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A New P,N-Chelating Ligand Combining Phosphaferrocene and Azacymantrene Units

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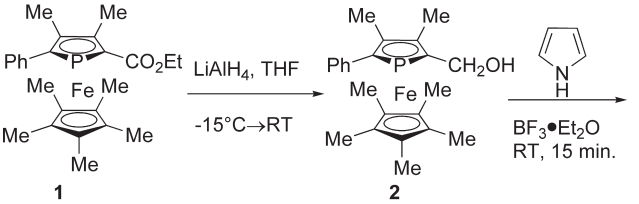
Supporting Information

ABSTRACT: A 2-(ethoxycarbonyl)ferrocene is transformed into a 2-(pyrrolylmethyl)phosphaferrocene, whose reaction with $Mn_2(CO)_{10}$ yields a 2-(azacymantrenylmethyl)phosphaferrocene. This new ligand gives a chelate with $Mo(CO)_4$ whose structure shows that molybdenum is displaced from the P−lone pair axis by 16.5°, indicating that the lone pair is less directional than the N lone pair. It appears that P behaves as a stronger donor than does N in this case.

P,N-chelating ligands derived from phosphaferrocenes have proven their worth in asymmetric catalysis since the work of Fu on phosphaferrocene-oxazolines.[1,2] Other nitrogen heterocycles such as pyridines, pyrazoles, and imidazoles[3−6] have also been combined with phosphaferrocenes in such chelating systems. In this report, we wish to describe and structurally characterize another member of this family based on phosphaferrocenes and azacymantrenes. The use of azacymantrenes offers additional possibilities in asymmetric catalysis resulting from the combination of their own planar chirality with that of phosphaferrocenes. These possibilities will be investigated later.

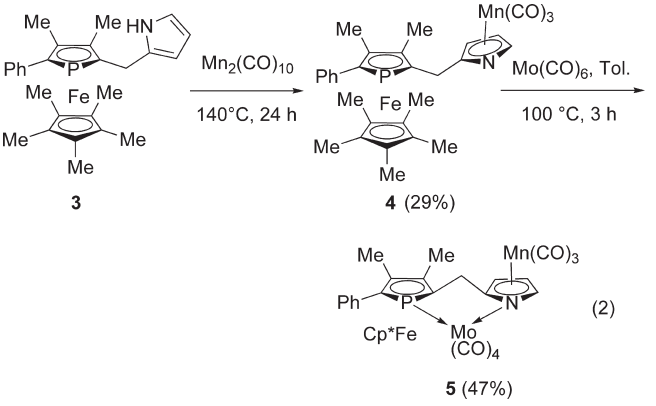
RESULTS AND DISCUSSION

We started from the functional phosphaferrocene **1**, synthesized as shown in Scheme 1. The phenyl substitution is needed for improving the stability of the system. The phospholide ions resulted from the successive [1,5]-shifts of phenyl and ethoxycarbonyl substituents as described in the literature.[7] Phosphaferrocene **1** was then converted into its pyrrolylmethyl derivative **3**, as shown in eq 1. The yield of the conversion of **1** into **3** was satisfactory (61%).



1 **2** **3** (1)

All our attempts at synthesizing η^5-pyrrolyl complexes through the pyrrolide ion failed, probably because the phosphaferrocene unit is poorly stable in nucleophilic media. We were finally successful when using the direct reaction of **3** with manganese carbonyl (eq 2).



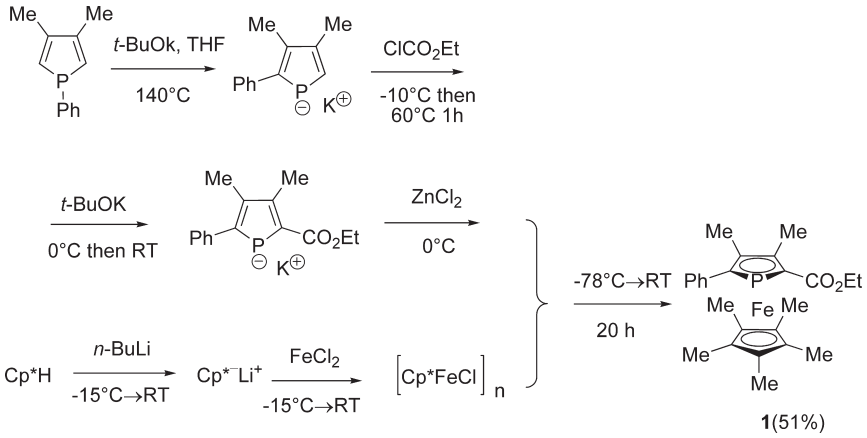
3 **4** (29%) **5** (47%) (2)

