe_2(\eta^1\text{-}C_5H_4)\}(dppe)]$ (**2**) in 90 % yield [Eq. (1)].[10]



(1)

The $^{31}P\{^1H\}$ NMR spectrum of **2** consisted of slightly broad AB doublets at $\delta = 109.4$ and 108.5 ppm[11] with the same coupling constant ($^2J(P,P) = 27.2$ Hz); they were assigned to the diastereotopic phosphine atoms coordinated to the iron center. In the $^{29}Si\{^1H\}$ NMR spectrum, a single broad resonance signal appeared at $\delta = -8.72$ ppm, which is shifted slightly upfield compared to that of **1** ($\delta = -4.6$ ppm).

Figure 1 shows the molecular structure of **2** determined by X-ray crystallography.[12] The photoproduct **2** possesses a

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[*] Dr. M. Tanabe,[+] S. C. Bourke, D. E. Herbert, Dr. A. J. Lough, Prof. Dr. I. Manners
Department of Chemistry
University of Toronto
80 St. George Street, Toronto, ON M5S3H6 (Canada)
Fax: (+1) 416-978-6157
E-mail: imanners@chem.utoronto.ca

[+] Present address:
Chemical Resources Laboratory
Tokyo Institute of Technology
4259 Nagasuta, Midori-ku, Yokohama 226-8503 (Japan)

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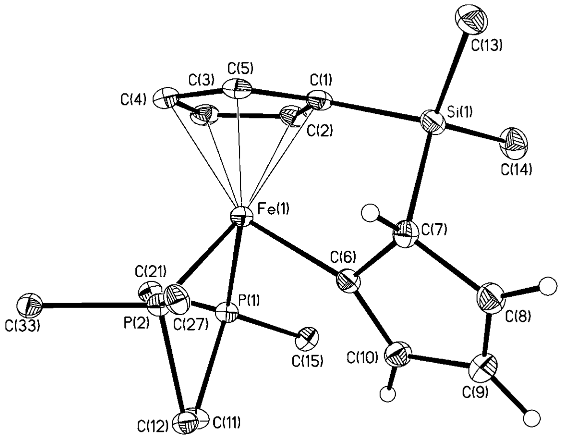


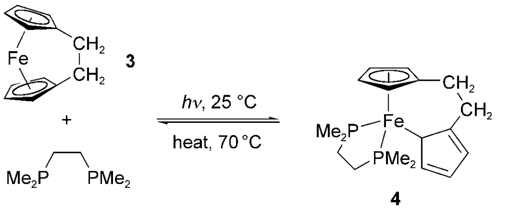
Figure 1. ORTEP drawing of **2** with 30% thermal ellipsoidal plots. Hydrogen atoms are depicted only for the η^1-Cp ring. Phenyl groups of the phosphine ligand are omitted for clarity. Selected bond lengths [Å] and angles [°]: Fe(1)-$Cp_{centroid}$ 1.736(2), Fe(1)-P(1) 2.1543(6), Fe(1)-P(2) 2.1544(6), Fe(1)-C(6) 2.015(2), Si(1)-C(1) 1.862(2), Si(1)-C(7) 1.884(2), C(6)-C(7), 1.524(3), C(6)-C(10) 1.367(3), C(7)-C(8) 1.483(3), C(8)-C(9) 1.343(4), C(9)-C(10) 1.464(3); $Cp_{centroid}$-Fe(1)-C(6) 119.7(9), $Cp_{centroid}$-Fe(1)-P(1) 129.8(9), $Cp_{centroid}$-Fe(1)-P(2) 131.5(9), C(1)-Si(1)-C(7) 99.42(10), Fe(1)-C(6)-C(7) 118.01(16), Si(1)-C(7)-C(6) 100.07(14).

piano-stool geometry around the Fe center. The C(1)-Si(1)-C(7) angle (99.42(10)°) is larger than that of **1** (95.7(4)°),[9] and the angle β (14.0(3)°) of **2**, between the plane of the cyclopentadienyl carbon atoms and the C(1)-Si(1) bond, has decreased significantly (from 37.0(6)° for **1**),[9] indicating that the ring strain is less in **2** than in **1**. The bond lengths for C(6)−C(10) (1.367(3) Å) and C(8)−C(9) (1.343(4) Å) in the σ-bonded Cp ring are shorter than other bond lengths (average 1.490(3) Å), indicating that the double bonds are located in these positions.

