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Note

π-Excess aromatic σ^2P ligands: Unprecedented reductive C–C coupling of neopentylbenzazaphosphole at the P=CH–N group by $Fe_3(CO)_{12}$ to an heterocyclic 1,2-bis(phosphido)-$Fe_2(CO)_6$ complex

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Dedicated to Prof. Dr. Dr. h.c. Wilhelm Keim on the occasion of his 80th birthday.

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ABSTRACT

The aromatic P=CH–N heterocycle **1** with dicoordinated phosphorus (σ^2P) reacts with $Fe_3(CO)_{12}$ in toluene or benzene under reductive C–C coupling and coordination of the $[Fe_2(CO)_6]^{2+}$ fragment to the μ_2-bridging 1,2-bis(phosphido)$Fe_2(CO)_6$ chelate complex **2** (rac/*meso* 4:1 to 2:1). This reaction illustrates the potential of $Fe_3(CO)_{12}$ for C–C coupling reactions of easily reducible unsaturated heterocycles which may act as both, substrate and ligands for coordination of the resulting $Fe_2(CO)_6$ fragment. The products were identified by characteristic NMR data of the bis(dihydrobenzazaphospholide) ligands and *rac*-**2**·1.5 $CDCl_3$ by crystal structure analysis.

Introduction

Reactivity studies of aromatic P ligands towards transition metal compounds were focused so far mainly on phosphabenzenes [1]. The knowledge about complexes formed with likewise aromatically stabilized N-heterocyclic σ^2P ligands [2,3] is, apart from M(0) carbonyl complexes [3,4], still sparse and hints at changed coordination properties [3,5–7]. Recent studies of complexes of annulated 1,3-azaphospholes with non-zerovalent d^{10} metals reveal exclusively μ-bridging and/or bent κ*P* coordination [6,7], atypical and rare for phosphinine d^{10} metal complexes [1,8], whereas d^8-metal complexes of *1H*-1,3-benzazaphospholes are less stable than related phosphinine complexes and add any trace of moisture at the P=C bond [9]. We now found also distinct reactivity towards $Fe_3(CO)_{12}$, a metal(0) carbonyl cluster with M–M bonds. Whereas phosphinines react with related $Os_3(CO)_{12}$ [10] or $Mn_2(CO)_{10}$ [11] clusters to μ_2-*P*-bridged bis(phosphinine)$M_n(CO)_m$ complexes, an unprecedented Fe(0)-mediated reductive C–C coupling of two P=CH–N heterocycles and formation of a μ_2-bridged bis(phosphido) $Fe_2(CO)_6$ complex was observed, illuminating the potential of $Fe_3(CO)_{12}$ for C–C coupling reactions and a new route to 1,2-diphosphido-$Fe_2(CO)_6$ chelate complexes.

Results and discussion

The reactivity study of *1H*-1,3-benzazaphospholes towards $Fe_3(CO)_{12}$ was performed with compound **1** as a representative model. This species is convenient accessible [12] and suitable for NMR reaction monitoring by strong CMe_3 and characteristic PCH and NCH proton and ^{13}C NMR signals. In toluene at room temperature, the reaction is rather slow. ^{31}P and ^{1}H NMR monitoring after 15 h displayed a mixture of unconverted **1** (δ = 70.4 ppm), the product *rac*-**2** (δ = 165.2 ppm) and a transient, not completely identified 1-neopentyl-1,3-benzazaphosphole iron(0)carbonyl complex (δ = 71.7 ppm), ^{31}P and NCH_2 proton integral ratios (49:42:9). Complete conversion of **1** was achieved by subsequent heating at 60 °C for 15 h (Scheme 1). The ^{31}P NMR spectrum then

