

ELECTRONIC SUPPLEMENTARY INFORMATION FOR

Synthesis, Reactivity, Structures, and Dynamic Properties of Gyroscope Like Iron
Carbonyl Complexes based upon Dibridgehead Diphosphine Cages:
Pre- vs. Post-Metathesis Substitutions as Routes to Adducts with Neutral Dipolar
Fe(CO)(NO)(X) Rotors.

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EXPERIMENTAL SECTION (continued)

Additional NMR data (alternative solvents and temperatures; relevant to Figure 5).

9c-Cl (CD₂Cl₂, δ in ppm): ¹³C{¹H} (125 MHz, 25 °C; CH₂ peaks only) 30.8 (virtual t, ³J_{CP}, ⁵J_{CP} = 6.8 Hz, ^{s1} PCH₂CH₂CH₂), 28.1 (s, CH₂), 27.8 (s, CH₂), 27.2 (s, CH₂), 27.0 (s, CH₂), 26.9 (virtual t, ¹J_{CP}, ³J_{CP} = 12.8 Hz, ^{s1} PCH₂), 23.7 (s, PCH₂CH₂); ¹³C{¹H} (125 MHz, –85 °C; CH₂ peaks only) 30.4, 29.7, 29.3 (3m, 3PCH₂CH₂CH₂), 27.1-23.9 (overlapping signals, CH₂), 23.3, 22.7, and 22.0 (3br(s), 3PCH₂CH₂).

9c-I (C₆D₅Cl, δ in ppm): ¹³C{¹H} (125 MHz, 100 °C; CH₂ peaks only) 30.5 (virtual t, ³J_{CP}, ⁵J_{CP} = 6.5 Hz, ^{s1} PCH₂CH₂CH₂), 28.1 (s, CH₂), 27.8 (s, CH₂), 27.6 (s, CH₂), 27.5 (s, CH₂), 23.9 (s, PCH₂CH₂); ¹³C{¹H} (125 MHz, –40 °C; CH₂ peaks only) 31.0, 30.3, 29.7 (3m, 3PCH₂CH₂CH₂), 28.2-26.3 (overlapping signals, CH₂), 24.5, 24.2, and 23.6 (3s, 3PCH₂CH₂).

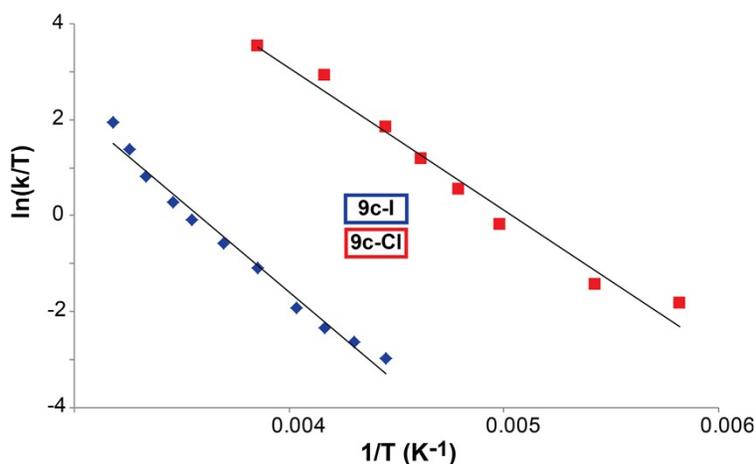


Figure s1. Eyring plots involving rate constants for the processes that renders the (CH₂)₁₄ bridges of **9c-Cl** and **9c-I** equivalent.

Additional Synthetic Procedures and Characterization (all compounds *not* bearing the index "c" in Schemes 2-5; "c" indicates the family of complexes derived from precursors with the phosphine ligand P((CH₂)₆CH=CH₂)₃, including gyroscope like complexes with P(CH₂)₁₄P segments).

trans-Fe(CO)(NO)(Cl)(P((CH₂)₇CH=CH(CH₂)₇)₃P) (**7d-Cl**). *trans*-Fe(CO)(NO)(Cl)-(P((CH₂)₇CH=CH₂)₃)₂, (**6d-Cl**; ^{s2} 0.101 g, 0.104 mmol), CH₂Cl₂ (55 mL; the resulting solution

is 0.0020 M in **6d-Cl**), and Grubbs' catalyst (0.015 g, 0.018 mmol, 18 mol%) were combined in a procedure analogous to that for **7c-Cl**. An identical workup gave **7d-Cl** as a red-brown waxy solid (0.032 g, 0.037 mmol, 35%, mixture of *E/Z* isomers).

