ChemPubSoc Europe

DOI: 10.1002/cplu.201402195

CHEMPLUSCHEM Full Papers

Functionalized Tri- and Tetraphosphine Ligands as a General Approach for Controlled Implantation of Phosphorus Donors with a High Local Density in Immobilized Molecular Catalysts

Matthieu Beaupérin,[a] Radomyr Smaliy,[a] Hélène Cattey,[a] Philippe Meunier,[a] Jun Ou,[b] Patrick H. Toy,[b] and Jean-Cyrille Hierso*[a, c]

Supported phosphine ligands are auxiliaries of topical academic and industrial interest in catalysis promoted by transition metals. However, both controlled implantation and controlled conformation of ligands should be achieved to produce immobilized catalysts that are able to structurally "copy" efficient homogeneous systems. We provide herein a general synthetic strategy for assembling a new class of branched tetra- and triphosphine ligands with a unique controlled rigid conformation, and thus providing a high local density of phosphorus atoms for extended coordination to the metal center. We prepared new functionalized cyclopentadienyl (Cp) salts to design polyphosphines that were "ready for immobilization". These protected Cp fragments might also be of synthetic utility for generating other supported metallocenes. Tetra- and triphosphines were then formed and diversely functionalized for immobilization on virtually any kind of support. As evidenced by ^{31}P NMR spectroscopy and the strong "through-space" spin–spin ^{TS}J(P,P) coupling observed between P atoms, these modified polyphosphines induce, when immobilized on a support, a high local concentration of phosphorus donors that are spatially very close to each other (3–5 Å). These functionalized ligands have been incorporated into polystyrene to give either soluble or insoluble polymers and on inorganic supports such as silica. We report the catalytic performance at 0.05–0.5 mol% low palladium loading of the resulting immobilized polyphosphine ligands. This study provides proof-of-concept of supported catalytic materials built from modular polyphosphines with a novel approach to structurally controlled polydentate heterogeneous catalysts.

Introduction

The separation and recycling of molecular catalysts from reactions is a scientific challenge with environmental and economic implications.[1,2] The "holy grail" in molecular catalysis would arguably be to combine within the same system the virtues of high activity and selectivity attributed to homogeneous catalysis, and the technical and commercial advantages of catalyst separation and recycling from heterogeneous systems. In this respect, many techniques have been developed that have aimed at the immobilization of catalytic systems with the use of different solid supports,[3,4] and the development of multiphasic reaction conditions.[5] These remarkable advances have shown that heterogenized species can be in many instances promising challengers to their homogeneous molecular catalyst counterparts. However, a single universal solution to the problems of separation, catalyst instability and activity, metal leaching, and control of single-site molecular catalysts has yet to be reported.

Among the auxiliaries of easy access and industrial-scale interest, supported phosphine ligands are currently used in transition-metal catalysis,[6] and some simple examples are commercially available, such as triphenylphosphine polystyrene (PS–PPh_3) and diphenylphosphinomethyl polystyrene (PS–CH_2PPh_2). In systems that use such auxiliaries, in addition to mass-transfer problems, the structural similarity between the homogeneous molecular catalysts and their corresponding immobilized analogues is often not exact. As a result, this can negatively affect reactivity and/or selectivity when compared with the parent homogeneous catalysts.

Efficient palladium-catalyzed cross-coupling in solution is usually achieved in the presence of a two- to fourfold excess

[a] Dr. M. Beaupérin, Dr. R. Smaliy, Dr. H. Cattey, Prof. Dr. P. Meunier, Prof. Dr. J.-C. Hierso
Université de Bourgogne
Institut de Chimie Moléculaire (ICMUB)
UMR-CNRS 6302, 9 avenue Alain Savary
21078 Dijon (France)
Fax: (+33) (0)3 80393682
E-mail: hiersojc@u-bourgogne.fr

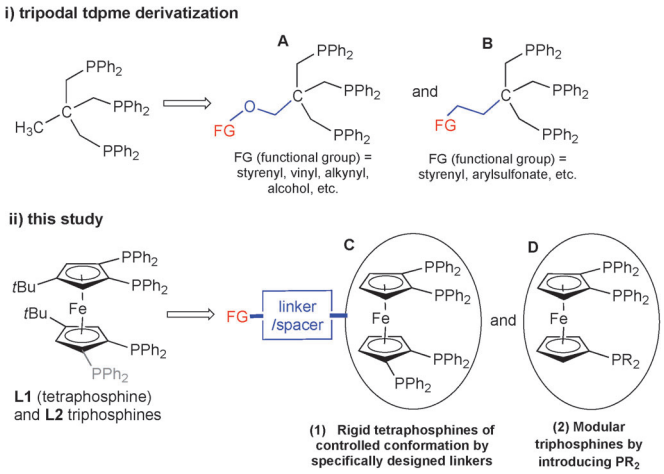
[b] Dr. J. Ou, Prof. Dr. P. H. Toy
The University of Hong Kong
Department of Chemistry
Pokfulam Road, Hong Kong (P. R. China)

[c] Prof. Dr. J.-C. Hierso
Institut Universitaire de France (IUF)-France

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/cplu.201402195. It contains the preparation details for all CpLi salts, functionalized polyphosphines, and immobilized ligands; spectroscopic data for new compounds; ^{31}P NMR spectroscopic simulation for second-order spectra and conformational views of molecular structures.

amount of phosphine ligands relative to the metal center. Phosphines allow for the stabilization of Pd^0/Pd^{II} as 14 to 18 e^- species (i.e., "$Pd(PR_3)_n$" with $n = 2–4$, R = aryl or alkyl).[7] Conversely, whatever the nature of the support for immobilized monophosphine ligands, the unavoidable high dispersion of the coordinating sites on the support renders it improbable for multiple remote donors to coordinate the same metal center. In more rigid and/or insoluble supports this issue for supported molecular catalysts is even more pronounced. Thus, to provide immobilized single-molecular catalysts able to accommodate three or four coordinating ligands to a given metal center, a controlled implantation of donors with a high local density must be achieved. Finding a general solution to this challenge is a driving force of the present study.

Polydentate ligands, which are known to form thermally and kinetically more stable complexes with metal catalyst than monodentate ones, have been proposed for attachment to solid supports by Bianchini et al.,[8] Gade et al.[9] and others,[10] and triphosphine-supported polymers have been developed.[11] These pioneering investigations have been limited to functionalization of the tripodal phosphine ligand 1,1,1-tris[(diphenylphosphino)methyl]ethane (tdpme; Scheme 1, compounds A and B) despite the wide variety of linear, tripodal, and other branched polydentate phosphines available.[12]



Scheme 1. Polyphosphines functionalized for immobilization on supports: (i) State-of-the-art tripodal species, and (ii) rigid and modular branched tri- and tetraphosphines, a new class of ligands.

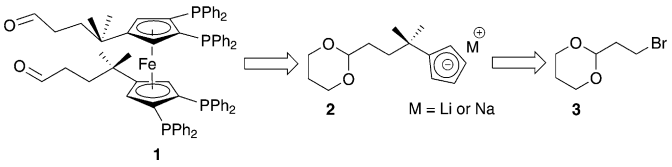
We provide herein a general synthetic pathway for assembling a new class of branched tetra- and triphosphine ligands with a controlled rigid conformation. These species are diversely functionalized for immobilization on virtually any kind of support. As demonstrated by ^{31}P NMR spectroscopy and the strong through-space spin–spin $^{TS}J(P,P)$ coupling observed, these modified polyphosphines induce, when immobilized on a support, a high local concentration of phosphorus donors spatially very close to each other (Scheme 1, compounds C and D). We demonstrate that the specific conformation of polyphosphines in which the phosphorus atoms are in close spatial vicinity is conserved in the modified polyphosphines. Accordingly, these functionalized ligands have been supported on polystyrene, thereby providing easy access to either soluble or insoluble materials. These modular functionalized polyphosphines were also used for the controlled implantation of donors onto commercial silica. We report the catalytic performance at 0.05–0.5 mol% palladium loading of the supported polyphosphine ligands and their recyclability. Carbon–carbon bond formation by Suzuki reaction and an unprecedented heterogeneous direct C–H functionalization of heteroaromatics with demanding chloroarene substrates was also successfully achieved.

