Comparing the asymmetric dppf-type ligands with their semi-homologous counterparts[☆]

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A B S T R A C T

Two series of asymmetric ferrocene diphosphines, namely the dppf-type ligands $R_2PfcPPh_2$ (protected as BH_3 adducts; fc = ferrocene-1,1′-diyl) and their semi-homologous counterparts $R_2PfcCH_2PPh_2$ (both in free and BH_3-protected form), with diverse PR_2 groups (R = cyclohexyl, isopropyl and *tert*-butyl), were prepared and further converted into the respective phosphine selenides, $R_2P(Se)fcP(Se)Ph_2$ and $R_2P(Se)fcCH_2P(Se)Ph_2$, which were in turn used to evaluate the electronic properties of these diphosphines through $^1J_{SeP}$ coupling constants. When reacted with $[PdCl_2(MeCN)_2]$ or $[PdCl_2(cod)]$ (cod = cycloocta-1,5-diene), the dppf-type ligands exclusively afforded the chelate complexes $[PdCl_2(R_2PfcPPh_2\text{-}\kappa^2P,P')]$, whereas the more flexible, homologous ligands produced mixtures mainly containing the similar chelate complexes $[PdCl_2(R_2PfcCH_2PPh_2\text{-}\kappa^2P,P')]$ and the *P,P′*-bridged dimers $[PdCl_2(\mu(P,P')\text{-}R_2PfcCH_2PPh_2)]2$.

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1. Introduction

1,1′-Bis(diphenylphosphino)ferrocene (**1**; dppf) has become a truly iconic ferrocene ligand thanks to its unique coordination properties and numerous successful catalytic applications [1,2], which also triggered the search for analogous donors. Thus far, most attempts to modify the dppf structure have followed three main directions, namely (1) altering phosphine substituents, (2) replacing one of the phosphine groups by another functional moiety, and (3) introducing an additional substituent to the ferrocene core to provide planar-chiral ferrocene ligands. These approaches have already generated a vast family of ferrocene phosphines applicable as supporting ligands in coordination compounds and in a range of simple and enantioselective metal-catalyzed transformations [3].

Recently, we introduced an alternative approach to the design of ferrocene phosphines based on ligand desymmetrization by inserting a spacer group between the ferrocene scaffold and a directly bonded donor substituent. In the case of dppf, this approach using a simple methylene spacer led to its congener **2** [4] (Scheme 1). Coordination studies with this ligand and other,

similarly modified phosphinoferrocene donors [5] revealed considerable changes in coordination properties associated with increased molecular flexibility. These results and our recent findings demonstrating that even simple variations of substituents at the phosphine groups can markedly affect the coordination and catalytic behavior of phosphinoferrocene donors [6] have led us to investigate parallel series of dppf and type-**2** ligands with different phosphine substituents (Scheme 1). The properties of these diphosphines were compared by preparing and structurally characterizing Pd(II) complexes with these ligands and by analyzing the $^1J_{SeP}$ scalar coupling constants of the corresponding phosphine diselenides [7].

2. Results and discussion

2.1. Synthesis and characterization of dppf-type diphosphines and their derivatives

Asymmetric, dppf-like diphosphines with one PPh_2 substituent replaced by a dicyclohexylphosphino, diisopropylphosphino or di-*tert*-butylphosphino moiety were prepared by lithiation/phosphinylation of 1′-(diphenylphosphino)-1-bromoferrocene [8,9] and were isolated as air-stable borane adducts **3a-c** (Scheme 2) rather than the corresponding, oxidation-sensitive phosphines **1a-c** [10]. This procedure typically afforded minor amounts of $FcPPh_2 \cdot BH_3$ (Fc = ferrocenyl) resulting from unwanted protonolysis of the

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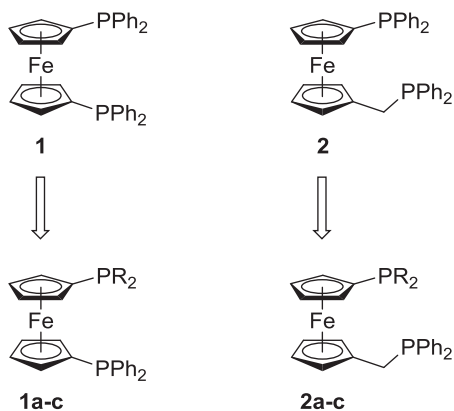
Scheme 1.

R = cyclohexyl (Cy; **a**), *i*-Pr (**b**), *t*-Bu (**c**).

lithiated intermediate. Fortunately, this side product could be separated by chromatography.