All inequivalent proton and carbon signals for the differently coordinated Cp rings were assigned by ^{1}H-^{1}H and ^{1}H-^{13}C COSY NMR spectroscopic methods at −40 °C. Interestingly, one signal in each Cp ring was observed at higher field (δ = 2.82 ppm for η^1-Cp; δ = 3.03 ppm for η^5-Cp). Upon raising the temperature of the solution to 25 °C, all signals in the ^{1}H and ^{31}P{^{1}H} NMR spectra appeared broadened suggesting fluxional behavior around the Fe center.

Remarkably, on heating at 70 °C in [D$_6$]benzene for 3 h, photoproduct **2** underwent dissociation of the dppe ligand and quantitative retroconversion into **1** [Eq. (1)]. This thermal reaction clearly indicates that, at elevated temperatures, the ring-strained ferrocenophane **1** and dppe are thermodynamically favored compared with the photoproduct **2**. This can be attributed to the greater entropy of the species on the left side of Equation (1) and the enthalpic preference for η^5-Cp coordination. It appears that **2** is metastable at room temperature and that its formation relies on the photoactivation of **1**.

To explore the generality of this surprising reversible reaction, we investigated the analogous chemistry of the ethane-bridged [2]ferrocenophane **3** (α = 21.6(4)°)[13] which has a similar degree of ring strain as **1**. Another ring-slipped Fe complex, [{Fe(η^5-C_5H_4)CH_2CH_2(η^1-C_5H_4)}(dmpe)] (**4**), was obtained from the photolysis of **3** in the presence of 1,2-bis(dimethylphosphanyl)ethane (dmpe) in THF at room temperature [Eq. (2)]. Recrystallization of the crude product from toluene/hexane at −55 °C afforded **4** as dark red crystals in 83% yield.[14] Heating of **4** in [D$_8$]toluene for 3 h at 70 °C also led to a quantitative reverse haptotropic rearrangement with dissociation of the dmpe ligand.



(2)

Complex **4** was also fully characterized by one- and two-dimensional NMR spectroscopic methods at low temperature and the crystal structure was determined by X-ray diffraction (Figure 2).[12] The piano-stool Fe center, capped by an η^5-Cp ligand, also possesses a chelating dmpe ligand. The C(1)−C(6) bond was found to lie almost in plane with the η^5-Cp ligand (β = 1.9(3)°), indicating that the structure contains no significant ring strain. The two double bonds in the η^1-Cp ring were located at C(8)−C(9) (1.352(8) Å) and C(10)−C(11) (1.350(8) Å), supported by the conformation around C(12) which is not suited to an sp^2 carbon center. Analysis of **4** in the solid state indicated that the η^1-Cp geometry is a tautomer of that in **2**.

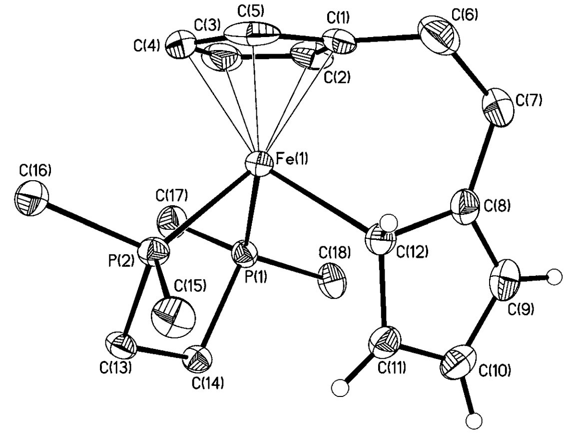


Figure 2. ORTEP drawing of **4** with 30% thermal ellipsoidal plots. Hydrogen atoms are depicted only for the η^1-Cp ring. Selected bond lengths [Å] and angles [°]: Fe(1)-$Cp_{centroid}$ 1.717(5), Fe(1)-P(1) 2.1674(15), Fe(1)-P(2) 2.1776(14), Fe(1)-C(12) 2.201(5), C(1)-C(6) 1.491(8), C(6)-C(7) 1.516(9), C(7)-C(8) 1.512(7), C(8)-C(9) 1.352(8), C(8)-C(12) 1.476(7), C(9)-C(10) 1.428(8), C(10)-C(11) 1.350(8), C(11)-C(12) 1.465(7); $Cp_{centroid}$-Fe(1)-C(12) 120.1(2), $Cp_{centroid}$-Fe(1)-P(1) 125.1(2), $Cp_{centroid}$-Fe(1)-P(2) 128.0(2), C(1)-C(6)-C(7) 111.6(5), C(6)-C(7)-C(8) 113.5(5), C(7)-C(8)-C(12) 124.6(5), Fe(1)-C(12)-C(8) 110.6(3).

