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# C – O bond activation and subsequent decarbonylation of ester promoted by $Fe(PMe_3)_4$



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#### A R T I C L E I N F O

#### ABSTRACT

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Organic halides are commonly employed as electrophilic coupling partners in transition-metal-catalyzed cross-coupling reactions for the construction of carbon-carbon and carbon-heteroatom bonds [1]. Recently, phenolic derivatives as electrophiles attract much attention [2] since they are cheap and easily available. Iron-catalyzed C<sub>phenol</sub>-O bond activation for the synthesis of trizoles was reported by Shi [2b]. The C-O bond activation of benzyl alcohols with Grignard reagents was studied with Fe, Co and Ni complexes in direct arylation and alkylation [2c]. Phenol-derived electrophiles, such as aryl sulfonates, have also been investigated [3]. Esters, as one kind of phenol derivatives, could be used to construct C-C [4] and C-N [5] bonds. Shi reported the cross-coupling of aryl/alkenyl pivalates with organozinc reagents through nickel-catalyzed C-O bond activation under mild reaction conditions [6]. In general, there are two possible forms of the C-O bond activation for aryl esters: C<sub>acyl</sub>-O or C<sub>arvloxy</sub>-O bond activation. The reaction of electron-rich hydrido iron complex supported by diphosphine ligands with methyl benzoate delivered Cmethoxy-O bond activation product [7], but the related mechanism was not fully discussed [8]. Liu published a theoretical analysis of the Ni-catalyzed cross-coupling reaction of aryl esters and explained the excellent selectivity of C – O bond activation [9]. These results indicate that the  $C_{acvl}$  – O bond cleavage is involved in the oxidative addition of carboxylate esters and this process is reversible. These calculated results are in good agreement with the experimental results.

In this work, it is found that the  $C_{acyl}$ -O bond cleavage occurred, when aryl ester is treated with electron-rich iron(0) complex, Fe(PMe<sub>3</sub>)<sub>4</sub>, but the final product is a carbonyl organoiron(II) phenolate complex. This implies that a decarbonylation ensued after the C-O bond activation. The present work provides a new strategy on C-O

The reactions of 8-quinolinyl esters with iron(0) complex supported by trimethylphosphine ligands afforded four hexa-coordinate chelate-[C,N] iron(II) carbonyl complexes **5–8** via  $C_{acyl} - O$  bond activation and subsequent decarbonylation. Complexes **5–8** were characterized through IR, <sup>1</sup>H NMR, <sup>31</sup>P NMR and elemental analysis. The crystal structures of complexes **5–8** were determined by X-ray diffraction.

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bond activation with nitrogen atom as an anchoring group. To our knowledge, this could be the first example of iron(0)-promoted C–O bond activation.

The reactions of ester 1-4 [10] with Fe(PMe<sub>3</sub>)<sub>4</sub> [11] afforded the hexa-coordinate Fe(II) carbonyl complexes **5–8** via C–O bond activation and subsequent decarbonylation (Eq. (1)) [12].



The iron(II) complexes **5–8** were obtained as red crystals in the yields of 62–87% by crystallization from pentane at -30 °C. Complexes **5–8** in the solid state are stable for several days at room temperature. In the IR spectra of complexes **5–8**, the stretching vibrations of the terminal carbonyl group are situated at 1892 (**5**), 1888 (**6**) 1889 (**7**) and 1876 (**8**) cm<sup>-1</sup> respectively. In the <sup>1</sup>H NMR spectra of the four complexes, the resonances of PMe<sub>3</sub> ligands were recorded as a triplet at 0.73 (**5**), 0.53 (**6**), 0.79 (**7**) and 0.89 (**8**) ppm respectively. Only one <sup>31</sup>P NMR signal was observed at 20.4 (**5**), 33.2 (**6**), 36.0 (**7**) and 36.4 (**8**) ppm. These data imply that two trimethylphosphine ligands are in *trans*orientation. All of the spectroscopic information indicates that complexes **5–8** have a hexa-coordination geometry.

