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Sterically Hindered Ortho-Substituted Phosphatriptycenes as Configurationally Stable P-Chirogenic Triarylphosphines

--Manuscript Draft--

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Abstract:	Ortho-substituted and unsymmetrical 9-phospha-triptycenes were synthesized via two synthetic approaches involving densely functionalized ortho-halogenated triarylmethane or phosphine precursors. Ortho-substituents turned out to impose a considerable steric shielding but had only a limited influence on the Lewis and Brønsted basicity of 9-phosphatripytycene, due to the tricyclic cage-shaped structure with the aryl rings p-systems orthogonal to the phosphorus electron pair. A series of Au(I) and Rh(I) complexes were analysed in the solid state to determine Tolman electronic parameters, cone angles and buried volumes of the ortho-substituted phosphatriptycenes. Quantum chemical calculations of electronic and steric descriptors revealed that these cage-shaped phosphines are electron-poor and that single methyl substituent is enough to provide the largest effect on steric shielding reported so far in triarylphosphines. An unsymmetrically substituted 9-phosphatriptycene was resolved by chiral HPLC, opening the avenue towards stable P-chirogenic triarylphosphines with unlimited configurational stability for new catalyst development in asymmetric transition-metal catalysis.
Author Comments:	Dear Editors, Dear Nathalie Weickgenannt, the development of new classes of bulky and chiral phosphines and the determination of their reactivity, steric and electronic properties is of high current interest in the fields of frustrated Lewis pairs chemistry, transition metal catalysis, and organocatalysis. Neither ortho-substituted, nor unsymmetrically substituted phosphatriptycenes were reported so far, due to their challenging syntheses involving unprecedent functionalization methods for obtaining their precursors (halogenated triarylmethanes and triarylphosphines). We have now developed two straightforward and expeditious methods to obtain a series of tricyclic cage-shaped phosphines, and have systematically quantified their electronic and steric properties experimentally and computationally. These unprecedented phosphines were employed as ligands for preparing Au and Ru complexes used as catalysts in TM catalysis, and fully characterized them in solution and in the solid state. Finally, a chiral phosphatriptycene was resolved by chiral HPLC, opening a whole new area in the field of chiral P-ligands, since these phosphines have an unlimited configurational stability owing to their cage-shaped structure (no P umbrella inversion and no racemisation is possible). We think that this fundamental work will not only guide further synthetic applications with these new phosphorus ligands, but will also drive further applications in enantioselective synthesis (e.g. catalysts development for frustrated Lewis pair and TM catalysis). As it will attract the attention of mechanistically, structurally and computationally interested synthetic organic and organometallic chemists, we consider Angewandte Chemie as the best medium for publishing these results and believe that this work will attract the interest of a broad readership. Yours sincerely, Raphaël Robiette Guillaume Berionni
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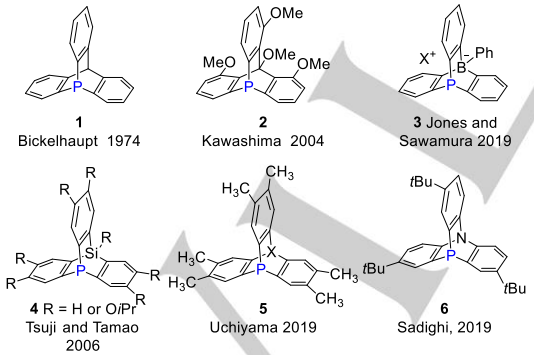
Sterically Hindered Ortho-Substituted Phosphatriptycenes as Configurationally Stable P-Chirogenic Triarylphosphines

Lei Hu, Damien Mahaut, Nikolay Tumanov, Johan Wouters, Laurent Collard, Raphaël Robiette,* and Guillaume Berionni*

Abstract: Ortho-substituted and unsymmetrical 9-phospha-triptycenes were synthesized via two synthetic approaches involving densely functionalized ortho-halogenated triarylmethane or phosphine precursors. Ortho-substituents turned out to impose a considerable steric shielding but had only a limited influence on the Lewis and Brønsted basicity of 9-phosphatripytycene, due to the tricyclic cage-shaped structure with the aryl rings π-systems orthogonal to the phosphorus electron pair. A series of Au(I) and Rh(I) complexes were analysed in the solid state to determine Tolman electronic parameters, cone angles and buried volumes of the ortho-substituted phosphatriptycenes. Quantum chemical calculations of electronic and steric descriptors revealed that these cage-shaped phosphines are electron-poor and that single methyl substituent is enough to provide the largest effect on steric shielding reported so far in triarylphosphines. An unsymmetrically substituted 9-phosphatriptycene was resolved by chiral HPLC, opening the avenue towards stable P-chirogenic triarylphosphines with unlimited configurational stability for new catalyst development in asymmetric transition-metal catalysis.

