

Supplementary information

CO Insertion in Lithiated Diene–Tricarbonyliron Complexes

Tatsuo Okauchi,* Takao Teshima, Mitsuru Sadoshima, Hidekazu Kawakubo, Kouta Kagimoto, Yoko Sugahara, and Mitsuru Kitamura

*Department of Applied Chemistry, Kyushu Institute of Technology, Sensui-cho, Tobata,
Kitakyushu 804-8550, Japan*
e-mail: okauchi@che.kyutech.ac.jp

Contents

p. 2–8: Experimental procedures and characterization data for the new compounds

Experimental Procedures

General. All reactions were performed under a nitrogen atmosphere with magnetic stirring. Column chromatography on silica gel was performed with Fuji Silysia BW-127ZH. Preparative TLC was performed on Wakogel B-5F/TLC-cards (20×20×0.7 cm). Commercial solution of ⁿBuLi (1.53 M in hexane) were used. Fe(CO)₅ was purchased from Aldrich. Organic solvents were purified and dried by standard procedures. Tricarbonyl(1-4η-5,5-dimethyl-1,3-cyclohexadien-2-ol)iron was prepared by method of P. Eilbracht and R. Jelitte, *Chem. Ber.* **1983**, *116*, 243.

NMR spectra were recorded on a JEOL JNM-A500 spectrometer at 500 MHz (¹H NMR), 126 MHz (¹³C NMR) or on a Bruker Avance 400 spectrometer at 400 MHz (¹H NMR), 101 MHz (¹³C NMR). Chemical shifts are reported in ppm relative to TMS as internal standard. MS were measured on a JEOL JMS-SX102A system. Infrared spectra were recorded on a JEOL JIR-WINSPEC50 spectrometer.

General Procedure for the Preparation of Iron–diene Complex **1b** and **1c**

To a suspension of 1.5 equiv of NaH in THF (2 mL) was added dropwise tricarbonyl(1-4η-5,5-dimethyl-1,3-cyclohexadien-2-ol) iron (0.379 mmol) in THF (2 mL) at 0 °C. After being stirred for 1 h, bis(dimethylamino)chlorophosphate (1.5 equiv) was added to the reaction mixture. The reaction was quenched by addition of phosphate buffer (pH = 7), and the mixture was filtrated through Celite 545. After usual workup, the crude product was purified by column chromatography on silica gel to give **1b**. The compounds **1b** and **1c** had the following properties.

General Procedure for the Preparation of Iron–diene Complex **1a** and **1d-f**

To 1.1 equiv of sodium hexamethyldisilazane in THF (2 mL) was added dropwise methyl vinyl ketone (0.38 mmol) in THF (2 mL) at -78 °C. After being stirred for 1 h, bis(dimethylamino)chlorophosphate (1.5 equiv) was added to the reaction mixture. The mixture was allowed to warm to room temperature over 2 h. After one night of stirring at room temperature, the reaction was quenched by addition of phosphate buffer (pH = 7). After usual

workup, the crude product was purified by column chromatography on silica gel to give a dienylyl phosphonate. The dienylyl phosphonate was treated by 1.5 equiv of benzalacetone tricarbonyliron in toluene at 80 °C for 10 h. The reaction mixture was filtrated through Celite 545 and concentrated in vacuo. The residue was purified by column chromatography on silica gel to give **1a** and **1d-f**. *syn-1a* and *anti-1a* were separated by silica gel chromatography. **1a** and **1d-f** had the following properties.