The molecular structures of complexes **5–8** confirm a hexacoordination octahedral geometry in the crystals (Figs. 1–4) [13]. In

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**Fig. 1.** Molecular structure of **5**, selected bond distances (Å) and angles (°): N1 – Fe1 2.017(2), Fe1–C7 1.715(3), Fe1–O2 2.012(2), Fe1–C17 2.013(3), Fe1–P2 2.2352(8), Fe1–P1 2.2368(8), O1–C7 1.165(4); C7–Fe1–O2 176.6(1), P2–Fe1–P1 173.85(3), N1–Fe1–P1 92.71(7), C10–Fe1–P2 174.71(5), C17–Fe1–P1 86.86(8), C17–Fe1–P2 87.26(8), N1–Fe1–P2 93.38(7), O2–Fe1–P1 91.43(6), O2–Fe1–N1 80.94(9), C7–Fe1–P1 90.47(9).

the molecular structure, the iron atom is centered in an octahedron with one N, one O, two C and two P atom(s) at the apical positions. A fivemembered metallacycle is formed through the [C,N]-chelate coordination. Owing to the trans-influence, the CO ligand is located opposite to the phenolate-O atom in all of the four structures. Unlike the *trans*-orientation of the two phosphine ligands in complexes 5, 7 and **8**, the two phosphine ligands in complex **6** are in the *cis*-positions. It could be conjectured that this difference is related to the orthomethyl group in the quinoline ring because this is the only variation between complexes 5 and 6. It might also be caused by packing effect during the crystallization since the two phosphine ligands in complex **6** are also in the *trans*-positions in the solution. This was verified by the NMR data in the solution. The C≡O bond distances of complexes **5–8** (ca. 1.16 Å) are in the normal range. For  $Fe - O_{phenolate}$  bonds, complex **6** has the shortest distance (1.983(1) Å), while complex **5** has the largest distance (2.012(2) Å) among the four complexes.



**Fig. 2.** Molecular structure of **6**, selected bond distances (Å) and angles (°): N1 – Fe1 2.047(2), Fe1 – C15 1.722(2), Fe1 – O2 1.983(1), Fe1 – C10 2.029(2), Fe1 – P2 2.2920(7), Fe1 – P1 2.2179(9), O1 – C15 1.162(3); C15 – Fe1 – O2 172.44(8), N1 – Fe1 – P1 165.14(5), C10 – Fe1 – P2 174.71(5), C15 – Fe1 – N1 104.78(8), C15 – Fe1 – P1 88.11(7), N1 – Fe1 – P2 89.16(5), C10 – Fe1 – P1 86.67(5), O2 – Fe1 – P1 85.62(4), O2 – Fe1 – N1 82.01(6), C15 – Fe1 – C10 91.84(9).



**Fig. 3.** Molecular structure of **7**, selected bond distances (Å) and angles (°): N1 – Fe1 2.018(2), Fe1 – C7 2.014(2), Fe1 – O2 2.004(1), Fe1 – C8 1.722(2), Fe1 – P2 2.2524(5), Fe1 – P1 2.2415(5), O1 – C8 1.166(4); C8 – Fe1 – O2 172.45(7), P2 – Fe1 – P1 175.35(2), N1 – Fe1 – C7 169.43(7), O2 – Fe1 – N1 80.75(6), N1 – Fe1 – C8 91.78(7), C8 – Fe1 – C7 98.70(8), O2 – Fe1 – C7 88.74(6), N1 – Fe1 – P1 92.62(5), C7 – Fe1 – P2 88.82(5), O2 – Fe1 – P2 87.23(4).

However, for Fe–N bonds, complex **6** has the largest distance (2.047(2) Å) among them. This also may be due to the strong *trans*-influence of the trimethylphosphine ligand in complex **6**. Because of the coordination of *n*-pentyl group, Fe1–C7(sp<sup>3</sup>) bond length with 2.062(5) Å in complex **8** is a little bit longer than the other three Fe1–C(sp<sup>2</sup>) bonds. Complex **8** is very stable in the air. No expected  $\beta$ -H elimination product with regard to the *n*-pentyl group was observed. This confirms that the formally negatively-charged *n*-pentyl group well bonds with the central Fe(II) atom at room temperature, especially with the support of the strong backbonding between the iron center and the carbonyl ligand.