NMR (CDCl₃, δ in ppm): ¹H (500 MHz) 5.44-5.24 (m, 6H, *CH*=), 2.31-2.11 (m, 12H, *CH*₂), 2.09-1.94 (m, 12H, *CH*₂), 1.89-1.64 (m, 12H, *CH*₂), 1.64-1.49 (m, 12H, *CH*₂), 1.50-1.18 (m, 48H, *CH*₂); ³¹P{¹H} (202 MHz) 42.1 (s, 25%), 42.0 (s, 25%), 41.9 (s, 20%), 39.7 (s, 30%).

***trans*-Fe(CO)(NO)(Br)(P((CH₂)₇CH=CH(CH₂)₇)₃P)** (**7d-Br**). A Schlenk flask was charged with *trans*-Fe(CO)(NO)(Br)(P((CH₂)₇CH=CH₂)₃)₂, (**6d-Br**; ^{s2} 0.110 g, 0.109 mmol), CH₂Cl₂ (55 mL; the resulting solution is 0.0020 M in **6d-Br**), and Grubbs' catalyst (0.016 g, 0.020 mmol, 18 mol%), and fitted with a condenser. The solution was refluxed. After 16 h, additional catalyst was added (0.005 g, 0.007 mmol, 6 mol%). After another 20 h, the solvent was removed by oil pump vacuum. The residue was filtered through neutral alumina (2.5 × 2.5 cm) using 1:1 v/v hexane/CH₂Cl₂. The solvent was removed from the filtrate by oil pump vacuum to give **7d-Br** as a red-brown waxy solid (0.030 g, 0.033 mmol, 30%, mixture of *E/Z* isomers).

NMR (CDCl₃, δ in ppm): ¹H (500 MHz) 5.46-5.21 (m, 6H, *CH*=), 2.15-1.88 (m, 12H, *CH*₂), 1.84-1.52 (m, 24H, *CH*₂), 1.50-1.00 (m, 54H, *CH*₂); ³¹P{¹H} (202 MHz) 42.2 (s, 23%), 42.0 (s, 30%), 41.9 (s, 12%), 39.7 (s, 12%), 39.7 (s, 23%).

***trans*-Fe(CO)(NO)(Cl)(P((CH₂)₈CH=CH(CH₂)₈)₃P)** (**7e-Cl**). A Schlenk flask was charged with *trans*-Fe(CO)(NO)(Cl)(P((CH₂)₈CH=CH₂)₃)₂, (**6e-Cl**; ^{s2} 0.131 g, 0.125 mmol), CH₂Cl₂ (65 mL; the resulting solution is 0.0020 M in **6e-Cl**), and Grubbs' catalyst (0.019 g, 0.023 mmol, 18 mol%), and fitted with a condenser. The solution was refluxed. After 12 h, additional catalyst was added (0.006 g, 0.008 mmol, 6 mol%). After another 24 h, the solvent was removed by oil pump vacuum. The residue was filtered through neutral alumina (2.5 × 2.5 cm) using 2:1 v/v hexane/CH₂Cl₂. The solvent was removed from the filtrate by oil pump vacuum to give **7e-Cl** as a red-brown waxy solid (0.049 g, 0.051 mmol, 41%, mixture of *E/Z* isomers).

NMR (CDCl₃, δ in ppm): ¹H (500 MHz) 5.45-5.25 (m, 6H, *CH*=), 2.07-1.82 (m, 24H, *CH*₂), 1.80-1.64 (m, 12H, *CH*₂), 1.64-1.44 (m, 24H, *CH*₂), 1.42-1.14 (m, 42H, *CH*₂); ³¹P{¹H}

(202 MHz) 49.3 (s, 57%), 49.1 (s, 41%), 48.9 (s, 2%).

$\overline{\text{trans-Fe}(\text{CO})(\text{NO})(\text{Br})(\text{P}((\text{CH}_2)_8\text{CH}=\text{CH}(\text{CH}_2)_8)_3\text{P})}$ (**7e-Br**). A Schlenk flask was charged with *trans*-Fe(CO)(NO)(Br)(P((CH₂)₈CH=CH₂)₃)₂, (**6e-Br**; ^{s2} 0.125 g, 0.115 mmol), CH₂Cl₂ (60 mL; the resulting solution is 0.0020 M in **6e-Br**), and Grubbs' catalyst (0.017 g, 0.021 mmol, 18 mol%), and fitted with a condenser. The solution was refluxed. After 48 h, the solvent was removed by oil pump vacuum. The residue was filtered through neutral alumina (2.5 × 2.5 cm) using 1:1 v/v hexane/CH₂Cl₂. The solvent was removed from the filtrate by oil pump vacuum to give **7e-Cl** as a red-brown waxy solid (0.042 g, 0.041 mmol, 36%, mixture of *E/Z* isomers).

NMR (CDCl₃, δ in ppm): ¹H (500 MHz) 5.56-5.28 (m, 6H, *CH*=), 2.17-2.01 (m, 12H, *CH*₂), 1.92-1.61 (m, 24H, *CH*₂), 1.61-1.46 (m, 24H, *CH*₂), 1.44-1.10 (m, 42H, *CH*₂); ³¹P{¹H} (202 MHz) 41.8 (s, 59%), 41.7 (s, 34%), 41.6 (s, 7%).