Tricarbonyl[1-4 η -2-bis(dimethylamino)phosphoryloxy-4,6 β -dimethyl-1,3-cyclohexadiene]-iron (*syn-1a*): 17% yield, yellow oil; ¹H NMR (500 MHz; CDCl₃; Me₄Si) δ 1.03 (3H, d, $J = 7.0$ Hz), 1.02-1.05 (1H, m), 1.54 (3H, s), 1.88 (1H, dd, $J = 10.5, 15.0$ Hz), 2.26-2.32 (1H, m), 2.69 (6H, d, $J = 10.5$ Hz), 2.70 (6H, d, $J = 10.0$ Hz), 3.32 (1H, dd, $J = 2.0, 3.5$ Hz), 5.74 (1H, s); ¹³C NMR (126 MHz; CDCl₃; Me₄Si) δ 25.0, 25.6, 34.8, 36.4 (d, $J_{\text{P-C}} = 4.2$ Hz), 36.5 (d, $J_{\text{P-C}} = 4.2$ Hz), 38.7, 63.3 (d, $J_{\text{P-C}} = 3.2$ Hz), 64.8, 81.9 (d, $J_{\text{P-C}} = 3.2$ Hz), 126.9 (d, $J_{\text{P-C}} = 3.2$ Hz), 211.5; MS (FAB/NPOE) m/z 399 (M+H⁺); HRMS (FAB/NPOE) calcd for C₁₅H₂₄O₅N₂PFe (M+H⁺) 399.0772, found 399.0733.

Tricarbonyl[1-4 η -2-bis(dimethylamino)phosphoryloxy-4,6 α -dimethyl-1,3-cyclohexadiene]-iron (*anti-1a*): 33% yield, yellow oil; ¹H NMR (500 MHz; CDCl₃; Me₄Si) δ 0.98 (3H, d, $J = 7.0$ Hz), 1.16 (1H, dd, $J = 5.0, 15.3$ Hz), 1.60 (3H, s), 1.73 (1H, dd, $J = 8.0, 15.8$ Hz), 1.97-2.03(1H, m), 2.69 (6H, d, $J = 10.0$ Hz), 2.72 (6H, d, $J = 10.0$ Hz), 3.15 (1H, t, $J = 2.0$ Hz), 5.54 (1H, s); ¹³C NMR (126 MHz; CDCl₃; Me₄Si) δ 21.8, 25.2, 29.6, 36.4 (d, $J_{\text{P-C}} = 4.2$ Hz), 36.5 (d, $J_{\text{P-C}} = 4.2$ Hz), 82.2 (d, $J_{\text{P-C}} = 3.2$ Hz), 126.7 (d, $J_{\text{P-C}} = 4.2$ Hz), 211.8; MS (FAB/NPOE) m/z 399 (M+H⁺); HRMS (FAB/NPOE) calcd for C₁₅H₂₄O₅N₂PFe (M+H⁺) 399.0772, found 399.0797.

Tricarbonyl[1-4 η -2-bis(dimethylamino)phosphoryloxy-5,5-dimethyl-1,3-cyclohexadiene]-iron (1b**):** 90% yield, yellow oil; IR (KBr) 2049, 1963, 1467, 1313, 1240, 1170 cm⁻¹; ¹H NMR (500 MHz; CDCl₃; Me₄Si) δ 0.96 (3H, s), 0.99 (3H, s), 1.62 (1H, dd, $J = 3.1, 14.7$ Hz), 1.73 (1H, dd, $J = 3.1, 15.0$ Hz), 2.47 (1H, d, $J = 6.7$ Hz), 2.69 (3H, s), 2.71 (3H, s), 2.73 (3H, s), 2.75 (3H, s), 3.45 (1H, dt, $J = 2.4, 2.8$ Hz), 5.57 (1H, dd, $J = 1.8, 6.4$ Hz); ¹³C NMR (126 MHz; CDCl₃;

Me₄Si) δ 30.7, 34.1, 35.1, 36.5 (d, $J_{\text{P-C}} = 4.1$ Hz), 36.6 (d, $J_{\text{P-C}} = 4.1$ Hz), 43.2, 57.3 (d, $J_{\text{P-C}} = 3.1$ Hz), 64.6, 75.5 (d, $J_{\text{P-C}} = 4.1$ Hz), 130.7 (d, $J_{\text{P-C}} = 2.1$ Hz), 211.2. Anal. Calcd for C₁₅H₂₃FeN₂O₅P: C, 45.25; H, 5.82; N, 7.04. Found: C, 45.34; H, 5.89; N, 6.99.