In summary, we reported the first  $Fe(PMe_3)_4$  induced  $C_{acyl}-O$  activation and subsequent decarbonylation of 8-quinolinyl esters. In this process, the quinoline-N atom as an anchoring group plays an important role, therefore a chelate ring is formed. The chelation effect thermodynamically facilitates the C-O bond cleavage. It has been experimentally confirmed that no similar  $C_{acyl}-O$  bond activation occurred in the reaction of 1-naphthyl ester with Fe(PMe\_3)\_4. The crystal structures of complexes **5–8** show an octahedral coordination.



**Fig. 4.** Molecular structure of **8**, selected bond distances (Å) and angles (°): N1 – Fe1 2.010(4), Fe1 – C7 1.714(6), Fe1 – O2 2.008(3), Fe1 – C17 2.062(5), Fe1 – P2 2.246(2), Fe1 – P1 2.235(2), O1 – C7 1.166(6); C7 – Fe1 – O2 178.1(2), C10 – Fe1 – P2 174.71(5), P2 – Fe1 – P1 177.54(7), C7 – Fe1 – C17 93.0(2), O2 – Fe1 – N1 81.3(2), N1 – Fe1 – C7 100.6(2), O2 – Fe1 – C17 85.1(2), N1 – Fe1 – P1 90.6(1).

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#### Appendix A. Supplementary material

CCDC 951489 (**5**), 951490 (**6**), 951491 (**7**) and 951494 (**8**) contain the supplementary crystallographic data. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ ccdc.cam.ac.uk. Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.inoche.2013.12.026.

#### References

- [1] J. Hassan, M. Sévignon, C. Gozzi, E. Schulz, M. Lemaire, Chem. Rev. 102 (2002) 1359–1469;
  - J.-P. Corbet, G. Mignani, Chem. Rev. 106 (2006) 2651–2710; E. Negishi, Acc. Chem. Res. 15 (1982) 340–348.
- [2] B.M. Rosen, K.W. Quasdorf, D.A. Wilson, N. Zhang, A.-M. Resmerita, N.K. Garg, V. Percec, Chem. Rev. 111 (2011) 1346–1416; W. Yan, Q. Wang, Y. Chen, J.L. Petersen, X. Shi, Org. Lett. 12 (2010) 3308–3311; D.G. Yu, X. Wang, R.Y. Zhu, S. Luo, X.B. Zhang, B.Q. Wang, L. Wang, Z.J. Shi, J. Am.
- Chem, Soc. 134 (2012) 14638-14641.
   W.K. Chow, C.M. So, C.P. Lau, F.Y. Kwong, J. Org. Chem. 75 (2010) 5109–5112;
- B. Bhayana, B.P. Fors, S.L. Buchwald, Org. Lett. 11 (2009) 3954–3957; R.H. Munday, J.R. Martinelli, S.L. Buchwald, J. Am. Chem. Soc. 130 (2008) 2754–2755.
- [4] B.T. Guan, Y. Wang, B.-J. Li, D.-G. Yu, Z.-J. Shi, J. Am. Chem. Soc. 130 (2008) 14468–14470;
- G.A. Molander, F. Beaumard, Org. Lett. 12 (2010) 4022–4025.
  [5] T. Gerfaud, L. Neuville, J.P. Zhu, Angew. Chem. Int. Ed. 48 (2009) 572–577;
- [3] I. Geriada, E. Kettinic, J. 21d, Angew. Chem. Int. Ed. 49 (2003) 572–577,
   T. Shimasaki, M. Tobisu, N. Chatani, Angew. Chem. Int. Ed. 49 (2010) 2929–2932.
   [3] F. Michael E. Michael K. G. Guidella, J. Chem. Chem. 101 (1977)
- [6] E. Wenkert, E.L. Michelotti, C.S. Swindell, J. Am. Chem. Soc. 101 (1979) 2246–2247;
   B.J. Li, Y.Z. Li, X.Y. Lu, J. Liu, B.T. Guan, Z.J. Shi, Angew. Chem. Int. Ed. 47 (2008) 10124–10127.
- [7] S.D. Ittel, C.A. Tolman, A.D. English, J.P. Jesson, J. Am. Chem. Soc. 100 (1978) 7577–7585.
- [8] C.A. Tolman, S.D. Ittel, A.D. English, J.P. Jesson, J. Am. Chem. Soc. 101 (1979) 1742–1751.
- [9] Z. Li, S.L. Zhang, Y. Fu, Q.X. Guo, L. Liu, J. Am. Chem. Soc. 131 (2009) 8815–8823.
- [10] M.A. Altmeyer, A. Marschner, R. Schiffmann, C.D. Klein, Bioorg. Med. Chem. Lett. 20 (2010) 4038–4044.
- [11] H.H. Karsch, H.-F. Klein, H. Schmidbaur, Chem. Ber. 110 (1977) 2200-2212.
- [12] Synthesis of **5**: A solution of compound **1** (0.50 g, 2.0 mmol) in THF (50 ml) was added to the solution of Fe(PMe<sub>3</sub>)<sub>4</sub> (0.72 g, 2.0 mmol) in THF (50 ml) at -80 °C. This mixture was allowed to warm to 20 °C and stirred for 6 h to form a brown solution. The volatiles were transferred under vacuum, and the residue was extracted with pentane (40 ml) and diethyl ether (30 ml) respectively. Crystallization from pentane at -30 °C afforded brown single crystals of **5** (0.74 g, 81%) suitable for X-ray analysis. Anal. Calcd for **5**,  $c_{21}H_{29}\text{FeNO}_2P_2$  (457.25 g mol<sup>-1</sup>): C, 55.16; H, 6.39; N, 3.06. Found: C, 55.42; H, 6.63; N, 2.97. IR (Nujol mull. cm<sup>-1</sup>): 3049  $\nu(C_{Ar}-H)$ , 1892  $\nu(CO)$ , 1591 $\nu(C=N)$ , 1562  $\nu(C=C)$ , 942  $\rho(PMe_3)$ . <sup>1</sup>H NMR (300 MHz,  $C_6D_6$ , 297 K):  $\delta$  0.73 (t', <sup>2</sup>J(PH) + <sup>4</sup>J(PH) = 7.8 Hz, 18H, PCH<sub>3</sub>), 6.61

