



NOTE

Synthesis and Characterization of Dicobalt-Iron Complex $(\mu_3\text{-S})\text{FeCo}_2(\text{CO})_7[\text{P}(m\text{-MeC}_6\text{H}_4)_3]_2$

WEI GAO

School of Pharmacy, Henan University of Traditional Chinese Medicine, Zhengzhou 450046, P.R. China

Corresponding author: E-mail: weigao415@aliyun.com

Received: 30 June 2014;

Accepted: 12 September 2014;

Published online: 26 May 2015;

AJC-17287

Treatment of dicobalt-iron complex $(\mu_3\text{-S})\text{FeCo}_2(\text{CO})_9$ (**1**) with $\text{P}(m\text{-MeC}_6\text{H}_4)_3$ in CH_2Cl_2 afforded the dicobalt-iron complex $(\mu_3\text{-S})\text{FeCo}_2(\text{CO})_7[\text{P}(m\text{-MeC}_6\text{H}_4)_3]_2$ (**2**) in 49 % yield. The new complex **2** was structurally characterized by IR, ^1H NMR, $^{31}\text{P}\{^1\text{H}\}$ NMR and $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy.

Keywords: Dicobalt-iron complex, Monophosphine, Carbonyl substitution.

In recent years, iron-sulfur complexes have received special attention due to their structures in relevance with the biological enzymes¹⁻⁸. The parent complex $(\mu_3\text{-S})\text{FeCo}_2(\text{CO})_9$ was reported many years ago⁹ and its derivatives with monophosphine or diphosphine ligands were also produced by carbonyl substitution¹⁰. Our recent studies concern on the carbonyl substitution of complex **1** with a monophosphine $\text{P}(m\text{-MeC}_6\text{H}_4)_3$ in a mild condition. In this paper, we report the synthesis and characterization of the dicobalt-iron complex $(\mu_3\text{-S})\text{FeCo}_2(\text{CO})_7[\text{P}(m\text{-MeC}_6\text{H}_4)_3]_2$ with a monodentate phosphine ligand.

Reaction and operation was carried out under a dry, oxygen free nitrogen atmosphere with standard Schlenk and vacuum line techniques. Complex **1** was prepared according to the literature procedures. $\text{P}(m\text{-MeC}_6\text{H}_4)_3$ was available commercially and used as received. IR spectra were recorded on a Nicolet 670 FTIR spectrometer. ^1H ($^{31}\text{P}\{^1\text{H}\}$, $^{13}\text{C}\{^1\text{H}\}$) NMR spectra were obtained on a Bruker Avance 500 MHz spectrometer.

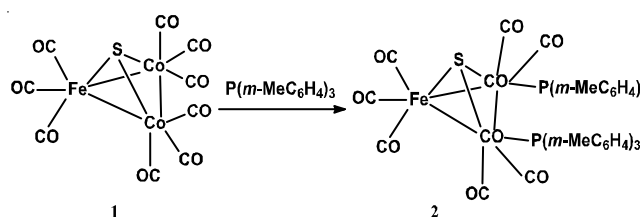
Synthesis: A solution of $(\mu_3\text{-S})\text{FeCo}_2(\text{CO})_9$ (**1**) (0.092 g, 0.2 mmol) and $\text{P}(m\text{-MeC}_6\text{H}_4)_3$ (0.122 g, 0.4 mmol) in CH_2Cl_2 (10 mL) was stirred at room temperature overnight. The solvent was reduced *in vacuo* and the residue was subjected to TLC separation using petroleum ether as eluent. From the main brown band afforded 0.098 g (49 %) of **2** as a black solid. IR (KBr, ν_{max} , cm^{-1}): $\nu_{\text{C=O}}$ 2045 (vs), 2005 (vs), 1981 (vs), 1934 (vs), 1923 (vs). ^1H NMR (500 MHz, CDCl_3): 7.38-7.34 (m, 4H, PhH), 7.25-7.21 (m, 8H, PhH), 2.35 (s, 9H, 3CH₃) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (200 MHz, CDCl_3 , 85 % H_3PO_4): 46.06 (s) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): 211.08 (C=O), 137.87 (t, $J_{\text{P-C}} = 4.9$ Hz, *o*-PhC), 134.89 (d, $J_{\text{P-C}} =$

