

# 단 신

## Methyl-Fe( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)(CO)<sub>2</sub>과 1,2-Bis(diphenylphosphino)ethane의 반응

權 赫 鵬

한남대학교 화학과

(2000. 11. 22 접수)

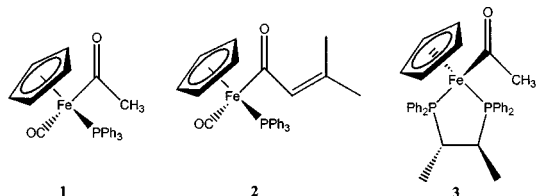
## Reaction of Methyl-Fe( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)(CO)<sub>2</sub> with 1,2-Bis(diphenylphosphino)ethane

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(Received November 22, 2000)

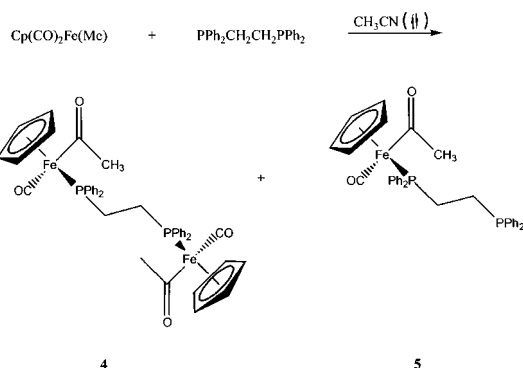
Organoiron complexes have been playing an important role in the development of useful methodologies in organic synthesis.<sup>1</sup> Among those organoiron complexes, acyl-( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Fe(CO)(PPh<sub>3</sub>) (**1**) and related complexes have been well studied as effective reagents for stereo-selective organic transformations.<sup>2,3</sup> Along with those chiral iron-acyl complexes, cyclopentadienyl iron complexes with chelate diphosphine were also studied with limited success of cationic complexes.<sup>4</sup> On the other hand, bidentate chiral diphosphines have been extensively studied over the past several decades and have proved to have excellent stereocontrol, especially with transition metals as catalysts.<sup>5</sup> Therefore, we have initiated studies on the reaction of methyl( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Fe(CO)<sub>2</sub> with bidentate diphosphine as a continuing effort for the synthesis of chiral iron complexes **2** and **3**.<sup>6</sup> In this note, we report an initial result of this reaction.



As a model of chiral chelating diphosphine ligands, 1,2-bis(diphenylphosphino) ethane (DPPE, PPh<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>) was selected for this reaction. A ligand substitution reaction of methyl-( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Fe(CO)<sub>2</sub> with 1,2-bis(diphenylphosphino)ethane (DPPE) was carried out in tetrahy-

drofuran reflux. The progress of the reaction was monitored by IR. This reaction was completed after 30 h of THF reflux. In acetonitrile reflux, the reaction was completed within 16 h in an almost quantitative yield to two chiral iron complexes, *i.e.*, a dinuclear complex **4** and a mononuclear complex **5** with 1:2 ratio.

Instead of the thermal reaction, photochemical ligand substitution was attempted and none of the desired chelate product was again obtained under various reaction conditions, *i.e.*, the amount of DPPE, irradiation period, reaction temperature, solvent, and light source.



## EXPERIMENTAL SECTION

Tetrahydrofuran and acetonitrile were freshly distilled under nitrogen from sodium/benzophenone and calcium hydride, respectively. The following chemicals were pur-

chased from Aldrich and used as received: 1,2-bis(diphenylphosphino)ethane, Fp dimer, activated neutral alumina and basic alumina, ~150 mesh. Infrared spectra were recorded on a Perkin-Elmer Spectrum 1000 FT-IR spectrophotometer. NMR spectra were measured at 300 MHz on a Varian Mercury 300 spectrometer. All <sup>1</sup>H NMR absorptions were expressed in parts per million ( $\delta$ ) relative to tetramethylsilane (Me<sub>4</sub>Si) as an internal standard. All <sup>31</sup>P NMR absorptions were expressed in parts per million ( $\delta$ ) relative to 85% phosphoric acid (H<sub>3</sub>PO<sub>4</sub>) as an external standard. Melting points were determined on a Mel-Temp II capillary melting point apparatus and reported uncorrected. Analytical TLC was conducted on precoated aluminum plates available from Merck (neutral aluminium oxide 60 F<sub>245</sub>, Type E). Elemental analyses were performed by M-H-W Laboratories in Phoenix, AZ. All reactions were run under a nitrogen atmosphere with a mineral oil bubbler so the system was maintained under a positive nitrogen pressure unless otherwise stated.

**Reaction of MeFe( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)(CO)<sub>2</sub> and 1,2-bis(diphenylphosphino)ethane.** A yellow solution of MeFe( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)(CO)<sub>2</sub> (192 mg, 1 mmole) and 1,2-bis(diphenylphosphino)ethane (410 mg, 1.03 mmole) in acetonitrile (25 mL) was stirred at reflux for 16 h. Solvent removed to give brown oil, which was purified by column chromatography on basic alumina with EtOAc-CHCl<sub>3</sub> (CHCl<sub>3</sub>/EtOAc=20) as eluent to yield ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)(CO)(COCH<sub>3</sub>)Fe(PPh<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>) (1) (194 mg, 0.247 mmole, 49% yield based on methyl-Fp) and ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)(CO)(COCH<sub>3</sub>)Fe(PPh<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>) (2) (292 mg, 0.495 mmole), 49% yield based on methyl-Fp) as orange solids.

( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)(CO)(COCH<sub>3</sub>)Fe(PPh<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)Fe( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)(CO)(COCH<sub>3</sub>) (4): mp. 65-70 °C; IR (KBr disk,  $\nu$ CO, cm<sup>-1</sup>) 1922, 1602; <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS,  $\delta$ ) 2.45-2.05 (m, 4H, -CH<sub>2</sub>H<sub>2</sub>-), 2.44 (s, 3H, Me), 2.48 (s, 3H, Me), 4.4 (d,  $J$ =1.1 Hz, 10H, Cp), 7.2-7.4 (m, 20H, Ph); <sup>31</sup>P {H} NMR (CDCl<sub>3</sub>, 85% H<sub>3</sub>PO<sub>4</sub>, external,  $\delta$ ) 76 (s). Anal. Calcd. for C<sub>42</sub>H<sub>40</sub>FeP<sub>2</sub>O<sub>4</sub>: C, 64.47; H, 5.15. Found: C, 64.57; H, 5.26.

( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)(CO)(COCH<sub>3</sub>)Fe(PPh<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)(5): mp. 56-60 °C; IR (KBr disk,  $\nu$ CO, cm<sup>-1</sup>) 1912, 1602; <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS,  $\delta$ ) 1.65-1.8 (m, 1H, -CHH-), 1.9-2.09 (m,

1H, -CHH-), 2.2-2.32 (m, 1H, -CHH-), 2.4-2.6 (m, 1H, -CHH-), 2.48 (s, 3H, Me), 4.34 (d,  $J$ =1.1 Hz, 5H, Cp), 7.25-7.45 (m, 20H, Ph); <sup>31</sup>P {H} NMR (CDCl<sub>3</sub>, H<sub>3</sub>PO<sub>4</sub> (85%, external, ) 75.2 (d,  $J$ =37 Hz), -11.6 (d,  $J$ =37 Hz). Anal. Calcd for C<sub>34</sub>H<sub>32</sub>FeP<sub>2</sub>O<sub>2</sub>: C, 69.16; H, 5.46. Found: C, 68.99; H, 5.46.

## REFERENCES

- (a) Koerner Von Gustorf, E. A.; Grevels, F. W. *The Organic Chemistry of Iron*, Fisher, I., Eds.; Academic Press: New York, 1978. (b) Wilkinson, G.; Stone, F. G. A.; Abel, E. W., Eds.; *In Comprehensive Organometallic Chemistry*, Pergamon Press: Oxford, U. K., 1982; vol. 4, pp. 243-649. (c) *ibid*, vol 8, pp. 939-1012. (d) Abel, E. W.; Stone, F. G. A.; *In Comprehensive Organometallic Chemistry II*, Wilkinson, G., Eds.; Pergamon Press: Oxford, U. K., 1995; vol. 7, pp. 1-289. (e) Abel, E. W.; Stone, F. G. A.; Wilkinson, G., Eds.; *In Comprehensive Organometallic Chemistry II*, Pergamon Press: Oxford, U. K., 1995; vol. 12.
- (a) Davies, S. G. *Pure Appl. Chem.* **1988**, 60, 13. (b) Davies, S. G.; Bashirdes, G.; Coote, S. J.; Goodfellow, C. L.; McNally, J. P. *New Aspects of Organic Chemistry*, Yoshida, J.; Shiba, T.; Ohshiro, Y., Eds.; VCH: Basel, 1990; vol 1, p 81. (c) Davies, S. G.; Dupont, J.; Easton, R. J. C. *Tetrahedron Asymmetry* **1990**, 1, 279. (d) Davies, S. G.; Polywka, R.; Warner, P. *Tetrahedron* **1990**, 46, 4847.
- Liebskind, L. S.; Welker, M. E.; Fengl, R. W. *J. Am. Chem. Soc.* **1986**, 108, 6328.
- (a) Riely, P. E.; Capshaw, C. E.; Pettit, R. *Inorg. Chem.* **1978**, 17, 408. (b) Sellmann, D.; Kleinschmidt, E. *Angew. Chem. Int. Ed. Engl.* **1975**, 14, 571. (c) Brunner, H.; Rahman, A. F. M. *J. Orgnomet. Chem.* **1981**, 214, 373. (d) Brunner, H.; Rahman, A. F. M.; Bernal, I. *Inorg. Chim. Acta.* **1984**, 83, L93. (e) Davies, S. G.; Simpson, S. J. *J. Chem. Soc. Dalton Trans.* **1983**, 981.
- (a) Whitesell, J. K. *Chem. Rev.* **1989**, 89, 1581. (b) Ojima, I. *Catalytic Asymmetric Synthesis*; VCH: New York, 1993; pp 445-470.
- (a) Kwon, H. B.; Ojima, I. *Bull. Korean Chem. Soc.* **1994**, 15, 849. (b) Kwon, H. B.; Oh, H. S.; Hwang, I. C. *78th Annual Meeting of Korean Chemical Society, Abstract* 1996, p 231.