Tricarbonyl[1-4η-2-bis(dimethylamino)phosphoryloxy-1,3-cyclohexadiene]iron (1c): 77% yield, yellow crystal; ¹H NMR (500 MHz; CDCl₃; Me₄Si) δ 1.47-1.56 (2H, m), 1.74-1.76 (2H, m), 2.69 (6H, d, $J = 10.0$ Hz), 2.72 (6H, d, $J = 10$ Hz), 2.79-2.82 (1H, m), 3.52 (1H, d, $J = 2.0$ Hz), 5.63 (1H, d, $J = 6.0$ Hz); ¹³C NMR (126 MHz; CDCl₃; Me₄Si) δ 23.2, 24.7, 36.3 (d, $J_{\text{P-C}} = 4.2$ Hz), 36.4 (d, $J_{\text{P-C}} = 4.2$ Hz), 51.3, 57.7 (d, $J_{\text{P-C}} = 3.2$ Hz), 78.1 (d, $J_{\text{P-C}} = 3.2$ Hz), 130.2, 210.9; MS (FAB/NPOE) m/z 371 (M+H⁺); HRMS (FAB/NPOE) calcd for C₁₃H₂₀O₅N₂PFe (M+H⁺) 371.0459, found 371.0457.

Tricarbonyl[1-4η-2-bis(dimethylamino)phosphoryloxy-4-methyl-1,3-cyclohexadiene]iron (1d): 52% yield, yellow solid; IR (ATR) 2035, 1954, 1454, 1309, 1205, 1066 cm⁻¹; ¹H NMR (400 MHz; CDCl₃; Me₄Si) δ 1.40-1.47 (1H, m), 1.56-1.63 (1H, m), 1.61 (3H, s), 1.80-1.84 (2H, m), 2.70 (12H, dd, $J = 10.2, 12.3$ Hz), 3.39 (1H, d, $J = 2.3$ Hz), 5.60 (1H, s); ¹³C NMR (126 MHz; CDCl₃; Me₄Si) δ 25.3, 25.6, 30.0, 36.4 (d, $J_{\text{P-C}} = 4.2$ Hz), 36.4 (d, $J_{\text{P-C}} = 4.2$ Hz), 56.5 (d, $J_{\text{P-C}} = 3.2$ Hz), 67.3, 81.6 (d, $J_{\text{P-C}} = 3.2$ Hz), 127.6 (d, $J_{\text{P-C}} = 3.2$ Hz), 211.4; MS (FAB/NPOE) m/z 385 (M+H⁺); HRMS (FAB/NPOE) calcd for C₁₄H₂₂O₅N₂PFe (M+H⁺) 385.0616, found 385.0633.

Tricarbonyl[1-4η-2-bis(dimethylamino)phosphoryloxy-1,3-butadiene]iron (1e): 49% yield, yellow crystal; yellow solid; IR (ATR) 2046, 1959, 1454, 1311, 1172, 1068 cm⁻¹; ¹H NMR (500 MHz; CDCl₃; Me₄Si) δ -0.34 (1H, dd, $J = 2.5, 8.5$ Hz), 0.47 (1H, d, $J = 4.5$ Hz), 1.49 (1H, dd, $J = 2.3, 6.8$ Hz), 2.29 (1H, d, $J = 3.0$ Hz), 2.70 (6H, d, $J = 10.0$ Hz), 2.74 (6H, d, $J = 10.5$ Hz), 5.71 (1H, t, $J = 7.5$ Hz); ¹³C NMR (126 MHz; CDCl₃; Me₄Si) δ 31.2, 36.4 (d, $J_{\text{P-C}} = 4.2$ Hz), 36.5 (d, $J_{\text{P-C}} = 4.0$ Hz), 37.2 (d, $J_{\text{P-C}} = 3.0$ Hz), 76.8 (d, $J_{\text{P-C}} = 3.2$ Hz), 131.4 (d, $J_{\text{P-C}} = 3.2$ Hz), 210.2; MS (FAB/NPOE) m/z 345 (M+H⁺); HRMS (FAB/NPOE) calcd for C₁₁H₁₈O₅N₂PFe (M+H⁺) 345.0303, found 345.0301.