(dd, J = 4.8 Hz, 1H,  $H_{quinoline-6}$ ), 6.72 (d, J = 7.8 Hz, 1H,  $H_{quinoline-7}$ ), 7.34 (d, J = 7.8 Hz, 1H,  $H_{quinoline-5}$ ), 7.34 (m, J = 7.8Hz, 5H,  $C_6H_5$ ), 7.95 (d, J = 7.2 Hz, 1H,  $H_{quinoline-5}$ ), 7.34 (m, J = 7.8Hz, 5H,  $C_6H_5$ ), 7.95 (d, J = 7.2 Hz, 1H,  $H_{quinoline-5}$ ), 7.34 (m, J = 7.8Hz, 5H,  $C_6H_5$ ), 7.95 (d, J = 7.2 Hz, 1H,  $H_{quinoline-5}$ ), 7.95 (d,  $H_{quin$  $H_{quinoline-2}$ , R.68 (dd, J = 1.5 Hz, 1H,  $H_{quinoline-3}$ ), 901 (d, J = 7.8 Hz, 1H,  $H_{quinoline-2}$ ) ppm. <sup>31</sup>P NMR (121 MHz, C<sub>6</sub>D<sub>6</sub>, 297 K):  $\delta$  20.4 (s, *P*CH<sub>3</sub>) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, 297 K):  $\delta$  169.1, 168.9, 168.5, 147.7, 146.7, 144.4, 139.3, 134.1, 130.2, 129.8, 125.7, 125.1, 121.4, 120.7, 113.7, 107.4, 12.9 (t',  ${}^{1}J(PC) + {}^{3}J(PC) =$ 23 Hz, PCH<sub>3</sub>) ppm.Complexes 6-8 were synthesized according to the similar method as that for complex 5. Synthesis of 6: Complex 6 as yellow crystals was obtained in the yield of 62%. Anal. Calc. for **6**, C<sub>23</sub>H<sub>3</sub>FeNO<sub>2</sub>P<sub>2</sub> (471.28 g mol<sup>-1</sup>): C, 58.62; H, 6.63; N, 2.97. Found: C, 59.02; H, 6.70; N, 3.12. IR (Nujol mull, cm<sup>-1</sup>): 3063  $\nu(C_{Ar}-H)$ , 1888  $\nu(CO)$ , 1600  $\nu(C=N)$ , 1564  $\nu(C=C)$ , 947  $\rho(PMe_3)$ . 1H NMR (300 MHz, C6D6, 297 K):  $\delta$  0.53 (t', <sup>2</sup>J(PH) + <sup>4</sup>J(PH) = 6.0 Hz, 18H, PCH<sub>3</sub>), 2.68 (s, 3H, Ar-CH<sub>3</sub>), 6.41 (d, J = 8.4 Hz, 1H, H<sub>quinoline-7</sub>), 6.53 (dd, J = 6 Hz, 1H, Hquinoline-5), 7.01 (m, 1H, C6H5), 7.10 (m, 1H, Hquinoline-6), 7.24 (m, 4H, C6H5), NMR (121 MHz, C6D6, 297 K): δ 33.2 (s, PCH3) ppm. <sup>13</sup>C NMR (75 MHz, CDCI3, 297 K): δ 169.1, 166.4, 166.0, 165.6, 157.9, 147.0, 142.8, 139.6, 135.4, 128.9, 128.1, 125.7, 125.1, 123.5, 120.7, 114.3, 107.5, 29.1, 13.4 (t',  ${}^{1}J(PC) + {}^{3}J(PC) = 23$  Hz, PCH3) ppm.Synthesis of **7**: Complex **7** as yellow crystals was obtained in the yield of 72%. Anal. Calcd for **7**,  $C_{22}H_{28}$ CIFeNO<sub>2</sub>P<sub>2</sub> (491.69 g mol<sup>-1</sup>): C, 53.74; H, 5.74; N, 2. 85. Found: C, 53.87; H, 5.69; N, 2. 