$\overline{\text{trans-}[\text{Fe}(\text{CO})_2(\text{NO})(\text{P}((\text{CH}_2)_8\text{CH}=\text{CH}(\text{CH}_2)_8)_3\text{P})]^+ \text{BF}_4^-}$ (**8e⁺ BF₄⁻**). A Schlenk flask was charged with *trans*-[Fe(CO)₂(NO)(P((CH₂)₈CH=CH₂)₃)₂]⁺ BF₄⁻ (**5e⁺ BF₄⁻**; ^{s2} 0.300 g, 0.266 mmol), CH₂Cl₂ (175 mL, the resulting solution is 0.0015 M in **5e⁺ BF₄⁻**), Grubbs' catalyst (ca. half of 0.023 g, 0.027 mmol, 10 mol%), and fitted with a condenser. The solution was refluxed. After 24 h, the remaining catalyst was added. After another 24 h, the solvent was removed by oil pump vacuum to give crude **8e⁺ BF₄⁻** as a red-brown oil (0.308 g, 0.296 mmol).

NMR (C₆D₆, δ in ppm): ¹H (400 MHz): 5.80-5.47 (m, 6H, *CH*=), 2.50 (m, 12H, *CH*₂), 2.07 (m, 24H, *CH*₂), 1.47-1.33 (m, 60H, *CH*₂); ³¹P{¹H} (162 MHz): 58.7 (s, 68%), 58.3 (s, 27%), 57.6 (s, 3%), 57.1 (s, 2%).

$\overline{\text{trans-}[\text{Fe}(\text{CO})_2(\text{NO})(\text{P}((\text{CH}_2)_{18})_3\text{P})]^+ \text{BF}_4^-}$ (**4e⁺ BF₄⁻**). A Fischer-Porter bottle was charged with crude **8e⁺ BF₄⁻** (0.308 g, 0.295 mmol), ClRh(PPh₃)₃ (0.028 g, 0.030 mmol, 10 mol%), CH₂Cl₂ (30 mL), and H₂ (5 atm). The solution was stirred at 23 °C. After 24 h, the solvent was removed by oil pump vacuum to give crude **4e⁺ BF₄⁻** as a red-brown crude product (0.320 g, 0.305 mmol).

NMR (C₆D₆, δ in ppm): ¹H (400 MHz): 1.53 (m, 24H, *CH*₂), 1.34 (m, 84H, *CH*₂);

$^{31}\text{P}\{^1\text{H}\}$ (162 MHz): 56.8 (overlapping peaks, 5% impurity), 55.9 (s, 80%), 55.4 (overlapping peaks, 10% impurity), 55.1 (overlapping peaks, 5% impurity).

***trans*- $\overline{\text{Fe}(\text{CO})(\text{NO})(\text{Br})(\text{P}((\text{CH}_2)_{18})_3\text{P})}$ (**9e-Br**)**. A Schlenk flask was charged with crude $4\text{e}^+ \text{BF}_4^-$ (0.320 g, 0.305 mmol) and CH_2Cl_2 (40 mL). Then $\text{Bu}_4\text{N}^+ \text{Br}^-$ (excess) was added with stirring. After 16 h, the solvent was removed by oil pump vacuum. The residue was filtered through a plug of silica (2.5×2.0 cm) using CH_2Cl_2 . The solvent was removed from the filtrate by oil pump vacuum to give crude **9e-Br** as a pale orange solid.

$^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, C_6D_6 , δ in ppm): 45.4 (s, 5% impurity), 45.0 (s, 80%, **9e-Br**), 44.8 (overlapping peaks, 15% impurity). MS:^{s3} 1011 (**9e-Br**⁺, 5%), 984 (**[9e-Br-CO]**⁺, 20%), 954 (**[9e-Br-CO-NO]**⁺, 100%), 903 (**[9e-Br-CO-Br]**⁺, 60%), 818 (**[9e-Br-CO-NO-Br-Fe]**⁺, 30%), 836 (**[9e-Br-CO-NO-Br-Fe+O]**⁺, 20%), 852 (**[9e-Br-CO-NO-Br-Fe+2O]**⁺, 5%).

REFERENCES

(s1) Hersh, W. H. *J. Chem. Educ.* **1997**, *74*, 1485-1488. The *J* values given represent the apparent coupling between adjacent peaks of the triplet.

(s2) Lang, G. M.; Skaper, D.; Shima, T.; Otto, M.; Wang, L.; Gladysz, J. A. *Aust. J. Chem.* **2015**, *68*, 1342-1351.

(s3) FAB, 3-NBA, *m/z* (relative intensity, %); the most intense peak of the isotope envelope is given.