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Carbometalated Complexes Possessing Tripodal Pseudo-C_3-Symmetric Triptycene-Based Ligands

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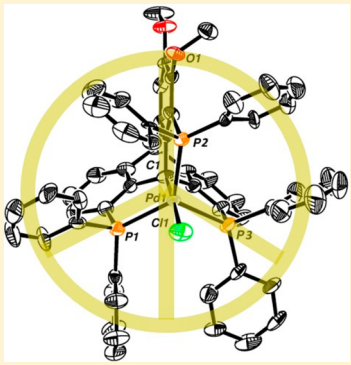
Supporting Information

ABSTRACT: New air-stable tripodal triphosphine ligands 1,8,13-tris-(diisopropylphosphino)-2,3-dimethoxytriptycene ($\mathbf{P_3T1}$) and 1,8,13-tris-(diphenylphosphino)-2,3-dimethoxytriptycene ($\mathbf{P_3T2}$) are presented and discussed. Their synthesis is based on the first practical synthesis of 1,8,13-tribromotriptycene. Reaction with palladium leads to the formation of new pseudo-C_3-symmetric carbometalated complexes: namely, $\mathbf{Pd(P_3T1)Cl}$ and $\mathbf{Pd(P_3T2)Cl}$. The catalytic activity of the new ligands and complexes was tested in the palladium-catalyzed chemoselective transfer hydrogenation of α,β-unsaturated ketones.



After more than 50 years of intensive research, numerous catalytic transformations have become routine for manufacturing fine and bulk chemicals on both academic and industrial scales. The breakthrough toward popularizing catalysis in organic synthesis came three decades ago after understanding that ligands can strongly affect and modify the intrinsic catalytic performance of late transition metals (Rh, Ru, Pd, Ir, Pt, and others). Since then, thousands of structurally different (mainly multidentate) ligands have been synthesized and tested for numerous metal-catalyzed reactions. However, despite the structural diversity of commercially available and reported scaffolds, C_3-symmetric ligands are still quite rare and, therefore, less explored.[1]

Most of the C_3-symmetric ligands known to date possess hard donors (N- or O-based) and, therefore, are more suitable for the synthesis of main-group- or early-transition-metal complexes.[2] Examples of ligands coordinating late transition metals through phosphorus and their applications in chiral molecular recognition and catalysis are less common, but some have appeared in the literature.[3] However, metalated C_3-symmetric complexes possessing a direct C/Si/N(sp^3)−M bond have been even less studied.[4] These compounds often possess unique reactivity, arguably because of the singular electronic and steric properties of the metal site originating from the strong σ-donating character of the anionic C(sp^3)-hybridized carbon in combination with the coordination sphere of unusual geometry.[5]

Our group has a longstanding interest in developing catalysts based on carbometalated PC(sp^3)P pincer ligands, especially those derived from a dibenzobarrelene-based scaffold.[6] Our interest in these compounds stems from the fact that, unlike the case for many known classes of PC(sp^3)P pincer ligands, synthesis of dibenzobarrelene derivatives is very modular because it is accomplished through the use of reliable Diels−Alder cycloaddition methodology, which guarantees facile access to a readily modifiable platform with tailored steric and electronic properties.[7] In addition, the rigidity of the frame and the lack of available labile α- and β-hydrogens can be translated into robustness and conformational stability, along with exceptional σ-donation of the metalated bridgehead sp^3-hybridized carbon. Following this initial interest and keeping in mind that triptycene-based ligands, in general, have gained a high reputation in catalysis,[8] extending the bis(dialkylphosphino)-tripticene system to the symmetrically substituted tris-(dialkylphosphino)tripticene was quite natural and logical.

Herein, we report the synthesis and characterization of a new class of triptycene-based triphosphines ($\mathbf{P_3T1}$ and $\mathbf{P_3T2}$), their coordination to Pd(II), and the benchmarking catalytic tests in the Pd(II)-catalyzed chemoselective transfer hydrogenation of α,β-unsaturated ketones.

The ligands $\mathbf{P_3T1}$ and $\mathbf{P_3T2}$ were prepared in three steps from the readily accessible starting materials, as presented in Scheme 1. Initially, 1,8-dibromoanthracene (**1**) is converted into 1,13-dibromo-6,7-dimethoxytriptycene (**2**) using a slightly modified literature protocol[9] in 63% yield. A successive electrophilic bromination of **2** results in the formation of a 1:1 mixture of the syn- and anti-substituted tribromide **3**. Fortunately, the desired $\mathbf{3}_{syn}$ can be selectively crystallized out in 42% yield, obviating tedious chromatographic isolation.

