

Synthesis, structure, and reactivity of fluorous phosphorus/carbon/phosphorus pincer complexes derived from $P(CH_2)_5P$ backbones

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Dedicated to Professor Dr. Wolfgang A. Herrmann in appreciation of his many contributions to inorganic and organometallic chemistry.

Abstract

Reactions of the diphosphine $H_2P(CH_2)_5PH_2$ and fluorous alkenes $H_2C=CHR_{fn}$ (excess; $R_{fn} = (CF_2)_{n-1}CF_3$; $n = \mathbf{a}, 6$; $\mathbf{b}, 8$; $\mathbf{c}, 10$) at $60^\circ C$ in the presence of AIBN give the precursors $(R_{fn}CH_2CH_2)_2P(CH_2)_5P(CH_2CH_2R_{fn})_2$ ($\mathbf{2a-c}$; 68–74%). These react with $Pd(O_2CCF_3)_2$ in $CF_3C_6F_5$ at $80^\circ C$ to give the title complexes $(R_{fn}CH_2CH_2)_2P(CH_2)_2CH(CH_2)_2P(CH_2CH_2R_{fn})_2Pd(O_2CCF_3)$ ($\mathbf{5a-c}$, 51–18%). Addition of LiCl to $\mathbf{5b}$ gives $(R_{f8}CH_2CH_2)_2P(CH_2)_2CH(CH_2)_2P(CH_2CH_2R_{f8})_2PdCl$ ($\mathbf{6b}$, 97%); subsequent reaction with MeLi affords the corresponding methyl complex (97%). A solvate of $\mathbf{6b}$ is crystallographically characterized. The structure exhibits $CH_2CH_2R_{f8}$ groups with nearly anti C–C–C conformations, extending in parallel above and below the palladium square plane to create fluorous lattice domains. Reactions of $\mathbf{2b}$ and other metal complexes are described; in the cases of $(PhCN)_2PdCl_2$ or $(COD)_2PtCl_2$ ($CF_3C_6H_5$, room temperature), bimetallic species in which two MCl_2 moieties are bridged by two diphosphines appear to form. The $CF_3C_6F_{11}$ /toluene partition coefficients of $\mathbf{2a-c}$ and $\mathbf{5a-c}$ establish high fluorophilicities; despite the lower fluorine weight%, those of $\mathbf{5a-c}$ are slightly greater ((97.4–99.7):(2.6–0.3) versus (95.3–99.3):(4.7–0.7)).
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Keywords: Pincer; Fluorous; Radical addition; Palladium; Platinum; Iridium; Partition coefficient

1. Introduction

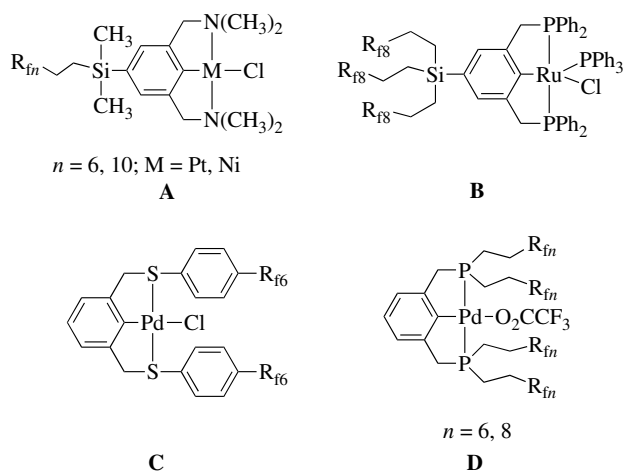
Pincer ligands and their complexes continue to play increasingly important roles in metal-catalyzed reactions [1]. Systems based upon aliphatic backbones [2–4] as opposed to the more usual arene-based tethers have provided several notable recent developments [2g,3e,4d]. A variety of approaches to recoverable pincer ligands and complexes have been reported [5–14]. These efforts have included fluorous derivatives [13,14], which can be recycled

by a variety of liquid/liquid and liquid/solid biphasic techniques [15]. Representative examples are provided in Scheme 1 (A–D) [13,14]. However, to our knowledge there have been no attempts to immobilize pincer complexes with aliphatic backbones.

We have described several fluorous arene-based phosphorus/carbon/phosphorus or $PC(sp^2)P$ pincer ligands and metal complexes, as exemplified by D in Scheme 1 [14]. However, the ligands were much more difficult to prepare than their non-fluorous counterparts. New types of side-reactions were encountered, and significantly lower yields were obtained. Thus, our attention was drawn to analogs with aliphatic backbones. A variety of convenient protocols for synthesizing aliphatic fluorous phosphines

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Scheme 1. Representative fluorous pincer complexes ($R_{fn} = (\text{CF}_2)_{n-1}\text{-CF}_3$).

have been developed in our laboratory [16] and we were optimistic that these could be applied to pincer systems without difficulty.