40.1 Hz, *i*-PhC), 134.27 (t, $J_{\text{P-C}} = 6.2$ Hz, *o*-PhC), 130.80 (s, *p*-PhC), 130.46 (t, $J_{\text{P-C}} = 4.6$ Hz, *m*-PhC), 127.96 (t, $J_{\text{P-C}} = 4.6$ Hz, *m*-PhC), 21.51 (s, CH₃) ppm.

As shown in **Scheme-I**, treatment of the dicobalt-iron complex **1** with 2 equivalents of $\text{P}(m\text{-MeC}_6\text{H}_4)_3$ in CH_2Cl_2 at room temperature afforded the dicobalt-iron complex **2** with monophosphine ligand in 49 % yield. The new complex **2** was air-stable black solids, which has been characterized by IR, ^1H NMR, $^{31}\text{P}\{^1\text{H}\}$ NMR and $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy.

Infrared spectrum: As shown in Fig. 1, the IR spectrum of complex **2** showed five strong absorption bands in the range of 2045-1923 cm^{-1} for the terminal carbonyls and the values are moved towards lower frequencies relative to complex **1** (2106, 2067, 2054, 2041, 2029 and 1973 cm^{-1})¹¹ because $\text{P}(m\text{-MeC}_6\text{H}_4)_3$ is stronger electron-donating than CO.

^1H NMR spectrum: As shown in Fig. 2, the ^1H NMR spectrum of the title complex **2** displayed two multiplets at δ 7.38-7.34 and 7.25-7.21 ppm for the phenyl protons and a singlet at δ 2.35 ppm for the methyl protons.



Scheme-I: Synthesis of the title complex **2**

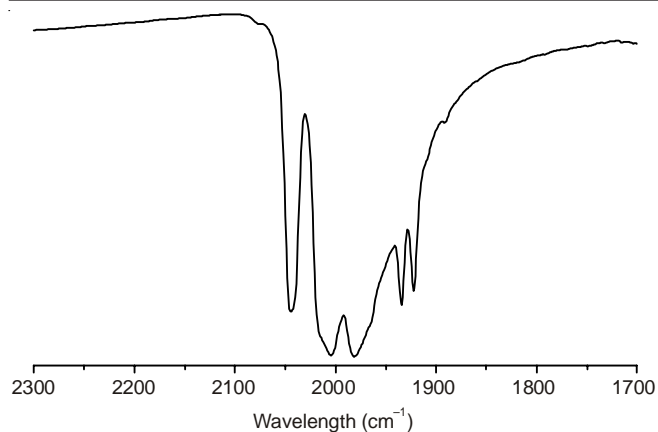
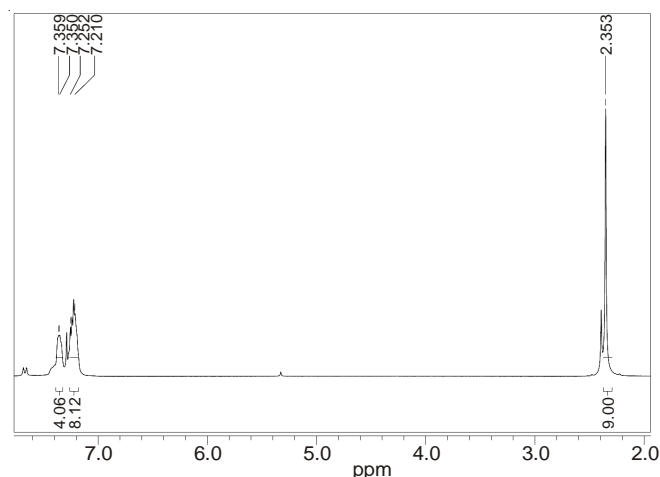
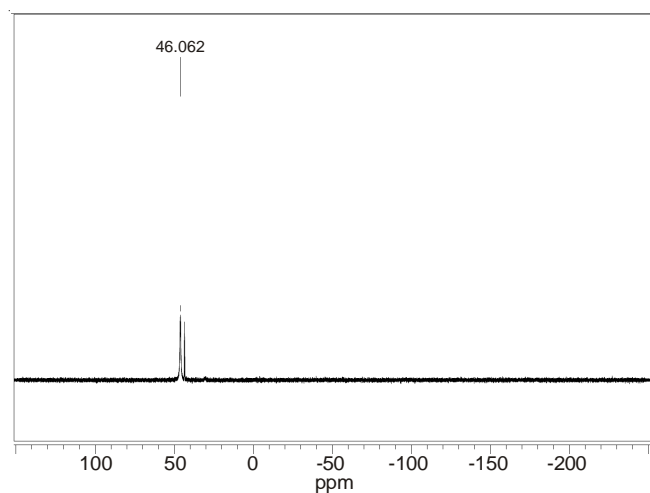