Surprisingly, an extensive literature search revealed that syntheses of symmetrically halogenated triptycenes are extremely rare and generally report on the synthesis of inseparable mixtures of isomers.[10] Thus, the reported protocol represents the first practical synthesis of 1,8,13-halogenated triptycene—a

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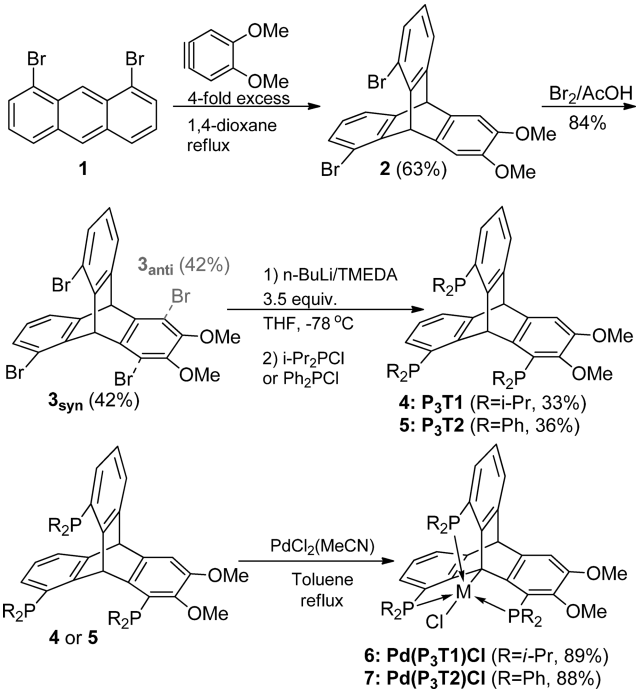
Scheme 1. Synthesis of the New Pseudo-C_3-Symmetric Triptycene-Based Ligands and Complexes



valuable synthetic intermediate.[11] Finally, phosphination of $\mathbf{3}_{syn}$ was carried out by sequential treatment with *n*-BuLi/TMEDA and the corresponding chlorodialkylphosphine. Both $\mathbf{P_3T1}$ (**4**) and $\mathbf{P_3T2}$ (**5**) were synthesized in approximately equal yields (33−35%).

NMR spectroscopy unequivocally validates the desired structure. For example, ^{31}P NMR of $\mathbf{P_3T1}$ displays two resonances for two different phosphine types: a doublet centered at −8.27 ppm (J = 10 Hz) for phosphines installed onto unsubstituted rings and a triplet appearing at 6.17 ppm (J = 10 Hz) for the MeO substituents neighboring the phosphine (AB_2 system).[12] Since six bonds separate all phosphorus nuclei, the splitting must originate from through-space interactions of the phosphines if they still converge at the same point, apparently in proximity to the central methine hydrogen. Indeed, the lack of free rotation can be clearly concluded from the ^{1}H NMR by the perfectly resolved anisochronous methyl groups within each of the isopropylphosphine substituents (please see the Supporting Information).[13] Furthermore, whereas peripheral methine hydrogen appears as an expected singlet at 5.25 ppm, the front hydrogen is shifted strongly downfield (7.93 ppm) and is split virtually into a quartet, which supports this assessment. Both of these phenomena have been described for bis-phosphine compounds of this type.[14] NMR spectra of the ligand $\mathbf{P_3T2}$ are less indicative, however, but exhibit similar patterns and are presented in the Supporting Information.

With the ligands at hand, we performed a series of complexation studies. Thus, for example, when $\mathbf{P_3T1}$ (**4**) and $\mathbf{P_3T2}$ (**5**) react stoichiometrically with $PdCl_2(MeCN)_2$ in toluene at 100 °C for 48 h, the carbometalated $\mathbf{Pd(P_3T1)Cl}$ (**6**) and $\mathbf{Pd(P_3T2)Cl}$ (**7**) form as orange solids in 83−89% isolated yields. ^{31}P{^{1}H} NMR spectra taken from the new compounds **6** and **7** displayed an expected AB_2 pattern, but with well-expressed secondary effects. The stronger influence of the second-order splitting in **6** and **7** is due to a stronger through-metal P_a−P_b coupling in the complexes versus a weak through-space coupling in the corresponding free ligands ($J_{P_a-P_b}$ = 212 Hz in $\mathbf{Pd(P_3T1)Cl}$ (**6**) versus J = 10 Hz for $\mathbf{P_3T1}$ and $J_{P_a-P_b}$ = 218 Hz in $\mathbf{Pd(P_3T2)Cl}$ (**7**) versus J = 18 Hz for $\mathbf{P_3T2}$ that correspond to $\Delta\nu/J$ = 20 for **6** and $\Delta\nu/J$ = 5 for **7**). In both cases, the triplet signal assigned to the phosphine in the substituted ring (P_a) of the free ligand now appears as a multiplet arising from the second-order splitting consisting of four transition lines centered at δ_P 55.76 ppm ($J_{P_a-P_b}$ = 212 Hz) for **6** and at δ_P 30.92 ppm ($J_{P_a-P_b}$ = 218 Hz) for **7**. The parent doublet signal ascribed to the phosphines on the unsubstituted rings of $\mathbf{P_3T1}$ and $\mathbf{P_3T2}$ is now situated at δ_P 34.8 ppm for **6** and 24.4 ppm for **7** and is also seen as a four-transition-line multiplet. The absence of the front methine hydrogen and the perfectly resolved isopropyl methyl groups in the ^{1}H NMR of **6** confirm their rigid (i.e., metalated) structure.

