

Supporting Information

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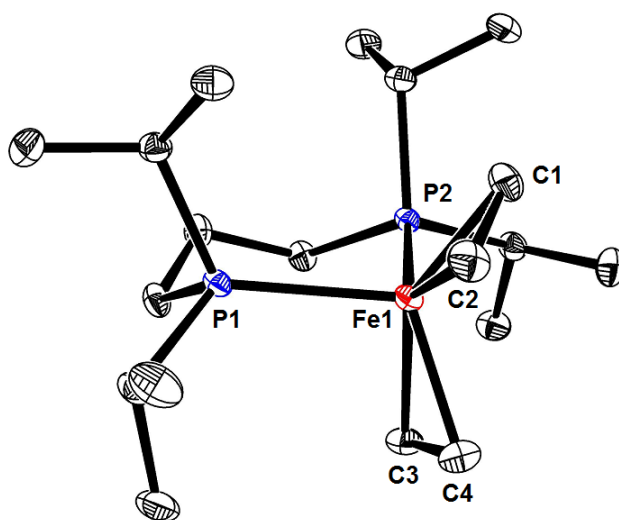
**Elementary Steps of Iron Catalysis: Exploring the Links between Iron Alkyl and Iron Olefin Complexes for their Relevance in C–H Activation and C–C Bond Formation\*\***

*Alicia Casitas, Helga Krause, Richard Goddard, and Alois Fürstner\**

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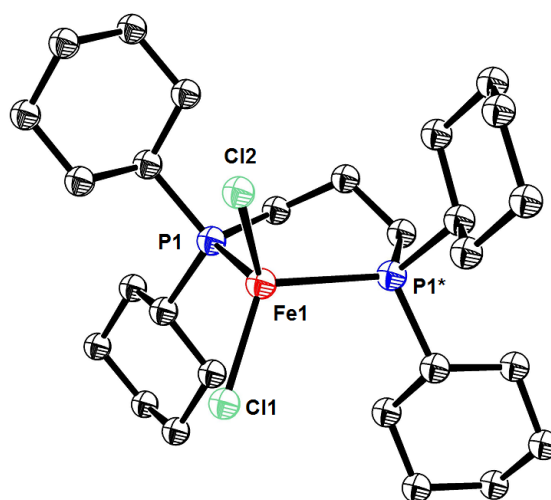
## CRYSTALLOGRAPHIC SUMMARY

CCDC 1026194 (**1**), CCDC 1026195 (**6**), CCDC 1026196 (**25**), CCDC 1026197 (**20**), CCDC 1026198 (**14**), CCDC 1026199 (**11**), CCDC 1026200 (**2**) contain the supporting 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](http://www.ccdc.cam.ac.uk/data_request/cif).



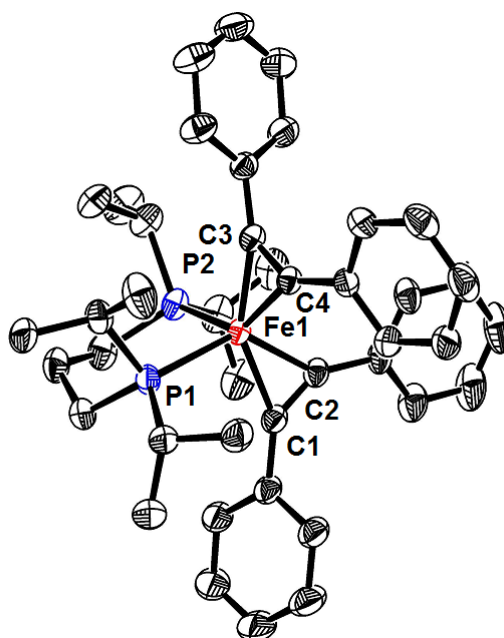
**Figure S-1.** Structure of complex **1** in the solid state.

**X-ray Crystal Structure Analysis of Complex 1:**  $C_{19}H_{42}FeP_2$ ,  $M_r = 388.32 \text{ g} \cdot \text{mol}^{-1}$ , blue plate, crystal size  $0.04 \times 0.02 \times 0.01 \text{ mm}^3$ , monoclinic, space group  $P2_1/n$ ,  $a = 9.329(5) \text{ \AA}$ ,  $b = 15.761(8) \text{ \AA}$ ,  $c = 15.064(8) \text{ \AA}$ ,  $\beta = 103.815(10)^\circ$ ,  $V = 2150.9(19) \text{ \AA}^3$ ,  $T = 100 \text{ K}$ ,  $Z = 4$ ,  $D_{calc} = 1.199 \text{ g} \cdot \text{cm}^3$ ,  $\lambda = 0.71073 \text{ \AA}$ ,  $\mu(Mo-K\alpha) = 0.847 \text{ mm}^{-1}$ , Gaussian integration absorption correction ( $T_{min} = 0.97$ ,  $T_{max} = 0.99$ ), Bruker-AXS Kappa Mach3 APEX-II diffractometer,  $2.34 < \theta < 35.21^\circ$ , 78842 measured reflections, 9537 independent reflections, 7125 reflections with  $I > 2\sigma(I)$ . Structure solved by direct methods and refined by full-matrix least-squares against  $F^2$  to  $R_1 = 0.034$  [ $I > 2\sigma(I)$ ],  $wR_2 = 0.084$ , 207 parameters, H atoms riding,  $S = 1.014$ , residual electron density  $0.5 / -0.4 \text{ e} \text{ \AA}^{-3}$ . CCDC-1026194.



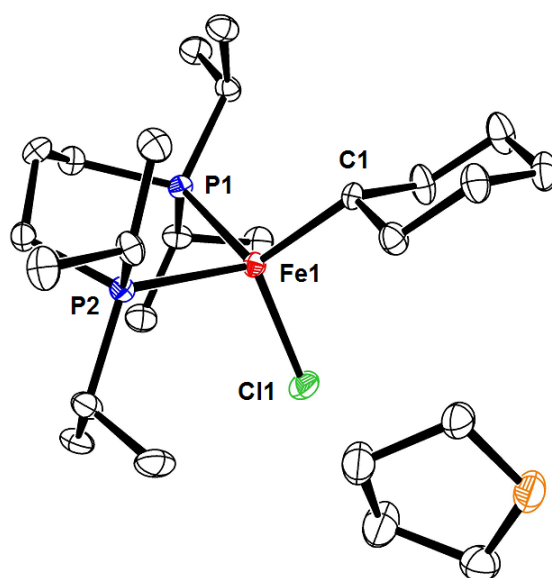
**Figure S-2.** Structure of complex **2** in the solid state.

**X-ray Crystal Structure Analysis of Complex 2:**  $C_{27}H_{50}Cl_2FeP_2$ ,  $M_r = 563.36 \text{ g} \cdot \text{mol}^{-1}$ , colorless plate, crystal size  $0.14 \times 0.12 \times 0.12 \text{ mm}^3$ , orthorhombic, space group  $Pnma$ ,  $a = 16.2465(6) \text{ \AA}$ ,  $b = 22.4774(10) \text{ \AA}$ ,  $c = 7.9309(3) \text{ \AA}$ ,  $V = 2896.20(19) \text{ \AA}^3$ ,  $T = 100 \text{ K}$ ,  $Z = 4$ ,  $D_{calc} = 1.292 \text{ g} \cdot \text{cm}^{-3}$ ,  $\lambda = 0.71073 \text{ \AA}$ ,  $\mu(Mo-K\alpha) = 0.830 \text{ mm}^{-1}$ , Gaussian integration absorption correction ( $T_{min} = 0.89$ ,  $T_{max} = 0.92$ ), Bruker AXS Enraf-Nonius KappaCCD diffractometer,  $2.723 < \theta < 33.125^\circ$ , 85062 measured reflections, 5624 independent reflections, 5156 reflections with  $I > 2\sigma(I)$ . Structure solved by direct methods and refined by full-matrix least-squares against  $F^2$  to  $R_1 = 0.022$  [ $I > 2\sigma(I)$ ],  $wR_2 = 0.057$ , 151 parameters, H atoms riding,  $S = 1.081$ , residual electron density  $0.4 / -0.4 \text{ e} \text{ \AA}^{-3}$ . CCDC-1026200.



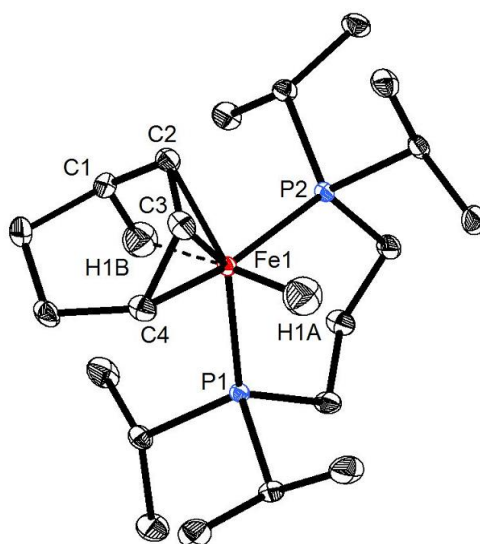
**Figure S-3.** Structure of complex **6** in the solid state; the disorder of one of the isopropyl substituents as well as disordered hexane in the unit cell are not shown for the sake of clarity.