The variable-temperature ^{31}P{^{1}H} NMR spectra exhibited two doublets at δ = 81.0 and 78.9 ppm (^2J(P,P) = 39 Hz) at −40 °C that coalesce to give a single signal at 79.0 ppm upon warming to 20 °C. Figure 3 depicts the ^{1}H NMR spectra of **4**

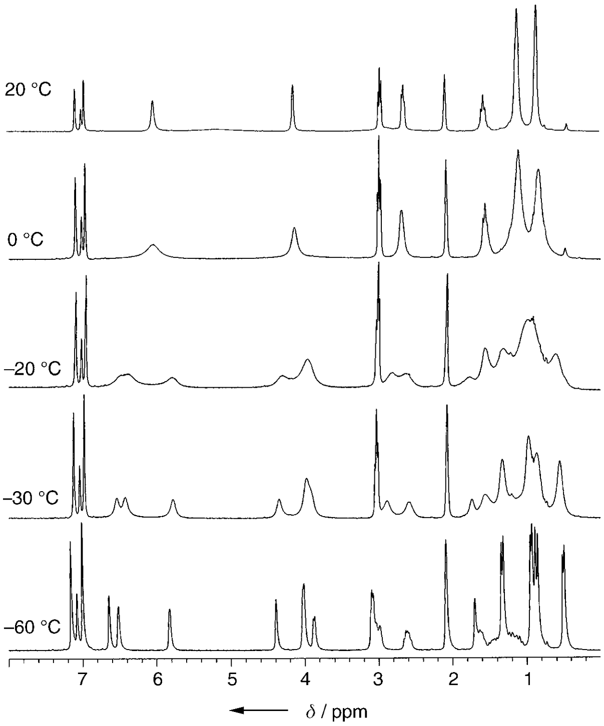
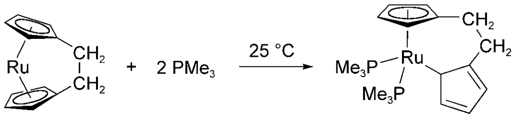


Figure 3. Variable-temperature ^{1}H NMR spectra of **4** between −60 and 20 °C in [D$_8$]toluene.

between −60 and 20 °C. At −60 °C, eight signals attributed to the two inequivalent Cp rings were observed in the range $\delta =$ 1.70–6.64 ppm. Upon raising the temperature to −20 °C all signals attributable to **4** broadened and coalesced around 0 °C, indicating the same coalescence temperature for both the η^1- and η^5-Cp rings. At 20 °C, two widely broadened signals ($\delta =$ 4.6–5.6 ppm for the η^1-ring; $\delta = 2.8$–3.1 ppm for the η^5-ring; not clearly visible in the spectra) suggest slower fluxional behavior. The fluxional behavior of σ-bonded Cp rings such as that in [Fe(η^1-Cp)(η^5-Cp)(CO)$_2$] has been well studied over the past four decades.[15] The η^1-Cp ring of this species is involved in a fluxional process that consists of successive 1,2-shifts, observable on the NMR time scale, while the η^5-Cp ring signals display no coalescence due to more rapid ring rotation. The dynamic nature of the NMR spectrum of **4** suggests fluxional behavior, which may involve fast successive 1,2-shifts of the η^1-Cp ring and slow coordination mode exchange between the two Cp ligands.

At this point, we investigated the analogous reaction of the more highly ring-strained, ethane-bridged [2]ruthenocenophane **5** which possesses a larger tilt angle of 29.6(5)° by virtue of the larger covalent radius of Ru relative to Fe.[16] When **5** was reacted with excess PMe$_3$ *without* photoirradiation the new complex [{Ru(η^5-C$_5$H$_4$)CH$_2$CH$_2$(η^1-C$_5$H$_4$)}(PMe$_3$)$_2$] (**6**) was formed in a quantitative yield [Eq. (3)].