Despite the unambiguous identification of the new compound, single crystals of $\mathbf{Pd(P_3T1)Cl}$ (**6**) and $\mathbf{Pd(P_3T2)Cl}$ (**7**) (CCDC 1578676 and CCDC 1578674, correspondingly), grown by the slow diffusion of hexane into their saturated solutions in chloroform at room temperature, were subjected to X-ray diffraction analysis. Selected crystallographic parameters and the ORTEP drawingare presented in Figure 1. As expected, the

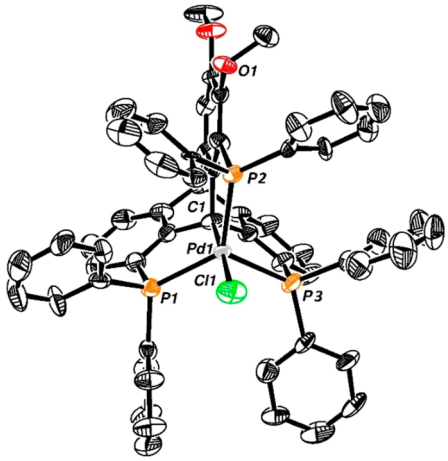


Figure 1. ORTEP drawing (50% probability ellipsoids) of $\mathbf{Pd(P_3T2)Cl}$ (**7**). Hydrogen atoms and solvent molecules are omitted for clarity.

palladium center in C(sp^3)-metalated complexes has almost a perfect trigonal-bipyramidal shape. For example, for $\mathbf{Pd(P_3T2)Cl}$,[15] the observed Cl1−Pd1−C1 angle is 176.6° and for P1−Pd1−P2, P2−Pd1−P3, and P1−Pd1−P3 the angles range from 118.6 to 122.8°. As expected, the Pd−Cl bond in $\mathbf{Pd(P_3T2)Cl}$ is slightly longer than the corresponding bond in the previously reported anthracene-based two-dimensional pincer complexes owing to a stronger trans influence exerted by the sp^3-hybridized carbon.[7b,16]

Chemoselective transfer hydrogenation of α,β-unsaturated ketones was chosen to benchmark the catalytic activity of the new complexes.[17] We chose this particular transformation because it is mediated by Pd-hydride species whose stability/reactivity balance is responsible for the higher efficiency and selectivity of the catalysts. We hypothesized that chemoselectivity will greatly benefit from the structural and conformational stability of the tripodal triptycene-based complexes. On the other hand, the electron-rich nature of the palladium centers will enhance the reactivity of the Pd-hydride intermediates. Moreover, this

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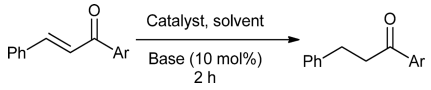
transformation is of great importance in organic synthesis.[18] It is often carried out in the presence of silicon or boron hydrides,[19] hydrogen,[18b,20] or hydrogen surrogates such as alcohols[21] and formates.[22] However, of all these alternatives, the use of alcohol as an environmentally friendly, safe, and cost-efficient hydrogen source is the most important one.