**X-ray Crystal Structure Analysis of Complex 6:**  $C_{49}H_{54}FeP_2$ ,  $M_r = 760.71 \text{ g} \cdot \text{mol}^{-1}$ , red-brown block, crystal size  $0.532 \times 0.356 \times 0.310 \text{ mm}^3$ , monoclinic, space group  $P2_1/c$ ,  $a = 14.8314(19) \text{ \AA}$ ,  $b = 14.3770(18) \text{ \AA}$ ,  $c = 21.717(3) \text{ \AA}$ ,  $\beta = 109.819(2)^\circ$ ,  $V = 4356.5(10) \text{ \AA}^3$ ,  $T = 100 \text{ K}$ ,  $Z = 4$ ,  $D_{calc} = 1.160 \text{ g} \cdot \text{cm}^3$ ,  $\lambda = 0.71073 \text{ \AA}$ ,  $\mu(Mo-K\alpha) = 0.451 \text{ mm}^{-1}$ , Gaussian integration absorption correction ( $T_{min} = 0.88$ ,  $T_{max} = 0.91$ ), Bruker-AXS Kappa Mach3 APEX-II diffractometer,  $1.459 < \theta < 34.081^\circ$ , 148686 measured reflections, 17841 independent reflections, 13690 reflections with  $I > 2\sigma(I)$ , Structure solved by direct methods and refined by full-matrix least-squares against  $F^2$  to  $R_1 = 0.050 [I > 2\sigma(I)]$ ,  $wR_2 = 0.157$ , 560 parameters; badly disordered solvent was modelled by 13 C-atoms with partial occupancy, otherwise H atoms riding; one of the isopropyl groups was partially disordered (0.685(5) : 0.315(5),  $S = 1.089$ , residual electron density  $0.8 / -0.6 \text{ e} \text{ \AA}^{-3}$ . CCDC-1026195.



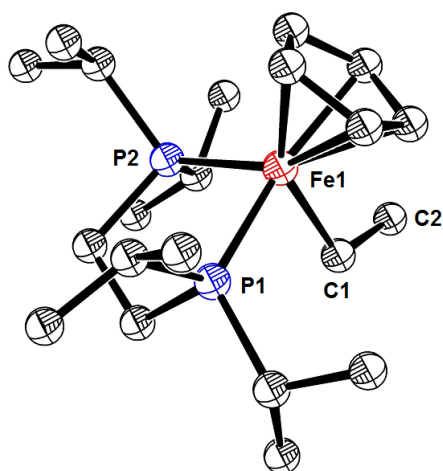
**Figure S-4.** Structure of complex **11** in the solid state.

**X-ray Crystal Structure Analysis of Complex 11:**  $C_{25}H_{53}ClFeOP_2$ ,  $M_r = 522.91 \text{ g} \cdot \text{mol}^{-1}$ , red plate, crystal size  $0.10 \times 0.06 \times 0.06 \text{ mm}^3$ , monoclinic, space group  $P2_1$ ,  $a = 8.9503(4) \text{ \AA}$ ,  $b = 16.2564(7) \text{ \AA}$ ,  $c = 10.3102(5) \text{ \AA}$ ,  $\beta = 106.289(4)^\circ$ ,  $V = 1439.91(12) \text{ \AA}^3$ ,  $T = 100 \text{ K}$ ,  $Z = 2$ ,  $D_{calc} = 1.206 \text{ g} \cdot \text{cm}^3$ ,  $\lambda = 0.71073 \text{ \AA}$ ,  $\mu(Mo-K\alpha) = 0.742 \text{ mm}^{-1}$ , Gaussian integration absorption correction ( $T_{min} = 0.84$ ,  $T_{max} = 0.93$ ), Bruker AXS Enraf-Nonius KappaCCD APEX-II diffractometer,  $2.668 < \theta < 28.031^\circ$ , 17356 measured reflections, 6789 independent reflections, 6064 reflections with  $I > 2\sigma(I)$ . Structure solved by direct methods and refined by full-matrix least-squares against  $F^2$  to  $R_1 = 0.051 [I > 2\sigma(I)]$ ,  $wR_2 = 0.162$ , 279 parameters, absolute structure parameter =  $0.014(19)$  (2576 quotients), H atoms riding,  $S = 1.051$ , residual electron density  $0.5 / -1.1 \text{ e} \text{ \AA}^{-3}$ . CCDC-1026199.



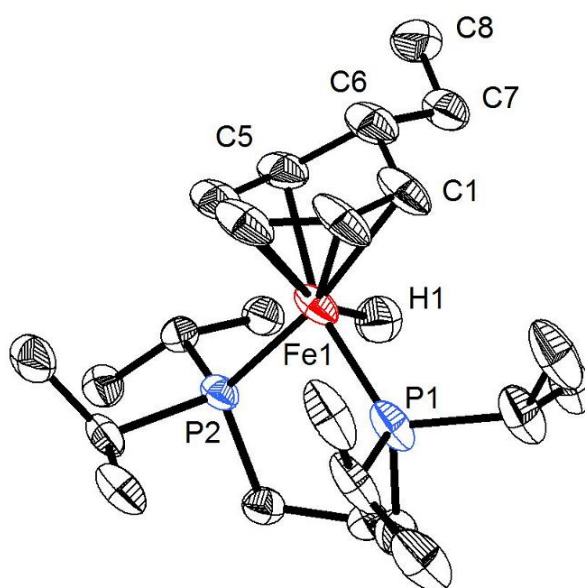
**Figure S-5.** Structure of complex **14** in the solid state; the hydrogen atoms engaged with the iron center have been localized in a difference Fourier map and their positions refined

**X-ray Crystal Structure Analysis of Complex 14:**  $C_{21}H_{44}FeP_2$ ,  $M_r = 414.35 \text{ g} \cdot \text{mol}^{-1}$ , orange plate, crystal size  $0.24 \times 0.16 \times 0.08 \text{ mm}^3$ , monoclinic, space group  $Cc$ ,  $a = 17.527(3) \text{ \AA}$ ,  $b = 8.6665(16) \text{ \AA}$ ,  $c = 15.632(3) \text{ \AA}$ ,  $\beta = 109.570(3)^\circ$ ,  $V = 2237.2(7) \text{ \AA}^3$ ,  $T = 100 \text{ K}$ ,  $Z = 4$ ,  $D_{calc} = 1.230 \text{ g} \cdot \text{cm}^{-3}$ ,  $\lambda = 0.71073 \text{ \AA}$ ,  $\mu(Mo-K\alpha) = 0.819 \text{ mm}^{-1}$ , Gaussian integration absorption correction ( $T_{min} = 0.84$ ,  $T_{max} = 0.94$ ), Bruker-AXS Kappa Mach3 APEX-II diffractometer,  $2.467 < \theta < 31.085^\circ$ , 32140 measured reflections, 7150 independent reflections, 6969 reflections with  $I > 2\sigma(I)$ , Structure solved by direct methods and refined by full-matrix least-squares against  $F^2$  to  $R_1 = 0.020$  [ $I > 2\sigma(I)$ ],  $wR_2 = 0.051$ , 237 parameters, absolute structure parameter =  $-0.001(3)$  (3370 quotients), H-atoms attached to C1 and the hydride H-atom were refined with isotropic atomic displacement parameters, otherwise H atoms riding,  $S = 1.066$ , residual electron density  $0.3 / -0.2 \text{ e} \cdot \text{\AA}^{-3}$ . CCDC-1026198.



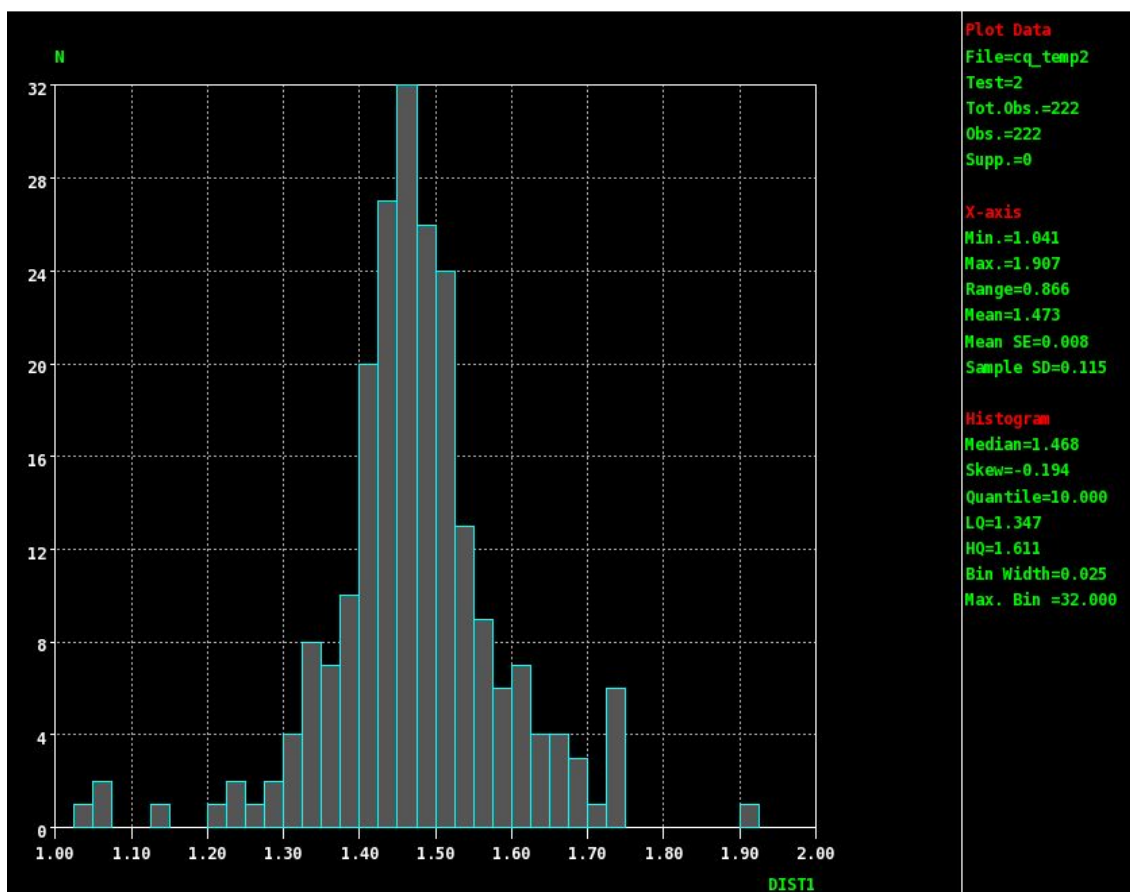
**Figure S-6.** Structure of complex **20** in the solid state.