Phosphatriptycenes and their heteroatom bridged analogues **1**-**6** are increasingly used as ligands in Rh,[1] Ir,[2] Pt[3] and Pd[4] organometallic complexes applied in homogeneous and heterogeneous transition-metal catalysis.[5] Meta-substituted 9-phosphatriptycenes such as **4**-**6** are readily accessible in a few steps,[6] but this type of substitution has a small impact on the steric hindrance around the phosphorus atom, as indicated by the Tolman cone angle of 151° for **6**,[7] only slightly higher than in triphenylphosphine (145°).[8]



Scheme 1. Reported 9-phospha and phospha-hetero triptycenes.

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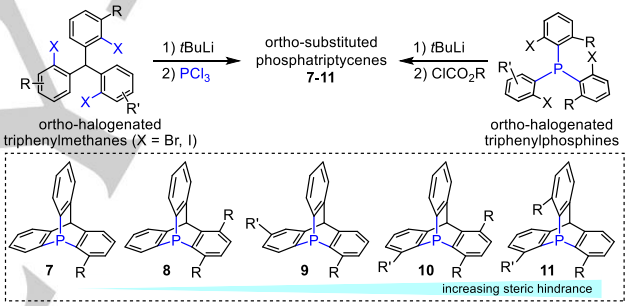
Supporting information for this article is given via a link at the end of the document.

In contrast, the synthesis of ortho-substituted 9-phospha-triptycenes **7**-**11** (Scheme 2) with better shielding of phosphorus is much more challenging, and since the first report on 9-phosphatriptycene **1** in 1974, no examples of ortho-substituted 9-phosphatriptycenes have been reported so far.[9]

We now achieved the first synthesis of the sterically hindered ortho-substituted 9-phosphatriptycenes **7**-**10** via two synthetic approaches involving densely functionalized ortho-halogenated triarylmethanes or phosphines precursors (Scheme 2). Owing to their P atom embedded in a tricyclic cage-shape scaffold, no rotation, inversion or flipping at P[10] is allowed in the unsymmetrically substituted 9-phosphatriptycenes **9**-**11**,opening the path to a new class of configurationally stable P-chirogenic triaryphosphines.[11]



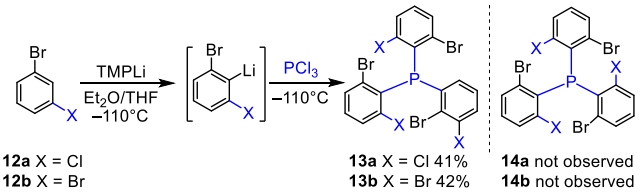
Scheme 2. Phosphatriptycene derivatives **7**-**11** synthesized and studied in this work (**11**: attempted synthesis).

The steric and electronic properties of the ortho-substituted 9-phosphatriptycenes **7**-**11** were determined by characterizing their Rh and Au complexes by X-ray diffraction analysis and by NMR and IR spectroscopies, giving access to their σ-donating and π-accepting abilities (Tolman electronic parameters), and steric hindrance (cone angles, buried volumes).[12]

Quantum chemical calculations of their proton affinity (PA) and methyl cation affinity (MCA) were performed to evaluate their Brønsted and Lewis basicities and their He_8_ring steric descriptor was computed to rationalize the steric hindrance imposed by the ortho-substituents. The resolution of both enantiomers of an unsymmetrical phosphatriptycene was performed by chiral HPLC to establish the proof of concept that enantiopure phosphatriptycenes with unlimited configurationally stability could be accessed.