The catalysts **Pd(P$_3$T1)Cl** and **Pd(P$_3$T2)Cl** were initially tested in the conjugate reduction of benzalacetophenone ((*E*)-chalcone). Brief experimentation showed that the primary alcohols were generally superior over the secondary alcohols as solvents for the described transformation (e.g., 1-butanol or 1-propanol versus 2-butanol or 2-propanol), whereas ethanol and methanol led to no conversion. For example, 68% of the corresponding saturated product in >99% selectivity forms in refluxing 1-PrOH in the presence of 1 mol % of **Pd(P$_3$T1)Cl** and 10 mol % of K_3PO_4 as a base. A significantly lower yield, yet with excellent selectivity (25% and >99%, respectively), were observed under the same substrate:catalyst:base ratio in 2-propanol (Table 1, entries 1 and 2). We assume that the Pd−H bond formation is more difficult when sterically demanding alcohols interact with a cribbed palladium center. On the other hand, the excellent chemoselectivity of the presumed **Pd(P$_3$T1)-H** species also originates from the singular steric environment around the catalytic site. The diminished activity of the lower primary alcohols can be rationalized by the lower reaction temperature. Further improvement was achieved using boiling *n*-butanol in the presence of 10 mol % of K_2CO_3 and 0.5 mol % of equally reactive **Pd(P$_3$T1)Cl** or **Pd(P$_3$T2)Cl** (Table 1, entry 3). It is noteworthy that this reaction does not require oxygen, moisture-free conditions, or special equipment; therefore, the procedure can be performed in air using the standard grade solvents.

Table 1. Representative Results of the Transfer Hydrogenation of Enones Catalyzed by Pd(P$_3$T1)Cl

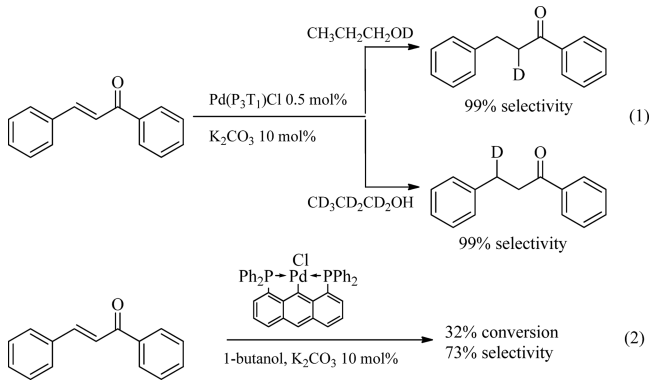


entry	conditions[a]	Ar	yield (sel), %[b]
1	**6** 1 mol % K_3PO_4, *n*-PrOH	phenyl	68 (99)
2	**6** 1 mol % K_3PO_4, *i*-PrOH	phenyl	25 (99)
3	**6** 0.5 mol % K_3PO_4, *n*-PrOH	phenyl	89 (99)
4	**6** 0.5 mol % K_3PO_4, *n*-PrOH	4-MeO-phenyl	92 (99)
5	**6** 0.5 mol % K_3PO_4, *n*-PrOH	1-naphthyl	73 (99)
6	**6** 0.5 mol % K_3PO_4, *n*-PrOH	2-furyl	72 (99)

[a]Other conditions: 0.5 mol % of **Pd(P$_3$T1)Cl**, 10 mol % of K_2CO_3 in refluxing *n*-butanol (or as stated in the table). [b]Isolated yield; selectivity according to NMR integration.

To test the general applicability of the new Pd complexes, a limited number of various α,β-unsaturated ketones were allowed to react under the optimized conditions. Substituted and unsubstituted, aromatic, and heteroaromatic enones were transfer-hydrogenated to provide the desired products in high yields and with excellent selectivity (Table 1, entries 4−6).

In order to confirm that the reaction is indeed mediated by the presumed Pd−H species and not by colloidal palladium that can, in principle, form, upon decomposition of the complexes, we carried out a mercury test as well as two deuterium-labeling experiments for the transfer hydrogenation of chalcone. Thus, the presence of metallic mercury in the reaction vessel showed no influence on the outcome. On the other hand, the use of $CH_3CH_2CH_2OD$ as a hydrogen source afforded an α-deuterated product, whereas the reaction using $CD_3CD_2CD_2OH$ afforded the product exclusively deuterated at the β-position (eq 1)—the selectivity cannot be achieved if the process is mediated by the ligand-free particle catalysts. Finally, employment of the previously reported anthracene-based two-dimensional pincer complexes of palladium led to diminished conversion and poor selectivity under the same reaction conditions (eq 2).



To conclude, we have disclosed for the first time synthesis and coordination studies of unprecedented air-stable tripodal ligands (**P$_3$T1** and **P$_3$T2**) based on a pseudo-C_3-symmetric triptycene derivative. The whole synthesis relies on the first practical synthesis of 1,8,13-tribromotriptycene. The catalytic activity of the new palladium complexes was tested in palladium-catalyzed chemoselective transfer hydrogenation of α,β-unsaturated ketones showing uniqueness of the reported scaffold. Further coordination and catalytic studies of this new family of tripodal ligands, including those that are chiral and enantiopure, will be reported soon.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.7b00907.

Experimental procedures, X-ray crystallographic data for all structures, and spectroscopic data (PDF)

Accession Codes

CCDC 1578674 and 1578676 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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