Supplementary Information

A new PC(sp^3)P ligand and its coordination chemistry with low-valent iron, cobalt and nickel complexes

Gengyu Zhu, Xiaoyan Li, Guoqiang Xu, Lin Wang, Hongjian Sun*

School of Chemistry and Chemical Engineering, Key Laboratory of Special Functional Aggregated Materials, Ministry of Education, Shandong University, Shanda Nanlu 27, 250100 Jinan, People's Republic of China

General methods Standard vacuum techniques were used in the manipulations of volatile and air-sensitive materials. Solvents were dried by known procedures and distilled under nitrogen before use. The compounds $Fe(PMe_3)_4$,[1] $Co(PMe_3)_4$,[2] $Co(Me)(PMe_3)_4$,[2] $Ni(PMe_3)_4$,[3] $Ni(Me)_2(PMe_3)_3$[4] and dipyrromethane[5] were prepared according to literature procedures. All other chemicals were used as received without further purification. IR spectra were recorded on a Bruker ALPHA FT-IR instrument from Nujol mulls between KBr disks. NMR spectra were recorded on Bruker Avance 300 MHz spectrometers. Melting points were measured in capillaries sealed under N_2 and were uncorrected. Elemental analyses were carried out on an Elementar Vario ELIII instrument.

[PCH_2P] (1) To a solution of dipyrromethane (500 mg, 3.42 mmol) in 40 mL THF NaH (684 mg, 17.1 mmol) was added slowly at 25 °C. The resulting suspension was stirred for 1.5 h and was then treated dropwise with a solution of Ph_2PCl (1.54 g, 6.84 mmol) in 10 mL THF. The reaction mixture was stirred for 10 h. All volatiles were removed under vacuum, and the residue was extracted with diethyl ether. The crude product was purified by column chromatography on silica gel (EtOAc: petroleum ether = 8 : 1) under N_2 to give a colorless viscous oil. Yield: 62% (1.1 g, 2.14 mmol). ^1H NMR (300 MHz, $CDCl_3$, 298 K): δ (ppm) 4.81 (s, 2H, -C*H*$_2$-), 6.31 (br s, 2H, py-*H*), 6.43 (t, *J* = 3.0 Hz, 2H, py-*H*), 6.65 (t, *J* = 1.5 Hz, 2H, py-*H*), 7.08-7.10 (m, 12H, Ar-*H*), 7.33 - 7.39 (m, 8H, Ar-*H*). ^{13}C NMR (75 MHz, $CDCl_3$, 298 K): δ (ppm) 25.4 (t, *J* = 18.0 Hz, -*C*H$_2$-), 109.9 (t, *J* = 2.2 Hz), 110.4 (s), 122.7 (d, *J* = 6.7 Hz), 127.3 (d, *J* = 6.4 Hz), 128.1 (s), 131.2 (d, *J* = 22.5 Hz), 136.2-136.5 (m). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$, 298 K): δ (ppm) 35.1 (s).

[PCHP]Fe(H)(PMe_3)$_2$ (2) [PCH_2P] (**1**) (700 mg, 1.36 mmol) in 30 mL THF was combined with a solution of $Fe(PMe_3)_4$ (500 mg, 1.39 mmol) in 20 mL THF with stirring at 0 °C. The reaction mixture was allowed to warm slowly to room temperature and stirred for 24 h. During this time the color of the solution gradually changed to dark brown. The volatiles were removed under vacuum, and the residue was extracted with pentane and diethyl ether. Complex **2** (660 mg, 0.91 mmol) was isolated as golden yellow needles in 67% yield from diethyl ether at -20 °C. m.p.: >108 °C dec. Anal. Calcd for $C_{39}H_{46}FeN_2P_4$ (722.51 g/mol): C, 64.83; H, 6.42; N, 3.88. Found: C, 65.02; H, 6.31; N, 3.67. IR (Nujol, KBr): 3075, 3050 (Ar-H), 1922 (Fe-H), 1545 (ArC=C), 936 (PMe_3) cm^{-1}. ^1H NMR (300 MHz, benzene-*d*$_6$, 298 K):δ (ppm) -13.36 (tdd, *J* = 71.1, 32.7, 20.7 Hz, 1H, Fe*H*), 0.76 (d, *J* = 5.4 Hz, 9H, P*Me*$_3$), 0.87 (d, *J* = 6.3 Hz, 9H, P*Me*$_3$), 4.30 (d, *J* = 13.8 Hz, 1H, FeC*H*), 6.39 (br s, 2H, py-*H*), 6.63 (br s, 2H, py-*H*), 6.70 (m, 2H, py-*H*), 7.11 (m, 6H, Ar-*H*), 7.18 (m, 6H, Ar-*H*)), 7.71 (m, 4H, Ar-*H*), 8.02 (m, 4H, Ar-H). ^{31}P{^{1}H} NMR (121 MHz, benzene-d_6, 298 K): δ (ppm) 8.4 (dt, *J* = 30 and 20 Hz, 1P, *P*Me_3), 14.2 (dt, *J* = 30 and 20 Hz, 1P, *P*Me_3), 123.0 (t, *J* = 20 Hz, 2P, *P*Ph_2).