The pyrrole complexation mainly affords a major product ($\delta(^{31}P)$ −54.2 ppm) but a minor isomer ($\delta(^{31}P)$ −54.7 ppm) is also formed (major/minor ratio 94/6). This is, no doubt, a consequence of the steric repulsion between the two bulky FeCp* and $Mn(CO)_3$ complexing groups. Azacymantrenylmethylphosphaferrocene **4** easily gives the molybdenum chelate **5**, which was characterized by X-ray crystal structure analysis (Figure 1). This structure gave us some information on the ligating properties of **4**. There is some strain in the chelate ring, as indicated by the reduction of the tetrahedral angle at the CH_2 bridge down to 106.5° and the decrease of the P−Mo−N angle from 90° to 80.5°. This strain is accommodated by the deviation of the P−Mo bond from the P−lone-pair axis by 16.5° and the N−Mo bond from the N−lone-pair axis by only 3.5°. This result

Received: December 10, 2010
Published: February 16, 2011

   dx.doi.org/10.1021/om101160w | *Organometallics* 2011, 30, 1738–1740

Scheme 1. Synthesis of the Starting Phosphaferrocene



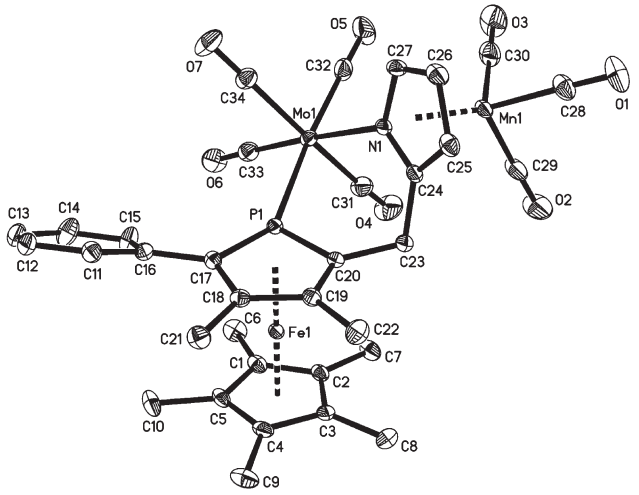


Figure 1. X-ray crystal structure of chelate **5**. Selected bond lengths (Å) and angles (deg): P1−Mo1 = 2.5143(5), N1−Mo1 = 2.3210(18), Mo1−C32 = 1.976(2), C32−O5 = 1.158(3), Mo1−C33 = 1.964(2), C33−O6 = 1.156(3); P1−Mo1−N1 = 80.48(4), C17−P1−C20 = 91.49(9), C24−N1−C27 = 105.85(17), C20−C23−C24 = 106.51(16).

clearly shows that the P−lone-pair axis is much less directional than the N−lone-pair axis. A similar finding has been very recently reported in the literature for chelates derived from a 2-(2-pyridyl)phosphinine.[8] Also noteworthy is the fact that N is planar ($\sum$(angles at N) = 358.1°), whereas P is slightly pyramidal ($\sum$(angles at P) = 352.2°). As a general rule, η^5-phospholyl complexes are weaker donors and better acceptors than the corresponding η^5-pyrrolyl complexes. However, it is known that the ancillary ligands play a major role in the nucleophilicity of these complexes. For example, azacymantrene is protonated at manganese,[9] whereas, upon replacement of one CO by one triphenylphosphine, the protonation takes place at nitrogen.[10] In our case, using the lengthening of the Mo−*trans*-CO bond as a criterion, it seems clear that P and N have comparable donating properties (1.976(2) vs 1.964(2) Å) and this is probably due to the presence of the Cp* ligand.

It is likely that a ligand such as **4** can find some use in catalysis, but this is not the only possibility. The recent discovery that phosphaferrocene complexes can have interesting nonlinear optical properties[11] adds another possible application.