**X-ray Crystal Structure Analysis of Complex 20:**  $C_{21}H_{42}FeP_2$ ,  $M_r = 412.33 \text{ g} \cdot \text{mol}^{-1}$ , orange plate, crystal size  $0.12 \times 0.12 \times 0.05 \text{ mm}^3$ , triclinic, space group  $P1$ ,  $a = 8.2104(16) \text{ \AA}$ ,  $b = 8.449(3) \text{ \AA}$ ,  $c = 17.999(3) \text{ \AA}$ ,  $\alpha = 90.430(15)^\circ$ ,  $\beta = 96.781(15)^\circ$ ,  $\gamma = 116.538(14)^\circ$ ,  $V = 1106.7(5) \text{ \AA}^3$ ,  $T = 100 \text{ K}$ ,  $Z = 2$ ,  $D_{calc} = 1.237 \text{ g} \cdot \text{cm}^{-3}$ ,  $\lambda = 0.71073 \text{ \AA}$ ,  $\mu(Mo-K\alpha) = 0.827 \text{ mm}^{-1}$ , Gaussian integration absorption correction ( $T_{min} = 0.90$ ,  $T_{max} = 0.96$ ), Bruker AXS Enraf-Nonius KappaCCD diffractometer,  $2.701 < \theta < 30.019^\circ$ , 18819 measured reflections, 6425 independent reflections, 5660 reflections with  $I > 2\sigma(I)$ . Structure solved by direct methods and refined by full-matrix least-squares against  $F^2$  to  $R_1 = 0.034 [I > 2\sigma(I)]$ ,  $wR_2 = 0.090$ , 225 parameters, H atoms riding,  $S = 1.043$ , residual electron density  $0.6 / -0.6 \text{ e} \text{ \AA}^{-3}$ . CCDC-1026197.



**Figure S-7.** Structure of complex **25** in the solid state; the hydrogen atom H1 forming the Fe–H bond has been localized in a difference Fourier map and its position refined with isotropic atomic displacement parameter (Fe–H  $1.40(4) \text{ \AA}$ ).

**X-ray Crystal Structure Analysis of Complex 25:**  $C_{23}H_{46}FeP_2$ ,  $M_r = 440.39 \text{ g} \cdot \text{mol}^{-1}$ , orange block, crystal size  $0.59 \times 0.45 \times 0.27 \text{ mm}^3$ , monoclinic, space group  $P2_1/n$ ,  $a = 8.4397(8) \text{ \AA}$ ,  $b = 16.6736(15) \text{ \AA}$ ,  $c = 16.8811(15) \text{ \AA}$ ,  $\beta = 95.026(4)^\circ$ ,  $V = 2366.4(4) \text{ \AA}^3$ ,  $T = 100 \text{ K}$ ,  $Z = 4$ ,  $D_{calc} = 1.236 \text{ g} \cdot \text{cm}^{-3}$ ,  $\lambda = 1.54178 \text{ \AA}$ ,  $\mu(Cu-K\alpha) = 6.399 \text{ mm}^{-1}$ , Empirical absorption correction ( $T_{min} = 0.03$ ,  $T_{max} = 0.30$ ), Bruker AXS X8 Proteum diffractometer,  $3.73 < \theta < 67.81^\circ$ , 51802 measured reflections, 4246 independent reflections, 3711 reflections with  $I > 2\sigma(I)$ . Structure solved by direct methods and refined by full-matrix least-squares against  $F^2$  to  $R_1 = 0.058 [I > 2\sigma(I)]$ ,  $wR_2 = 0.158$ , 248 parameters, hydride H-atom refined, otherwise H atoms riding,  $S = 1.039$ , residual electron density  $0.8 / -0.6 \text{ e} \text{ \AA}^{-3}$ . CCDC-1026196.



**Figure S-8.** Frequency-distance histogram for non-bridging Fe–H bonds taken from the Cambridge Structure Database (222 structures); accordingly, the expected Fe–H bond distance is 1.47(12) Å (drawn with Vista - A Program for the Analysis and Display of Data Retrieved from the CSD. Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, England).

## Procedures

**General.** All manipulations were carried out under argon atmosphere using Schlenk techniques. The solvents were purified by distillation over the indicated drying agents and were transferred under argon: THF, Et<sub>2</sub>O (Mg-anthracene), hexane, pentane, [D<sub>8</sub>]-THF (Na/K). NMR: Spectra were recorded on a DPX 300 or AV 400 in the solvents indicated; chemical shifts ( $\delta$ ) are given in ppm, coupling constants ( $J$ ) in Hz. MS (EI): Finnigan MAT 8200 (70 eV), HRMS: Finnigan MAT 95, Bruker APEX III FT-ICR-MS (7 T magnet); Elemental analyses: H. Kolbe, Mülheim/Ruhr. All commercially available compounds (Lancaster, Fluka, Aldrich) were used as received unless stated otherwise.

[FeCl<sub>2</sub>(THF)<sub>1,5</sub>]<sup>1</sup> and bis(diisopropylphosphino)propane (dipp)<sup>2</sup> were prepared according to literature procedures.

<sup>1</sup> S. D. Ittel, A. D. English, C. A. Tolman, J. P. Jesson, *Inorg. Chim. Acta*, **1979**, *33*, 101-106.

<sup>2</sup> K. Tani, E. Tanigawa, Y. Tatsuno, S. Otsuka, *J. Organomet. Chem.* **1985**, *279*, 87-101.

**Representative Procedure for the [2+2+2] Cyclotrimerization of Alkynes. Hexaethylbenzene.**

A solution of 3-hexyne (36 mg, 0.437 mmol) in THF (1 mL) was added to a solution of complex **1** (17 mg, 0.043 mmol) in THF at  $-50^{\circ}\text{C}$ . The cooling bath was removed and the solution allowed to reach ambient temperature, during which time the color changed from turquoise via gray-green to dark brown. After stirring for 1 h, the solvent was removed and the residue was purified by flash chromatography (hexanes/EtOAc, 4:1) to give the title compound as a colorless syrup which solidified upon standing (35 mg, 97%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 2.61 (q,  $J$  = 7.5 Hz, 12H), 1.17 ppm (t,  $J$  = 7.5 Hz, 18H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 137.8, 22.1, 15.7 ppm; MS (EI):  $m/z$  (%): 247 (14), 246 (73), 231 (100), 217 (17), 173 (6), 161 (7), 147 (8), 133 (5), 105 (3), 55(3). The data are in good accord with those reported in the literature.<sup>3</sup>

**Tris(hexamethylene)benzene.** Prepared analogously as a colorless solid (22 mg, 81%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 2.86-2.83 (m, 12 H), 1.65 (br m, 12H), 1.36-1.34 ppm (m, 12H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 136.5, 31.3, 28.0, 26.7 ppm; MS (EI):  $m/z$  (%): 325 (26), 324 (100), 281 (21), 253 (6), 211 (6), 185 (6), 143 (4), 55(4). The data are in good accord with those reported in the literature.<sup>3</sup>

**Representative Procedure for the Iron-Catalyzed Pyridine Synthesis: Dimethyl 1,4-dimethyl-3-phenyl-6,7-dihydro-5H-cyclopenta[c]pyridine-6,6-dicarboxylate.** Dimethyl 2,2-di(but-2-yn-1-yl)-malonate 97 mg, 0.41 mmol) was added to a turquoise solution of complex **1** (16 mg, 0.041 mmol) in THF (2 mL) at  $-50^{\circ}\text{C}$ , causing a color change to red-brown. Next, an excess of benzonitrile (412 mg, 4 mmol) was added, which caused yet another color change to greenish-brown. The cooling bath was removed and the mixture allowed to reach ambient temperature. After stirring for 2 h, all volatile materials were distilled off and the residue was purified by flash chromatography (hexanes/EtOAc, 10:1) to give the title compound as a pale yellow solid (123 mg, 88%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.43-7.32 (m, 5H), 3.77 (s, 6H), 3.62 (s, 2H), 3.58 (s, 2H), 2.46 (s, 3H), 2.17 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 171.8, 156.9, 150.3, 149.3, 140.5, 132.3, 129.0, 128.0, 127.5, 124.2, 59.3, 53.1, 40.1, 39.1, 21.7, 16.0; Ms (ESI pos): 340 ( $[\text{M}+\text{H}]^+$ ), 339. The data are in good accord with those reported in the literature.<sup>4</sup>

**Dimethyl 1,3,4-trimethyl-6,7-dihydro-5H-cyclopenta[c]pyridine-6,6-dicarboxylate.** Prepared analogously as a pale yellow solid (70 mg, 61%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 3.70 (s, 6H), 3.48 (s, 4H), 2.38 (s, 3H), 2.34 (s, 3H), 2.10 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 171.7, 154.5, 149.4, 148.2, 131.1, 124.4, 60.2, 59.4, 53.0, 39.7, 38.8, 21.8, 21.4, 14.9, 14.0; MS (EI):  $m/z$  (%): 277 (36), 218 (100), 217 (38), 186 (12), 158 (43), 115 (7), 59 (5). The data are in good accord with those reported in the literature.<sup>4</sup>

**Dimethyl 3-butyl-1,4-dimethyl-6,7-dihydro-5H-cyclopenta[c]pyridine-6,6-dicarboxylate.** Prepared analogously as a pale yellow syrup (84 mg, 78%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 3.72 (s, 6H), 3.50 (s, 2H), 3.49 (s, 2H), 2.69 (t, 2H), 2.36 (s, 3H), 2.15 (s, 3H), 1.50-1.63 (m, 2H), 1.32-1.39 (m, 2H), 0.89 (t,  $J$  = 7.2 Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 171.8, 158.5, 149.6, 148.6, 131.0, 123.9, 59.3, 53.0, 39.9, 38.9, 35.0, 31.7, 22.8, 21.5, 16.7, 14.5, 13.9; MS (EI):  $m/z$  (%):

<sup>3</sup> A. Das, C. Dash, M. Yousufuddin, M. A. Celik, G. Frenking, H. V. R. Dias, *Angew. Chem. Int. Ed.* **2012**, *51*, 3940.

<sup>4</sup> K. Kase, A. Goswami, K. Ohtaki, E. Tanabe, N. Saino, S. Okamoto, *Org. Lett.* **2007**, *9*, 931.