92. IR (Nujol mull, cm<sup>-1</sup>): 3086  $\nu$ (C<sub>Ar</sub>-H), 1889  $\nu$ (CO), 1599  $\nu$ (C=N), 1562  $\nu$ (C=C), 940  $\rho$ (PMe<sub>3</sub>). <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>, 297 K):  $\delta 0.79$  (t<sup>2</sup>, <sup>2</sup>*J*(PH) + <sup>4</sup>*J*(PH) = 7.8 Hz, 18H, PCH<sub>3</sub>), 6.63 (dd, *J* = 4.8 Hz, 1H, H<sub>quinoline-6</sub>), 6.70 (d, *J* = 7.8 Hz, 1H, H<sub>quinoline-7</sub>), 6.99 (m, *J* = 2.7 Hz, 1H, H<sub>quinoline-6</sub>) H<sub>phenyl-4</sub>), 7.22(ddd, J = 7.2 Hz, 1H, H<sub>phenyl-5</sub>), 7.34 (d, J = 7.8 Hz, 1H, H<sub>quinoline-5</sub>), 7.45 (t, J = 7.8 Hz, 1H, H<sub>quinoline-4</sub>), 7.49 (dd, J = 7.8 Hz, 1H, H<sub>phenyl-6</sub>), 7.55 (dd, J = 7.8 Hz, 1H, H<sub>phenyl-3</sub>), 8. 78 (m, J = 5.1 Hz, 1H, H<sub>quinoline-3</sub>), 9. 20 (ddd, J = 7.2 Hz, 1H, H<sub>quinoline-2</sub>) ppm. <sup>31</sup>P NMR (121 MHz, C<sub>6</sub>D<sub>6</sub>, 297 K):  $\delta$  36.0 (s, PCH<sub>3</sub>) ppm.<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, 297 K):  $\delta$  168.6, 168.4, 168.0, 150.4, 148.0, 146.8, 141.9, 134.5, 130.3, 129.8, 127.8, 122.7, 122.6, 121.5, 114.0, 107.7, 13.2  $(t', {}^{1}J(PC) + {}^{3}J(PC) = 24 \text{ Hz}, PCH_{3}) \text{ ppm.Synthesis of } \mathbf{8}: \text{ Complex } \mathbf{8} \text{ as yellow}$ crystals was obtained in the yield of 87 %. Anal. Calcd for 8, C21H35FeNO2P2 (451.29 g mol<sup>-1</sup>) C, 55.89; H, 7.82; N, 3.10. Found: C, 55.66; H, 7.95; N, 3.02. IR (Nujol mull, cm<sup>-1</sup>): 3050  $\nu$ (C<sub>Ar</sub>-H), 1876  $\nu$ (CO), 1591  $\nu$ (C=N), 1559  $\nu$ (C=C), 943  $\rho$ (PMe<sub>3</sub>). 1H NMR (300 MHz, C6D6, 297 K):  $\delta$  0.89 (t', <sup>2</sup>J(PH) + <sup>4</sup>J(PH) = 7.2 Hz, 18H, PCH3), 1.19 (t, J = 6.9 Hz, 3H, CH<sub>3</sub>), 1.30 (m, 4H, CH2CH2), 1.77 (qd, 4H, CH2CH2), 6.59 (dd, J = 8.4 Hz, 1H, H<sub>quinoline-6</sub>), 6.70 (d, J = 7.8 Hz, 1H, H<sub>quinoline-7</sub>), 7.30 (d, J = 7.8 Hz, 1H, H<sub>quinoline-5</sub>), 7.45 (t, J = 7.8 Hz, 1H, H<sub>quinoline-3</sub>), 7.51 (d, J = 9 Hz, 1H, H<sub>quinoline-4</sub>), 8.57 (d, J = 2.7 Hz, 1H, H<sub>quinoline-2</sub>) ppm. 31P NMR (121 MHz, C6D6, 297 K): δ 36.4 (s, PCH<sub>3</sub>) ppm. <sup>13</sup>C NMR (75 MHz, CDCl3, 297 K): δ 169.4, 147.3, 146.4, 133.7, 130.0, 129.6, 121.2, 113.8, 107.8, 38.3, 35.8, 22.6, 14.5, 12.9,  $12.6 (t', {}^{1}J(PC) + {}^{3}J(PC) = 23 Hz, PCH_{3}) ppm.$ 