Tricarbonyl[1-4η-2-bis(dimethylamino)phosphoryloxy-5-methyl-1,3-hexadiene]iron (1f): 32% yield, yellow solid; IR (ATR) 2042, 1948, 1462, 1308, 1223, 1068 cm⁻¹; ¹H NMR (500 MHz; CDCl₃; Me₄Si) δ 0.26 (1H, t, *J* = 8.8 Hz), 0.45 (1H, d, *J* = 4.5 Hz), 1.04 (3H, dd, *J* = 0.8, 6.8 Hz), 1.10 (3H, dd, *J* = 0.8, 6.3 Hz), 1.52-1.59 (1H, m), 2.18-2.19 (1H, m), 2.69 (6H, dd, *J* = 1.3, 10.3 Hz), 2.74 (6H, dd, *J* = 1.0, 10.0 Hz), 5.58 (1H, d, *J* = 7.5 Hz); ¹³C NMR (126 MHz; CDCl₃; Me₄Si) δ 24.6, 26.0, 33.9, 36.3, 36.4 (d, *J*_{P-C} = 4.2 Hz), 36.5 (d, *J*_{P-C} = 4.2 Hz), 64.5, 79.6 (d, *J*_{P-C} = 4.2 Hz), 128.6 (d, *J*_{P-C} = 3.2 Hz); MS (FAB/NPOE) *m/z* 387 (M+H⁺); HRMS (FAB/NPOE) calcd for C₁₄H₂₄O₅N₂PFe (M+H⁺) 387.0772, found 387.0761.

General Procedure for CO insertion of Iron Complex 1a-f: To a solution of LDA (0.22 mmol) in THF (2 mL) and P(OMe)₃ (0.12 mmol) was added dropwise a THF (1 mL) solution of iron complex **1** (0.1 mmol). After being stirred for 2.0 h at -78 °C, a Et₂O (1 mL) solution of CF₃SO₃H (0.5 mmol) was added. The mixture was stirred for 2 h at -78 °C, and phosphate buffer (pH = 7) was added. After usual workup, the crude product was purified by silica gel chromatography (AcOEt) to give **2a-f**. The compounds **2a-f** had the following properties.

Dicarbonyl[1-4η-2-bis(dimethylamino)phosphoryloxy-3-formyl-4,6-dimethyl-1,3-cyclohexadiene](trimethoxyphosphine)iron (*syn*-2a and *anti*-2a)

The ¹H and ¹³C NMR, and MS were recorded on a mixture of *syn*-2a and *anti*-2a:

¹H NMR (500 MHz; CDCl₃; Me₄Si) (for *syn*-2a) δ 1.05 (3H, d, *J* = 7.0 Hz), 1.33 (1H, dt, *J* = 15.3, 5.0 Hz), 1.82 (3H, d, *J* = 4.0 Hz), 1.88 (1H, ddd, *J* = 7.9, 7.9, 15.6 Hz), 1.97-2.05 (1H, m), 2.68 (6H, d, *J* = 10.0 Hz), 2.71 (6H, d, *J* = 10.0 Hz), 2.96 (1H, dd, *J* = 1.2, 9.8 Hz), 3.60 (9H, d, *J* = 12.0 Hz), 10.38 (1H, s); ¹³C NMR (126 MHz; CDCl₃; Me₄Si) (for *syn*-2a) δ 22.3, 23.4, 30.4 (d, *J*_{P-C} = 7.2 Hz), 36.4 (d, *J*_{P-C} = 4.1 Hz), 36.6 (d, *J*_{P-C} = 4.0 Hz), 43.6 (d, *J*_{P-C} = 3.1 Hz), 51.4 (d, *J*_{P-C} = 2.0 Hz), 65.4 (d, *J*_{P-C} = 12.4 Hz), 67.6 (d, *J*_{P-C} = 8.3 Hz), 84.0, 130.1 (d, *J*_{P-C} = 2.1 Hz), 192.5, 213.7 (d, *J*_{P-C} = 33.0 Hz), 218.4 (d, *J*_{P-C} = 9.3 Hz); ¹H NMR (500 MHz; CDCl₃; Me₄Si) (for *anti*-2a) δ 1.02 (3H, d, *J* = 7.0 Hz), 1.10 (1H, ddd, *J* = 14.6, 9.3, 4.9 Hz), 1.74 (3H, d, *J* = 3.7 Hz), 1.87-1.93 (1H, m), 2.40-2.47 (1H, m), 2.72 (6H, d, *J* = 10.5 Hz), 2.74 (6H, d, *J* = 10.1 Hz), 3.36 (1H, dd, *J* = 3.1, 7.7 Hz), 3.60 (9H, d, *J* = 11.6 Hz), 10.45 (1H, s); ¹³C NMR (126 MHz; CDCl₃;