319 (3), 290 (8), 277 (100), 219 (12), 158 (8). The data are in good accord with those reported in the literature.<sup>5</sup>

**Complex [(dipp)FeCl<sub>2</sub>] (2).** A flame-dried two-necked round-bottomed flask equipped with a magnetic stir bar and connected to the Ar line was charged with FeCl<sub>2</sub>·THF<sub>1.5</sub> (4.5 g, 0.019 mol) and THF (50 mL) under Ar. A solution of bis(diisopropylphosphino)propane (dipp, 5.2 g, 0.019 mol) in THF (5 mL) was slowly added via cannula to the resulting suspension and stirring was continued overnight. For work up, all volatile materials were distilled off in vacuum, the remaining pale-pink solid was suspended in diethyl ether (25 mL) and the suspension was stored at –30°C overnight. The solvent was siphoned off by cannula and the resulting solid dried in vacuum to give the title complex as a crystalline material (6.9 g, 91 %). Single crystals suitable for X-ray diffraction were grown from a saturated solution in THF by lowering the temperature. MS (EI): *m/z* (%): 404 (6) [M, <sup>37</sup>Cl], 402 (10) [M, <sup>35</sup>Cl], 233 (100), 148 (10), 43 (7); HRMS (EI): calcd for C<sub>15</sub>H<sub>34</sub>Cl<sub>2</sub>FeP<sub>2</sub>: 402.08622 [M, <sup>35</sup>Cl]; found: 402.08648; Anal. calcd (%) for C<sub>15</sub>H<sub>34</sub>Cl<sub>2</sub>FeP<sub>2</sub>: C 44.69; H 8.50; P 15.37; found: C 44.63, H 8.55, P 15.37.

**Complex [(dippe)FeCl<sub>2</sub>] (7).**<sup>6</sup> Prepared analogously from FeCl<sub>2</sub>·THF<sub>1.5</sub> (2.9 g, 0.012 mol) and bis(diisopropylphosphino)ethane (dippe, 3.3 g, 0.013 mol) as a crystalline material (4.3 g, 90%) MS (EI): *m/z* (%): 390 (7) [M, <sup>37</sup>Cl], 388 (11) [M, <sup>35</sup>Cl], 219 (100), 43 (44). HRMS (EI): calcd for C<sub>14</sub>H<sub>32</sub>Cl<sub>2</sub>FeP<sub>2</sub>: 388.07057 [M, <sup>35</sup>Cl]; found: 388.07086; Anal. calcd (%) for C<sub>14</sub>H<sub>32</sub>Cl<sub>2</sub>FeP<sub>2</sub>: C 43.22; H 8.29; P 15.92; found: C 43.54, H 8.10, P 15.79.

**Complex [(dipp)(η<sup>2</sup>-C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>Fe] (1).** A flame-dried two-necked round-bottomed flask equipped with a magnetic stir bar, a gas inlet and a connection to the Ar line was charged with (dipp)FeCl<sub>2</sub> (1.27 g, 3.15 mmol) and THF (20 mL). Ethylene was bubbled through this mixture at –5°C for 30 min. EtMgBr (3 M in Et<sub>2</sub>O, 3.15 mL, 9.45 mmol) was then added dropwise while keeping the ethylene flow, causing an immediate color change from pale yellow to dark turquoise-blue. The resulting mixture was stirred for 1 h under ethylene at –5 °C. For work up, all volatile materials were removed under vacuum at –10°C to leave a dark-brown residue. Extraction of the solid with cold hexane and filtration at –40 °C afforded a clear turquoise-blue solution, which was evaporated in vacuo at –10°C to give the title complex as a turquoise-blue powder (0.9 g, 77%). The material is highly air sensitive and thermally unstable at ≥ 0 °C, but can be stored at –80°C under Ar for prolonged periods of time without noticeable decomposition. Single crystals suitable for X-ray diffraction were grown from a saturated solution in hexanes by lowering the temperature to –80°C. Anal. calcd (%) for C<sub>19</sub>H<sub>42</sub>FeP<sub>2</sub>: C 58.76, H 10.90, Fe 14.38, P 15.95; found: C 58.57, H 10.97, Fe 14.37, P 15.87.

**Complex [(dipp)Fe(η<sup>2</sup>-PhC≡CPh)<sub>2</sub>] (6).** *Method A:* A flame-dried three-necked round-bottomed flask, equipped with a magnetic stir bar, a gas inlet and a connection to the Ar line, was charged with (dipp)FeCl<sub>2</sub> (462 mg, 1.15 mmol) and THF (10 mL). The resulting solution was cooled to –5°C and saturated with ethylene by bubbling the gas through the solution for 30 min. EtMgBr (3 M in Et<sub>2</sub>O, 1.15 mL, 3.44 mmol) was added dropwise while keeping the ethylene flow, causing a color change from pale yellow to turquoise. The resulting mixture was

<sup>5</sup> H. Zhang, Z. Ouyang, Y. Liu, Q. Zhang, L. Wang, L. Deng, *Angew. Chem. Int. Ed.* **2014**, *53*, 8432.

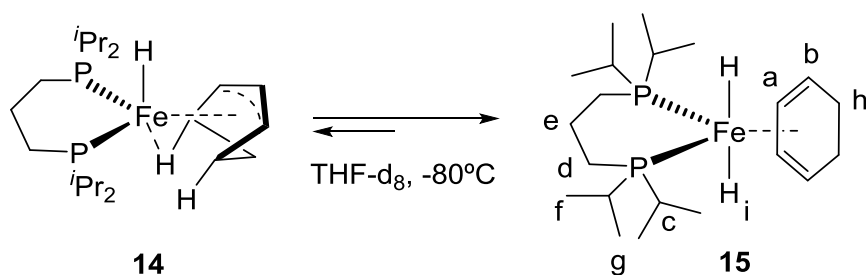
<sup>6</sup> A. R. Hermes, G. S. Girolami, *Inorg. Chem.* **1988**, *27*, 1775-1781.

stirred for 1 h under ethylene at  $-5^{\circ}\text{C}$ . The flask was then purged with Ar to remove the ethylene before a solution of diphenylacetylene (0.41 mg, 2.29 mmol) in THF (4 mL) was added by cannula, causing the immediate formation of a deep red solution. After stirring for 1 h at  $-5^{\circ}\text{C}$ , the solvent was removed in vacuo at  $-10^{\circ}\text{C}$  to leave a dark brown residue. The solid was extracted with cold hexane and all insoluble materials were filtered off at  $-10^{\circ}\text{C}$  to afford a clear red solution. The solvent was concentrated until the precipitation of solid material started to occur. At this point, the resulting solution was slowly cooled from  $-20^{\circ}\text{C}$  to  $-70^{\circ}\text{C}$ . The solvent was removed by cannula and the remaining solid was rinsed with cold  $\text{Et}_2\text{O}$  at  $-70^{\circ}\text{C}$  and dried in vacuo to give the title complex as a dark red crystalline material. The filtrate was concentrated and the residue again recrystallized to give a second crop of the title complex (558 mg combined, 70%). Single crystals suitable for X-ray diffraction were grown from a saturated solution of the complex in hexane by lowering the temperature from  $-20^{\circ}\text{C}$  to  $-80^{\circ}\text{C}$ . In the solid, the complex is stable at room temperature.

*Method B:* A flame-dried three-necked round-bottom flask, equipped with a magnetic stir bar, a gas inlet and connected to the Ar line, was charged with magnesium turnings (65.3 mg, 2.69 mmol) and THF (3 mL). In a separate Schlenk flask, a suspension of  $\text{FeBr}_2$  (205 mg, 0.95 mmol) in THF (15 mL) was stirred at ambient temperature for 1 h before a solution of dippp (289 mg, 1.04 mmol) in THF (2 mL) and diphenylacetylene (347.4 mg, 1.95 mmol) were successively added. The resulting mixture was transferred into a dropping funnel and slowly added to the stirred suspension of the magnesium at  $0^{\circ}\text{C}$ . After stirring at this temperature for 24 h, the solvent was removed in vacuo. The remaining dark brown solid was extracted with cold pentane and the suspension was filtered at  $-40^{\circ}\text{C}$ . The dark red filtrate was concentrated to ca. 1/3 of the initial volume and the product crystallized by lowering the temperature to  $-85^{\circ}\text{C}$ . The resulting crystals were filtered off at  $-70^{\circ}\text{C}$ , rinsed with cold  $\text{Et}_2\text{O}$  at  $-70^{\circ}\text{C}$  and dried in vacuo to give the title complex in the form of red crystals (338 mg, 53%). Anal. calcd (%) for  $\text{C}_{43}\text{H}_{54}\text{FeP}_2$ : C 74.99; H 7.90; Fe 8.11; P 8.99; found: C 74.83, H 7.87, Fe 8.09; P 8.91.

**Complex [(dipp)(cyclohexyl)(Cl)Fe] (11).** A flame-dried Schlenk flask, equipped with a magnetic stir bar and a connection to the Ar line, was charged with (dipp)FeCl<sub>2</sub> (341 mg, 0.85 mmol) and THF (6 mL) under Ar. The solution was cooled to  $-35^{\circ}\text{C}$  before cyclohexylmagnesium chloride (2 M in  $\text{Et}_2\text{O}$ , 0.42 mL, 0.85 mmol) was slowly added via syringe, causing an immediate color change from pale-yellow to deep red. After stirring for 2 h at  $-35^{\circ}\text{C}$ , the solution was concentrated to ca. 1/2 of the initial volume under vacuum while keeping the temperature at  $-35^{\circ}\text{C}$ . Cold  $\text{Et}_2\text{O}$  was added to precipitate the magnesium salts. The suspension was filtered at  $-40^{\circ}\text{C}$  and the solvent was removed in vacuo at  $-35^{\circ}\text{C}$  to afford a red solid which was recrystallized from the minimum amount of THF by decreasing the temperature from  $-35^{\circ}\text{C}$  to  $-85^{\circ}\text{C}$  over the course of 24 h. The solvent was decanted and the remaining solid material was rinsed with cold  $\text{Et}_2\text{O}$  and dried in vacuo at  $-40^{\circ}\text{C}$  to give the title complex in the form of red crystals (195 mg, 51 %). The material is highly air sensitive and thermally unstable ( $\geq 0^{\circ}\text{C}$ ) but can be stored at  $-80^{\circ}\text{C}$  for prolonged periods of time without noticeable decomposition. Single crystals suitable for X-ray diffraction were grown from a saturated solution in THF by slowly decreasing the temperature from  $-35^{\circ}\text{C}$  to  $-80^{\circ}\text{C}$ . Because of the sensitivity of the complex, no correct combustion analysis could be obtained.