Results and Discussion

The lack of supported polyphosphines reported in the literature might be attributed to the challenging requirements for the selective and efficient functionalization of the backbone of such sophisticated ligands.[13] Indeed, the introduction of phosphino groups at an early stage of the design sequence renders subsequent modifications much more difficult. Protection and deprotection procedures for phosphorus donors might be necessary, and the loss of phosphine during the overall process could be considerable. We became interested in the challenge of providing a general access to supported tri- and tetraphosphine ligands of controlled conformation based on the ferrocene backbone (Scheme 1C and 1D). To the best of our knowledge, no tetradentate phosphine has been implanted on a support to date, and we have shown that the ferrocene platform polyfunctionalized with three or four phosphorus atoms gives access to molecular palladium catalysts with excellent performance in topical homogeneous C–C,[14] C–N,[15] and C–O (and C–S)[16] cross-coupling reactions, as well as direct C–H functionalization.[17,18]

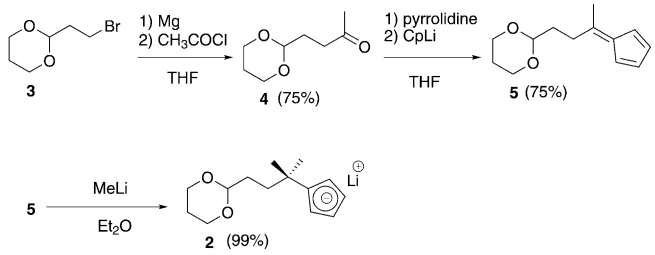
Functionalized ferrocenyl tetraphosphine ligands ready for immobilization

To achieve its anchorage on a solid support, the tetraphosphine ligand **L1** (Scheme 1, and analogous **L2** triphosphines) needs to be modified by the introduction of a reactive handle. This point of attachment should preferably be positioned far enough away from the four phosphino groups to keep the active catalytic site uncluttered. The steric hindrance induced by the two bulky *tert*-butyl groups in **L1** is essential to be reproduced since this feature gives a *cisoid* conformation to such type of ligands. This specific conformation is at the origin of the close proximity of donor atoms in solution and in the solid state. Accordingly, unique spectroscopic[19] and catalytic properties[14–18] are associated with the presence of bulky *tert*-butyl groups on the ferrocenylphosphines. The preservation and control of the close proximity of the phosphorus atoms in the supported ligands is thus critical. Considering these prerequisites, we envisioned that the tetraphosphine derivative **1** would be a valuable target (Scheme 2). Compound **1** possesses a carbonyl group that could be readily utilized and modified to achieve attachment of the tetraphosphine motif to a large variety of supports.



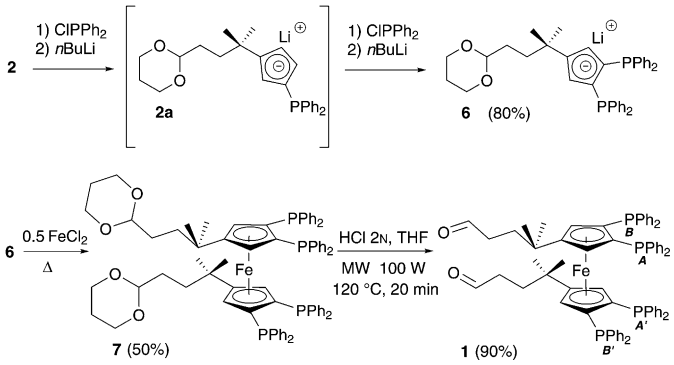
Scheme 2. Retrosynthetic analysis for the synthesis of functionalized ferrocenyl polyphosphine **1** by assembly of cyclopentadienyl blocks.

We reasoned that the two *gem*-methyl groups in the linker attached to the cyclopentadienyl rings (Cp) might serve as *tert*-butyl mimetic groups for the control of the ferrocene platform conformation. An acetal group was chosen to protect the carbonyl group since it should be stable towards the strongly basic conditions usually employed in the assembly of ferrocene derivatives from cyclopentadienyl compounds. Thus, functionalized polyphosphine **1** was obtained by treating two equivalents of the diphosphino lithium salt derived from the Cp salt **2** with one equivalent of $FeCl_2$ after cleavage of the acetal protecting groups (Scheme 2). Lithium or sodium Cp salt **2** was prepared from the commercially available 2-(2-bromoethyl)-1,3-dioxane (**3**), which includes both a masked carbonyl group and a versatile bromide group. The direct synthesis of compound **2** by addition on 6,6-dimethylfulvene of the Grignard derivative of **3** (or alternatively the nucleophilic lithium derivative) did not proceed at all.[20] However, bromide **3** could be converted into the corresponding Grignard reagent, which in turn could be directly added to acetyl chloride to afford ketone **4** in 75% yields after purification (Scheme 3).



Scheme 3. Synthesis of CpLi salt **2** including an acetal group.

The addition was conducted slowly to minimize the competing formation of 4-bromobutyl acetate from tetrahydrofuran (THF) ring opening by the organomagnesium intermediate, followed by reaction on acetyl chloride. This side reaction was found to be difficult to avoid since the Grignard reagent could only be generated in THF. The addition of pyrrolidine on ketone **4** and subsequent reaction with CpLi gave the 6,6-disubstituted fulvene **5** in 75% yield after purification (Scheme 3). This diene was treated with MeLi to afford Cp salt **2** in quantitative yield. Two sequential one-pot phosphination reactions using Cp lithium salt **2** afforded 1,2-bis(diphenylphosphino)-4-[4-(1,3-dioxan-2-yl)-2-methylbutyl] cyclopentadienyl lithium **6** in 80% overall yield (Scheme 4). Reaction of **6** with $FeCl_2$ afforded the protected ferrocenyl tetraphosphine **7** in 50% yield after purification. The acetal groups of **7** were hydrolyzed using acidic conditions and microwave irradiation to give the desired tetraphosphine dialdehyde **1** in 90% yield (Scheme 4). Surprisingly, other methods tested for this deprotection were found to be unsuccessful.[21]



Scheme 4. Synthesis of tetraphosphines **1** and **7**.

Gratifyingly, solution ^{31}P NMR spectroscopy of the functionalized polyphosphines **7** and **1** confirmed the success of our strategy in achieving the desired *cisoid* conformation of ferrocenylphosphines by control with *gem*-dimethyl groups. Typical AA′BB′ spin system signatures, which highlight the mutual proximity of the phosphorus atoms in **L1**,[19] were obtained for both functionalized polyphosphines **7** and **1**. Only minor differences in chemical shifts and coupling constants were found in comparison to **L1** (Table 1). The existence of a strong "through-space" coupling $^{TS}J(A,A')$ between internal heteroannular phosphorus atoms arises from the overlap of the phosphorus lone pairs.[22] In addition, strong $^3J(A,B)$ and $^3J(A',B')$ values between homoannular phosphorus are detected, which results mostly from the overlap of P lone pairs.[23] These coupling constants dramatically depend on the spatial proximity of the concerned atoms, and thus attest to the ligand conformation in solution. Consequently, ^{31}P NMR spectroscopy of samples in solution supports a similar *cisoid* conformation for **L1**, **7**, and **1**. This was confirmed in the solid state by an X-ray diffraction structure of the acetal-functionalized polyphosphine **7** (Figure 1). As expected, this tetraphosphine bears two acetal groups positioned on the Cp rings that do not encumber the coordination sites of the polyphosphine. The ferrocene backbone adopts a *cisoid* conformation analogous to the one observed in the

Table 1. ^{31}P NMR spectroscopic data for **L1**, **7**, and **1**.[a]

	$\delta_{AA'}$ [ppm]	$\delta_{BB'}$ [ppm]	$J(A,A')$ [Hz]	$J(A,B)=J(A',B')$ [Hz]	$J(B,B')$ [Hz]
L1	−28.6	−32.2	59.8	74.5	0
7	−30.4	−34.4	64.3	74.7	0
1	−31.0	−35.0	61.0	73.4	0

[a] Spectrum at 297 K in $CDCl_3$; δ and J values from simulated spectra at ±0.1 ppm and ±0.1 Hz. Lower-field $\delta_{AA'}$ is attributed to internal phosphorus atoms and $\delta_{BB'}$ to peripheral phosphorus atoms (see **1** in Scheme 4). All other J coupling constants involving the AA′BB′ ^{31}P spin system have zero values.

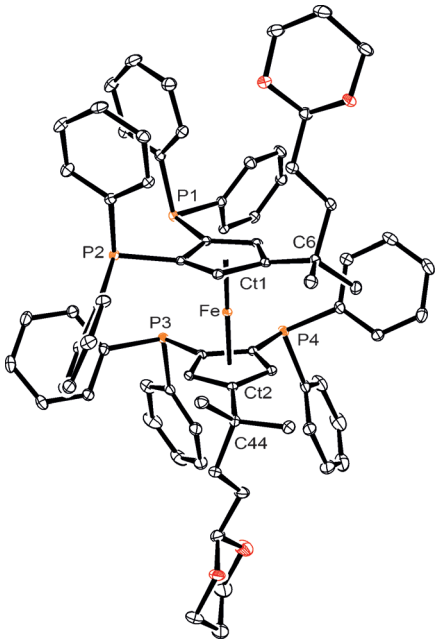


Figure 1. Molecular structure of the acetal-functionalized tetraphosphine **7** (hydrogen atoms are omitted for clarity) showing its *cisoid* conformation. Selected geometrical parameters: P1-Ct1-Ct2-P3, −9.90(5)°; P1-Ct1-Ct2-P4, 58.86(5)°; P2-Ct1-Ct2-P3, 57.84(5)°; P1···P3, 3.6737(8) Å.