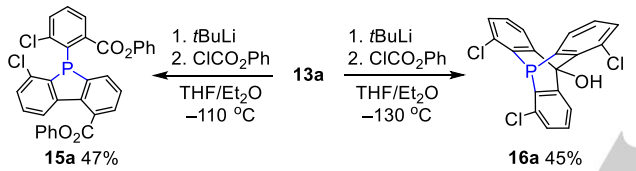
The first step in our synthetic approach to obtain tris-ortho-substituted phosphatriptycene **11** was the preparation of the sterically crowded ortho-substituted halogenated triaryl-phosphines **13**-**14** (Scheme 3). The directed ortho-lithiation of **12a**-**b** with lithium amides was performed at low temperature to avoid benzyne formation. However, quenching the intermediate aryl-lithium species with PCl_3 did not lead to expected hexa-ortho-substituted phosphines **14a-b** (Scheme 3).

Instead, NMR spectroscopy and single-crystal X-ray diffraction (SCXRD) revealed the formation of the arylphosphines **13a**-**b** with only five halogens in ortho-positions, the sixth halogen being located in the meta position, presumably due to an halogen migration occurring even at this low temperature.[13]



Scheme 3. Synthesis of ortho-halogenated triarylphosphines **13a**-**b**. For their single-crystal X-ray structures, see the Supporting Information.

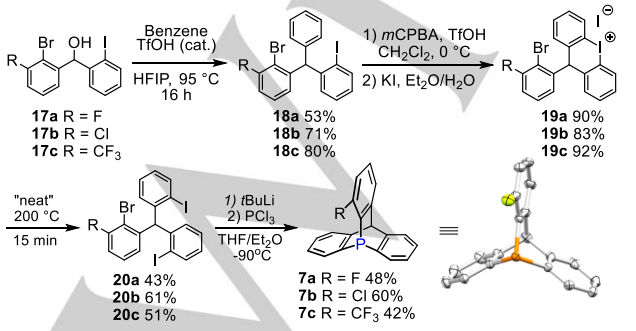
Although we failed to obtain the hexa-ortho-substituted phosphines **14a**-**b**, which are the direct precursors of the tris-ortho-substituted phosphatriptycene **11**, we still decided to show that **13a** can be converted into ortho-substituted phospha-triptycenes such as **16** (Scheme 4). The triple Br/Li exchange on **13a** with *t*BuLi followed by quenching with phenyl chloroformate produced either the phosphino-fluorene **15a** or the substituted phosphatriptycene **16** depending on the reaction temperature.



Scheme 4. Synthesis of unsymmetrical phosphino fluorene **15a** and triptycene **16a**. For the X-ray structure of **15a** and synthetic details, see the SI.

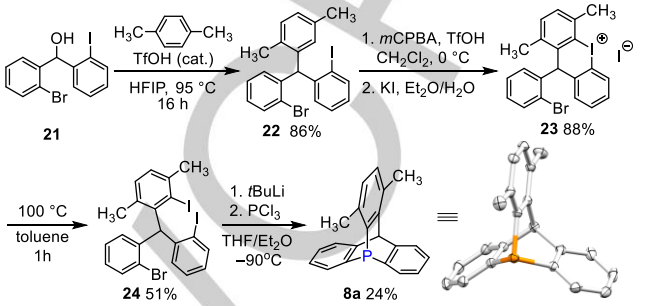
Since the initially planned synthetic approach toward ortho-substituted phosphatriptycenes suffered from several limitations and low yields, we focused on the second synthetic approach involving ortho-halogenated triphenylmethane precursors.

Based on the method of Moran,[14] the Friedel-Crafts reactions of **17a**-**c** produced **18a**-**c** in good yields (Scheme 5). Consecutive iodine oxidation with *m*CPBA, regioselective intramolecular S_EAr cyclization and TfO^-/I^- anion metathesis[15] led to the cyclic iodonium salts **19a**-**c** in high yields. Thermally induced ring-opening of **19a**-**c** by S_NAr reactions with iodide[15] provided the halogenated triarylmethanes **20a**-**c** in good isolated yields. Then, a triple halogen/lithium exchange and the trapping with PCl_3 yielded the novel ortho-substituted 1-fluoro-, 1-chloro- and 1-trifluoromethyl-9-phosphatriptycenes (**7a**-**c**).



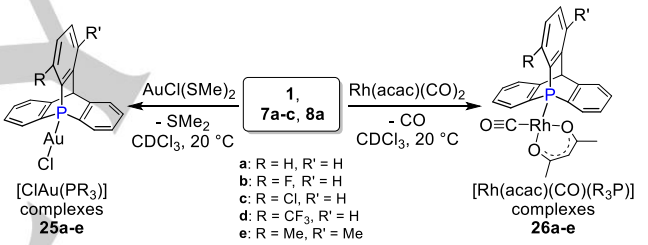
Scheme 5. Synthesis of ortho substituted 9-phosphatriptycene **7a**-**c** and X-ray structure of **7b** with ellipsoids represented at the 50% level.