Me₄Si) (for **anti-2a**) δ 23.7, 24.8, 36.0 (d, $J_{\text{P-C}} = 8.3$ Hz), 36.6 (d, $J_{\text{P-C}} = 3.1$ Hz), 37.4 (d, $J_{\text{P-C}} = 4.1$ Hz), 40.1, 51.6 (d, $J_{\text{P-C}} = 3.1$ Hz), 61.9 (d, $J_{\text{P-C}} = 11.4$ Hz), 68.1 (d, $J_{\text{P-C}} = 7.2$ Hz), 83.5, 130.8 (d, $J_{\text{P-C}} = 2.1$ Hz), 192.2, 212.9 (d, $J_{\text{P-C}} = 29.2$ Hz), 217.5 (d, $J_{\text{P-C}} = 11.4$ Hz); MS (FAB/NPOE) m/z 523 (M+H⁺); HRMS (FAB/NPOE) calcd for C₁₈H₃₃O₈N₂PFe (M+H⁺) 523.1062, found 5231098.

Dicarbonyl[1-4 η -2-bis(dimethylamino)phosphoryloxy-3-formyl-5,5-dimethyl-1,3-

cyclohexadiene](trimethoxyphosphine)iron (2b): IR (ATR) 1988, 1928, 1678, 1377, 1309, 1171 cm⁻¹; ¹H NMR (500 MHz; CDCl₃; Me₄Si) δ 0.93 (3H, s), 1.06 (3H, s), 1.78-1.84 (2H, m), 2.57 (1H, d, $J = 5.5$ Hz), 2.70 (6H, d, $J = 10.5$ Hz), 2.77 (6H, d, $J = 10.5$ Hz), 3.59 (9H, d, $J = 11.5$ Hz), 3.70 (1H, s), 10.27 (1H, s); ¹³C NMR (126 MHz; CDCl₃; Me₄Si) δ 31.0, 34.0 (d, $J_{\text{P-C}} = 2.1$ Hz), 34.2, 36.4 (d, $J_{\text{P-C}} = 4.2$ Hz), 36.7 (d, $J_{\text{P-C}} = 4.2$ Hz), 43.6, 52.0 (d, $J_{\text{P-C}} = 4.0$ Hz), 60.6 (d, $J_{\text{P-C}} = 8.3$ Hz), 60.7, 81.1 (d, $J_{\text{P-C}} = 3.2$ Hz), 132.5, 191.8; MS (FAB/NPOE) m/z 523 (M+H⁺); HRMS (FAB/NPOE) calcd for C₁₈H₃₃O₈N₂P₂Fe (M+H⁺) 523.1062, found 523.1089.

Dicarbonyl[1-4 η -2-bis(dimethylamino)phosphoryloxy-3-formyl-1,3-cyclohexadiene](trimet

hoxyphosphine)iron (2c): ¹H NMR (500 MHz; CDCl₃; Me₄Si) δ 1.41-1.47 (1H, m), 1.60-1.67 (1H, m), 1.81-1.84 (1H, m), 1.90-1.95 (1H, m), 2.71 (6H, d, $J = 10.0$ Hz), 2.75 (6H, d, $J = 10.0$ Hz), 2.91 (1H, d, $J = 2.5$ Hz), 3.61 (9H, d, $J = 11.5$ Hz), 3.72 (1H, s), 10.25 (1H, s); ¹³C NMR (126 MHz; CDCl₃; Me₄Si) δ 23.3 (d, $J_{\text{P-C}} = 4.2$ Hz), 26.0 (d, $J_{\text{P-C}} = 2.0$ Hz), 36.5 (d, $J_{\text{P-C}} = 3.0$ Hz), 36.6 (d, $J_{\text{P-C}} = 4.0$ Hz), 47.1 (d, $J_{\text{P-C}} = 2.0$ Hz), 51.8 (d, $J_{\text{P-C}} = 4.2$ Hz), 61.6 (d, $J_{\text{P-C}} = 3.2$ Hz), 83.2 (d, $J_{\text{P-C}} = 3.0$ Hz), 132.9, 190.9; MS (FAB/NPOE) m/z 495(M+H⁺); HRMS (FAB/NPOE) calcd for C₁₆H₂₉O₈N₂P₂Fe (M+H⁺) 495.0749, found 495.0759.