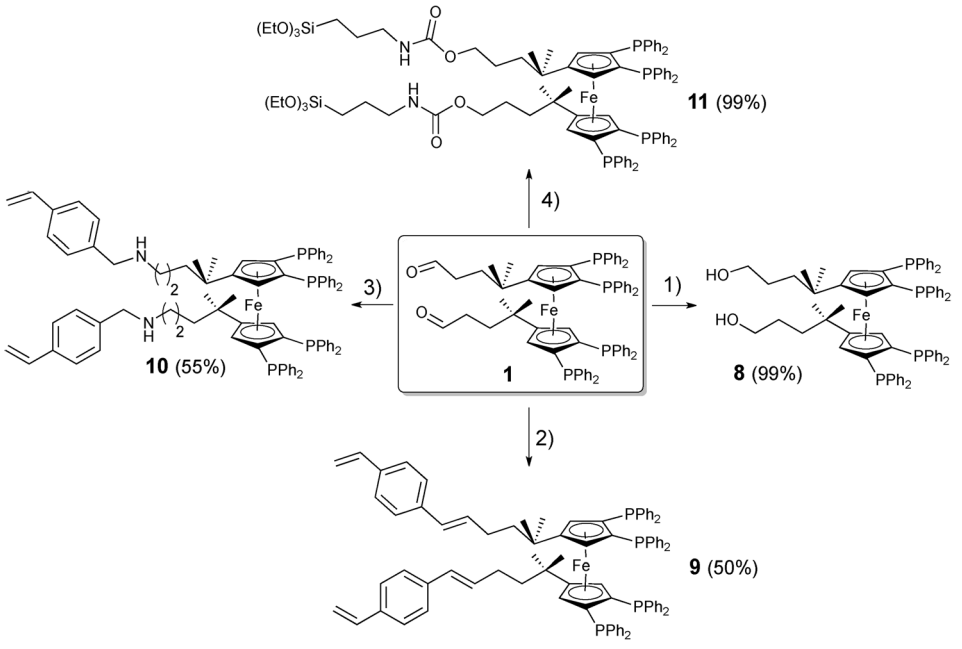
molecular structure for **L1**, with small dihedral angles P1-Ct1-Ct2-P3 of 9.90(5)° (2.72° for **L1**; see also the molecular structure projection in the Supporting Information).

The carbonyl groups of tetraphosphine **1** have to be modified according to the immobilization mode used and depending on the solid support. This will guarantee efficient covalent bonding of the ligand to the support. The carbonyl derivative can be grafted directly on preformed Merrifield-type resins. Alternatively, a styrenyl moiety has to be introduced for processing tetraphosphine immobilization within a polymeric resin, which would be formed by co-polymerization with styrene. An alkyltriethoxysilane chain has to be added for anchoring of the ligand on inorganic supports such as functionalized silica, or to alternatively perform the synthesis of a functionalized material by means of a sol–gel process. Therefore, tetraphosphine **1** was modified to give the new functionalized polyphosphines **8**–**11** (Scheme 5).

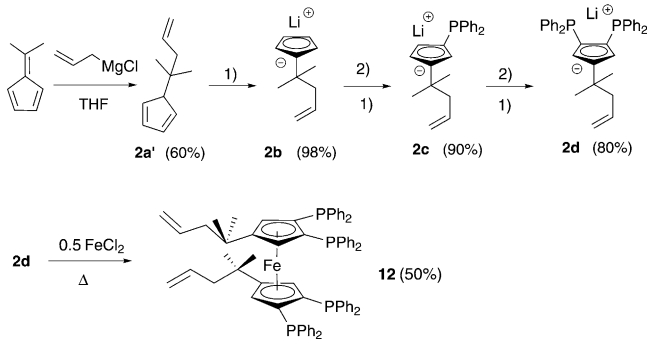
Diol **8** was quantitatively obtained from reduction of **1** with $LiAlH_4$ in THF. From **8**, we aimed to introduce a terminal styrenyl moiety through an ether linkage, but *p*-vinylbenzylchloride or iodide did not react appropriately with the corresponding alkoxide and instead produced the undesired quaternization of phosphines (as evidenced by ^{31}P NMR spectroscopy with a shift from $\delta = -30$ to 20 ppm). To avoid tedious sequences of phosphorus protection/deprotection, we generated the styrenyl derivative **9** by means of a Wittig reaction using **1**. We alternatively obtained it from the phosphonium salt of *p*-vinylbenzyl iodide, and a Julia–Kocienski olefination with a sulfonylbenzothiazole. Polyphosphine **9** was produced in 35–50% yield using these methods. The preparation of polyphosphine **10** was achieved by reductive amination of **1** with *p*-vinylbenzylamine in dichloroethane (DCE; 55% yield). The multinuclear NMR spectroscopic characterization of the functionalized polyphosphines **8**–**11** confirmed the conservation of the desired polydentate ligand *cisoid* conformation for all these compounds.

Although we introduced various functional groups (FGs) efficiently on the metallocene backbone of a tetraphosphine (Scheme 1), we were also interested in tuning the length of the linker (Scheme 1) and accessing other useful functionalities. Therefore, by following a similar strategy, we synthesized vinyl-functionalized ferrocenyl tetraphosphine **12** (Scheme 6). Such vinyl groups could potentially allow for further relevant modifications by means of olefin copolymerization, olefin metathesis, hydrosilylation, hydroboration, Heck coupling etcetera. In the tetraphosphine **12** the FG is in the γ position, closer to the Cp ring.

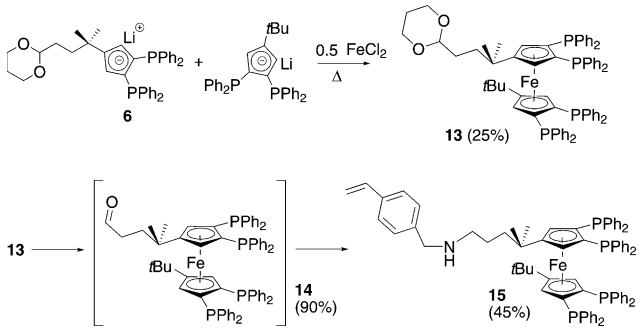
The reaction of 6,6-dimethylfulvene with allylmagnesium chloride led to the 1-functionalized cyclopentadiene **2a′** (Scheme 6).[24] Our attempts to position the vinyl group in the β position of the Cp ring by using vinyl-magnesium halides



Scheme 5. Synthesis of tetraphosphines **8**–**11**. Conditions: (1) $LiAlH_4$/THF, 0 °C, 1 h; (2) triphenyl(4-vinylbenzyl) phosphonium iodide/NaH, THF, RT (20 °C), 0.5 h; (3) triacetoxyborohydride, *p*-vinylbenzylamine, DCE, RT, 15 h; and (4) from **8**: (3-isocyanatopropyl)triethoxysilane/NEt_3, DCE, RT, 20 h.



Scheme 6. Synthesis of the vinyl ferrocenyltetraphosphine **12**. Conditions: (1) *n*BuLi/*n*-hexane, −80 °C; (2) $ClPPh_2$/toluene.



Scheme 7. Synthesis of the monofunctionalized-tetraphosphines **13**–**15**.

failed. Lithiation of **2a**′ with *n*BuLi quantitatively converted it into **2b**. Two successive phosphination/lithiation reactions using chlorodiphenylphosphine and *n*BuLi selectively gave **2d** in 70% overall yield. Ferrocenyl polyphosphine **12** was obtained by treating $FeCl_2$ with **2d**. ^1H and ^{31}P NMR spectroscopy in solution and single-crystal X-ray diffraction in the solid state (Figure 2) for the vinylferrocenyl phosphine **12** confirmed the presence of the vinyl moiety and perfect conservation of a *cisoid* conformation for the polyphosphine with a dihedral angle P1-Ct1-Ct2-P3 of 7.38(5)° (see also the molecular structure projection in the Supporting Information).

The monofunctionalized analogues **13**–**15** of the difunctionalized tetraphosphines **1**, **7**, and **10** were also synthesized (Scheme 7). Compound **13** was formed from the appropriate Cp lithium salt mixture, with a statistical coproduction of the symmetric compounds **L1** and **7**. These phosphines were easily separated by column chromatography. The ^{31}P spin systems found for **13**–**15** support a *cisoid* conformation for the ferrocene backbone. However, they do not resemble the AA′BB′ spin systems of tetraphosphines **L1**, **7**, **1**, and **10** (see Table 1). Indeed, owing to the dissymmetric nature of **13**–**15**, the spin systems obtained show an additional complexity. This is illustrated by very rarely reported intricate ABCD patterns (Figure 3, top).