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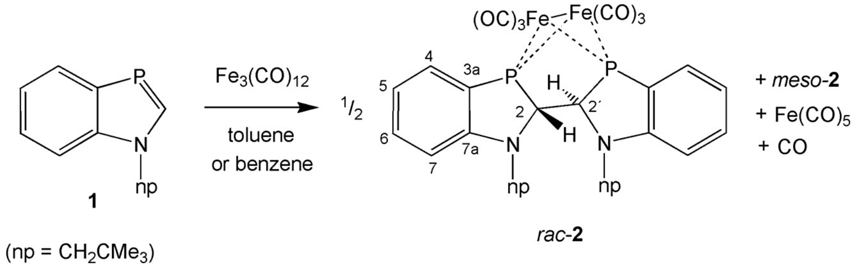

Scheme 1. Reaction of the π-excess aromatic ligand **1** with $Fe_3(CO)_{12}$.

exhibited the major signal of *rac*-**2** along with an only slightly shifted, but much weaker signal of *meso*-**2** (δ = 166.1 ppm), and trace signals for two unidentified compounds at δ = 76.7 and 125.1 ppm (^{31}P integral ratio 80:16:2:2). After cooling to room temperature a major part of *rac*-**2** precipitated as ochre powder. Washing with hexane and drying under vacuum furnished this compound in pure state, yield 46%. The filtrate was containing the residual *rac*-**2** along with *meso*-**2** and the unidentified trace compounds, ^{31}P integral ratio 54:35:6:5. When the reaction was repeated in C_6D_6, complete conversion was observed at room temperature (20–22 °C), yield of **2** 86% (by ^{31}P integration after ca. 30 h), but the diastereoselectivity was lower, *rac*/*meso* ratio 67:33%. The^{13}C NMR spectrum indicated a strong signal at δ = 211 ppm for $Fe(CO)_5$ besides the product signals.

The mechanism of the reaction of **1** with $Fe_3(CO)_{12}$ was not investigated within this study. The ease of the formation of **2** compared to very slow reaction of **1** with the mononuclear 3d-metal carbonyl $Cr(CO)_6$ with terminal CO, suggests however, that the reaction starts by replacement of weaker coordinating μ_2-CO ligands by compound **1**. In contrast to thermally very stable (κ*P*-benzazaphosphole)$Cr(CO)_5$ complexes, accessible with Cr(THF)$(CO)_5$ [4], the primary benzazaphosphole iron(0) carbonyl complex, observed in toluene, is much less stable and converts to *rac*-**2**. On heating at 60 °C also a minor amount of *meso*-**2** is formed while the intermediate benzazaphosphole iron(0) carbonyl species disappears.

Structure elucidation

The solution NMR data of *rac*-**2** and *meso*-**2** reveal conversion of **1** to a dimer, partly saturated in the five-membered ring. Conclusive are in particular the replacement of the =CH-2 signals by those of saturated CH-2, the strong low-frequency shifts of the signals of $^{13}C_q$-3a in α-position of phosphorus and of the CH-7 and CH-5 proton and ^{13}C nuclei by the +M-effect of nitrogen in the non-aromatic dihydrobenzazaphosphole ring. Further characteristic features are the pseudotriplet couplings of the NCH_2 protons and various ^{13}C ring nuclei with two phosphorus nuclei. The relatively large P–C coupling constants of the pseudotriplets of C-2, $|^1J + ^2J|$ = 66.4 and 65.0 Hz in *rac*-**2** and *meso*-**2**, respectively, indicate coordination of phosphorus to iron, and the high-frequency phosphorus resonance, similar to that observed in *o*-phenylene-bis(μ-*tert*-butylphosphido)$Fe_2(CO)_6$ (δ = 180 ppm) [13], suggests formation of bis(μ-phosphido) complexes. The final identification of the *rac*-**2** diastereoisomers succeeded by crystal structure analysis of its $CDCl_3$ solvate (see below). The oily minor product with similar NMR data represents then the *meso*-diastereoisomers with the CH-2 protons at the same side. Increased steric hindrance at the opposite side may be the reason for the lower abundance compared to the solid *rac*-**2**. The two NCH_2 protons are then not longer equivalent and display an AB coupling pattern. The above mentioned transient benzazaphosphole iron(0) carbonyl complex was indicated by the diminished $^2J_{PCH}$ coupling constant (31.2 Hz), conclusive for coordination at **1** [6] (without coordination $^2J_{PCH}$ = 38 Hz [12]), by the changed coupling pattern of H-4 to a triplet appearance with $^3J_{PH} \approx ^3J_{HH}$, a slight downfield shift of H-7 and a small $^4J_{PH}$ coupling of the NCH_2 protons. All these changes are close to those observed in the κ*P*-LM$(CO)_5$ complexes of **1** [4a] (M = Cr, Mo, W; L = coordinated benzazaphosphole). The phosphorus coordination shift of the intermediate is small, $\Delta\delta_{\text{complex-}\mathbf{1}}$ = 1.3 ppm, just between that of the κ*P*-LCr$(CO)_5$ and κ*P*-LMo$(CO)_5$ complexes of **1** ($\Delta\delta$ = 12.6 and −5.8 ppm [4a]). For a variety of 2-substituted κ*P*-LM$(CO)_5$ benzazaphosphole complexes [4b] the trends of the ^{13}C and ^{31}P chemical shifts and P–C coupling constants are the same.