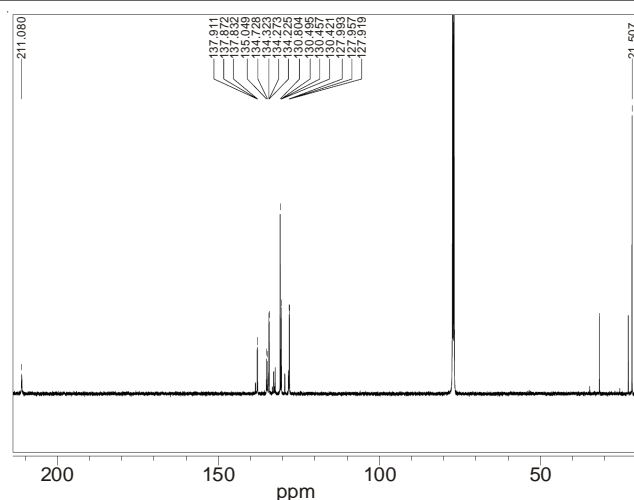
Fig. 1. IR spectrum of the title complex 2

Fig. 2. ^1H NMR spectrum of the title complex 2

$^{31}\text{P}\{^1\text{H}\}$ NMR spectrum: As shown in Fig. 3, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the title complex 2 exhibited a singlet at δ 46.06 ppm for the phosphorus atom of $\text{P}(\text{m-MeC}_6\text{H}_4)_3$ coordinated to the cobalt atoms.

Fig. 3. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the title complex 2

$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum: As shown in Fig. 4, the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of the title complex 2 demonstrated a singlet at δ 211.08 ppm for the terminal carbonyls, four triplets at δ 137.87, 134.27, 130.46 and 127.96 ppm, a doublet at δ 134.89 ppm and a singlet at δ 130.80 ppm for the phenyl carbons and a singlet at δ 21.51 ppm for the methyl carbons.

Fig. 4. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of the title complex 2

ACKNOWLEDGEMENTS

The author gratefully acknowledge the financial support by the Doctoral Research Fund of Henan University of Traditional Chinese Medicine.