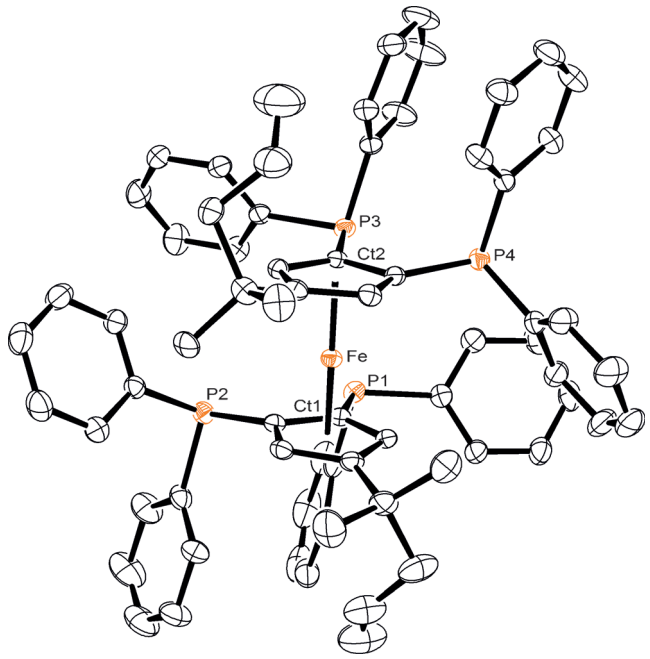


Figure 2. Molecular structure of the vinyl-functionalized tetraphosphine **12** (disorder of 1,1-dimethylbut-3-enyl groups and hydrogen atoms are omitted for clarity). Selected geometrical parameters: P1-Ct1-Ct2-P3, 7.38(5)°; P1-Ct1-Ct2-P4, −60.11(5)°; P2-Ct1-Ct2-P3, −60.66(5)°; P1···P3, 3.5987(8) Å.

The simulation of these second-order spectra (Figure 3, middle) allowed us to determine the ^{31}P NMR spectroscopic chemical shifts and coupling constants, as exemplified for tetraphosphine **13** (Figure 3). Thus, four different but proximate chemical shifts are obtained for the anisochronous phosphino groups (Figure 3, bottom). Different ^3J(A,B), ^3J(C,D), and ^{TS}J(B,C) values were obtained, which are consistent with the values obtained for ^{TS}J(A,A) and ^3J(A,B)=^3J(A′,B′) in the symmetrical ferrocenylphosphine analogues; this ascertained the controlled conformation of the monofunctionalized tetraphosphines **13** and **15** (second-order ^{31}P NMR spectroscopic simulations in the Supporting Information).

Immobilization of functionalized tetraphosphines onto organic and inorganic supports

To test the reactivity of the modified polyphosphines, we first achieved the direct anchoring of dialdehyde **1** on a polymeric support. Compound **1** was treated with a commercially available mesoporous aminomethylpolystyrene resin (PL-AMS) in the presence of sodium triacetoxyborohydride in DCE. Since **1** has a deep red color, the originally white polymer beads displayed a pink coloration at the end of the reaction that was conserved after repeated washing of the resin. The grafting ratio was determined by phosphorus elemental analysis and a loading of 0.99% P was achieved (0.32 mmol g^{-1}). Solid-state ^{31}P NMR (cross-polarization magic angle spinning, CP-MAS) was performed. This established that no oxidation of phosphine occurred during the immobilization. The corresponding spectrum showed a broad singlet centered at $\delta = -27.0$ ppm (see the Supporting Information), which roughly corresponds to the average chemical shift of phosphorus atoms in the original ligand. From this insoluble resin the presence of only one

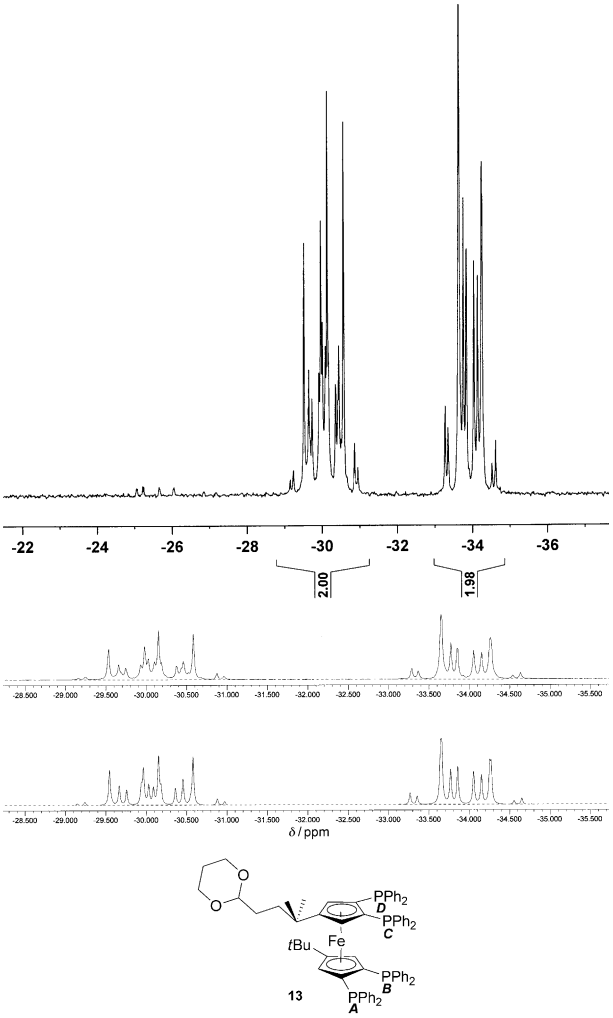
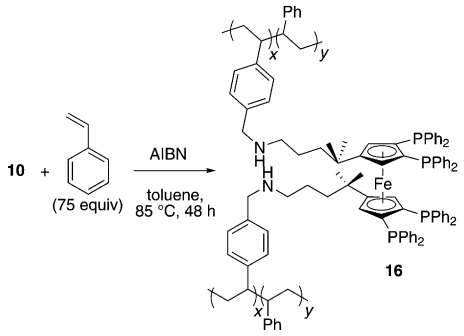


Figure 3. ^{31}P NMR spectra of the ABCD spin system for the tetraphosphine **13** (top), and experimental and simulated enhancement spectra (middle). Chemical shift (δ) for **13** ($\pm$0.1 ppm) and J constants ($\pm$0.6 Hz): $\delta_A = -33.9$, $\delta_B = -29.9$, $\delta_C = -30.3$, $\delta_D = -34.0$ ppm, J(A,B) = 73.3, J(B,C) = 61.6, J(C,D) = 74.2 Hz. All other J coupling constants involving the ABCD ^{31}P spin system have zero values.

strong phosphorus signal is informative of the success of immobilization; however, no fine structure could be obtained to definitively confirm the preservation of the ligand conformation.

With a view toward having better control over the immobilization process on a polymeric support, and to tune the solubility properties of the resulting resins, we performed radical copolymerizations with styrene of the styrenyl-functionalized tetraphosphines **9** and **10**. Copolymerization of styrene with vinyl-functionalized tetraphosphine **12** was unsatisfactory, likely owing to reaction kinetics being too different for the structurally dissimilar monomers, and thus no detectable incorporation of phosphine ligands was achieved. Because of the cross-linking internal double bond in the δ position to Cp, monomer **9** was difficult to incorporate properly into a polystyrene matrix, and only traces of phosphorus were detected by elemental analysis of the resulting resins formed ($<$30 μmol g^{-1}).



Scheme 8. Synthesis of polystyrene-supported tetraphosphine **16**.

Conversely, styrenyl tetraphosphine **10** was found to be suitable to form with styrene either soluble or insoluble supported polyphosphine, depending on the experimental conditions. The radical polymerization of **10** with styrene and azobisisobutyronitrile (AIBN) initiator in toluene at 85 °C for 48 hours afforded, after removal of the solvent, compound **16** (Scheme 8) as the first non-cross-linked polystyrene-supported tetraphosphine. This orange polymer is soluble in most common organic solvents except for methanol and *n*-hexane.

The elemental analysis of **16** indicated a phosphorus loading of 1.05% (0.34 mmol g^{-1}), and ^{31}P NMR spectroscopy in CD_2Cl_2 showed two broad signals centered at $\delta = -30.0$ and -34.0 ppm (Figure 4). These chemical shifts are fully consistent with those of the non-supported parent ligand, thereby attesting to the non-oxidized state of the phosphorus atoms. The presence of two signals evidenced in the supported ligand a differentiation between internal and peripheral phosphorus atoms. Gratifyingly, this confirmed the expected conservation of the specific *cisoid* conformation of the tetraphosphine in the polymer.