EXPERIMENTAL SECTION

All reactions were performed under nitrogen using solvents purified and dried by standard standards. Nuclear magnetic resonance spectra were obtained using a JEOL ECA 400 or Bruker AV400 spectrometer operating at 400 MHz for ^{1}H, 100.56 MHz for ^{13}C, and 161.89 MHz for ^{31}P. Chemical shifts are expressed in parts per million downfield from internal TMS (^{1}H and ^{13}C) and external 85% H_3PO_4 (^{31}P). All coupling constants (J values) are reported in hertz (Hz). MS spectra were obtained in the ESI mode on a Thermo Finnigan LCQ DECA XP MAX. X-ray crystallographic analyses were performed on a Bruker X8 APEX diffractometer. 3,4-Dimethyl-1-phenylphosphole was prepared according to the literature.[12] Pyrrole was distilled before use. Other reagents were commercially available and were used without further purification.

Synthesis of Phosphaferrocene 1. A mixture of 3,4-dimethyl-1-phenylphosphole (2 g, 10.6 mmol) and *t*-BuOK (1.44 g, 12.7 mmol) in THF (10 mL) were stirred in a pressure tube for 14 h at 140 °C (^{31}P NMR: δ +70.1 ppm). The brown solution was transferred to a two-neck round-bottom flask, and ethyl chloroformate (1.4 g, 12.7 mmol.) was added slowly to the solution at −10 °C. The reaction mixture was stirred at room temperature for 20 min and then heated to 60 °C for 1 h. *t*-BuOK (1.49 g, 13.3 mmol) was added to the mixture at 0 °C, and the mixture was stirred at room temperature for 3 h (^{31}P NMR: δ +106.9 ppm). $ZnCl_2$ (1.81 g, 13.3 mmol) was added to the phospholide solution at 0 °C. The mixture was stirred at 0 °C for 5 min and then at room temperature for 30 min. In a separate flask, Cp*Li was prepared by adding *n*-BuLi (5.2 mL, 8.2 mmol.) to 1,2,3,4,5-pentamethylcyclopentadiene (1.25 mL, 8 mmol) in dry THF at −15 °C and stirred at −15 °C for 5 min and then at room temperature for 30 min. The suspension solution of Cp*Li was then added quickly to the $FeCl_2$ solution in THF at −15 °C. The mixture was stirred at room temperature for 30 min to obtain $[Cp^*FeCl]_n$. The phospholide/$ZnCl_2$ solution was then added dropwise to the dark green $[Cp^*FeCl]_n$ solution at −78 °C, and the resulting mixture was slowly warmed to room temperature and stirred at room temperature for 20 h. Purification was performed via cold column chromatography on silica using 2/1 hexane/dichloromethane. The orange-red band collected gives a red solid (2.44 g, 5.42 mmol), and the yield was 51% from 3,4-dimethyl-1-phenylphosphole.

^{31}P NMR ($CDCl_3$): δ −39.5. ^{1}H NMR ($CDCl_3$): δ 1.27 (t, 3H, $^3J_{HH}$ = 7.2 Hz, CH_2CH_3), 1.57 (s, 15H, CH_3), 2.10 (s, 3H, CH_3), 2.30 (s, 3H, CH_3), 4.04−4.18 (m, 2H, OCH_2), 7.08−7.35 (m, 5H, Ph). ^{13}C NMR ($CDCl_3$): δ 9.64 (s, Cp* Me), 12.74 (s, Me), 13.55 (s, Me), 14.43 (s, Me), 59.86 (s, OCH_2), 79.04 (d, $^1J_{CP}$ = 55.5 Hz, =CP), 83.51 (s, Cp* C), 93.39 (d, $^2J_{CP}$ = 5.8 Hz, =CMe), 95.81 (d, $^2J_{CP}$ = 5.0 Hz, =CMe), 102.56 (d, $^1J_{CP}$ = 53.5 Hz, =CP), 125.73 (s, Ph CH para), 127.75 (s, Ph

dx.doi.org/10.1021/om101160w |*Organometallics* 2011, 30, 1738–1740

CH), 129.54 (d, $^3J_{CP}$ = 9.5 Hz, Ph CH), 139.05 (d, $^2J_{CP}$ = 17.8 Hz, Ph C ipso), 172.97 (d, $^2J_{CP}$ = 17.9 Hz, C═O). HRMS: *m*/*z* calcd for $C_{25}H_{32}O_2PFe$ $(M + H)^+$ 451.1498, found 451.1489.