We next extended our synthetic method to produce 1,4-disubstituted 9-phosphatriptycenes. The Friedel-Crafts alkylation of *p*-xylene with the benzhydrylium ion, generated from **21**, and triflic acid gave access to **22** in good yield (Scheme 6). Oxidation of the iodine atom of **22** with *m*CPBA and intramolecular S_EAr cyclization gave the iodonium salt **23**. Subsequent S_NAr substitution provided **24**, which after triple halogen/lithium exchange and trapping with PCl_3 led to **8a**.



Scheme 6. Synthesis of the 1,4-disubstituted 9-phosphatriptycene **8a** and its X-ray structure with ellipsoid represented at the 50% level.

To evaluate the steric and electronic properties of these cage-shaped phosphines, we prepared the Au(I) and Rh(I) complexes of 9-phosphatriptycene **1** and of its substituted analogues **7**-**8** and characterized them by NMR, FTIR and SCXRD (Scheme 7).



Scheme 7. Formation of the gold complexes [AuCl(R_3P)] and rhodium complexes [Rh(acac)(CO)(R_3P)] of 9-phosphatriptycenes **1** and **7**-**8**. All reactions were quantitative except for **7c**, see the SI page S23.

The σ-donating and π-accepting abilities (Tolman electronic parameters) of the phosphatriptycenes were derived from the IR stretching frequency (ν_{CO}) of the *cis* carbonyl ligand in the Rh complexes **26** in CH_2Cl_2 solutions (Table 1). The frequencies are comparable to these in the complexes of the electron-poor (*p*-CF_3-C_6H_4)$_3$P and (*p*-Cl-C_6H_4)$_3$P phosphines, showing that 9-phosphatriptycenes are weak σ electron-donor but strong π acceptor ligands. Ortho substituents were found to have minor effects on the electronic properties of phosphatriptycenes (max deviation of ν_{CO} is of 5 cm^{-1}) since their aryl ring π-systems are orthogonal and not conjugated to the P lone pair.[16]

To evaluate the Brønsted and Lewis basicities of these phosphines, we performed quantum chemical calculations of the proton affinity (PA) and methyl cation affinity (MCA). The Brønsted and Lewis basicities of **7**-**8** turned out to be only moderately affected by ortho-substitution (see Table 1). Linear correlation of PA versus pK_a (see SI) indicated that pK_a(H_2O) ranges from -1.58 to 0.03 between **7c** and **8a**, which are all weaker Brønsted bases than PPh_3 and comparable to (*p*-CF_3-C_6H_4)$_3$P.[21]

Thus, ortho substituents have a negligible effect on the electronic properties of phosphatriptycenes due to the near absence of conjugation between the triptycene aryl rings orbitals and the orthogonal P lone pair.[16] In contrast, a huge impact on the steric shielding is anticipated since ortho-substituents are maintained in very close proximity to the P-lone pair, and aryl rings are prevented from rotating by the cage-shaped structure.

Table 1. Computed[17] and experimental reactivity parameters and electronic descriptors for PPh_3 and 9-phosphatriptycenes **1** and **7**-**8**. The $^3J_{P\text{-}F}$ coupling constants in Hz are indicated in square brackets.

Parameters	PPh_3	**1** H	**7a** F	**7b** Cl	**7c** CF_3	**8a** CH_3
^{11}P NMR / ppm [$^3J_{P\text{-}F}$ / Hz]	22.2	-64.4	-83.4 [*d* 36.1]	-72.5	-69.7 [*q* 51.7]	-74.9
^{11}P NMR in $Au(R_3P)Cl$	33.3[a]	-1.9	-19.4 [*d* 22.8]	-10.7	-5.6 [*q* 17.2]	-13.4
^{11}P NMR in Rh complex	48.6[b]	4.4	-11.6 [*d* 11.4]	-0.5	0.5 [*q* 11.7]	-3.0
$J_{P\text{-}Rh}$ / Hz	177[b]	189	192	196	200	188
ν_{CO} / Rh (cm^{-1})	1978[b]	1985[c]	1983	1983	1980	1982
PA[d]	248	236	233	234	232	237
pK_a[e]	3.28	-0.42	-1.24	-1.17	-1.58	0.03
MCA[d]	113	103	101	101	99	104

[a] Reference 18; [b] Reference 19; [c] Reference 20; [d] PA and MCA stand for the proton and methyl cation affinities, in kcal/mol; [e] Obtained by linear correlation of PA versus pK_a of selected reference phosphines, see SI.

