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Heterobimetallic complexes with ferrocenyl-substituted phosphaheterocycles

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ABSTRACT

The ferrocenyl-substituted phosphaheterocycles racemic 1-(1,3,2-dithiaphosphorinan-2-yl)-2-*N*,*N*-dimethylaminomethylferrocene (*rac*-**4**) and racemic 1-(1,3,2-dioxaphosphorinan-2-yl)-2-*N*,*N*-dimethylaminomethylferrocene (*rac*-**5**) have been prepared and their coordination chemistry has been studied. Compounds *rac*-**4** and *rac*-**5** act as bidentate *P*,*N* ligands in *rac*-[$Mo(CO)_4$(**4**-κ*P*,*N*)] (*rac*-**6**) and *rac*-[$Mo(CO)_4$(**5**-κ*P*,*N*)] (*rac*-**7**), and as monodentate ligands in *rac*-[$RuCl_2$(**5**-κ*P*)(η^6-cymene)] (*rac*-**8**) and *rac*-[AuCl(**4**-κ*P*)] (*rac*-**9**). Compounds *rac*-**4** to *rac*-**9** were fully characterised by NMR (^{1}H, ^{13}C, ^{31}P) and IR spectroscopy, mass spectrometry, single-crystal X-ray crystallography, and elemental analysis. Furthermore, preliminary studies on *rac*-**5** in the rhodium(I)-catalysed hydroformylation of ethyl methacrylate were carried out and showed a preference for the branched aldehyde.

1. Introduction

Phosphorus-containing heterocycles have been known for more than one century and have always attracted much interest [1–3]. The development of new and effective synthetic methods for cyclic, rigid, bulky phosphorus(III) ligands which might offer improved performance in homogeneous catalysis is one of the current challenges in organophosphorus chemistry [4]. Among these heterocycles, five- (phospholanes) [5–7] and six-membered (phosphorinanes) rings [8–10] are the best studied. 1*H*-Phosphorinane was first obtained in 1962 by Wagner [11,12] and Braid [13] by a multistep synthesis which included an intramolecular Michaelis–Arbuzov reaction, a Grignard reaction, hydrolysis, and reduction. Lambert et al. developed a simplified synthesis of phosphorinanes and described their conformation [14,15]. Heteroatom-containing phosphorinanes, so-called heterophosphorinanes, containing two oxygen [16–19], sulfur [16,19,20] or nitrogen [16] atoms or two different donor atoms (O,S [21] or O,N [16,17,22,23]) can be synthesised from bifunctional linear precursors and trichlorophosphine via HCl elimination [24–26]. Like phosphorinanes, they exhibit the chair, boat and twist conformations typical of six-membered rings. The preferred conformation depends on the incorporated heteroatoms and the substituent on the phosphorus atom. Axial positions are typically favoured for substituents at phosphorus due to interaction of the lone pair of electrons of the phosphorus atom with the σ^* orbitals of the C–X bond (n(P) → σ^*(C–X)) [27]. Compounds with equatorial orientation of the substituents are rare [27,28]. Phosphorinanes are applied in therapeutic agents and pesticides as well as in catalysis [29].

Ferrocene has proved to be a versatile substituent for phosphines due to its rich chemistry, stability and redox properties [2,3,30,31]. In the last decades, ferrocene-substituted phosphaheterocycles such as FerroTANEs (1,1′-bis(phosphetano)ferrocenes) [32,33] and FerriESPHOS (diazaphospholane) [34] (Fig. 1) have attracted much interest. The combination of a chiral bis-phosphine with the characteristics of ferrocene in FerroTANEs and FerriESPHOS derivatives makes them suitable for a wide range of applications [30,35].

We now report the synthesis of ferrocenyl-substituted heterophosphorinanes (*rac*-**4** and *rac*-**5**) and transition metal complexes thereof (*rac*-**6**, *rac*-**7**, *rac*-**8** and *rac*-**9**) as well as some preliminary studies on the catalytic activity of the corresponding rhodium(I) complexes in hydroformylation.

2. Experimental

2.1. General considerations

All manipulations were carried out by using standard Schlenk techniques under an atmosphere of dry, high-purity nitrogen.