Synthesis of Phosphaferrocene 3. Lithium aluminum hydride (80 mg, 2 mmol.) was added to 2-phenyl-5-(ethoxycarbonyl)phosphaferrocene **1** (450 mg, 1 mmol) in dry THF (10 mL) at −15 °C. The reaction mixture was slowly warmed to room temperature and stirred for 2 h. Excess $LiAlH_4$ was quenched with a small amount of ethyl acetate and 2 drops of deionized water. The solvents were evaporated, and the resulting precipitate was dissolved in freshly distilled pyrrole (10 mL). $BF_3 \cdot OEt_2$ (0.13 mL, 1 mmol) was added to the pyrrole solution, the mixture was stirred for 15 min, and a small amount of triethylamine was then added. Purification was performed via cold column chromatography on silica using 20/1 hexane/ethyl acetate. The dark orange band collected gives a red oil (279 mg, 0.61 mmol), and the yield was 61%.

Complex ***2***. ^{31}P NMR ($CDCl_3$): δ −52.6. ^{1}H NMR ($CDCl_3$): δ 1.68 (s, 15H, Me Cp*), 2.09 (s, 3H, Me), 2.19 (s, 3H, Me), 4.09−4.30 (m, 2H, CH_2O), 7.12−7.16 (m, 1H Ph), 7.22−7.26 (m, 2H, Ph), 7.41−7.43 (m, 2H, Ph). ^{13}C NMR ($CDCl_3$): δ 10.46 (s, Cp* Me), 11.60 (s, Me), 14.18 (s, Me), 60.83 (d, $^2J_{CP}$ = 23.1 Hz, CH_2O), 82.81 (s, Cp* C), 90.70 (d, $^2J_{CP}$ = 3.8 Hz, ═*C*Me), 93.76 (d, $^2J_{CP}$ = 4.8 Hz, ═*C*Me), 95.13 (d, $^1J_{CP}$ = 55.8 Hz, ═CP), 98.52 (d, $^1J_{CP}$ = 53.6 Hz, ═CP), 125.48 (s, Ph CH para), 127.89 (s, Ph CH), 129.57 (d, $^3J_{CP}$ = 9.6 Hz, Ph CH), 140.04 (d, $^2J_{CP}$ = 17.4 Hz, Ph C ipso). HRMS: *m*/*z* calcd for $C_{27}H_{30}FeOP$ $(M + H)^+$ 409.1384, found 409.1379.

Complex ***3***. ^{31}P NMR ($CDCl_3$): δ −53.4. ^{1}H NMR ($CDCl_3$): δ 1.70 (s, 15H, Me Cp*), 1.95 (s, 3H, Me), 2.17 (s, 3H, Me), 3.31−3.47 (m, 2H, CH_2), 5.89−5.90 (t, 1H, CH), 6.04−6.06 (m, 1H, CH), 6.55−6.57 (m, 1H, N−CH), 7.10−7.14 (m, 1H, Ph), 7.20−7.24 (m, 2H, Ph), 7.40−7.43 (t, 2H, Ph), 7.91 (s, 1H, NH). ^{13}C NMR ($CDCl_3$): δ 10.20 (s, Cp* Me), 11.62 (s, Me), 14.27 (s, Me), 26.59 (d, $^2J_{CP}$ = 22.1 Hz, CH_2), 82.41 (s, Cp* C), 89.60 (d, $^2J_{CP}$ = 4.0 Hz, ═*C*Me), 93.47 (d, $^2J_{CP}$ = 5.0 Hz, ═*C*Me), 94.92 (d, $^1J_{CP}$ = 54.3 Hz, ═CP), 97.01 (d, $^1J_{CP}$ = 53.3 Hz, ═CP), 104.99 (s, Py CH), 108.02 (s, Py CH), 116.31 (s, Py CH), 125.17 (s, Ph CH para), 127.72 (s, Ph CH), 129.28 (d, $^3J_{CP}$ = 10.1 Hz, Ph CH), 131.41 (s, Py C), 140.25 (d, $^2J_{CP}$ = 17.1 Hz, Ph C ipso). HRMS: *m*/*z* calcd for $C_{27}H_{32}NPFe$ $(M + H)^+$ 458.1698, found 458.1700.

Synthesis of Phosphaferrocene 4. Phosphaferrocene **3** (338 mg, 0.74 mmol) and $Mn_2(CO)_{10}$ (293 mg, 0.75 mmol) were dissolved in dry toluene in a sealed tube. The mixture was heated to 145 °C for 24 h. Purification was performed via cold column chromatography on silica using hexane and then 15/1 hexane/ethyl acetate. The pale orange band collected gives a brown solid (130 mg, 0.21 mmol), and the yield was 29%.