5 **6** (3)

The solid-state structure of **6** was investigated by single-crystal X-ray crystallography.[12] The molecular structure (Figure 4) and the η^1-Cp ring geometry were similar to that seen for complex **4**. The Cp$_{\text{centroid}}$–Ru distance (1.863(3) Å) is longer than the Cp$_{\text{centroid}}$–Fe distance in **4** (1.717(5) Å) due to the larger size of the ruthenium atom. As expected from the reaction in the absence of UV-photoirradiation, the ring-slipped Ru complex **6** is the thermodynamically stable compound due to the high ring-strain energy of ruthenocenophane **5**. In fact, thermal treatment of **6** in [D$_8$]toluene (110 °C, 18 h) resulted in no detectable retroconversion to **5**. Similar, irreversible formation of a ring-slipped η^1-Cp complex [{Ru(η^5-Cp)(CH$_2$CH$_2$)(η^1-Cp)}(dmpe)] (**7**) was observed with **5** and the chelating diphosphine dmpe.

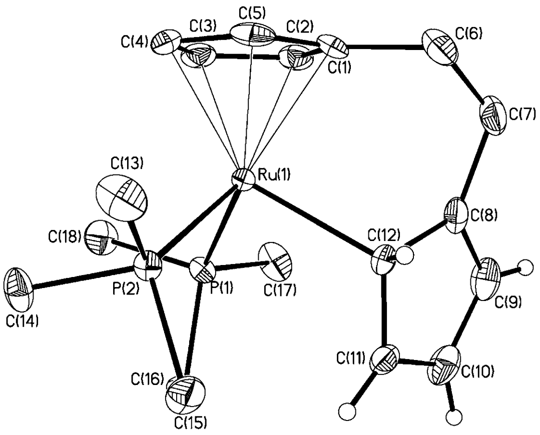


Figure 4. ORTEP drawing of **6** with 30% thermal ellipsoidal plots. Hydrogen atoms are depicted only for the η^1-Cp ring. Selected bond lengths [Å] and angles [°]: Ru(1)-Cp$_{\text{centroid}}$ 1.863(3), Ru(1)-P(1) 2.2710(6), Ru(1)-P(2) 2.2719(6), Ru(1)-C(12) 2.275(2), C(1)-C(6) 1.505(4), C(6)-C(7) 1.496(5), C(7)-C(8) 1.508(4), C(8)-C(12) 1.474(3), C(8)-C(9) 1.355(4), C(9)-C(10) 1.425(5), C(10)-C(11) 1.360(4), C(11)-C(12) 1.464(4); Cp$_{\text{centroid}}$-Ru(1)-C(12) 117.3(9), Cp$_{\text{centroid}}$-Ru(1)-P(1) 124.4(9), Cp$_{\text{centroid}}$-Ru(1)-P(2) 123.9(9), C(1)-C(6)-C(7) 112.8(3), C(6)-C(7)-C(8) 114.4(3), C(7)-C(8)-C(12) 126.0(3), Ru(1)-C(12)-C(8) 108.23(16).

In summary, ring-strained ferrocenophanes **1** and **3** were found to undergo photochemically and thermally reversible haptotropic shifts (η^5- to η^1-Cp) and the ring-slipped photoproducts **2** and **4** were isolated in the presence of appropriate phosphine ligands. In contrast, the highly ring-strained ruthenocenophane **5** was transformed irreversibly into the analogues **6** and **7** without UV-photoirradiation. We attribute these phenomena to the balance between the release of strain in the [1]- or [2]metallocenophane with the preference for η^5 coordination of the Cp ligand. For **1** and **3**, which possess moderate tilt angles and strain, photoactivation leads to **2** and **4**, which are metastable and retroconvert when heated at 70 °C. In contrast, the highly tilted [2]ruthenocenophane **5** possesses sufficient strain for the more thermodynamically stable species **6** and **7** to be formed irreversibly and without the need for photochemical activation. Currently, we are focusing on the detailed mechanism for the photochemically induced haptotropic rearrangement and the fluxional behavior of ring-slipped Fe and Ru complexes.