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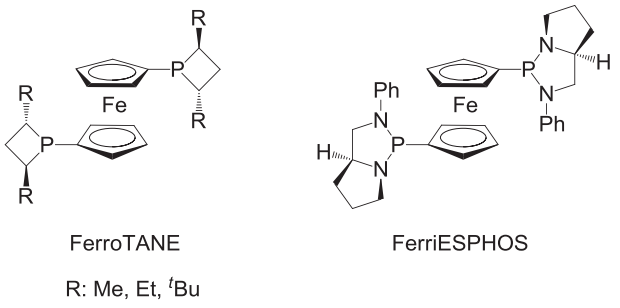

Fig. 1. FerroTANEs and FerriESPHOS [32–34].

Solvents were dried with an MB SPS-800 Solvent Purification System and stored over activated 4 Å molecular sieves. Deuterated solvents for NMR spectroscopy were purchased from Euriso-Top and Chemotrade GmbH. $CDCl_3$ was distilled from P_2O_5 and stored over activated 4 Å molecular sieves. C_6D_6 was dried with sodium, filtered and stored over potassium mirror. *N,N*-dimethylaminomethylferrocene (**1**) [36], 2-chloro-1,3,2-dithiaphosphorinane (**2**) [37,38] and 2-chloro-1,3,2-dioxaphosphorinane (**3**) [39] were synthesised according to literature procedures. Transition metal complexes, $[Mo(CO)_4(pip)_2]$ (pip = piperidine), $[\{RuCl_2(p\text{-cymene})\}_2]$ (cymene = 1-methyl-4-(1-methylethyl)benzene) and [AuCl(tht)] (tht = tetrahydrothiophene) were synthesised according to the literature [40–42]. PCl_3 was distilled prior to use. Other chemicals were obtained from commercial sources and were used as obtained. Spectra were recorded on a Bruker AVANCE DRX 400 NMR spectrometer at 400.13 (^{1}H NMR), 161.98 (^{31}P NMR) or 100.61 (^{13}C NMR). Tetramethylsilane (TMS) was used as internal standard for the ^{1}H NMR spectra and spectra of other nuclei were referred to TMS on the δ scale [43]. The signals of the ^{13}C NMR spectra were assigned by $^{13}C\{^{31}P\}$ experiments. ESI mass spectra were recorded on a Bruker-Daltonic FT-ICR-MS APEX II spectrometer (*m*/*z* values are given for the major isotopic combination only). FTIR spectra were recorded on a Perkin–Elmer Spectrum 2000 spectrometer. C, H, N analyses were performed with a Heraeus VARIO EL Analyser. Air-sensitive samples were prepared in a glove box. Melting points were determined in sealed glass capillaries under nitrogen and are uncorrected.