^{31}P NMR ($CDCl_3$): δ −54.2. ^{1}H NMR ($CDCl_3$): δ 1.70 (s, 15H, Cp*), 2.04 (s, 3H, Me), 2.18 (s, 3H, Me), 3.27 (m, 2H, CH_2), 5.00 (s, 1H Py), 5.02 (s, 1H, Py), 5.91 (1H, s, NCH═C), 7.11−7.42 (m, 5H, Ph). ^{13}C NMR ($CDCl_3$): δ 10.14 (s, Cp* Me), 11.91 (s, Me), 14.23 (s, Me), 29.13 (d, $^2J_{CP}$ = 21.7 Hz, $-CH_2-$), 82.59 (s, Cp* C), 89.47 (d, $^2J_{CP}$ = 3.9 Hz, ═*C*Me), 93.43 (d, $^2J_{CP}$ = 4.6 Hz, ═*C*Me), 94.37 (d, $^1J_{CP}$ = 54.9 Hz, ═CP), 97.69 (d, $^1J_{CP}$ = 53.5 Hz, ═CP), 104.88 (s, Py CH), 108.40 (s, Py CH), 116.40 (s, NCH═C), 125.26 (s, Ph CH para), 127.71 (s, Ph CH), 129.26 (d, $^3J_{CP}$ = 9.4 Hz, Ph CH), 130.90 (s, NCR═CH), 139.90 (d, $^2J_{CP}$ = 17.6 Hz, Ph C ipso), 223.17 (s, CO). HRMS: *m*/*z* calcd for $C_{31}H_{35}NO_3P^{55}MnFe$ $(M + H)^+$ 611.1084, found 611.1099.

Synthesis of Chelate Complex 5. A solution of phosphaferrocene **4** (178 mg, 029 mmol) and $Mo(CO)_6$ (80 mg, 0.3 mmol) in toluene was stirred at 100 °C for 3 h. Purification was performed via cold column chromatography on silica using hexane/ethyl acetate (10/1 to 4/1). The pale orange band collected gives a brown solid (111 mg, 0.135 mmol), and the yield was 47%. Crystals of **5** were grown from a solution of the compound in dichloromethane/methanol.

^{31}P NMR ($CDCl_3$): δ −5.6. ^{1}H NMR ($CDCl_3$): δ 1.70 (s, 15H, Cp*), 2.17 (s, 3H, Me), 2.28 (s, 3H, Me), 3.09−3.23 (m, 2H, CH_2), 4.97 (s, 1H, Py), 5.14 (s, 1H, Py), 6.43 (s, 1H, NC*H*═C), 7.15−7.43 (m, 5H, Ph). ^{13}C NMR ($CDCl_3$): δ 10.21 (s, Cp* Me), 11.84 (s, Me), 14.56 (s, Me), 26.16 (d, $^2J_{CP}$ = 14.5 Hz, $-CH_2-$), 82.53 (s, Py CH), 82.90 (d, J_{CP} = 10.4 Hz), 84.04 (s, Cp* C), 86.84 (s, Py CH), 88.02 (d, J_{CP} = 5.2 Hz), 88.22 (d, J_{CP} = 2.1 Hz), 91.83 (s, Py C) 112.13 (d, J_{CP} = 4.2 Hz, Py CH), 124.02 (d, $^1J_{CP}$ = 56.0 Hz), 125.95 (s, Ph CH para), 128.16 (s, Ph CH), 129.45 (d, $^3J_{CP}$ = 4.5 Hz, Ph CH), 136.84 (d, $^2J_{CP}$ = 14.5 Hz, Ph C ipso), 203.18 (d, J_{CP} = 12.5 Hz, Mo CO), 203.18 (d, J_{CP} = 12.5 Hz, Mo CO), 208.81 (d, J_{CP} = 10.4 Hz, Mo CO), 214.90 (d, J_{CP} = 41.5 Hz, Mo CO), 219.55 (d, J_{CP} = 8.3 Hz, Mo CO), 220.60 (s, Mn CO). HRMS: *m*/*z* calcd for $C_{35}H_{35}NO_7P^{55}MnFe^{98}Mo$ $(M + H)^+$ 820.9935, found 820.9938.

■ ASSOCIATED CONTENT

Supporting Information. Figures giving NMR data for all the new compounds and a CIF file giving the X-ray crystal structure analysis of compound **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENT

We thank the Nanyang Technological University in Singapore for financial support of this work. Thanks are also due to Dr. Li Yongxin (NTU) for the X-ray crystal structure analysis and to Ms. Ng Yong Xiang and Hui Yen Li Eunice for experimental help.

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