SCXRD showed that the 9-phosphatriptycene Rh complexes are square planar with P-Rh bonds of 2.22 Å, and the Au complexes are linear with P-Au bonds also of 2.22 Å on average (Figure 1 and Table 2). The crystallographic cone angle of 160° for the 9-phosphatriptycene **1** increases up to 187° for the methyl-substituted triptycene **8a**, representing one of the largest impacts known on the sterics of phosphines due to a single CH_3 substituent; for comparison, the effect of a CH_3 group substituent on PPh_3 (becoming Ph_2(otol)P) is only 6° (Table 2).

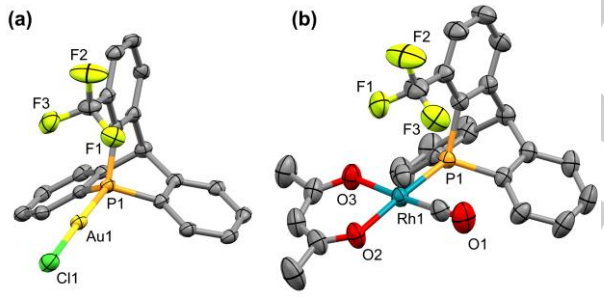
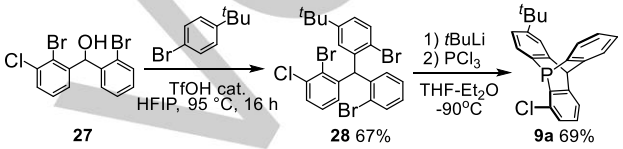


Figure 1. Structure of the Au (a) and Rh complexes (b) of **7c** in the solid state. Here and further structures are represented with ellipsoids at the 50% level; hydrogen atoms and solvate molecules are omitted for clarity. Labels are shown only for hetero-atoms.

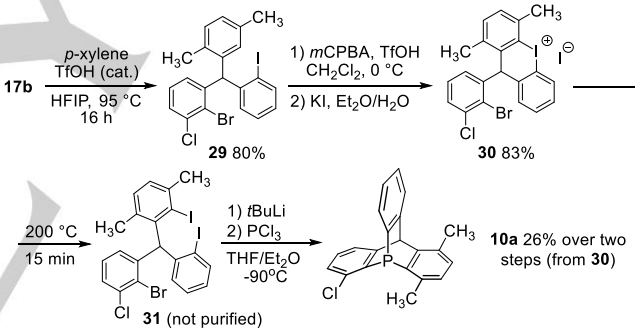
Due to the cage-shaped strained structure of these phosphines, the Tolman cone angles and buried volumes of the free and metal-complexed phosphatriptycenes are nearly identical, as shown by the similar buried volume of the free 9-phosphatriptycene **1** (30.7%), and in its complexes with Au (31.8%) and Rh (31.3%). The high steric bulkiness of CF_3 and Me substituted phosphatriptycenes **7c** and **8a** is also evidenced by the computed He_8_ring descriptor (21.1 and 18.5 kcal/mol, respectively), which is designed to mimic the non-bonded interactions between a P-donor ligand and other *cis* ligands in an octahedral complex (see SI for full details).[27]

Capitalizing on our new synthetic strategy toward ortho-substituted 9-phosphatriptycenes, we undertook the synthesis of the first unsymmetrically derivative **9a**. Treatment of the trityl precursor **28** with an excess of *t*BuLi followed by a trapping with PCl_3 provided **9a** in good isolated yield (Scheme 8).



Scheme 8. Synthesis of unsymmetrically substituted phosphatriptycene **9a**.

Using the same strategy, the bulky bis-ortho-substituted 9-phosphatriptycene **10a** with two different substituents in ortho-position could be obtained in four synthetic steps (Scheme 9).



Scheme 9. Synthesis of trisubstituted 9-phosphatriptycenes **10a**.

Single-crystal X-ray diffraction analyses provided the structures of the unsymmetrical phosphatriptycenes 9a and 10a (Figure 2), which were used for the determination of their crystallographic cone angle (Table 2). Both enantiomers of 9a were resolved by chiral HPLC (see the SI) illustrating the potential to obtain enantiopure P-chirogenic triarylphosphines with unlimited configurationally stability and with unprecedent stereoelectronic properties.