**Complex [(dippp)( $\eta^3$ -C<sub>6</sub>H<sub>9</sub>)Fe(H)] (14/15).** A flame-dried Schlenk flask, equipped with a magnetic stir bar and a connection to the Ar line, was charged with (dippp)FeCl<sub>2</sub> (438 mg, 1.09 mmol) and THF (10 mL). Freshly distilled cyclohexene (0.55 mL 5.43 mmol) was introduced and the resulting pale yellow solution was cooled to –30°C before cyclohexylmagnesium chloride (2 M in Et<sub>2</sub>O, 1.1 mL, 2.20 mmol) was slowly added via syringe. An immediate color change from pale yellow to deep red-orange was observed. The mixture was stirred at –30°C for 1.5 h before the solvent was removed in vacuo. The residue was extracted with cold pentane and the insoluble material was filtered off under Ar at –30°C to give a clear red-orange solution which was concentrated to ca. 1/3 of the initial volume. The product was crystallized from this solution at –78°C. The mother liquor was removed by canula, and the solid material was rinsed with cold Et<sub>2</sub>O and dried under high vacuum to give the title complex as an orange solid (358 mg, 79 %). Single crystals suitable for X-ray diffraction were grown from a saturated solution in THF by slowly decreasing the temperature from –30°C to –80°C. <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, THF-d<sub>8</sub>, –55°C):  $\delta$  = 75.3.



	$\delta$ <sup>1</sup> H (ppm) <sup>a</sup>	$\delta$ <sup>13</sup> C (ppm) <sup>a</sup>		$\delta$ <sup>1</sup> H (ppm)	$\delta$ <sup>13</sup> C (ppm)
a	4.65	73.02 (br)	f	1.04	19.70 (s)
b	1.95	32.02 (br)	g	1.04	18.78 (s)
c	1.88	29.48 (d)	h	0.97	23.30 (br)
d	1.69	23.59 (t)	i	–19.37	---
e	1.26	23.41 (t)			

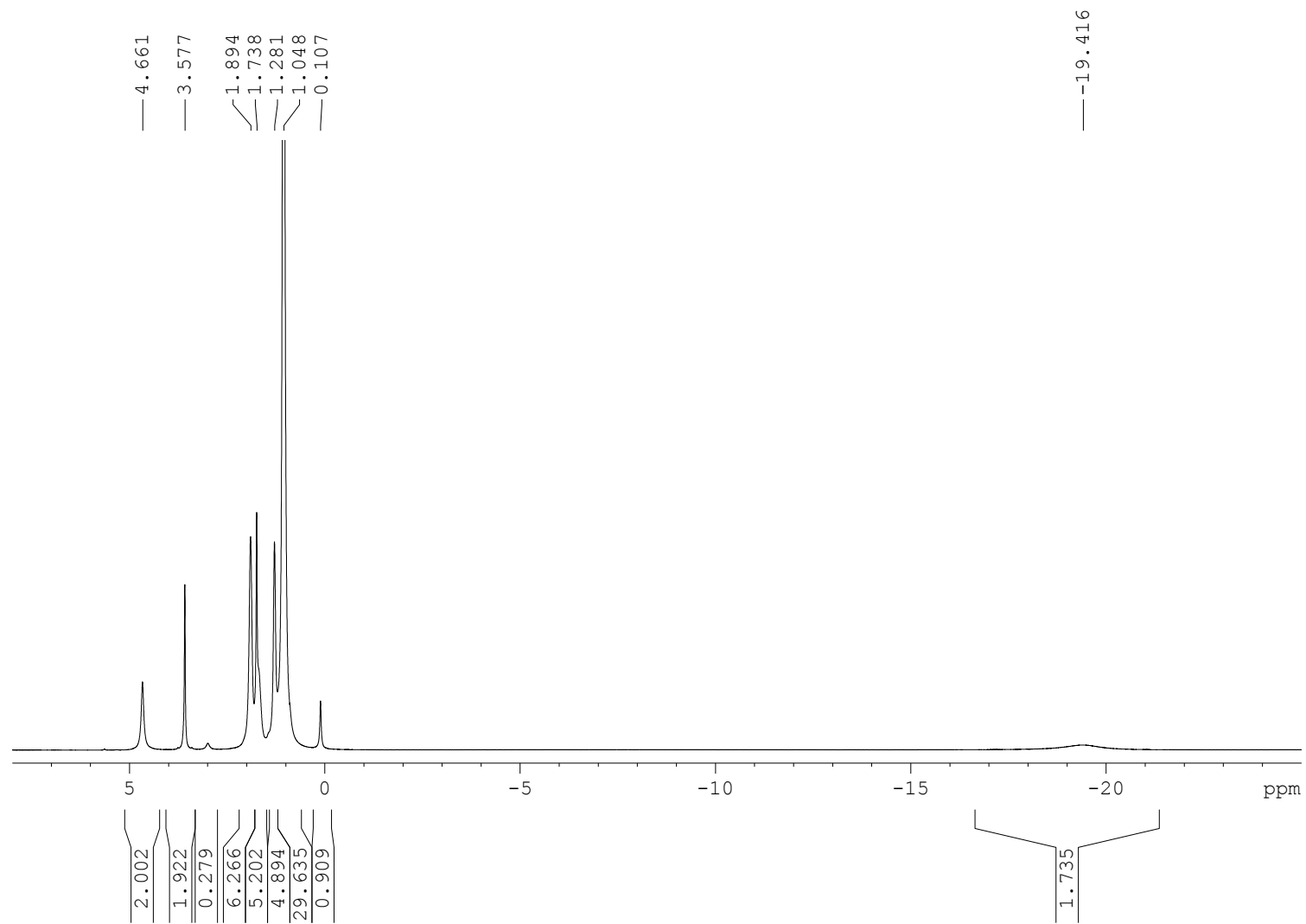
a) THF-d<sub>8</sub>, –80°C, 400 MHz for <sup>1</sup>H NMR and 100 MHz for <sup>13</sup>C NMR.

**Complex [(dippe)( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Fe(Et)] (20).** A flame-dried Schlenk flask, equipped with a magnetic stir bar, a gas inlet and a connection to the Ar line, was charged with (dippe)FeCl<sub>2</sub> (405 mg, 1.03 mmol) and THF (15 mL). Ethylene was bubbled through the resulting solution for 30 min at –20°C. Next, EtMgBr (3 M in Et<sub>2</sub>O, 0.69 mL, 2.08 mmol) was added dropwise while keeping the ethylene flow, causing an immediate color change from pale yellow to deep blue. After stirring the resulting solution at –20°C for 1.5 h, freshly distilled cyclopentadiene (0.43 mL, 5.24 mmol) was added dropwise, causing another color change from deep blue to red-brown. The temperature was slowly raised to 20°C and stirring was continued for 1 h. For work up, the

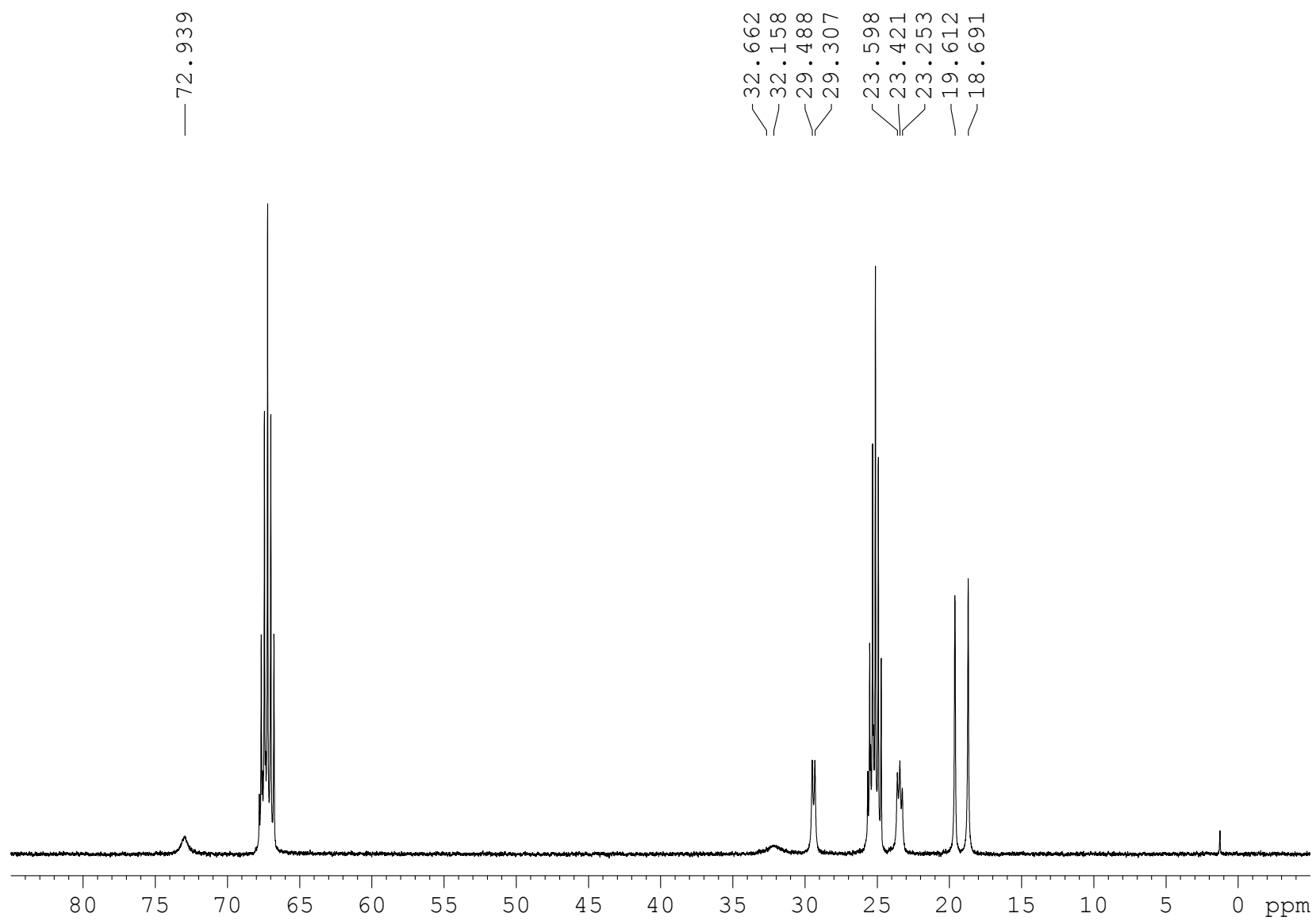
solvent was removed in vacuo and the resulting brown residue was repeatedly extracted with pentane to give a clear red solution. The product was isolated by crystallization upon lowering the temperature from 0°C to –85°C over the course of 24 h. The precipitate was filtered off at –30°C, rinsed with cold Et<sub>2</sub>O and dried in vacuo to give the title compound as a yellow crystalline solid (277 mg, 65%). Single crystals suitable for X-ray diffraction were grown from a saturated solution in pentane upon decreasing the temperature from 0°C to –35°C. <sup>1</sup>H NMR (500 MHz, THF-d<sub>8</sub>, –55°C): δ = 3.98 (5H), 2.26 (2H), 1.96 (2H), 1.56 (2H), 1.42-0.93 (29H), –0.13 (2H); <sup>13</sup>C NMR (126 MHz, THF-d<sub>8</sub>, 25°C): δ = 76.0, 31.7, 26.8, 22.6 (t, J<sub>PC+P'C</sub> = 35.8 Hz), 21.0, 20.6, 20.4, 20.3, 19.5, –11.4 (t, J<sub>PC+P'C</sub> = 46.4 Hz); <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, THF-d<sub>8</sub>, –55°C): δ = 110.6; MS (EI): *m/z* (%): 412 (14), 383 (100), 340 (23), 121 (14); HRMS (EI): calcd for C<sub>21</sub>H<sub>42</sub>FeP<sub>2</sub>: 412.21112; found: 412.21146 [M<sup>+</sup>].