2.2. Synthetic procedures

2.2.1. Racemic 1-(1,3,2-dithiaphosphorinan-2-yl)-2-*N*,*N*-dimethylaminomethylferrocene (rac-**4**)

1.01 mL of *n*-butyllithium (1.52 mmol, 1.5 M in *n*-hexane) was added to a solution of 0.34 g (1.38 mmol) of *N,N*-dimethylaminomethylferrocene (**1**) in diethyl ether (10 mL) and the solution was stirred for 12 h at room temperature. The solution was added to a solution of 0.31 g (1.80 mmol) of 2-chloro-1,3,2-dithiaphosphorinane in diethyl ether (5 mL) at −78 °C. The suspension was allowed to warm to room temperature overnight and filtered. After removal of the solvent, the crude product was obtained as an orange solid. Recrystallisation from a mixture of toluene (1 mL) and *n*-hexane (8 mL) gave orange crystals after storage at −60 °C. Yield: 0.32 g, 62%. Mp. 98 °C. ^{1}H NMR (C_6D_6/TMS, 400.13 MHz, 25 °C): δ 1.51 (br s, 2H, $SCH_2CH_2CH_2S$), 2.19 (s, 6H, $N(CH_3)_2$), 2.54 (br s, 2H, $SCH_2CH_2CH_2S$), 2.65–2.81 (m, 2H, $SCH_2CH_2CH_2S$), 3.19 (d, $^2J_{HH}$ = 12.8 Hz, 1H, CH_2N), 3.74 (d, $^2J_{HH}$ = 12.8 Hz, 1H, CH_2N), 4.11 (s, 6H, C_5H_5, C_5H_3), 4.31 (s, 1H, C_5H_3), 4.75 (s, 1H, C_5H_3) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6/TMS, 100.6 MHz, 25 °C): δ 28.0 (d, J_{CP} = 7.6 Hz, $SCH_2CH_2CH_2S$), 29.8 (d, J_{CP} = 9.2 Hz, $SCH_2CH_2CH_2S$), 30.7 (d, J_{CP} = 11.4 Hz, $CH_2CH_2CH_2S$), 45.4 (s, $N(CH_3)_2$), 58.3 (d, J_{CP} = 7.4 Hz, CH_2N), 70.6 (s, C_5H_5, C_5H_3), 72.4 (d, J_{CP} = 3.2 Hz, C_5H_3), 73.0 (d, J_{CP} = 3.7 Hz, C_5H_3), 74.7 (d, J_{CP} = 31.7 Hz, C_5H_3), 90.6 (d, J_{CP} = 26.7 Hz, CCH_2N) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6/TMS, 161.98 MHz): δ 49.5 ppm. MS (ESI pos.) *m*/*z*: 714 (100%) $[2M - N(CH_3)_2]^+$; 380 (14.6%) $[M + H]^+$. FTIR (KBr, $\tilde{\nu}$): 3923 (w), 3422 (w), 3089 (w), 2959 (m), 2934 (s), 2891 (m), 2854 (m), 2819 (m), 2771 (s), 1734 (w), 1696 (w), 1653 (w), 1558 (w), 1539 (w), 1521 (w), 1464 (w), 1452 (s), 1437 (w), 1421 (w), 1412 (w), 1387 (w), 1359 (m), 1295 (w), 1276 (w), 1261 (s), 1233 (s), 1178 (m), 1161 (m), 1138 (s), 1104 (s), 1071 (w), 1035 (s), 1022 (s), 997 (w), 904 (w), 863 (w), 846 (w), 839 (w), 817 (s), 640 (w), 623 (w), 537 (w), 503 (m), 485 (s), 459 (s), 426 (m), 411 (w), 406 (w) cm^{-1}. Elemental analysis calculated for $C_{16}H_{22}FeNPS_2$ (%): C 50.80, H 5.60, N 3.70; found: C 50.58, H 5.48, N 3.65.

