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Synthesis of racemic palladacycles from 2-ferrocenylphenylphosphines

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ABSTRACT

Transformation of 2-bromophenylferrocene into 2-(diphenylphosphino)-, 2-(dicyclohexylphosphino)-, or 2-(diisopropylphosphino)phenylferrocene is followed by facile room-temperature metallation with palladium acetate. The resulting acetate-ligated palladacycles are transformed readily into bridged-chloride, monomeric acetylacetonate, or monomeric hexafluoroacetylacetonate congeners.

Introduction

Palladacycles have been the subject of extensive investigation [1] with significant recent attention having focused on the use of these complexes as catalysts in organic synthesis [2]. Many palladacycles are based on ferrocene [3], and enantiopure planar chiral C–N palladacycles containing this metallocene, or a related cobalt sandwich complex, have found widespread application as catalysts in asymmetric synthesis [4]. Furthermore, racemic planar chiral C–N palladacycles have been utilised as precatalysts for Suzuki and Heck reactions [5], and in light of the ability of phosphorous ligands to stabilise palladium(0), some of these contain an additional phosphine ligand [5b–d]. Alternatively, C–P phosphapalladacycles are a simpler 'all-in-one' precatalyst [6] which led our group to introduce racemic complexes **1a–b** (Insert 1) as efficient precatalysts for the Suzuki reaction of aryl chlorides [7]. We have also described the synthesis of non-racemic **1a–b** by asymmetric transcyclometallation (up to 95% ee) [8] and asymmetric palladation (up to 65% ee) [9]. In this paper we describe in detail the synthesis, properties and ligand substitution chemistry of racemic phosphapalladacycles **1**. These have the potential to be exploited further as both catalysts and precatalysts in organic synthesis, in the knowledge that these complexes are also available in non-racemic form.

Results and discussion

The transformation of ferrocene **2** into 2-bromophenylferrocene **3** was achieved in low yield by lithation of ferrocene with *tert*-buytllithium [10] followed by transmetallation with zinc chloride and palladium catalysed cross-coupling with 1,2-dibromobenzene (Scheme 1). A simpler procedure, which became the method of choice, utilised a modification of the method previously reported by Little et al. involving diazotation of 2-bromoaniline followed by addition of ferrocene **2** [11]. Although the yield of this procedure was also modest, purification of the product from unreacted ferrocene by column chromatography was straight-forward enabling the isolation of multi-gram quantities of **3**. Synthesised similarly was 2-iodophenylferrocene **4**.

Addition of butyllithium to a solution of 2-bromophenylferrocene **3** in THF at −78 °C resulted in clean lithium–halogen exchange such that subsequent addition of either chlorodiphenylphosphine, chlorodicyclohexylphosphine or chlorodiisopropylphosphine resulted in the formation of phosphines

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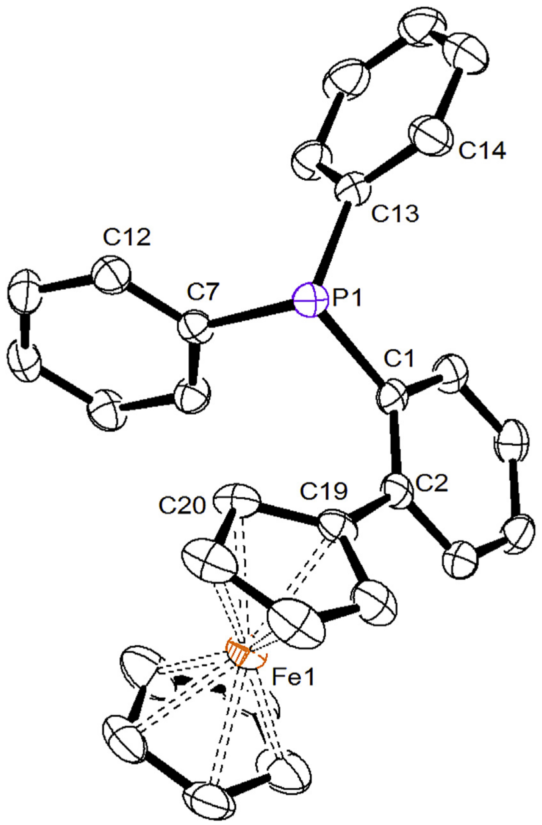

Fig. 1. A representation of **5a** from the X-ray analysis. Principal bond lengths [Å] include: C(2)–C(19) 1.509(3), P(1)–C(1) 1.8624(14), P(1)–C(7) 1.8487(14), P(1)–C(13) 1.8576(14). Principal torsion angles [°] include: C(1)–C(2)–C(19)–C(20) = 34.7(3), C(2)–C(1)–P–C(7) = −87.39(11), C(14)–C(13)–P(1)–C(1) = −88.07(12), C(12)–C(7)–P(1)–C(13) = −82.59(11).