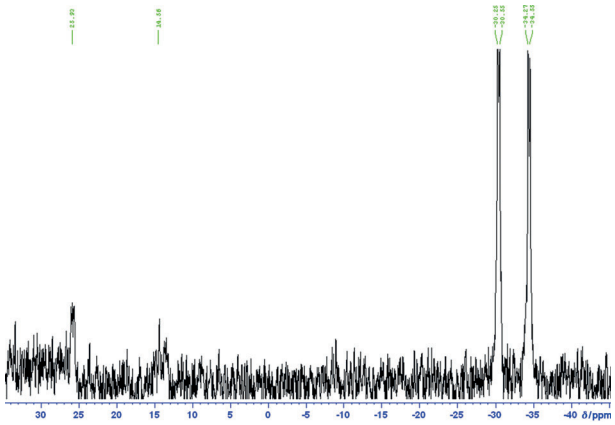


Figure 4. ^{31}P NMR spectra of a solution of polystyrene-supported tetraphosphine **16** in CD_2Cl_2. Distinct signals for peripheral and internal phosphorus are found at $\delta = -30.0$ and -34.0 ppm, respectively. Less than 10% traces of phosphine oxide are detectable at $\delta = 25.0$ ppm.

This conformation control for supported phosphines provides a localized high density of four proximate phosphorus atoms in the designed polymeric material. Additionally, the formation of an insoluble polystyrene-supported resin was ach-

ieved by incorporating a supplementary cross-linker such as divinylbenzene or the Jandajel cross-linker into the reacting mixture of **15** and styrene.[25] Accordingly, the morphology of soluble and insoluble polymer-supported tetraphosphines (named **15**-PS) is illustrated in Figure 5.

To further explore the versatility of our modified polyphosphines, we also achieved their immobilization on an inorganic support. The concept of dialkoxysilane **11** was inspired by silica-based condensation technology.[26] Phosphine **11** was immobilized on silica gel (0.035–0.070 mm, 60 Å) to give brown-red beaded powder (**11**-SiO_2), which were found insoluble in all the solvents tested (details in the Supporting Information).

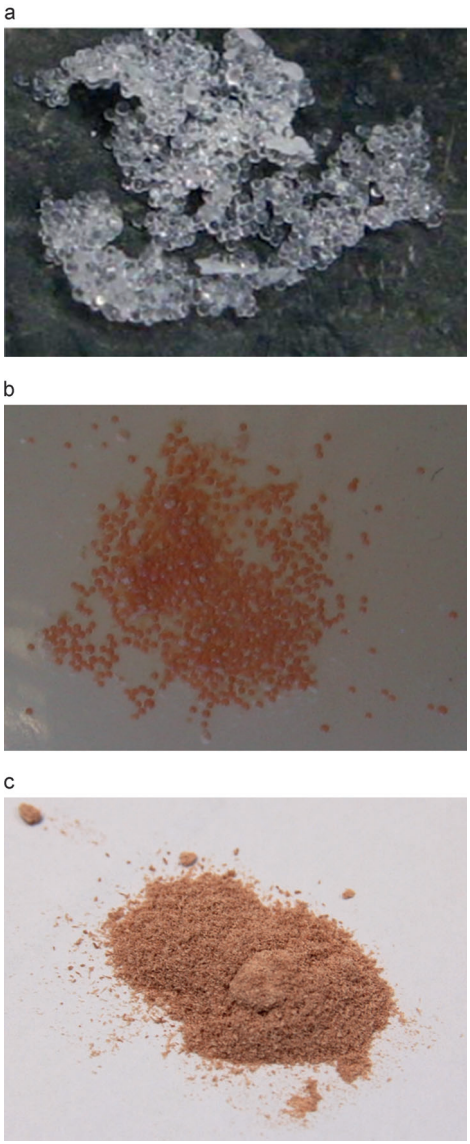


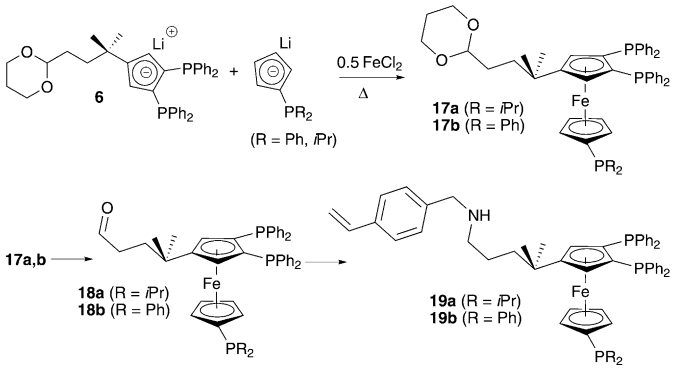
Figure 5. Polymeric materials: (a) Standard insoluble cross-linked polystyrene beads that do not incorporate a polyphosphine ligand (homogeneous dispersion 400–500 μm beads); (b) insoluble cross-linked polystyrene beads **15**-PS incorporating tetraphosphine ligand **15** (P loading 0.30 mmol g^{-1}, homogeneous dispersion 250–300 μm beads); (c) compound **16**, as soluble polystyrene powder incorporating tetraphosphine ligand **10** (P loading 0.34 mmol g^{-1}).

The corresponding solid-state ^{31}P NMR CP-MAS spectrum indicated a broad singlet centered at −30 ppm.

Stimulated by this preliminary proof-of-concept, we used our functionalized Cp salts to design dissymmetric modified triphosphines that were "ready for immobilization", in which the nature of the substituents on phosphino groups might differ (Scheme 1D). Such a powerful approach of modular formation of triphosphine towards immobilized ligands is described below.

Functionalized ferrocenyltriphosphines as modular ligands ready for immobilization

Based on the assembly of two different substituted Cp alkali-metal salts with iron dichloride, the triphosphines **17a,b**–**19a,b** (Scheme 9) were prepared. Great modularity is achieva-



Scheme 9. Synthesis of modular functionalized triphosphines **17a,b**–**19a,b** with various PR_2 groups (R = aryl, alkyl).

ble by this method of combining the protected salt **6** with another substituted cyclopentadienyl fragment. The characterization of functionalized ligands demonstrated the success of these syntheses with the typical chemical shift for the phosphorus atoms, as well as the signature of the FGs (see the Supporting Information). Functionalized triphosphine **19a** was then immobilized by radical copolymerization with styrene (60 equiv) and divinyl benzene (7 equiv) to give an insoluble resin with a 1.05% phosphorus content. The strategy we developed is thus applicable to the entire class of triphosphine ligands we have developed in recent years, and which contain the 1,2-bis(diphenylphosphino)-4-*tert*-butylcyclopentadienyl fragment.[27] Clearly, these cyclopentadienyl fragments and their derivatives might also be of synthetic utility to form other supported metallocenes such as titanocenes,[28] zirconocenes,[29] lanthanocenes[30] etcetera.

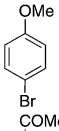
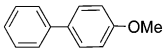
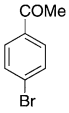
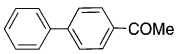
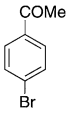
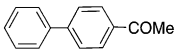
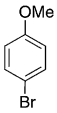
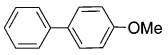
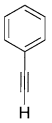
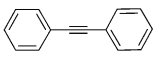
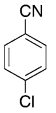
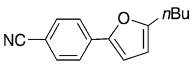
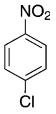
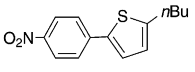
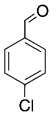
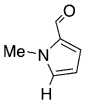
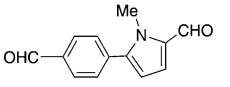
We next explored the performance of our set of immobilized polyphosphine ligands as catalytic materials in palladium-catalyzed reactions for which the homogeneous counterparts have been notably efficient at low catalyst loading.

Palladium-catalyzed C–C bond formation with immobilized polyphosphine catalysts

Palladium-catalyzed carbon–carbon bond formation is a powerful set of synthetic tools, which includes reactions between organometallic nucleophiles and organic halides such as the Suzuki and Sonogashira cross-couplings. Owing to the necessity of limiting costly and potentially toxic stoichiometric metallic reagents, research focus has recently shifted to the direct functionalization of substrates by C–H activation using aromatic and heteroaromatic starting materials. Recoverable or heterogeneous catalytic systems for direct arylation of C–H bonds are limited to very few examples.[31] The performance of the new supported polyphosphines at low palladium-catalyst loading was probed in Suzuki coupling of aryl bromides with phenyl boronic acid, in copper-free Sonogashira coupling with phenylacetylene, and in the direct C–H arylation of furane, thiophene, and pyrrole substrates with chloroarenes. With satisfactory conditions established for the use of the supported tetraphosphines **16** and **11**-SiO_2, and triphosphine **19a**-PS, pertinent results are summarized in Table 2. Noteworthy, the performance of the insoluble resin **15**-PS was poorer under similar conditions of solvent and temperature (conversion $<50\%$). Further study is needed to assert the stability and activity conservation of these catalysts.[1b,32] Nevertheless, these preliminary results show satisfactory consistency with the parent homogeneous polyphosphine catalysts, which inspired the present study, as illustrated in Table 2 for head-to-head comparisons with homogeneous counterparts and with PPh_3 and bis-(diphenylphosphino)ferrocene (dppf) ligands.