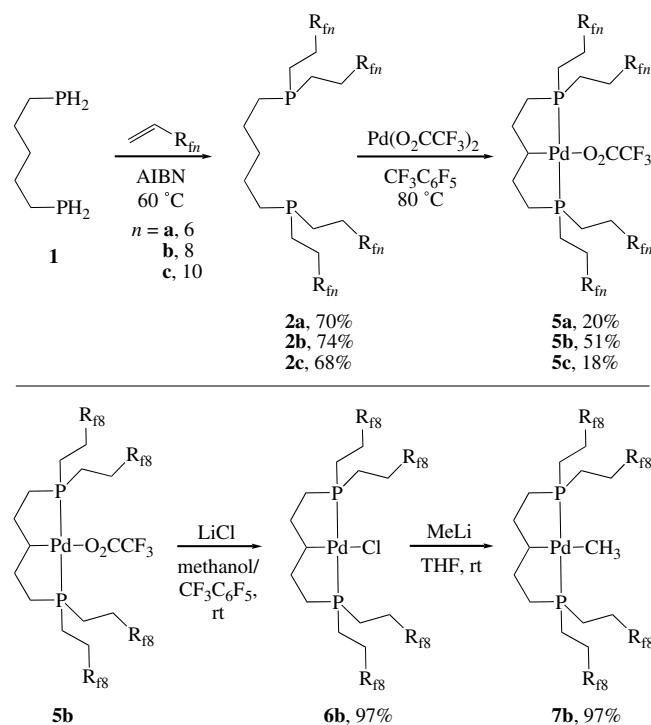
Accordingly, we set out to prepare fluorous 1,5-diphosphines of the formula $(R_{fn}\text{CH}_2\text{CH}_2)_2\text{P}(\text{CH}_2)_5\text{P}(\text{CH}_2\text{-CH}_2\text{R}_{fn})_2$, and define their coordination chemistry. Analogous non-fluorous ligands have been used as springboards to a variety of $\text{PC}(\text{sp}^3)\text{P}$ pincer complexes [2–4]. We report below (1) efficient high yield syntheses of such ligands, (2) their metalation to give fluorous palladium $\text{PC}(\text{sp}^3)\text{P}$ pincer complexes, (3) subsequent substitution reactions, (4) preliminary data involving adducts of other metals, (5) the crystallographic characterization an R_{f8} -based palladium complex, and (6) key phase properties of the preceding compounds.

2. Results

2.1. Diphosphine synthesis and characterization

We and others have described many free radical chain additions of $R_{3-x}\text{PH}_x$ species to fluorous terminal alkenes $\text{H}_2\text{C}=\text{CHR}_{fn}$ [14,16]. Thus, the known diprimary 1,5-diphosphine $\text{H}_2\text{P}(\text{CH}_2)_5\text{PH}_2$ (**1**) was synthesized from the corresponding 1,5-dibromide by a convenient and easily scalable Arbuzov/reduction sequence [17]. As shown in Scheme 2 (top), **1** and excess $\text{H}_2\text{C}=\text{CHR}_{fn}$ ($n = \mathbf{a}, 6; \mathbf{b}, 8; \mathbf{c}, 10$) were reacted neat at 60 °C in the presence of the radical initiator AIBN. Workups gave the fluorous ditertiary diphosphines $(R_{fn}\text{CH}_2\text{CH}_2)_2\text{P}(\text{CH}_2)_5\text{P}(\text{CH}_2\text{CH}_2\text{R}_{fn})_2$ (**2a–c**) as air sensitive liquids (**2a**) or solids (**2b,c**) in 68–74% yields on 3–5 g scales.

The diphosphines **2a–c** were characterized by microanalyses and NMR spectroscopy (^1H , ^{13}C , ^{19}F , ^{31}P), as summarized in Section 4. The chemical shifts and coupling constants associated with the $\text{P}(\text{CH}_2)_5\text{P}$ and $\text{P}(\text{CH}_2\text{-CH}_2\text{CF}_2)$ segments closely resembled those reported for related compounds earlier [2a,16].



Scheme 2. Synthesis of fluorous pincer ligands and palladium complexes.

As summarized in Table 1, the diphosphine **2a** was very soluble in the fluorous solvent $\text{CF}_3\text{C}_6\text{F}_{11}$ (perfluoro(methyl)cyclohexane)), the hybrid solvent $\text{CF}_3\text{C}_6\text{H}_5$ [18], and the non-fluorous solvent $\text{CF}_3\text{C}_6\text{F}_5$ [18]. It was moderately soluble in THF and CH_2Cl_2 . The homologs **2b** and **2c** exhibited progressively lower solubilities, consistent with R_{fn} length trends observed with other fluorous compounds [16a]. No dramatic changes in solubilities were noted at 60 °C. The $\text{CF}_3\text{C}_6\text{F}_{11}$ /toluene partition coefficients were determined by ^{19}F NMR as described in Section 4. As summarized in Table 2, values ranged from 95.3:4.7 (**2a**) to 99.3:0.7 (**2c**), indicative of high fluorophilicities.

2.2. Diphosphine derivatization

Reactions of non-fluorous 1,5-diphosphines $\text{R}_2\text{P}(\text{CH}_2)_5\text{-PR}_2$ with L_2PdCl_2 or L_2PtCl_2 species often give bimetallic complexes of the type **E** (Scheme 3) [2a,2b]. These can be converted at elevated temperatures to monometallic $\text{PC}(\text{sp}^3)\text{P}$ pincer complexes. Thus, **2b** and $(\text{PhCN})_2\text{PdCl}_2$ were combined in $\text{CF}_3\text{C}_6\text{F}_5$ at room temperature. A ^{31}P NMR spectrum of the reaction mixture showed one signal, suggesting the clean formation of a single complex (**3**). Workup gave a seemingly homogeneous material (97%), but FAB mass spectra did not give informative ion patterns. The ^{13}C NMR spectrum showed virtual triplets [19] for the $\text{PCH}_2\text{CH}_2\text{CF}_2$ signals, suggesting a *trans* geometry. An analogous reaction of **2b** and $(\text{COD})_2\text{PtCl}_2$ also appeared to give a single complex (**4**; 96%). The ^{31}P NMR spectrum showed one signal with a J_{PtP} value of 2680 Hz, diagnostic for PtCl_2 complexes with *trans*

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