Experimental Section

Basic experimental procedures and analytical equipment used were as noted elsewhere.[4b] The ligands dppe and dmpe were purchased from Aldrich, and trimethylphosphine was obtained from Strem. These phosphine reagents were used as received. The photoirradiation experiments were carried out with Pyrex-glass-filtered emission from a 125-W high-pressure mercury arc lamp (Philips). The emission lines of the mercury lamp were as follows: 578.0, 546.1, 435.8, 404.7, 365.0, 334.1, 313.0, and 302.5 nm.

Preparation of **2**: In the absence of light, dppe (359 mg, 0.9 mmol) was added to a slight excess of sila[1]ferrocenophane **1**[17] (242 mg, 1.0 mmol) dissolved in THF (5 mL). The solution was irradiated for 3 h, with stirring, in a cooling water bath at 5 °C. The reaction mixture was evaporated to dryness. Addition of hexane to the red residue followed by filtration allowed for collection of a red solid which was washed with hexane three times (2 mL), and dried in vacuo (517 mg, 90 % based on dppe). Recrystallization from THF/hexane, by slow evaporation, gave dark red crystals suitable for X-ray crystallography. All signals in the ^1H and $^{13}C\{^1H\}$ NMR spectra at 25 °C and −40 °C were characterized by 2D ^1H-^1H and ^1H-^{13}C NMR experiments. ^1H NMR (500 MHz, [D_8]toluene, −40 °C): $\delta = 7.88$ (br, 2H, Ph-*ortho*), 7.38 (s, 2H, Ph-*ortho*), 7.13–6.99 (Ph, overlapped with solvent), 6.69 (s, 1H, η^1-C_5H_4, CH=), 6.61 (s, 1H, η^1-C_5H_4, CH=), 5.33 (s, 1H, η^1-C_5H_4, CH=), 5.12 (s, 1H, η^5-C_5H_4), 4.70 (s, 1H, η^5-C_5H_4), 4.19 (s, 1H, η^5-C_5H_4), 3.03 (s, 1H, η^5-C_5H_4), 2.82 (s, 1H, η^1-C_5H_4, SiCH), 2.59 (br m, 1H, PCH_2), 2.17 (br d, 1H, PCH_2, ^2J(H,P) = 34 Hz), 1.87 (br m, 1H, PCH_2), 1.69 (br d, 1H, PCH_2, ^2J(H,P) = 27 Hz), 0.36 (br, 3H, $SiCH_3$), 0.13 ppm (br, 3H, $SiCH_3$); $^{13}C\{^1H\}$ NMR (75.4 MHz, [D_6]benzene, 25 °C): $\delta = 161.5$ (dd, η^1-C_5H_4, FeC=, ^2J(C,P) = 26, 38 Hz), 147.1 (Ph-*ipso*), 144.7 (η^1-C_5H_4, CH=), 141.0 (Ph-*ipso*), 140.7 (Ph-*ipso*), 139.5 (Ph-*ipso*), 135.6 (Ph-*ortho*), 134.0 (η^1-C_5H_4, CH=), 133.3 (η^1-C_5H_4, CH=), 131.3 (Ph-*ortho*), 129.8 (Ph), 129.1 (Ph), 103.2 (η^5-C_5H_4-*ipso*), 87.5 (η^5-C_5H_4), 84.0 (η^5-C_5H_4), 80.4 (η^5-C_5H_4), 74.9 (η^1-C_5H_4, SiCH), 73.6 (η^5-C_5H_4), 28.6 (dd, PCH_2, J(C,P) = 16, 34 Hz), 25.0 (br t, PCH_2), 0.11 ($SiCH_3$), −7.92 ppm ($SiCH_3$); $^{31}P\{^1H\}$ NMR (121.4 MHz, [D_6]benzene, 25 °C): $\delta = 109.4$ (d, J(P,P) = 27.2 Hz), 108.5 ppm (d, J(P,P) = 27.2 Hz); $^{29}Si\{^1H\}$ NMR (79.4 MHz, [D_6]benzene, 25 °C): $\delta = -8.72$ (br); MS analysis was not possible, as the sample decomposed in the spectrometer; elemental analysis: calcd for $C_{38}H_{38}FeP_2Si$ (%): C 71.25, H 5.98; found: C 70.95, H 6.00. A solution of **2** in [D_6]benzene, heated at 70 °C for 3 h in the absence of light, turned red in color and underwent a quantitative dissociation of the dppe ligand and reformation of the starting material **1**, as observed by ^1H NMR spectroscopy. The UV-photoirradiation of **1** with dmpe in THF at room temperature led to a dark red solution. However, a ^1H NMR spectrum of the reaction mixture showed the presence of **1** and free dmpe. In contrast, the photoirradiation of **1** with PMe_3 in [D_6]benzene at room temperature for 5 h afforded the ring-opened polymer $[fcSiMe_2]_n$ in 35 % yield ($M_n = 1.3 \times 10^4$, polydispersity index (PDI) = 1.45).[17a]