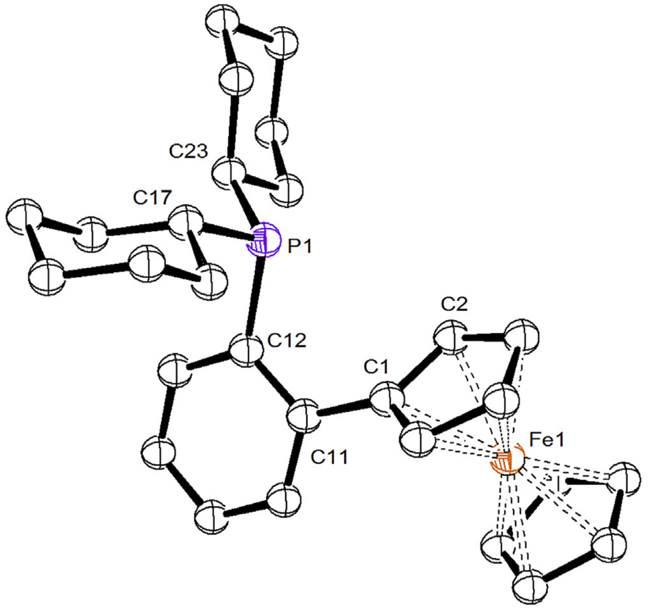

Fig. 2. A representation of **5b** from the X-ray analysis. Principal bond lengths [Å] include: C(1)–C(11) 1.479(3), P(1)–C(12) 1.848(2), P(1)–C(23) 1.851(2), P(1)–C(17) 1.752(4). Principal torsion angles [°] include: C(2)–C(1)–C(11)–C(12) −52.1(3), C(11)–C(12)–P(1)–C(17) −103.5(2), C(11)–C(12)–P(1)–C(23) 145.01(17).

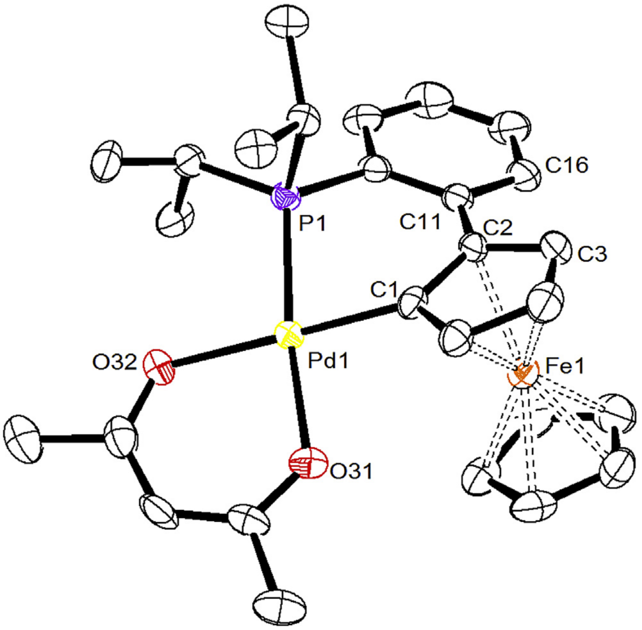

Fig. 3. A representation of **7c** from the X-ray analysis. Principal bond lengths [Å] include: Pd(1)–C(1) 1.988(6), Pd(1)–P(1) 2.2070(16), Pd(1)–O(31) 2.089(5), Pd(1)–O(32) 2.093(5). Principal angles [°] include: O(31)–Pd(1)–O(32) 89.07(19), C(1)–Pd(1)–P(1) 81.75(19). Principal torsion angles [°] include: O(31)–Pd(1)–C(1)–C(5) −35.0(5), C(3)–C(2)–C(11)–C(16) 25.9(10).

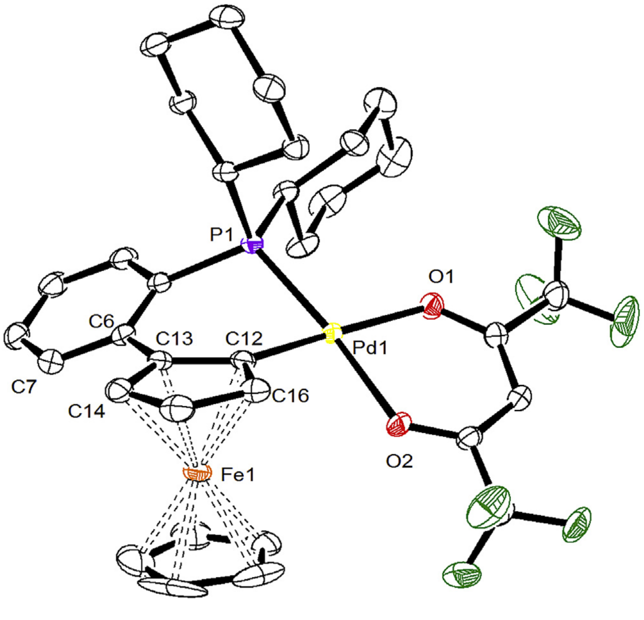

Fig. 4. A representation of **8b** from the X-ray analysis. Principal bond lengths [Å] include: Pd(1)–C(12) 1.974(2), Pd(1)–P(1) 2.2124(5), Pd(1)–O(1) 2.1309(15), Pd(1)–O(2) 2.1130(15). Principal angles [°] include: O(2)–Pd(1)–O(1) 86.04(6), C(12)–Pd(1)–P(1) 82.39(6). Principal torsion angles [°] include: C(16)–C(12)–Pd(1)–O(2) 34.31(17), C(7)–C(6)–C(13)–C(14) −23.1(3).