[13] Crystallographic data for **5**.  $C_{22}H_{29}FeNO_2P_2$ , Mr = 457.25, monoclinic, space group P2(1)/c, a = 13.1186(4) Å, b = 10.3241(4) Å, c = 16.7455(5) Å,  $\beta$  = 104.184(2) V = 2198.8(1) Å3, T = 298 K, Z = 4, Dc = 1.381 g/cm<sup>3</sup>,  $\mu = 0.849$  mm<sup>-1</sup>. A total of 14,958 reflections were collected, 4380 unique (Rint = 0.0534), R1 = 0.0417(for 4380 reflections with I > 2 sigma(I)), wR2 = 0.1018 (all data).Crystallographic data for **6**.  $C_{23}H_{31}FeNO_2P_2$ , Mr = 471.28, monoclinic, space group P2(1)/c, a = 8.1811(16) Å, b = 11.200(2) Å, c = 26.008(5) Å,  $\beta = 95.60(3)^{\circ}$  V = 2371.8(8) Å3, T = 298 K, Z = 4, Dc = 1.320 g/cm<sup>3</sup>,  $\mu$  = 0.789 mm<sup>-1</sup>. A total of 13,349 reflections were collected, 5232 unique (Rint = 0.0245), R1 = 0.0341 (for 5232 reflections with I > 2 sigma(I)), wR2 = 0.0848 (all data).Crystallographic data for 7.  $C_{22}H_{28}CIFeNO_2P_2$ , Mr = 491.69, monoclinic, space group P2(1)/n, a = 8.9167(8) Å, b = 26.1560(19) Å, c = 9.9759(8) Å,  $\beta = 97.551(7)$ V = 2306.5(3) Å3, T = 298 K, Z = 4, Dc = 1.416 g/cm<sup>3</sup>,  $\mu = 0.927$  mm<sup>-1</sup>. A total of 14,409 reflections were collected, 4701 unique (Rint = 0.0534), R1 = 0.0338 (for 4701 reflections with I > 2 sigma(I)), wR2 = 0.0972 (all data).Crystallographic data for **8**.  $C_{21}H_{35}FeNO_2P_2$ , Mr = 451.29, monoclinic, space group P2(1)/c, a = 15.0485(13) Å, b = 10.3042(6) Å, c = 15.6769 (6) Å,  $\beta = 110.559(6)^\circ$  V = 2276.1(3) Å3, T = 298 K, Z = 4, Dc = 1.317 g/cm<sup>3</sup>,  $\mu = 0.819 \text{ mm}^{-1}$ . A total of 9576 reflections were collected, 4545 unique (Rint = 0.0953), R1 = 0.0485 (for 4545 reflections with I > 2 sigma(I)), wR2 = 0.1100 (all data).