Preparation of **4**: The ligand dmpe (333 mg, 2.2 mmol) was added to a solution of ethane-bridged [2]ferrocenophane **3**[13a] (212 mg, 1.0 mmol) in THF (30 mL). The reaction mixture was irradiated for 2 h, with stirring at room temperature. The reaction conversion was estimated at 95 % by ^1H NMR spectroscopy. All volatile material in the reaction mixture was removed under high vacuum. The resulting material was dissolved in toluene and filtered through a celite-fritted glass disk. Recrystallization from toluene/hexane (10 mL, 4:1) at −55 °C gave dark red crystals (302 mg, 83 % yield). All signals in the ^1H and $^{13}C\{^1H\}$ NMR spectra at 20 and −60 °C were characterized by 2D ^1H-^1H and ^1H-^{13}C NMR experiments. ^1H NMR (300 MHz, [D_8]toluene, −60 °C): $\delta = 6.64$ (s, 1H, η^1-C_5H_4, CH=), 6.51 (s, 1H, η^1-C_5H_4, CH=), 5.82 (s, 1H, η^1-C_5H_4, CH=), 4.40 (s, 1H, η^5-C_5H_4), 4.02 (m, 2H, η^5-C_5H_4 and η^1-C_5H_4, overlapped signals), 3.87 (d, 1H, η^5-C_5H_4, ^3J(H,H) = 6.0 Hz), 3.08 (d, 2H, $CpCH_2$, ^3J(H,H) = 6.3 Hz), 3.02 (d, 1H, $CpCH_2$, ^3J(H,H) = 14 Hz), 2.61 (m, 1H, $CpCH_2$, ^3J(H,H) = 6.0 Hz), 1.70 (s, 1H, η^5-C_5H_4), 1.05–1.70 (4H, PCH_2), 1.33 (d, 3H, PCH_3, ^2J(H,P) = 7.5 Hz), 0.94 (d, 3H, PCH_3, ^2J(H,P) = 6.6 Hz), 0.87 (d, 3H, PCH_3, ^2J(H,P) = 10 Hz), 0.51 ppm (d, 3H, PCH_3, ^2J(H,P) = 6.6 Hz); $^{13}C\{^1H\}$ NMR (100.4 MHz, [D_8]toluene, −60 °C): $\delta = 157.4$ (η^1-C_5H_4-*ipso*, CH_2C=), 143.9 (η^1-C_5H_4, CH=), 118.2 (η^1-C_5H_4, CH=), 117.4 (η^1-C_5H_4, CH=), 94.4 (η^5-C_5H_4-*ipso*), 81.0 (η^5-C_5H_4), 80.1 (η^5-C_5H_4), 79.4 (η^5-C_5H_4), 56.3 (η^5-C_5H_4), 31.9 (dd, PCH_2, J(C,P) = 27, 14 Hz), 31.7 ($CpCH_2$), 30.8 ($CpCH_2$), 29.7 (dd, PCH_2, J(C,P) = 26, 15 Hz), 23.5 (d, PCH_3, J(C,P) = 27 Hz), 22.8 (η^1-C_5H_4, FeCH), 22.1 (d, PCH_3, J(C,P) = 25 Hz), 18.2 (d, PCH_3, J(C,P) = 9.5 Hz), 8.93 ppm (dd, PCH_3, J(C,P) = 4.5, 12 Hz); $^{31}P\{^1H\}$ NMR (121.4 MHz, [D_8]toluene, −40 °C): $\delta = 81.0$ (d, ^2J(P,P) = 39 Hz), 78.9 ppm (d, ^2J(P,P) = 39 Hz); $^{31}P\{^1H\}$ NMR (121.4 MHz, [D_8]toluene, 20 °C): $\delta = 79.0$ ppm; MS(CI, 70 eV): *m*/*z* (%): 362 (2.5) [M^+], 212 (100) [$M^+ - (PMe_2CH_2)_2$], 134 (65) [$Fe(C_5H_4CH_2)^+$], 122 (65) [$Fe(C_5H_5) + H^+$]; elemental analysis: calcd for $C_{18}H_{28}FeP_2$ (%): C 59.69, H 7.79; found: C 60.04, H 8.01. A solution of **4** in [D_6]benzene, heated at 70 °C for 3 h in the absence of light, was quantitatively converted into a mixture of dmpe and **3**, as observed by ^1H NMR spectroscopy. Although UV-photoirradiation of the solution of **3** in THF in the presence of dppe at 5 °C led to a slightly dark red color, the ^1H and $^{31}P\{^1H\}$ NMR spectra did not show any photoproducts. The photoreaction with a threefold excess of PMe_3 for 3 h in [D_6]benzene at room temperature led to polymerization to yield the yellowish insoluble polymer $[fcCH_2CH_2]_n$ in 66 % yield.[13b]