Table 2. Computed and experimental steric descriptors for phosphatriptycenes **1, 7-8** and **10**. The buried volume values (%Vbur) are calculated for M–P length at 2.00 Å with a sphere radius of 3.5 Å and bonds radii scaled by 1.17 as standard method.[22]

Parameters	PPh_3	Ph_2(otol)P	P(otol)$_3$	**1** H	**7a** F	**7b** Cl	**7c** CF_3	**8a** CH_3	**10a** CH_3+Cl
Cone angle (°)	145[a]	151[b]	194[a]	160[c]	167	173	186	187	196
P-Rh (Å)	2.242(2)[d]	2.242(2)[c]	--	2.225(1) 2.228(2)	2.223(2) 2.232(1)	2.225(2) --	2.230(1) --	--	-- --
P-Au (Å)	2.231(1)[d]	2.231(1)[d]	2.243(2)[e]	2.213(1)	--	--	2.220(1) 2.215(1)	--	--
%V_{Bur}	29.6[a]	29.6[a]	46.7[a]	31.3[f]	33.5	36.3[g]	41.3	36.0	41.9
He_8_steric (kcal/mol)	8.0[h]	8.0[h]	30.1[h]	9.3	12.5	18.6	21.1	18.5	35.2

[a] Cone angles and %V_{Bur} values from reference 22; [b] Reference 23; [c] Reference 20; [d] Reference 24; [d] Reference 25; [e] Reference 26; [f] Average value based on the structures of the free 9-phosphatriptycene (30.7%), and its complexes with Au (31.8%) and Rh (31.3%). [g] Value of 37.0% for the analogous ortho-Cl-phosphatriptycene **9a** (Scheme 8). [h] He_8_ring values from reference 12.

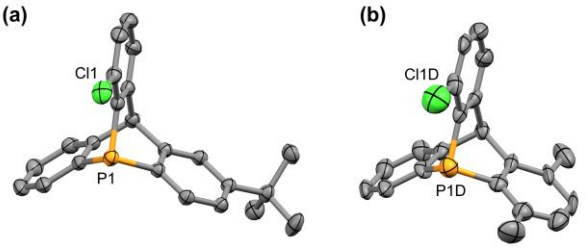


Figure 2. Structure of **9a** (a) and **10a** (b) in the solid state with ellipsoid represented at the 50% level. H atoms and toluene solvate molecule omitted.

Hence, using highly functionalized triphenylmethanes allowed us to access to ortho-substituted 9-phosphatriptycenes. As the P lone pair is not conjugated with the triptycene aryl rings, their Brønsted and Lewis basicities are less affected by substituents than in common triaryl-phosphines. However, as substituents are parallel to the P-lone pair axis in a cage-shaped strained phosphatriptycene core, the P environment becomes exceptionally shielded, resulting in very bullky phosphines.

Using phosphatriptycenes as electron poor P-ligands in cross-coupling reactions,[28] or for the design of electrophilic phosphonium cations[29] are ongoing in our laboratories. Owing to their tricyclic cage-shaped structures, ortho triptycenes constitute a new class of configurationally stable P-chirogenic phosphines, with highly modular steric hindrance, opening the way to further applications in asymmetric transition metal catalysis and frustrated Lewis pairs catalyzed hydrogenations.

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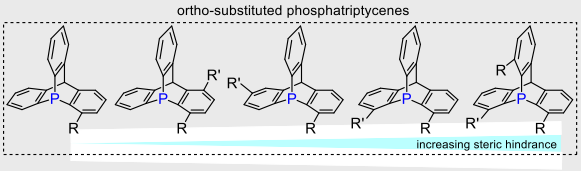

Bulky P-ligands: Ortho-substituted 9-phosphatriptycenes are cage-shaped phosphines featuring unprecedented steric and electronic parameters. Their Au(I) and Rh(I) complexes showed that ortho substituents are dramatically shielding the P atom. Unsymmetrically substituted 9-phosphatriptycenes are P-chirogenic triarylphosphines with unlimited configurational stability.

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Page No. – Page No.

Sterically Hindered Ortho-Substituted Phosphatriptycenes as Configurationally Stable P-Chirogenic Triarylphosphines

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