The cross-coupling of phenylboronic acid with bromobenzene was most efficiently achieved by using [Pd/**16**] (formed in situ; see the Experimental Section and the Supporting Information) at 0.5 mol% (80%). Electron-rich and electron-neutral bromoarenes gave reaction products in moderate (50%) to fairly good yield (65%) by using [Pd/**16**]. Significantly better performance was achieved by using the silica-supported system [Pd/**11**-SiO_2] (formed in situ), with yields above 80% for the coupling of 4-bromoanisole and 4-bromoacetophenone to phenyl boronic acid. The performance of supported triphosphine **19a**-PS was investigated in the copper-free Pd-catalyzed Sonogashira coupling of bromobenzene with phenylacetylene; it showed excellent performance (95%) and good potential for recycling. In general, efficient recycling of the catalysts after six runs has not been established. This is mainly due to accumulative loss of material during filtration. For the insoluble catalysts used at

Table 2. C–C bond formation from aryl halides and nucleophiles with immobilized polyphosphine catalysts.[a]

Catalyst [%]	Halide	Nucleophile	Product	Yield [%] (run)	TONs
0.5 mol% Pd/PPh_3	PhCl	$PhB(OH)_2$	Ph–Ph	5	10
0.5 mol% Pd/dppf	PhCl	$PhB(OH)_2$	Ph–Ph	38	76
0.5% mol% Pd/dppe	PhCl	$PhB(OH)_2$	Ph–Ph	44	88
0.5% mol% **L1**	PhCl	$PhB(OH)_2$	Ph–Ph	95	190
0.5 mol% [Pd/**16**]	PhBr	$PhB(OH)_2$	Ph–Ph	80 (1) 77 (2) 82 (3) 75 (4) 72 (5) 68 (6)	908
0.5 mol% [Pd/**16**]		$PhB(OH)_2$		50 (1) 49 (2) 37 (3)	272
0.05 mol% [Pd/**16**]		$PhB(OH)_2$		65	1300
0.05 mol% [Pd/**11**-SiO_2]		$PhB(OH)_2$		85	1700
0.5 mol% [Pd/**11**-SiO_2]		$PhB(OH)_2$		85 (1) 87 (2) 83 (3)	510
0.5 mol% [Pd/**19a**-PS]	PhBr			95 (1) 92 (2) 90 (3)	554
0.5 mol% [Pd/**19a**-PS]				68[b]	136
0.5 mol% [Pd/**19a**-PS]				49[b]	98
0.5 mol% [Pd/**19a**-PS]				23[b]	46

[a] Conditions: $[PdCl(\eta^3\text{-}C_3H_5)]_2$, 120 °C, DMF, 20 h. [b] $Pd(OAc)_2$, 150 °C for 40 h in *N*,*N*-dimethylacetamide, 2 equiv of tetra-*n*-butylammonium, yields based on GC analysis and NMR spectroscopy are the average value of two or more runs.

0.5 mol%, inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis of the filtrate indicated no significant leaching (< 10 ppm, less than 0.1% of the initial Pd loading). Accordingly, the hot filtration test showed the termination of the cross-coupling reactions by use of the filtrate recharged with reagents and bases.

The resulting cumulative turnover numbers (TONs; 270–1700) of the catalysts are satisfactory relative to their homogeneous counterparts tetraphosphine **L1** and triphosphine **L2** when used with chlorides (Table 2, first entries). However, **L1** and **L2** yielded TONs over 10000 with bromides under homogeneous conditions not reached by the supported ligands to date.[14]

The supported triphosphine **19a**-PS was also investigated in the coupling of chloroarenes to furane, thiophene, and pyrrole substrates by direct C2 C–H functionalization. These reactions were inspired by the excellent performance of the ferrocenyltriphosphines reported in these relevant reactions that eliminate the need for prefunctionalization of substrates for coupling.[17,18] We were glad to observe that these direct arylation reactions of heteroaromatics, which are typically promoted by triphosphines under homogeneous conditions,[17] were also achievable under heterogeneous conditions. The arylation of 2-*n*-butylfurane with 4-chlorobenzonitrile (68%) and the coupling of 2-*n*-butylthiophene to 4-chloronitrobenzene (49%) were achieved more efficiently than the C2 arylation of 1-methyl-2-formylpyrrole with 4-chlorobenzaldehyde (23%). All these coupling reactions tolerate a functionalization both on the chloroarene and heteroaromatic substrates and represent promising results towards difficult C–H functionalization with demanding chloroarenes under "greener" heterogeneous conditions.

Conclusion

In this study, we have delivered a general strategy for synthesizing unprecedented localized high-density phosphorus donor atoms in immobilized catalysts. Several reactive functional groups have been selectively introduced onto cyclopentadienyl rings, and these in turn allowed new synthetic pathways to the first supported rigid branched tetraphosphines, and to several modular triphosphines in which different phosphino groups can be introduced. These cyclopentadienyl fragments might also be of synthetic utility to form other supported metallocenes of interest. As a proof-of-concept, the modified ligands were supported on organic and inorganic supports elaborated by following different methodologies, which include copolymerization with styrene (with or without a cross-linker), direct grafting onto preformed polymers, and inorganic sol–gel condensation. The resulting materials were successfully used and recycled in low-metal-loading cross-coupling reactions. In particular, successful results have been obtained in direct C–H bond arylation with chloroarenes.

Overall, this study provides a new and general approach for supporting tetraphosphine ligands and modular triphosphines with highly controlled conformations. The use of ^{31}P NMR spectroscopy and "through-space" spin coupling of magnetically nonequivalent nuclei attest to the conformations, which were confirmed by X-ray structures. This study finally provides proof-of-concept of the synthetic utility of these new supported catalytic materials with a localized high density of donor atoms in C–C bond-formation reactions.[33] Further study in this area will aim to optimize the supports and supporting methods.

Experimental Section

General procedures

All reactions were performed under an argon atmosphere using Schlenk techniques. Full details of the preparation and characterization of modular ligands, their support, and catalytic use are provided as Supporting Information. The homogeneous polyphosphine counterparts to the modular functionalized polyphosphines presented herein are commercially available under the name HiersoPHOS (Strem Chemicals).

Synthesis of 1,1′,2,2′-tetrakis(diphenylphosphino)-4,4′-di[4-(1,3-dioxan-2-yl)-2-methylbut-2-yl]ferrocene (7)

A solution of **6** (3.1 g, 5.2 mmol) in toluene (10 mL) was added dropwise at 20 °C to a suspension of $FeCl_2$ (0.45 g, 3.55 mmol) in toluene (5 mL). The reaction mixture was then heated to reflux overnight and removed by filtration. Solvents were removed under reduced pressure, and the residue was washed with cold ethanol. When impurities were still present, purification by flash column chromatography on silica gel (eluent: AcOEt/heptane 1:4) was performed to yield **7** (3.2 g, 50%) as an orange-red powder. ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 8.42–6.45 (m, 40H; Ph), 4.47 (m, 2H; OCH_1), 4.15–4.06 (m, 8H; $4HCP + 4OCH_{6eq,8eq}$), 3.79 (m, 4H; $OCH_{6ax,8ax}$), 2.11 (m, 2H; CH_{7eq}), 1.51–1.21 (m, 10H; $2CH_{7ax} + 4H_2$, $4H_3$), 0.94, 0.10 ppm (s, 6H each, Me); ^{31}P{^{1}H} NMR ($CDCl_3$, 242.9 MHz): δ = −30.4 (AA′ spin system, 2P), −34.4 ppm (BB′ spin system, 2P); ^{13}C NMR ($CDCl_3$, 151 MHz): δ = 137.5–127.1 (m, 48C), 105.4 (s, 2C), 102.8 (s, 2C), 87.9 (dd, J(C,P) = 35.5 Hz, J(C,P) = 13 Hz, 2C), 79.4 (m, 2C), 72.7, 72.0 (s, 2C each), 67.0 (s, 4C), 41.7 (s, 2C), 32.8 (s, 2C), 31.0 (s, 2C), 26.9, 28.7 (s, 2C each), 26.0 ppm (s, 2C); MS: *m/z* calcd for $C_{76}H_{78}FeO_4P_4$ (1235.17): 1257.4092 [M+Na$^+$]; found: 1257.4037. σ = 0.030, err = 4.42 ppm.