[PCH_2P]Co(PMe_3)$_2$ (3) [PCH_2P] (**1**) (760 mg, 1.48 mmol) in 30 mL THF was combined with a solution of Co(PMe_3)$_4$ (550 mg, 1.51 mmol) in 20 mL THF with stirring at 0 °C. The mixture was stirred for 24 h at room temperature and the solution gradually changed from deep yellow to red brown. The solvent was removed under vacuum and the residue was extracted with pentane and diethyl ether. Complex **3** (740 mg, 1.02 mmol) was crystalized as dark red blocks in 69% yield from diethyl ether at 0 °C. m. p.: >123 °C dec. Anal. Calcd for $C_{39}H_{46}CoN_2P_4$ (725.59 g/mol): C, 64.55; H, 6.39; N, 3.86. Found: C, 64.72; H, 6.30; N, 3.72. IR (Nujol, KBr): 3053 (Ar-H), 1579 (ArC=C), 942 (PMe_3) cm^{-1}.

[PCHP]Co(PMe_3)$_2$ (4) [PCH_2P] (**1**) (840 mg, 1.63 mmol) in 40 mL diethyl ether was combined with a solution of Co(Me)(PMe_3)$_4$ (630 mg, 1.66 mmol) in 20 mL diethyl ether with stirring at -78 °C. The reaction mixture was warmed slowly to room temperature with the solution color changing from bright red to deep red. The mixture was kept stirring for 16 h, and a large amount of red powder precipitated from the solution. The powder was collected on a pad of Celite, washed with pentane, and extracted with diethyl ether. Complex **4** (1.0 g, 1.37 mmol) was isolated as dark red crystals in 84% yield at 0 °C. m.p.: >167 °C dec. Anal. Calcd for $C_{39}H_{45}CoN_2P_4$ (724.58 g/mol): C, 64.64; H, 6.26; N, 3.86. Found:. C, 65.05; H, 6.41; N, 3.92. IR (Nujol, KBr): 3051 (Ar-H), 1580 (ArC=C), 947 (PMe_3) cm^{-1}. ^{1}H NMR (300 MHz, benzene-d_6, 298 K): δ (ppm) 0.76 (d, *J* = 7.2 Hz, 9H, P*Me₃*), 1.06 (d, *J* = 5.7 Hz, 9H, P*Me₃*), 3.88 (d, *J* = 15.6 Hz, 1H, CoC*H*), 6.16 (s, 2H, py-*H*), 6.48 (m, 2H, py-*H*), 6.52 (s, 2H, py-*H*), 7.18 (m, 12H, Ar-*H*), 7.69 (m, 4H, Ar-*H*), 7.80 (m, 4H, Ar-*H*). ^{1}P{^{1}H} NMR (121 MHz, benzene-d_6, 298 K): δ (ppm) -11.4 (m, 1P, *P*Me_3), 9.6 (m, 1P, *P*Me_3), 91.6 (m, 2P, *P*Ph_2).