Preparation of **6**: A fivefold excess of PMe_3 (78 µL, 0.76 mmol) was added to a solution of ethane-bridged [2]ruthenocenophane **5**[16] (39 mg, 0.15 mmol) in [D_6]benzene (0.5 mL) at room temperature. The reaction mixture immediately turned from yellow to orange in color without UV-photoirradiation. A ^1H NMR spectrum of the reaction mixture showed the quantitative conversion into ring-slipped Ru complex **6**. The volatile material was removed under high vacuum to dryness. Recrystallization from hexane by slow evaporation gave orange crystals suitable for X-ray crystallography. ^1H NMR (300 MHz, [D_6]benzene, 25 °C): $\delta = 6.54$ (s, 2H, η^1-C_5H_4), 5.3–5.7 (br, 2H, η^1-C_5H_4), 4.10 (s, 2H, η^5-C_5H_4), 3.89 (s, 2H, η^5-C_5H_4), 3.00 (t, 2H, $CpCH_2$, ^3J(H,H) = 3.2 Hz), 2.43 (t, 2H, $CpCH_2$, ^3J(H,H) = 3.3 Hz), 1.04 ppm (t, 18H, PCH_3, ^2J(H,P) = 3.9 Hz); $^{31}P\{^1H\}$ NMR (121.4 MHz, [D_6]benzene, 25 °C): $\delta = 4.65$ ppm; MS(EI, 70 eV): *m*/*z* (%): 410 (19) [M^+], 258 (100) [$M^+ - 2PMe_3$], 180 (36) [$Ru(C_5H_5CH_2)^+$]. High-resolution MS for $C_{18}H_{30}P_2Ru$: calcd 410.086, found 410.087. Compound **6** did not show any retroconversion into ruthenocenophane **5** after 18 h at 110 °C in [D_8]toluene (^1H NMR).

Preparation of **7**: Excess dmpe (70 µL, 0.42 mmol) was added to a [D_6]benzene (0.5 mL) solution of ethane-bridged [2]ruthenocenophane **5** (5 mg, 0.019 mmol) at room temperature. The reaction mixture darkened from yellow to orange-yellow without UV-photoirradiation. A ^1H NMR spectrum of the reaction mixture showed quantitative conversion of the [2]ruthenocenophane into the ring-slipped Ru complex **7**. ^1H NMR (400 MHz, [D_6]benzene, 25 °C): $\delta =$ 6.32 (s, 2H, η^1-C_5H_4), 5.40 (br, 2H, η^1-C_5H_4), 4.56 (s, 2H, η^5-C_5H_4), 3.94 (s, 2H, η^5-C_5H_4), 2.96 (t, 2H, $CpCH_2$, ^3J(H,H) = 6.4 Hz), 2.46 (t, 2H, $CpCH_2$, ^3J(H,H) = 6.4 Hz), 1.61 (m, 4H, PCH_2), 1.17 ppm (m, 12H, PCH_3); $^{31}P\{^1H\}$ NMR (121.5 MHz, [D_6]benzene, 25 °C): $\delta =$ 54.2 ppm. ^1H NMR analysis of **7** in [D_6]benzene at 70 °C showed no evidence of retroconversion into [2]ruthenocenophane **5**. Partial decomposition of a solution of **7** in [D_8]toluene was observed at 85 °C but the remaining ring-slipped compound **7** showed no retroconversion into **5** even at 110 °C after 5 h.