**Complex [(dippp)(η<sup>5</sup>-C<sub>6</sub>H<sub>7</sub>Et-endo)Fe(H)] (25).** A flame-dried Schlenk flask, equipped with a magnetic stir bar, a gas inlet and a connection to the Ar line, was charged with (dippp)FeCl<sub>2</sub> (499.8 mg, 1.24 mmol) and THF (15 mL). Ethylene was bubbled through the stirred solution at –5°C for 30 min before EtMgBr (3 M in Et<sub>2</sub>O, 1.24 mL, 3.72 mmol) was added dropwise while keeping the ethylene flow, thus causing an immediate color change from pale yellow to turquoise-blue. After stirring the mixture at –5°C for 1.5 h, freshly distilled 1,3-cyclohexadiene (0.59 mL, 6.2 mmol) was slowly added, causing another color change to orange-brown. The temperature was gradually raised to 20°C and the resulting solution was stirred for 1 h before the solvent was removed in vacuo to leave a brown solid residue. Extractions with pentane gave a clean yellow solution from which the product was crystallized by lowering the temperature to –85°C over the course of 24 h. The resulting solid material was collected at –30°C, rinsed with cold Et<sub>2</sub>O and dried in vacuo to give the title complex in the form of an orange crystalline solid (217 mg, 40 %). Single crystals suitable for X-ray diffraction were grown from a saturated solution in pentane upon decreasing the temperature from 0°C to –85°C. <sup>1</sup>H NMR (500 MHz, THF-d<sub>8</sub>, –55°C, line broadening): δ = 6.14 (1H), 4.44 (2H), 2.22 (2H), 2.04 (1H), 1.64-0.73 (39H), –2.71 (1H); <sup>13</sup>C NMR (126 MHz, THF-d<sub>8</sub>, –55°C, line broadening): δ = 85.4, 74.6, 38.5, 36.2, 32.2, 28.8, 25.3 (under solvent peak), 21.7, 20.2, 19.5, 18.9, 18.4, 12.4; <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, THF-d<sub>8</sub>, –55°C): δ = 64.4; IR: 1840 cm<sup>–1</sup> (Fe-H); MS (ESI+): *m/z* 439.2; HRMS (ESI+): calcd for C<sub>23</sub>H<sub>45</sub>FeP<sub>2</sub>: 439.23457; found: 439.23404 [(M-H)<sup>+</sup>].

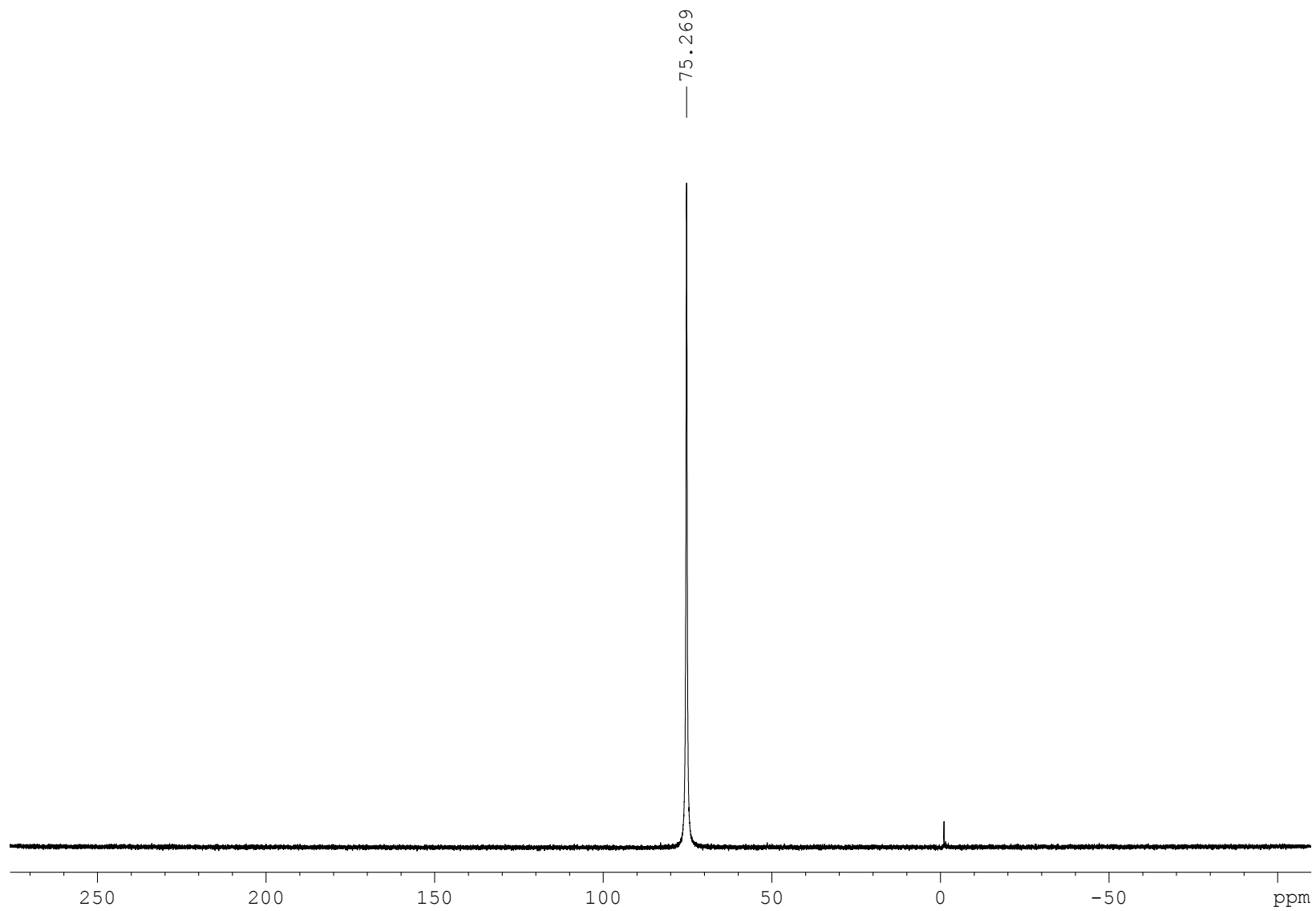
$^1\text{H-NMR}$  (400 MHz,  $-80^\circ\text{C}$ ,  $\text{THF-d}_8$ ) of  $\text{dipp}(\eta^3\text{-C}_6\text{H}_9)(\text{H})\text{Fe}$  (15)