Dicarbonyl[1-4 η -2-bis(dimethylamino)phosphoryloxy-3-formyl-4-methyl-1,3-

cyclohexadiene](trimethoxyphosphine)iron (2d): yellow solid, IR (ATR) 1981, 1928, 1686, 1466, 1377, 1308, 1201, 1026 cm⁻¹; ¹H NMR (500 MHz; CDCl₃; Me₄Si) δ 1.48-1.57 (1H, m), 1.62-1.70 (1H, m), 1.81 (3H, d, $J = 3.5$ Hz), 1.81-1.86 (1H, m), 1.92-2.00 (1H, m), 2.68 (6H, d, $J = 10.0$ Hz), 2.74 (6H, d, $J = 10.0$ Hz), 3.64 (9H, d, $J = 11.5$ Hz), 10.55 (1H, d, $J = 2.0$ Hz); ¹³C NMR (126 MHz; CDCl₃; Me₄Si) δ 23.7, 26.3 (d, $J_{\text{P-C}} = 8.2$ Hz), 31.5, 36.4 (d, $J_{\text{P-C}} = 4.1$ Hz),

36.6 (d, $J_{\text{P-C}} = 4.1$ Hz), 60.9 (d, $J_{\text{P-C}} = 6.2$ Hz), 64.6 (d, $J_{\text{P-C}} = 11.3$ Hz), 83.3, 131.3, 192.2, 212.8 (d, $J_{\text{P-C}} = 29.0$ Hz), 217.2 (d, $J_{\text{P-C}} = 10.3$ Hz); MS (FAB/NPOE) m/z 509(M+H⁺); HRMS (FAB/NPOE) calcd for C₁₇H₃₁O₈N₂P₂Fe (M+H⁺) 509.0905, found 509.0874.

Dicarbonyl[1-4η-2-bis(dimethylamino)phosphoryloxy-3-formyl-1,3-butadiene]

(trimethoxyphosphine)iron (2e): yellow solid, IR (ATR) 1998, 1936, 1678, 1460, 1373, 1338, 1219, 1178 cm⁻¹; ¹H NMR (500 MHz; CDCl₃; Me₄Si) δ -0.73 (1H, dd, $J = 1.8, 10.3$ Hz), 0.68 (1H, ddd, $J = 1.3, 4.3, 9.8$ Hz), 1.79 (1H, s), 2.57 (1H, d, $J = 4.0$ Hz), 2.71 (6H, d, $J = 10.0$ Hz), 2.77 (6H, d, $J = 10.0$ Hz), 3.68 (9H, d, $J = 11.5$ Hz), 10.54 (1H, s); ¹³C NMR (126 MHz; CDCl₃; Me₄Si) δ 26.8 (d, $J_{\text{P-C}} = 6.2$ Hz), 36.4 (d, $J_{\text{P-C}} = 4.2$ Hz), 36.6 (d, $J_{\text{P-C}} = 4.2$ Hz), 41.2 (d, $J_{\text{P-C}} = 4.2$ Hz), 51.8 (d, $J_{\text{P-C}} = 4.2$ Hz), 82.0 (d, $J_{\text{P-C}} = 2.1$ Hz), 136.2, 191.0, 209.8 (d, $J_{\text{P-C}} = 7.3$ Hz), 210.7 (d, $J_{\text{P-C}} = 19.8$ Hz); MS (FAB/NPOE) m/z 469 (M+H⁺); HRMS (FAB/NPOE) calcd for C₁₄H₂₇O₈N₂P₂Fe (M+H⁺) 469.0592, found 469.0610.