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[10] Similar photoirradiation of **1** in the presence of dmpe or PMe_3 was unsuccessful in terms of isolating Cp ring-slipped compounds like **2**; see the Experimental Section.

[11] These chemical shifts are similar to those of the dppe-coordinated Fe complex $[\{(\eta^5\text{-Cp})Fe(dppe)\}_2(\mu\text{-CH=CHCH=CH})]$: M.-C. Chung, X. Gu, B. A. Etzenhouser, A. M. Spuches, P. T. Rye, S. K. Seetharaman, D. J. Rose, J. Zubieta, M. B. Sponsler, *Organometallics* **2003**, *22*, 3485–3494.

[12] Crystallographic data for $C_{38}H_{38}FeP_2Si$ (**2**): $M_r = 640.56$, monoclinic, $P2_1/c$, $a = 8.9389(2)$, $b = 17.1939(2)$, $c = 20.8647(4)$ Å, $\beta = 95.7490(9)°$, $V = 3190.66(10)$ Å^3, $Z = 4$, $\mu = 0.637$ mm^{-1}, $\rho_{calcd} = 1.333$ Mg m^{-3}, 150(1) K, Nonius Kappa-CCD diffractometer using graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), dark red crystal ($0.28 \times 0.18 \times 0.10$ mm^3). Of 28009 reflections collected ($5.1 \leq 2\theta \leq 55.0°$), 7314 were independent ($R_{int} = 0.0553$). The data frames were integrated and scaled using the Denzo-SMN package.[18] Solution and refinement with SHELXTL-PC V6.12,[19] non-hydrogen atoms were refined with anisotropic parameters, hydrogen atoms were refined on calculated positions using a riding model, $R1 = 0.0401$, $wR2 = 0.1085$ (for all three structure determinations: $R1 = \Sigma(F_o - F_c)/\Sigma F_o$ for $I > 2\sigma(I)$, $wR2 = [\Sigma\{w(F_o^2 - F_c^2)^2\}/\Sigma\{w(F_o^2)^2\}]^{1/2}$) for all data), GOF = 1.035, $\Delta\rho_{max} = 0.370$ e Å^{-3}. Crystallographic data for $C_{18}H_{28}FeP_2$ (**4**): $M_r = 362.19$, monoclinic, $P2_1/c$, $a = 7.9539(4)$, $b = 13.9194(9)$, $c = 16.1807(8)$ Å, $\beta = 102.218(4)°$, $V = 1750.85(17)$ Å^3, $Z = 4$, $\mu = 1.036$ mm^{-1}, $\rho_{calcd} = 1.374$ Mg m^{-3}, 150(1) K, Nonius Kappa-CCD diffractometer using graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), dark red crystal ($0.10 \times 0.08 \times 0.06$ mm^3). Of 14784 reflections collected ($5.1 \leq 2\theta \leq 55.0°$), 4005 were independent ($R_{int} = 0.0879$). Solution and refinement as for **2**, $R1 = 0.0668$, $wR2 = 0.1702$, GOF = 1.076, $\Delta\rho_{max} = 0.845$ e Å^{-3}. Crystallographic data for $C_{18}H_{30}RuP_2$ (**6**): $M_r = 409.43$, orthorhombic, $P2_12_12_1$, $a = 9.13730(10)$, $b = 13.9938(2)$, $c = 15.1999(2)$ Å, $V = 1943.54(4)$ Å^3, $Z = 4$, $\mu = 0.964$ mm^{-1}, $\rho_{calcd} = 1.399$ Mg m^{-3}, 150(1) K, Nonius Kappa-CCD diffractometer using graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), dark red crystal ($0.16 \times 0.26 \times 0.26$ mm^3). Of 16976 reflections collected ($5.2 \leq 2\theta \leq 55.0°$), 4440 were independent ($R_{int} = 0.0364$). Solution and refinement as for **2**, $R1 = 0.0234$, $wR2 = 0.0561$, GOF = 1.124, $\Delta\rho_{max} = 0.758$ e Å^{-3}. CCDC-248005 (**2**), CCDC-248004 (**4**), and CCDC-248003 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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