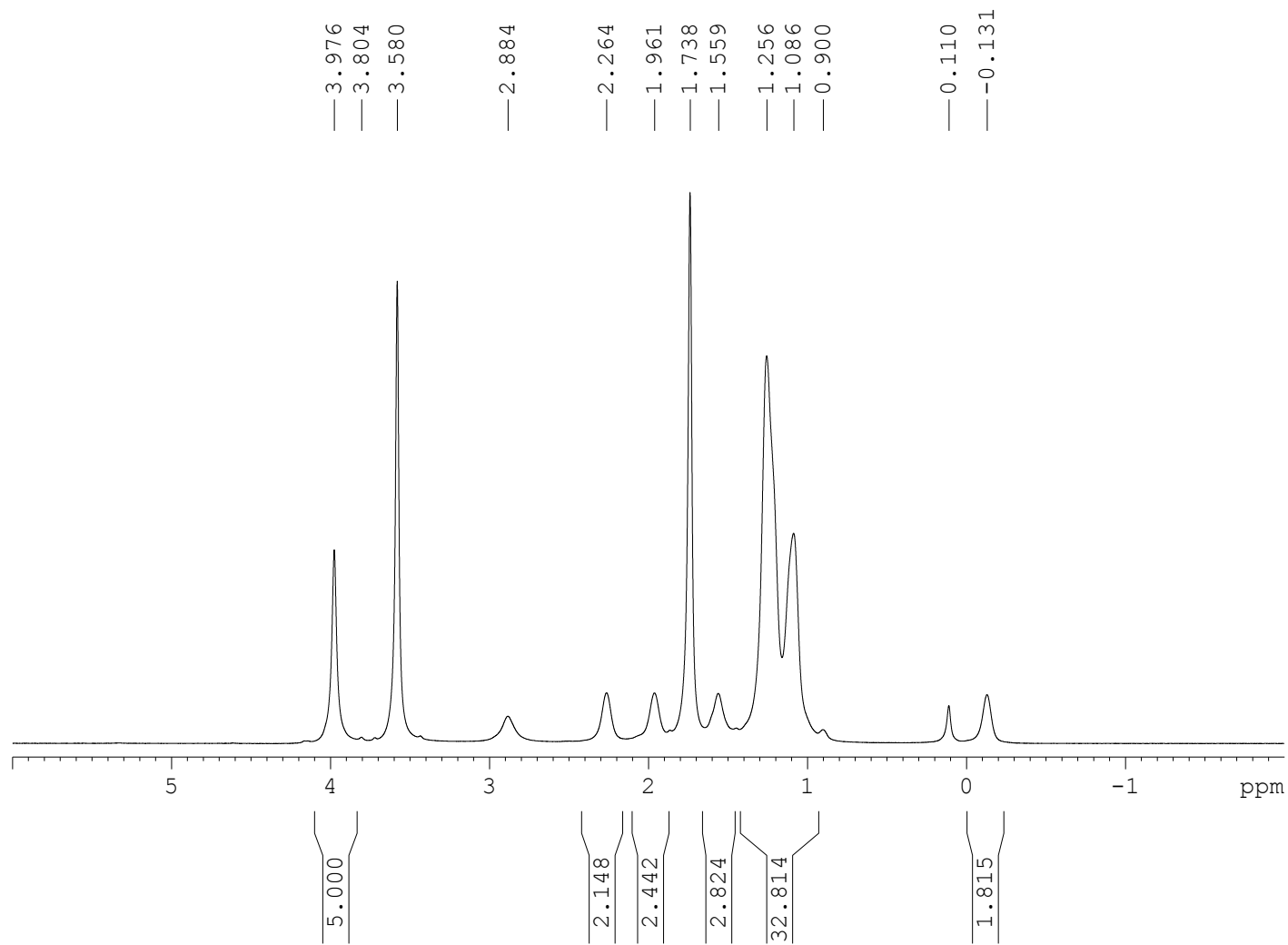
$^{13}\text{C}$ -NMR (100 MHz,  $-80^\circ\text{C}$ ,  $\text{THF-d}_8$ ) of  $\text{dippp}(\eta^3\text{-C}_6\text{H}_9)(\text{H})\text{Fe}$  (15)



$^{31}\text{P}\{^1\text{H}\}$ -NMR (162 MHz,  $-80^\circ\text{C}$ , THF- $d_8$ ) of  $\text{dippp}(\eta^3\text{-C}_6\text{H}_9)(\text{H})\text{Fe}$  (15)

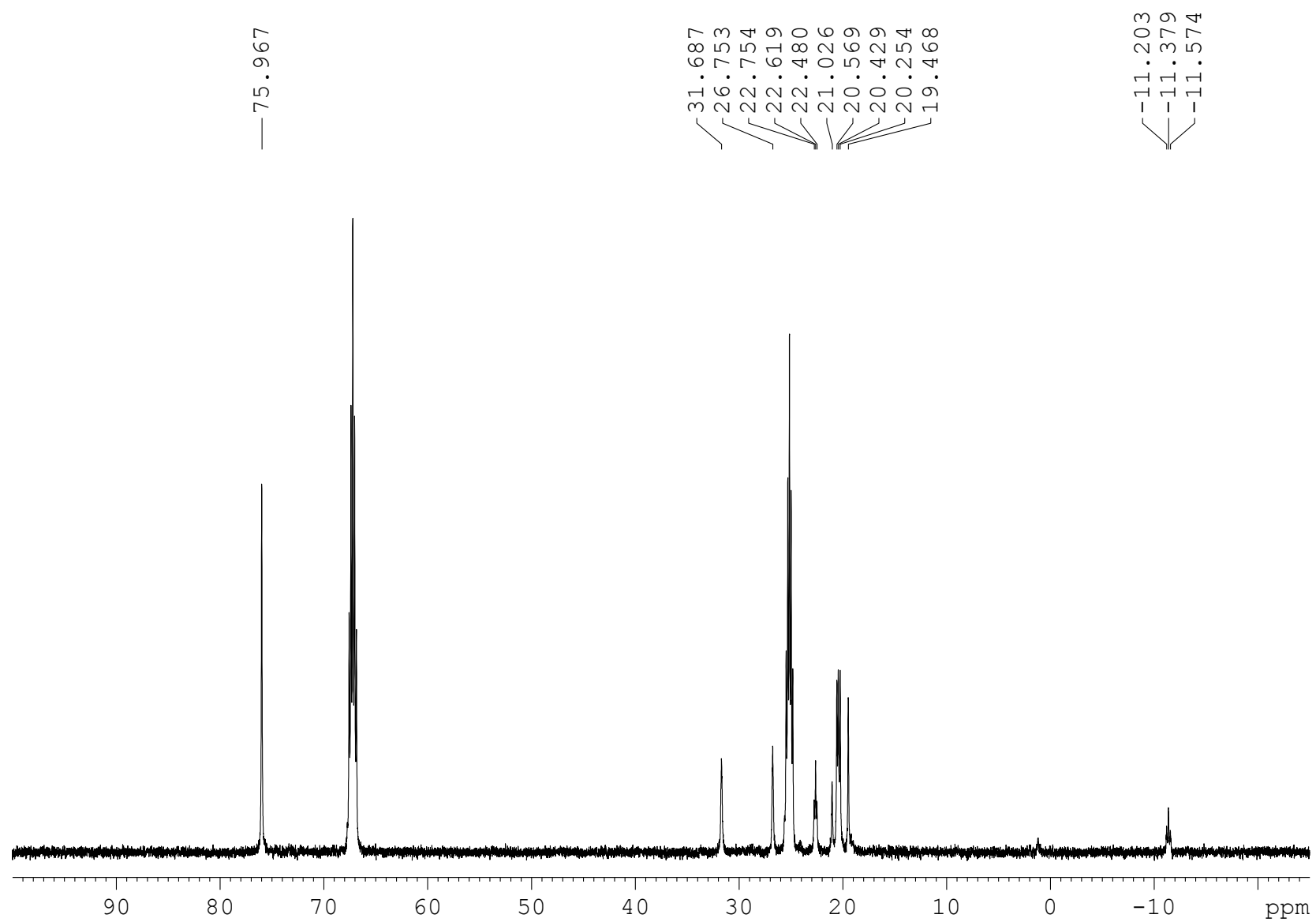


$^1\text{H-NMR}$  (500 MHz,  $-55^\circ\text{C}$ ,  $\text{THF-d}_8$ ) of  $(\text{dippe})(\eta^5\text{-C}_5\text{H}_5)(\text{Et})\text{Fe}$  (20)