Synthesis of 1,1′,2,2′-tetrakis(diphenylphosphino)-4,4′-di(4-oxo-2-methylbut-2-yl)ferrocene (1)

A hydrochloric acid solution (2 N, 5 mL) was added to a solution of **7** (0.3 g, 0.24 mmol) in THF (15 mL). The reaction mixture was stirred for 20 min under microwave irradiation (125 W), quenched by a solution of saturated aqueous sodium hydrogenocarbonate and extracted with CH_2Cl_2 (2×25 mL). The organic layer was dried over $MgSO_4$, and the solvents were removed under reduced pressure. The crude product was purified by flash column chromatography on silica gel (eluent: AcOEt/heptane 1:4) to yield **1** (0.245 g, 90%) as a red powder. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 9.77 (s, 2H), 8.37–6.48 (m, 40H), 4.18 (s, 2H), 4.04 (s, 2H), 2.20 (m, 4H), 1.54 (m, 4H), 0.97, 0.21 ppm (s, 6H each); ^{31}P{^{1}H} NMR ($CDCl_3$, 121.48 MHz) : δ = −31.0 (AA′, 2P), −35.0 ppm (BB′, 2P); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 202.0 (s, 2C), 138.7–127.4 (m, 48C), 105.1 (s, 2C), 88.8 (m, 2C), 80.0 (m, 2C), 72.4, 71.7 (s, 2C each), 40.2 (s, 2C), 37.7 (s, 2C), 32.8 (s, 2C), 28.0, 27.4 ppm (s, 2C each); FTIR: $\tilde{\nu}$ = 1721.8 cm^{-1} (CO) (full spectrum in the Supporting Information).

Owing to the reactivity of the formyl function, proper mass analyses were not obtained.

Synthesis of 1,1′,2,2′-tetrakis(diphenylphosphino)-4,4′-bis{5-[(3-triethoxysilyl)propylcarbamoyloxy]-2-methyl}pent-2-ylferrocene (11)

Tetraphosphine **1** (50 mg, 44 μmol) was dissolved in CH_2Cl_2 (1 mL). The addition of (3-isocyanatopropyl)triethoxysilane (24 μL, 44 μmol) to the reaction mixture was complemented with one drop of triethylamine. After 20 h at 20 °C, the solvent of the reaction was evaporated under reduced pressure to yield **11** (70 mg, 99%) as a red powder. ^{1}H NMR ($CDCl_3$, 500 MHz, 298 K): δ = 8.42–6.45 (m, 40H), 4.7 (s, 2H), 4.17, 4.04 (s, 2H each), 4.02 (t, ^3J = 6.5 Hz, 4H), 3.82 (q, ^3J = 7 Hz, 12H), 3.20 (q, ^3J = 6.5 Hz, 4H), 1.65 (m, 4H), 1.30 (m, 4H), 1.24 (t, ^3J = 7 Hz, 18H), 0.99, 0.13 (s, 6H each), 0.87 (m, 4H), 0.63 ppm (s, 4H); ^{31}P{^{1}H} NMR ($CDCl_3$, 202.5 MHz, 298 K): δ = −30.7 (AA′, 2P), −34.6 ppm (BB′, 2P); ^{13}C NMR ($CDCl_3$, 125.7 MHz, 298 K): δ = 157.1 (s, 2C), 139.1–127.5 (m, 48C; Ph), 105.8 (s, 2C), 88.5 (dd, J(C,P) = 13.8, 35.2 Hz, 2C), 79.9 (t, J(C,P) = 18.9 Hz, 2C), 72.7, 72.2 (s, 2C each), 65.6 (s, 2C), 58.8 (s, 6C), 43.8 (s, 2C), 43.3 (s, 2C), 35.7 (s, 2C), 28.9, 27.2 (s, 2C each), 25.1 (s, 2C), 23.7 (s, 2C), 18.6 (s, 6C), 8.0 ppm (s, 2C); MS: *m/z* calcd for $C_{90}H_{112}P_4FeO_{10}N_2Si_2$ (1617.77): 1616.61537 [M^+]; found: 1616.61284. σ = 0.1892, err = 1.3 ppm.

Grafting of triethoxysilane ligand 11 on silica gel (11-SiO_2)

In a Dean–Stark apparatus, silica gel (1.0 g, 16.64 mmol; Acros, 0.035–0.070 mm, 60 Å) was suspended in toluene (50 mL) and heated to reflux for 20 h. The silane ligand **11** (0.3 g, 185 μmol) dissolved in toluene (15 mL) was then added, and the mixture was heated to reflux for 5 h. After evaporation of toluene, the resulting mixture was treated with dichloromethane (20 mL), filtered, dried, and washed several times with dichloromethane, then dried under vacuum to give a red powder (1.06 g). The grafted silica was insoluble in all the organic solvent tested (THF, $CHCl_3$, CH_2Cl_2, toluene, Et_2O, ethyl acetate, *n*-hexane, methanol, *N*,*N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), *N*-methyl-2-pyrrolidone (NMP)). The grafting ratio of **11** was determined, and a 0.84% phosphorus loading was achieved (0.272 mmol g^{-1} of P, 0.068 mmol g^{-1} of ligand). ^{31}P NMR (CP-MAS; 121.48 MHz, 298 K): δ = −30.0 ppm.

Direct C–H arylation of heteroaromatics with chloroarenes using Pd/polystyrene 19a-PS

The aryl chloride (1 mmol), heteroaromatic derivative (2 mmol), KOAc (2 mmol, 196 mg), and Bu_4NBr (1 mmol, 322 mg) were introduced into a Schlenk tube equipped with a magnetic stirring bar and were purged several times with argon. In another tube, $Pd(OAc)_2$ (0.005 mmol, 1.12 mg) and **19a**-PS (0.005 mmol, 69.3 mg) were mixed in degassed dimethylacetamide (DMAc; 3 mL) and stirred for 30 min. After addition of the reagents to the catalyst, the Schlenk tube was placed in an oil bath that had been preheated to 150 °C, and the mixture was stirred for 40 h. The cooled mixture was filtered on paper to recover the catalyst. The solvent was removed by heating of the reaction vessel under vacuum, and the residue was charged directly onto a silica gel column. The products were eluted using diethyl ether/pentane.

Acknowledgements

Support provided by the ANR program for Sustainable Chemistry Development (ANR-09-CP2D-03 CAMELOT), the Région Bourgogne (3MIM program), and the CNRS is gratefully acknowledged. We thank Johnson Mattey for a generous gift of palladium. Thanks also go to B. Hanquet, J. Roger, A. Job, and S. Royer for their technical assistance.

Keywords: heterogeneous catalysis · immobilization · metallocenes · phosphane ligands · through-space interactions

[1] a) R. Chen, R. P. J. Bronger, P. C. J. Kamer, P. W. N. M. van Leeuwen, J. N. H. Reek, *J. Am. Chem. Soc.* **2004**, *126*, 14557; b) C. W. Jones, *Top Catal.* **2010**, *53*, 942; c) A. E. Collis, I. T. Horváth, *Catal. Sci. Technol.* **2011**, *1*, 912; d) *Heterogeneized Homogeneous Catalysts for Fine Chemicals Production: Materials and Processes* (Eds.: P. Barbaro, F. Liguori), Springer, Dordrecht, **2010**; e) *Recoverable and Recyclable Catalysts* (Ed.: M. Benaglia), Wiley, Chichester, **2009**.

[2] a) N. E. Leadbeater, M. Marco, *Chem. Rev.* **2002**, *102*, 3217; b) C. A. McNamara, M. J. Dixon, M. Bradley, *Chem. Rev.* **2002**, *102*, 3275; c) Q.-H. Fan, Y.-M. Li, A. S. C. Chan, *Chem. Rev.* **2002**, *102*, 3385; d) C. E. Song, S.-G. Lee, *Chem. Rev.* **2002**, *102*, 3495; e) Z. Wang, G. Chen, K. Ding, *Chem. Rev.* **2009**, *109*, 322; f) J. M. Fraile, J. I. García, J. A. Mayoral, *Chem. Rev.* **2009**, *109*, 360; g) A. F. Trindade, P. M. Gois, C. A. Afonso, *Chem. Rev.* **2009**, *109*, 418; h) P. Barbaro, F. Liguori, *Chem. Rev.* **2009**, *109*, 515; i) R. Akiyama, S. Kobayashi, *Chem. Rev.* **2009**, *109*, 594.

[3] For recent examples, see: a) D. T. Genna, A. G. Wong-Foy, A. J. Matzger, M. S. Sanford, *J. Am. Chem. Soc.* **2013**, *135*, 10586; b) Y. M. A. Yamada, Y. Yuyama, T. Sato, S. Fujikawa, Y. Uozomi, *Angew. Chem.* **2014**, *126*, 131; *Angew. Chem. Int. Ed.* **2014**, *53*, 127; c) T. Iwai, T. Harada, K. Hara, M. Sawamura, *Angew. Chem.* **2013**, *125*, 12548; *Angew. Chem. Int. Ed.* **2013**, *52*, 12322; d) T. Iwai, R. Tanaka, T. Harada, M. Sawamura, *Chem. Eur. J.* **2014**, *20*, 1057.