Orange crystals of *rac*-**2**·1.5 $CDCl_3$, grown by slow concentration of a solution of *rac*-**2** in $CDCl_3$, had poor quality, but allowed to collect structural data. While the principal structure is without doubt, the refinement and accuracy of bond lengths and angles were limited. Therefore, only characteristic structural aspects are discussed. The compound crystallized in the monoclinic space group $P2_1/c$ with four molecules in the unit cell, each two with *2S,2′S*-configuration (Fig. 1) and *2R,2′R*-configuration. The butterfly arrangement of the two planes P1–P2–Fe1 and P1–P2–Fe2 is typical for bis(phosphido)$Fe_2(CO)_6$ complexes, and the C–C and Fe–Fe bond lengths in **2** (1.533(10) and 2.6304(17) Å) are similar to those in ethylene-bis(μ-*tert*-butylphosphido)$Fe_2(CO)_6$ (1.53(2) and 2.624(2) Å), formed from the diphosphido complex (μ-

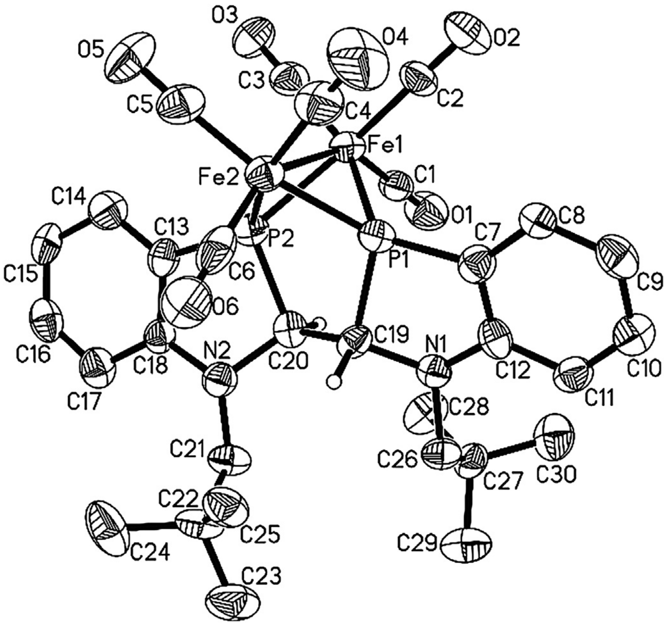

Fig. 1. Molecular structure of *2S,2′S*-**2**·1.5 $CDCl_3$ (ellipsoids with 50% probability, $CDCl_3$ and hydrogen atoms except at C19 and C20 omitted for clarity reasons).