REFERENCES

- (a) C.A. Mebi, D.S. Karr and B.C. Noll, *Polyhedron*, **50**, 164 (2013); (b) P.H. Zhao, Y.Q. Liu and X.A. Li, *Asian J. Chem.*, **25**, 5428 (2013); (c) X.F. Liu and B.S. Yin, *J. Coord. Chem.*, **63**, 4061 (2010); (d) C.G. Li, Y.F. Li, J.Y. Shang and T.J. Lou, *Transition Met. Chem.*, **39**, 373 (2014).
- (a) H.G. Cui, N.N. Wu, J.Y. Wang, M.Q. Hu, H.M. Wen and C.N. Chen, *J. Organomet. Chem.*, **767**, 46 (2014); (b) X.F. Liu, Z.Q. Jiang and Z.J. Jia, *Polyhedron*, **33**, 166 (2012); (c) B.S. Yin, T.B. Li and M.S. Yang, *J. Coord. Chem.*, **64**, 2066 (2011); (d) T.H. Yen, K.T. Chu, W.W. Chiu, Y.C. Chien, G.H. Lee and M.H. Chiang, *Polyhedron*, **64**, 247 (2013).
- (a) M. El-khateeb, M. Harb, Q. Abu-Salem, H. Görls and W. Weigand, *Polyhedron*, **61**, 1 (2013); (b) X.F. Liu, *J. Organomet. Chem.*, **750**, 117 (2014); (c) Y.L. Li, B. Xie, L.K. Zou, X.L. Zhang and X. Lin, *J. Organomet. Chem.*, **718**, 74 (2012); (d) W. Gao, J. Yuan and J. Yang, *Asian J. Chem.*, **25**, 9755 (2013).
- (a) S. Ghosh, G. Hogarth, N. Hollingsworth, K.B. Holt, S.E. Kabir and B.E. Sanchez, *Chem. Commun.*, **50**, 945 (2013); (b) X.F. Liu, *Inorg. Chim. Acta*, **421**, 10 (2014); (c) P.H. Zhao, X.H. Li, Y.F. Liu and Y.Q. Liu, *J. Coord. Chem.*, **67**, 766 (2014); (d) E.S. Donovan, G.S. Nichol and G.A.N. Felton, *J. Organomet. Chem.*, **726**, 9 (2013).
- (a) S. Ghosh, G. Hogarth, N. Hollingsworth, K.B. Holt, I. Richards, M.G. Richmond, B.E. Sanchez and D. Unwin, *Dalton Trans.*, **42**, 6775 (2013); (b) Y.L. Li, B. Xie, L.K. Zou, X. Lin, Y. Yang, S.S. Zhu and T. Wang, *Polyhedron*, **67**, 490 (2014); (c) X.F. Liu and H.Q. Gao, *J. Cluster Sci.*, **25**, 367 (2014); (d) W. Gao, L.Q. Tian and J. Yang, *Asian J. Chem.*, **26**, 2086 (2014).
- (a) C.G. Li, Y. Zhu, X.X. Jiao and X.Q. Fu, *Polyhedron*, **67**, 416 (2014); (b) P.H. Zhao, Y.F. Liu, K.K. Xiong and Y.Q. Liu, *J. Clust. Sci.*, **25**, 1061 (2014); (c) X.F. Liu, *Polyhedron*, **72**, 66 (2014); (d) W. Gao, J.Y. Zhang and J. Yang, *Asian J. Chem.*, **26**, 2089 (2014).
- (a) P.H. Zhao, Y.Q. Liu and G.Z. Zhao, *Polyhedron*, **53**, 144 (2013); (b) X.F. Liu and H.Q. Gao, *J. Cluster Sci.*, **25**, 495 (2014); (c) P.H. Zhao, S.N. Liu, Y.F. Liu and Y.Q. Liu, *J. Clust. Sci.*, **25**, 1331 (2014).
- (a) P.H. Zhao, W.T. Wang, Y.F. Liu and Y.Q. Liu, *Transition Met. Chem.*, **39**, 501 (2014); (b) P.H. Zhao, M. Zhang and G.Z. Zhao, *Asian J. Chem.*, **25**, 5068 (2013); (c) X.F. Liu, X.Y. Yu and H.Q. Gao, *Mol. Cryst. Liq. Cryst.*, **592**, 229 (2014).
- S. A. Khattab, L. Markó, G. Bor and B. Markó, *J. Organomet. Chem.*, **1**, 373 (1964).
- (a) L.J. Luo, X.F. Liu and H.Q. Gao, *J. Coord. Chem.*, **66**, 1077 (2013); (b) X.F. Liu and H.Q. Gao, *Polyhedron*, **65**, 1 (2013); (c) X.F. Liu, M.Y. Chen and H.Q. Gao, *J. Coord. Chem.*, **67**, 57 (2014).
- M. Cowie, R.L. Dekock, T.R. Wagenmaker, D. Seyferth, R.S. Henderson and M.K. Gallagher, *Organometallics*, **8**, 119 (1989).