[4] a) M. Waki, Y. Maegawa, K. Hara, Y. Goto, S. Shirai, Y. Yamada, N. Mizoshita, T. Tani, W.-J. Chun, S. Muratsugu, M. Tada, A. Fukuoka, S. Inagaki, *J. Am. Chem. Soc.* **2014**, *136*, 4003; b) D. Astruc, F. Chardac, *Chem. Rev.* **2001**, *101*, 2991.

[5] a) G.-J. ten Brink, I. W. C. E. Arends, R. A. Sheldon, *Science* **2000**, *287*, 1636; b) I. T. Horvath, J. Rabai, *Science* **1994**, *266*, 72.

[6] M. Guinó, K. K. (Mimi) Hii, *Chem. Soc. Rev.* **2007**, *36*, 608.

[7] a) C. Amatore, M. Azzabi, A. Jutand, *J. Am. Chem. Soc.* **1991**, *113*, 8375; b) A. Jutand, *Chem. Rev.* **2008**, *108*, 2300.

[8] a) C. Bianchini, D. G. Burnaby, J. Evans, P. Frediani, A. Meli, W. Oberhauser, R. Psaro, L. Sordelli, F. Vizza, *J. Am. Chem. Soc.* **1999**, *121*, 5961; b) P. Barbaro, C. Bianchini, V. Dal Santo, A. Meli, S. Moneti, R. Psaro, A. Scaffidi, L. Sordelli, F. Vizza, *J. Am. Chem. Soc.* **2006**, *128*, 7065.

[9] R. A. Findeis, L. H. Gade, *Eur. J. Inorg. Chem.* **2003**, 99.

[10] P. Schober, G. Huttner, L. Zsolnai, A. Jacobi, *J. Organomet. Chem.* **1998**, *571*, 279.

[11] C. Bianchini, A. Meli, M. Peruzzini, F. Vizza, F. Zanobini, *Coord. Chem. Rev.* **1992**, *120*, 193.

[12] a) J.-C. Hierso, R. Amardeil, E. Bentabet, R. Broussier, B. Gautheron, P. Meunier, P. Kalck, *Coord. Chem. Rev.* **2003**, *236*, 143; b) H. A. Mayer, W. C. Kaska, *Chem. Rev.* **1994**, *94*, 1239.

[13] R. A. Findeis, L. H. Gade, *Dalton Trans.* **2003**, 249.

[14] a) J.-C. Hierso, A. Fihri, R. Amardeil, P. Meunier, H. Doucet, M. Santelli, B. Donnadieu, *Organometallics* **2003**, *22*, 4490; b) J.-C. Hierso, A. Fihri, R. Amardeil, P. Meunier, H. Doucet, M. Santelli, V. V. Ivanov, *Org. Lett.* **2004**, *6*, 3473.

[15] a) M. Sophal, M. Platon, H. Cattey, H. J. Spencer, P. J. Low, J.-C. Hierso, *Catal. Commun.* **2014**, *51*, 10; b) M. Platon, J. Roger, S. Royer, J.-C. Hierso, *Catal. Sci. Technol.* **2014**, *4*, 2072; c) A. Fihri, J.-C. Hierso, A. Vion, D.-H. Nguyen, M. Urrutigoïty, P. Kalck, R. Amardeil, P. Meunier, *Adv. Synth. Catal.* **2005**, *347*, 1198.

[16] a) M. Platon, L. Cui, S. Mom, P. Richard, M. Saeys, J.-C. Hierso, *Adv. Synth. Catal.* **2011**, *353*, 3403; b) M. Platon, N. Wijaya, V. Rampazzi, L. Cui, Y.

Rousselin, M. Saeys, J.-C. Hierso, *Chem. Eur. J.* DOI: 10.1002/chem.201403337.
[17] D. Roy, S. Mom, M. Beaupérin, H. Doucet, J.-C. Hierso, *Angew. Chem.* **2010**, *122*, 6800; *Angew. Chem. Int. Ed.* **2010**, *49*, 6650.
[18] D. Roy, S. Mom, D. Lucas, H. Cattey, J.-C. Hierso, H. Doucet, *Chem. Eur. J.* **2011**, *17*, 6453.
[19] a) J.-C. Hierso, A. Fihri, V. V. Ivanov, B. Hanquet, N. Pirio, B. Donnadieu, B. Rebière, R. Amardeil, P. Meunier, *J. Am. Chem. Soc.* **2004**, *126*, 11077; b) J.-C. Hierso, D. Evrard, D. Lucas, P. Richard, H. Cattey, B. Hanquet, P. Meunier, *J. Organomet. Chem.* **2008**, *693*, 574.
[20] This is the classical way to produce *tert*-butyl cyclopentadienyl lithium, which is employed for the synthesis of **L1**.
[21] The other conditions we tested were unsuccessful or led to decomposition of polyphosphines.
[22] a) J.-C. Hierso, *Chem. Rev.* **2014**, *114*, 4838; b) J.-C. Hierso in *High Resolution Nuclear Magnetic Resonance Parameters: Understanding Molecules and their Electronic Structures* (Ed: R. H. Contreras), Elsevier, Amsterdam, **2014**.
[23] O. L. Malkina, V. G. Malkin, *Angew. Chem.* **2003**, *115*, 4471; *Angew. Chem. Int. Ed.* **2003**, *42*, 4335.
[24] D. Vos, P. Jutzi, *Synthesis* **2000**, 357.
[25] J. Lu, P. H. Toy, *Chem. Rev.* **2009**, *109*, 815.
[26] F. Hoffmann, M. Cornelius, J. Morell, M. Fröba, *Angew. Chem.* **2006**, *118*, 3290; *Angew. Chem. Int. Ed.* **2006**, *45*, 3216.
[27] V. V. Ivanov, J.-C. Hierso, R. Amardeil, P. Meunier, *Organometallics* **2006**, *25*, 989.
[28] a) W. Wang, M. Fujiki, K. Nomura, *J. Am. Chem. Soc.* **2005**, *127*, 4582; b) A. Gansäuer, C. Kube, K. Daasbjerg, R. Sure, S. Grimme, G. D. Fianu, D. V. Sadasivam, R. A. Flowers, *J. Am. Chem. Soc.* **2014**, *136*, 1663.
[29] a) S. Knüppel, G. Erker, R. Fröhlich, *Angew. Chem.* **1999**, *111*, 2048; *Angew. Chem. Int. Ed.* **1999**, *38*, 1923; b) B. Bosch, G. Erker, R. Froehlich, O. Meyer, *Organometallics* **1997**, *16*, 5449; c) G. Erker, G. Kehr, R. Fröhlich, *J. Organomet. Chem.* **2004**, *689*, 1402; d) J. A. Pool, E. Lobkovsky, P. J. Chirik, *J. Am. Chem. Soc.* **2003**, *125*, 2241.
[30] a) P. B. Hitchcock, M. F. Lappert, S. Tian, *Organometallics* **2000**, *19*, 3420; b) M. R. Douglass, T. J. Marks, *J. Am. Chem. Soc.* **2000**, *122*, 1824.
[31] For the first heterogeneous C–H bond arylation of furans and thiophenes with bromoarenes, see the recoverable system PdNPs@polypyrrole: a) V. A. Zinovyeva, M. A. Vorotyntsev, I. Bezverkhyy, D. Chaumont, J.-C. Hierso, *Adv. Funct. Mater.* **2011**, *21*, 1064; for C3 regioselective direct C–H functionalization of benzo[*b*]thiophenes with chloroarenes, see: b) D.-T. D. Tang, K. D. Collins, F. Glorius, *J. Am. Chem. Soc.* **2013**, *135*, 7450; for C–H bond functionalization with iodobenzene see: c) Ref. [3b]; for C–H phenylation of naphthalene using diphenyliodonium, see: d) T. H. Park, A. J. Hickman, K. Koh, S. Martin, A. G. Wong-Foy, M. S. Sanford, A. J. Matzger, *J. Am. Chem. Soc.* **2011**, *133*, 20138.
[32] a) M. Lamblin, L. Nassar-Hardy, J.-C. Hierso, E. Fouquet, F.-X. Felpin, *Adv. Synth. Catal.* **2010**, *352*, 33; b) N. T. S. Phan, M. Van Der Sluys, C. W. Jones, *Adv. Synth. Catal.* **2006**, *348*, 609.
[33] These functionalized polyphosphines, the methods for implantation of P donors on supports, and the catalytic applications at low loading are patented: J.-C. Hierso, M. Beaupérin, P. Meunier, FR Patent 2961813 A1 20111230, **2011**; WO 2012001601 A1 20120105, **2012**; US 2013158219 (A1), **2013**.

Received: June 28, 2014
Published online on August 26, 2014