2.2.2. Racemic 1-(1,3,2-dioxaphosphorinan-2-yl)-2-*N*,*N*-(dimethylaminomethyl)ferrocene (rac-**5**)

Compound *rac*-**5** was obtained from *N,N*-dimethylaminomethylferrocene (**1**) (5.0 g, 2.1 mmol) and 2-chloro-1,3,2-dioxaphosphorinane (**3**) (0.38 g, 2.7 mmol) as described for the synthesis of *rac*-**4**. Recrystallisation from a mixture of toluene (5 mL) and *n*-hexane (20 mL) gave orange crystals at −18 °C. Yield: 0.64 g, 90%. Mp. 120 °C. ^{1}H NMR (C_6D_6/TMS, 400.13 MHz, 25 °C): δ 0.82–0.86 (m, 1H, $OCH_2CH_2CH_2O$), 1.90–1.99 (m, 1H, $OCH_2CH_2CH_2O$), 2.20 (s, 6H, $N(CH_3)_2$), 3.15 (d, $^2J_{HH}$ = 12.9 Hz, 1H, CH_2N), 3.53–3.67 (m, 4H, $OCH_2CH_2CH_2O$), 3.67 (d, $^2J_{HH}$ = 12.4 Hz, 1H, CH_2N), 4.10 (m, 6H, C_5H_5, C_5H_3), 4.31 (s, 2H, C_5H_3) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6/TMS, 100.6 MHz, 25 °C): δ 29.2 (d, J_{CP} = 2.6 Hz, $OCH_2CH_2CH_2O$), 45.1 (s, $N(CH_3)_2$), 58.1 (d, J_{CP} = 5.3 Hz, CH_2N), 61.7 (s, $OCH_2CH_2CH_2O$), 62.5 (s, $OCH_2CH_2CH_2O$), 68.9 (s, C_5H_5), 69.9 (d, J_{CP} = 2.0 Hz, C_5H_3), 70.5 (s, C_5H_3), 72.9 (s, C_5H_3), 78.7 (d, J_{CP} = 46.4 Hz, C_5H_3), 88.7 (d, J_{CP} = 14.6 Hz, CCH_2N) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6/TMS, 161.98 MHz, 25 °C): δ 157.8 ppm. MS (ESI pos.) *m*/*z*: 348 (37.5%) $[M + H]^+$. FTIR (KBr, $\tilde{\nu}$): 3863 (w), 3839 (w), 3820 (w), 3772 (w), 3750 (w), 3736 (w), 3710 (w), 3701 (w), 3648 (w), 3094 (w), 2960 (s), 2869 (w), 2813 (w), 2769 (m), 2564 (w), 2444 (w), 2345 (w), 2331 (w), 1943 (w), 1824 (w), 1791 (w), 1772 (w), 1684 (w), 1653 (w), 1559 (w), 1466 (m), 1455 (m), 1436 (w), 1405 (w), 1368 (w), 1326 (w), 1261 (m), 1231 (m), 1179 (w), 1165 (w), 1133 (m), 1105 (w), 1064 (s), 1034 (w), 1022 (w), 939 (m), 929 (m), 886 (w), 858 (m), 818 (s), 801 (s), 707 (s), 667 (m), 616 (w), 575 (w), 536 (w), 522 (m), 477 (m), 435 (m), 412 (m) cm^{-1}. Elemental analysis calculated for $C_{16}H_{22}FeNO_2P$ (%): C 55.35, H 6.39, N 4.03; found: C 54.97, H 6.45, N 3.90.

2.2.3. Racemic [$Mo(CO)_4$(**4**-κ*P*,*N*)] (rac-**6**)

A solution of *rac*-**4** (0.05 g, 0.132 mmol) in dichloromethane (1 mL) was added slowly to a suspension of $[Mo(CO)_4(pip)_2]$ (0.048 g, 0.127 mmol) in a mixture of dichloromethane and *n*-hexane (5:1). The mixture was refluxed for a few minutes and then cooled to room temperature overnight. The solvent was evaporated and the residue dried *in vacuo*. Recrystallisation from a mixture of toluene (1 mL) and *n*-hexane (10 mL) gave red crystals at room temperature. Yield: 0.06 g, 81%. Mp. 185 °C. ^{1}H NMR (C_6D_6/TMS, 400.13 MHz, 25 °C): δ 1.42–1.56 (m, 2H, $SCH_2CH_2CH_2S$), 1.80 (s, 3H, $N(CH_3)_2$), 2.34 (d, $^2J_{HH}$ = 13.0 Hz, 1H, CH_2N), 2.39 (s, 3H, $N(CH_3)_2$), 2.58–2,69 (m, 2H, $SCH_2CH_2CH_2S$), 3.24–3.30 (m, 1H, $SCH_2CH_2CH_2S$), 3.41–3.47 (m, 1H, $SCH_2CH_2CH_2S$), 3.73 (s, 1H, C_5H_3), 3.96 (t, overlapped signals, 2H, each 1H of C_5H_3 and CH_2N), 4.07 (d, $^2J_{HH}$ = 13.0 Hz, 1H, CH_2N), 4.17 (s, 5H, C_5H_5), 4.79 (s, 1H, C_5H_3) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6/TMS, 100.6 MHz, 25 °C): δ 26.1 (d, J_{CP} = 8.2 Hz, $SCH_2CH_2CH_2S$), 30.3 (s, $SCH_2CH_2CH_2S$), 30.7 (s, $SCH_2CH_2CH_2S$), 52.0 (s, $N(CH_3)_2$), 59.9 (d, J_{CP} = 2.3 Hz, $N(CH_3)_2$), 67.1 (d, J_{CP} = 1.9 Hz, CH_2N), 69.5 (d, J_{CP} = 4.9 Hz, C_5H_3), 70.7 (s, C_5H_5), 72.9 (s, C_5H_3), 73.1 (d, J_{CP} = 8.8 Hz, C_5H_3), 75.4 (d, J_{CP} = 13.2 Hz, CCH_2N), 86.1 (d,