Dicarbonyl[1-4η-2-bis(dimethylamino)phosphoryloxy-3-formyl-5-methyl-1,3-hexadiene]

(trimethoxyphosphine)iron (2f): yellow oil, IR (ATR) 1988, 1930, 1682, 1460, 1376, 1306, 1225, 1176 cm⁻¹; ¹H NMR (400 MHz; CDCl₃; Me₄Si) δ -0.08 (1H, d, $J = 9.4$ Hz), 0.73 (1H, d, $J = 11.0$ Hz), 1.06 (3H, d, $J = 5.9$ Hz), 1.13 (3H, d, $J = 6.3$ Hz), 1.65-1.79 (1H, m), 2.20-2.35 (2H, m), 2.68 (6H, d, $J = 10.2$ Hz), 2.74 (6H, d, $J = 10.0$ Hz), 3.68 (9H, d, $J = 11.5$ Hz), 10.55 (1H, d, $J = 1.6$ Hz); ¹³C NMR (126 MHz; CDCl₃; Me₄Si) δ 25.7 (br), 26.1, 29.6, 36.5 (d, $J_{\text{P-C}} = 4.1$ Hz), 36.76015 (d, $J_{\text{P-C}} = 4.1$ Hz), 40.8 (d, $J_{\text{P-C}} = 8.3$ Hz), 51.8, 64.0 (br), 80.7, 133.7 (br), 192.5; MS (FAB/NPOE) m/z 511 (M+H⁺); HRMS (FAB/NPOE) calcd for C₁₇H₃₃O₈N₂P₂Fe (M+H⁺) 511.1062, found 511.1076.

Dicarbonyl[1-4η-3-acetyl-2-bis(dimethylamino)phosphoryloxy-5,5-dimethyl-1,3-

cyclohexadiene](trimethoxyphosphine)iron (4): To a THF solution (3 mL) of P(OMe)₃ (0.15 mmol) and LDA, prepared from diisopropylamine (0.30 mmol) and ⁿBuLi (0.28 mmol), was added a THF solution (1.5 mL) of **1b** at -78°C. After being stirred at -78°C for 2 h, a THF solution (1 mL) of MeI (0.63 mmol) was added dropwise at -78°C. The reaction mixture was stirred at -78°C for 0.5 h and at 0°C for 2 h. Then, phosphate buffer (pH = 7) was added. After usual workup, the crude product was purified by silica gel chromatography to give **4** (49.3 mg, 73% yield). The compounds **4** had the following properties: yellow oil, IR (ATR) 1994, 1920, 1673, 1462, 1360, 1311, 1225, 1155 cm⁻¹; ¹H NMR (400 MHz; CDCl₃; Me₄Si) δ 0.94 (3H, s), 1.04 (3H, s), 1.25 (1H, brs), 1.70 (1H, d, *J* = 15.1 Hz), 1.76 (1H, d, *J* = 14.8 Hz), 2.46 (3H, s), 2.71 (6H, d, *J* = 10.3 Hz), 2.76 (6H, d, *J* = 9.9 Hz), 3.58 (9H, d, *J* = 11.5 Hz), 3.71 (1H, brs); ¹³C NMR (101 MHz; CDCl₃; Me₄Si) δ 29.7, 31.0, 34.1, 34.2 (d, *J*_{P-C} = 2.9 Hz), 36.5 (d, *J*_{P-C} = 5.0 Hz), 36.7 (d, *J*_{P-C} = 4.1 Hz), 43.4, 52.0 (d, *J*_{P-C} = 5.5 Hz), 58.3 (t, *J*_{P-C} = 10.2 Hz), 62.3, 81.3, 130.1 (d, *J*_{P-C} = 2.6 Hz), 202.4; MS (FAB/NPOE) *m/z* 537 (M+H⁺); HRMS (FAB/NPOE) calcd for C₁₉H₃₅O₈N₂P₂Fe (M+H⁺) 537.1218, found 537.1182.