[PCH_2P]Ni(PMe_3)$_2$ (5) (a) [PCH_2P] (**1**) (810 mg, 1.57 mmol) in 40 mL diethyl ether was combined with a solution of Ni(PMe_3)$_4$ (580 mg, 1.60 mmol) in 20 mL diethyl ether with stirring at room temperature. The solution gradually changed from light yellow to orange-red with precipitation of a small amount of orange power in 16 h. The solvent was removed under vacuum, and the residue was extracted with pentane and diethyl ether. Complex **5** (890 mg, 1.23 mmol) was isolated as orange crystals in 78% yield from both pentane and diethyl ether at 0 °C. (b) [PCH_2P] (**1**) (790 mg, 1.54 mmol) in 40 mL diethyl ether was combined with a solution of Ni(Me)$_2$(PMe_3)$_3$ (600 mg, 1.53 mmol) in 20 mL diethyl ether with stirring at 0 °C. The solution was warmed slowly to room temperature and stirred for an additional 14 h. Complex **5** (830 mg, 1.14 mmol) was isolated by the same method described in (a) in 75% yield. m.p.: >129 °C dec. Anal. Calcd for $C_{39}H_{46}NiN_2P_4$ (725.37 g/mol): C, 64.58; H, 6.39; N, 3.86. Found: C, 64.48; H, 6.29; N, 3.81. IR (Nujol, KBr): 3054 (Ar-H), 1580, 1550 (ArC=C), 941 (PMe_3) cm^{-1}.

General procedure for attempted catalytic reduction To a 25 mL Schlenk tube containing a yellow solution of **2** (0.01 or 0.02 mmol) in 3 mL of solvent (THF, toluene or MeCN) were added benzaldehyde (1.0 mmol) and $(EtO)_3SiH$ (1.2 mmol). The reaction mixture was stirred at 25, 60 or

80 °C and monitored by TLC and GC. The solution turned colorless gradually upon heating, and no product was found.

X-ray crystallography Intensity data were collected on a Bruker SMART diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Summary of the crystal data, data collection and refinement for structures of **2**, **3**, **4** and **5** are given in **Table S1**. The structures were resolved by direct or Patterson methods with the SHELXS-97 program and were refined on F^2 with SHELXTL.[6] All non-hydrogen atoms were refined anisotropically. The iron hydride was located directly from the difference map and the position refined. The remaining hydrogen atoms were included in calculated positions and were refined using a riding model. CCDC 986904-986907 (**2-5**) 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.

Table S1. Crystal data for complexes **2**, **3**, **4** and **5**.

	2	**3**	**4**	**5**
Chemical formula	$C_{39}H_{46}FeN_2P_4$	$C_{39}H_{46}CoN_2P_4$	$C_{39}H_{45}CoN_2P_4$	$C_{39}H_{46}N_2NiP_4$
CCDC number	986904	986905	986906	986907
Formula Mass	722.51	725.59	724.58	725.37
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
a/Å	9.4130(19)	19.838(6)	19.854(4)	19.893(8)
b/Å	16.606(3)	10.326(3)	10.268(2)	10.313(4)
c/Å	25.818(5)	18.271(5)	17.816(4)	18.369(8)
α/°	90.00	90.00	90.00	90.00
β/°	91.83(3)	99.722(5)	99.49(3)	99.993(7)
γ/°	90.00	90.00	90.00	90.00
Unit cell volume/Å^3	4033.6(14)	3689.0(18)	3582.2(13)	3711(3)
Temperature/K	153(2)	273(2)	293(2)	273(2)
Space group	*P121/c1*	*P2(1)/c*	*P2(1)/c*	*P2(1)/c*
Formula units / cell, Z	4	4	4	4
Absorption coefficient, μ/mm^{-1}	0.560	0.669	0.688	0.725
No. of reflections measured	22760	20932	17409	21348
No. of independent reflections	7101	8228	6315	8356
R_{int}	0.1067	0.0679	0.0420	0.0622
Final R_1 values ($I > 2\sigma(I)$)	0.0814	0.0616	0.0381	0.0487
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.2436	0.1419	0.0878	0.0996
Final R_1 values (all data)	0.0945	0.1180	0.0548	0.1018
Final $wR(F^2)$ values (all data)	0.2548	0.1716	0.0970	0.1210
Goodness of fit on F^2	1.113	1.016	1.013	0.957

References

1. H.-F. Klein and H. H. Karsch, *Chem. Ber.* 1977, **110**, 2699.
2. H.-F. Klein and H. H. Karsch, *Chem. Ber.* 1975, **108**, 944.
3. H.-F. Klein and H. H. Karsch, *Chem. Ber.* 1976, **109**, 2515.
4. H.-F. Klein and H. H. Karsch, *Chem. Ber.* 1973, **106**, 1433.
5. J. K. Laha, S. Dhanalekshmi, M. Taniguchi, A. Ambroise and J. S. Lindsey, *Org. Process Res. Dev.* 2003, **7**, 799.
6. G. Sheldrick, *Acta Crystallogr.* 2008, **64**, 112.