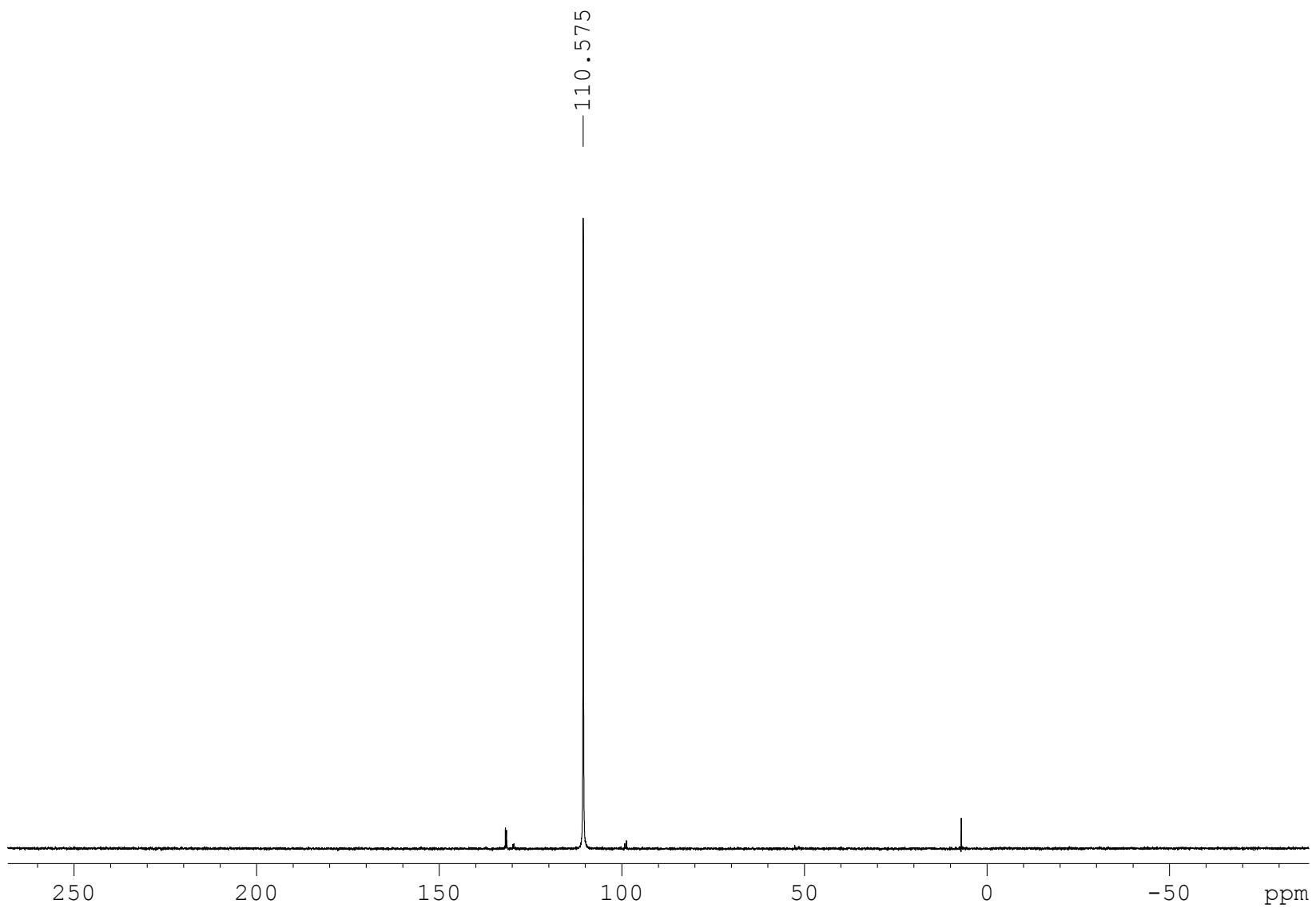




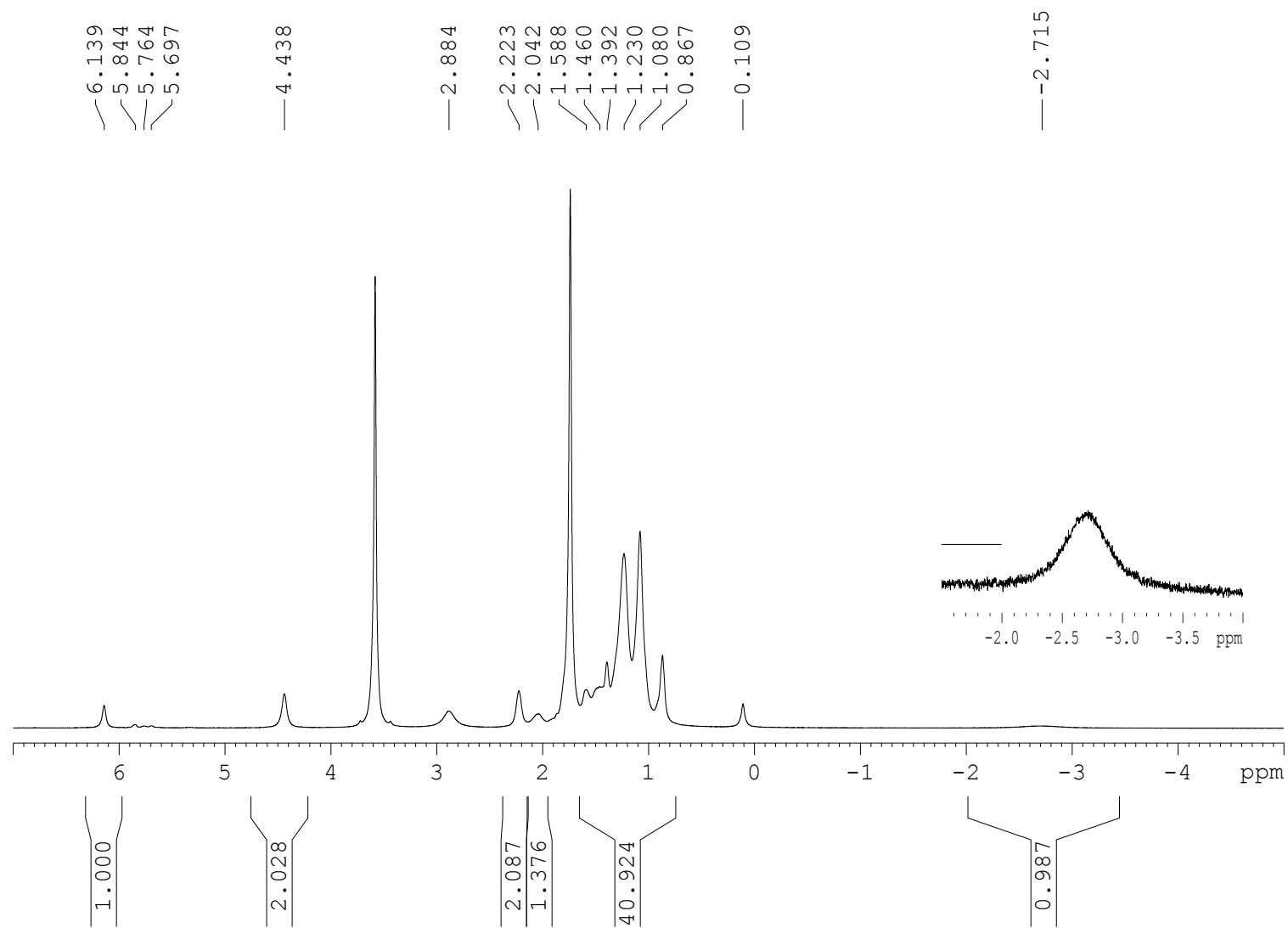
$^{13}\text{C}$ -NMR (126 MHz, 25°C, THF- $d_8$ ) of (dippe)( $\eta^5\text{-C}_5\text{H}_5$ )(Et)Fe (20)



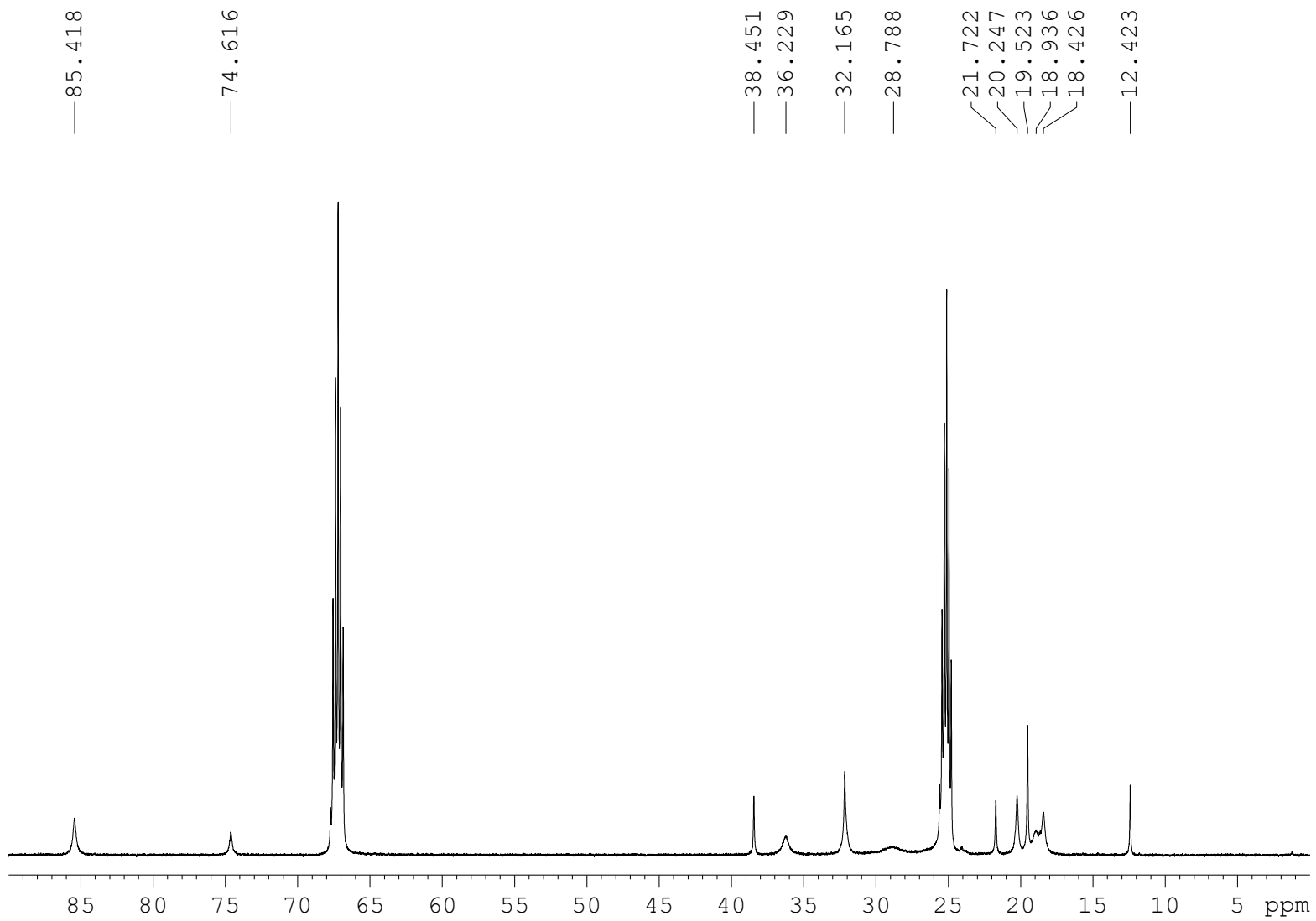
$^{31}\text{P}\{^1\text{H}\}$ -NMR (202 MHz,  $-55^\circ\text{C}$ ,  $\text{THF-d}_8$ ) of  $(\text{dippe})(\eta^5\text{-C}_5\text{H}_5)(\text{Et})\text{Fe}$  (20)



<sup>1</sup>H-NMR (500 MHz, -55°C, THF-d<sub>8</sub>) of (dipp)(η<sup>5</sup>-C<sub>6</sub>H<sub>7</sub>Et-endo)(H)Fe (25)



$^{13}\text{C-NMR}$  (126 MHz,  $-55^\circ\text{C}$ ,  $\text{THF-d}_8$ ) of  $(\text{dipp})_2(\eta^5\text{-C}_6\text{H}_7\text{Et-endo})(\text{H})\text{Fe}$  (25)



$^{31}\text{P}\{^1\text{H}\}$ -NMR (202 MHz,  $-55^\circ\text{C}$ ,  $\text{THF-d}_8$ ) of  $(\text{dipp})\{\eta^5\text{-C}_6\text{H}_7\text{Et-endo}\}(\text{H})\text{Fe}$  (25)