In the subsequent reactions, the borane protecting groups [11] in **3a-c** were removed by treatment with 1,4-diazabicyclo[2.2.2]octane (dabco) [12] in toluene (at elevated temperature). The resulting free phosphines **1a-c** were separated by flash chromatography and, after evaporation, converted into the respective phosphine selenides **4a-c** by reacting with KSeCN [13] in dichloromethane-methanol. In the complexation reactions, the eluate containing the free diphosphine was directly added to [PdCl$_2$(cod)] (cod = η^2:η^2-cycloocta-1,5-diene) dissolved in dichloromethane, producing the corresponding *P,P'*-chelate complexes **5a-c** as the sole products (Scheme 2). Notably, these simplified procedures avoiding the isolation of the air-sensitive diphosphines **1** provided the target compounds at generally good yields. For instance, the selenides **4** were isolated at 79% (**4a**), 53% (**4b**) and 40% (**4c**) yields after column chromatography and crystallization (Note: the relatively lower yield of **4c** can be explained by the higher solubility of this compound). Even the complexation reactions were accomplished with very good isolated yields, namely 74% for **5a**, and 49% for the remaining members of the series, **5b** and **5c**.
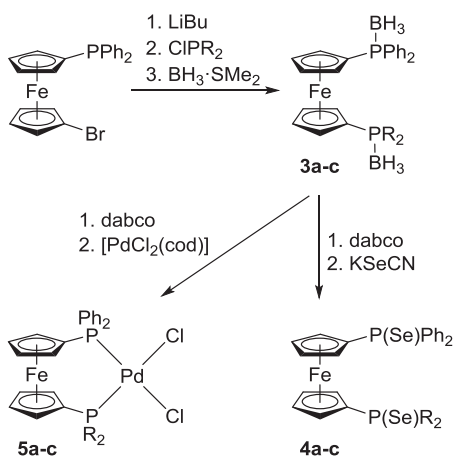
Compounds **3**–**5** were characterized by multinuclear NMR spectroscopy, electrospray ionization mass spectrometry (ESI MS) and elemental analysis. The ^{1}H and ^{13}C NMR spectra of **3**–**5** comprise the characteristic signals of the asymmetrically 1,1'-disubstituted ferrocene moiety and of the phosphine moieties. The presence of the protecting BH$_3$ groups in compounds **3a-c** is indicated by very broad, structured resonances due to six BH protons in the ^{1}H NMR spectra and broad, doublet-like signals in the ^{31}P{^{1}H} NMR spectra. The signals of the PPh$_2$·BH$_3$ moieties are found at $\delta_P \approx 16.3$, whereas those of the other phosphine substituents appear at lower fields (**3a**: δ_P 24.4, **3b**: δ_P 31.8, and **3c**: δ_P 45.4). Upon conversion to the selenides **4**, the ^{31}P NMR signals shift to lower fields, becoming sharp singlets associated with ^{77}Se satellites ($I = \frac{1}{2}$, natural abundance 7.6%; Note: for further discussion of the ^{31}P NMR parameters, see below). Finally, the ^{31}P NMR resonances of complexes **5a-c** are consistently shifted to even lower fields and split into doublets due to interactions between the non-equivalent phosphorus atoms, with $^2J_{PP} = 22$ Hz (in all compounds).

In addition to the conventional characterization, the solid-state structures of adducts **3b** and **3c** [14] and, mainly, the complete series of selenides **4a-c** and Pd(II) complexes **5a-c** were determined by single-crystal X-ray diffraction analysis. The molecular structures of adducts **3b** and **3c** are shown in Fig. 1. In the case of **3b**, the ferrocene substituents are rotated to an intermediate conformation between eclipsed anticlinal and staggered antiperiplanar [2a] with the torsion angle C1-Cg1-Cg2-C6 (τ), where Cg1 and Cg2 denote the centroids of the cyclopentadienyl rings C(1−5) and C(6−10), at −158.06(9)°. The cyclopentadienyl rings are mutually tilted by 7.06(8)°, which corresponds to individual Fe-C distances ranging from 2.019(1) to 2.072(2) Å. The lengths of the pivotal C-P bonds (C1-P1 1.793(1) Å and C6-P2 1.794(1) Å), as well as the P-B distances (P1-B1 1.927(2) Å and P2-B2 1.920(2) Å) in **3b** are similar to those observed in dppf·2BH$_3$ (1.790(3) Å and 1.922(4) Å, respectively)

Scheme 2. Synthesis of adducts **3** and their conversion into selenides **4** and Pd(II) complexes **5** (R = cyclohexyl (**a**), isopropyl (**b**), and *tert*-butyl (**c**); dabco = 1,4-diazabicyclo[2.2.2]octane, cod = η^2:η^2-cycloocta-1,5-diene).

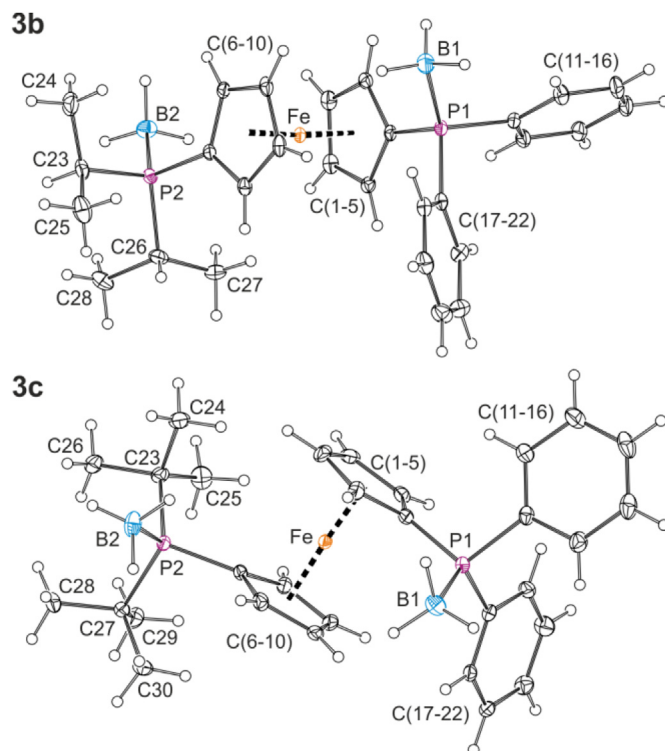**Fig. 1.** PLATON plots of the molecular structures of **3b** (top) and **3c** (bottom) showing the displacement ellipsoids at 30% probability level.