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Synthesis of all-*cis*-3-(2-diphenylphosphinoethyl)-1,2,4-tris(diphenylphosphinomethyl)cyclopentane (Ditricyp) from dicyclopentadiene

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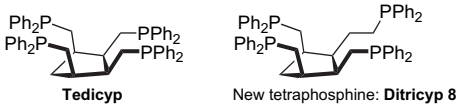
Abstract—A new tetraphosphine, all-*cis*-3-(2-diphenylphosphinoethyl)-1,2,4-tris(diphenylphosphinomethyl)cyclopentane (Ditricyp), has been synthesised in seven steps from commercially available dicyclopentadiene. The ozonolysis of dicyclopentadiene occurred first on the double bond of the bicycloheptene moiety. A very high chemoselective ozonolysis was observed at −60 °C leading to the diol after reductive treatment. From this diol, *cis*,*cis*,*cis*-3-(2-hydroxyethyl)-1,2,4-tri(hydroxymethyl)cyclopentane was obtained after a second ozonolysis. Mesylation and substitution with Ph_2PLi led to the title tetradiphenylphosphine Ditricyp. The efficiency of this new tetraphosphine ligand for palladium-catalysed coupling reactions has been studied. Satisfactory results in terms of substrate/catalyst ratio have been obtained for Suzuki, Negishi and Sonogashira couplings and also for Heck vinylation reaction. After chromatographic separation, one enantiomer of this ligand associated to palladium was able to induce enantioselective allylic alkylation with modest enantiomeric excess.

1. Introduction

The increasing importance of palladium-catalysed reactions such as the so-called Suzuki, Negishi or Sonogashira couplings and Heck vinylation has run parallel to the development of new ligands such as mono- or diphosphines and carbenes.[1–3] Recently, extensive efforts have been devoted to the design of new polypodal ligands.[4] In particular, transition-metal complexes of tripodal phosphines have begun to attract interest because of their potential as catalysts in several homogeneous catalysed reactions.[5] In contrast, tetraphosphine ligands have been poorly exploited in homogeneous catalysis.[6] A ferrocenyl tetraphosphine ligand gave good results in Suzuki and Heck reactions.[7] We have also reported the synthesis[8] and applications[8–12] of palladium-catalysed reactions of the tetraphosphine *cis*,*cis*,*cis*-1,2,3,4-tetrakis(diphenylphosphinomethyl)cyclopentane or Tedicyp, in which four diphenylphosphino groups are stereospecifically bound to the same face of the cyclopentane ring (Scheme 1).



Scheme 1.

Here, we wish to report the synthesis and the use of palladium-catalysed coupling reactions of the new tetrapodal phosphine ligand, all-*cis*-3-(2-diphenylphosphinoethyl)-1,2,4-tris(diphenylphosphinomethyl)cyclopentane (Ditricyp) **8** (Scheme 1).

2. Results and discussion

Ditricyp **8** was prepared in seven steps from commercially available *endo*-dicyclopentadiene **1** as illustrated in Scheme 2. Diene **1** was subjected to ozonolysis followed by reduction with $NaBH_4$ to give **2** in 95% yield.[13] Surprisingly, only little attention has been devoted to the ozonolysis of this diene.[14] We observed that the ozonolysis at −60 °C occurred with a high chemoselectivity, since only the double bond of the bicycloheptene moiety was cleaved to give **2** after reduction (ozonolysis at −15 °C gave directly the tetraol **5** after reduction, but its isolation was very difficult due to a very low solubility in organic solvents) (Scheme 2). The ^1H NMR spectra of the diol **2** were in accordance with the previously reported data,[15] and the structure was

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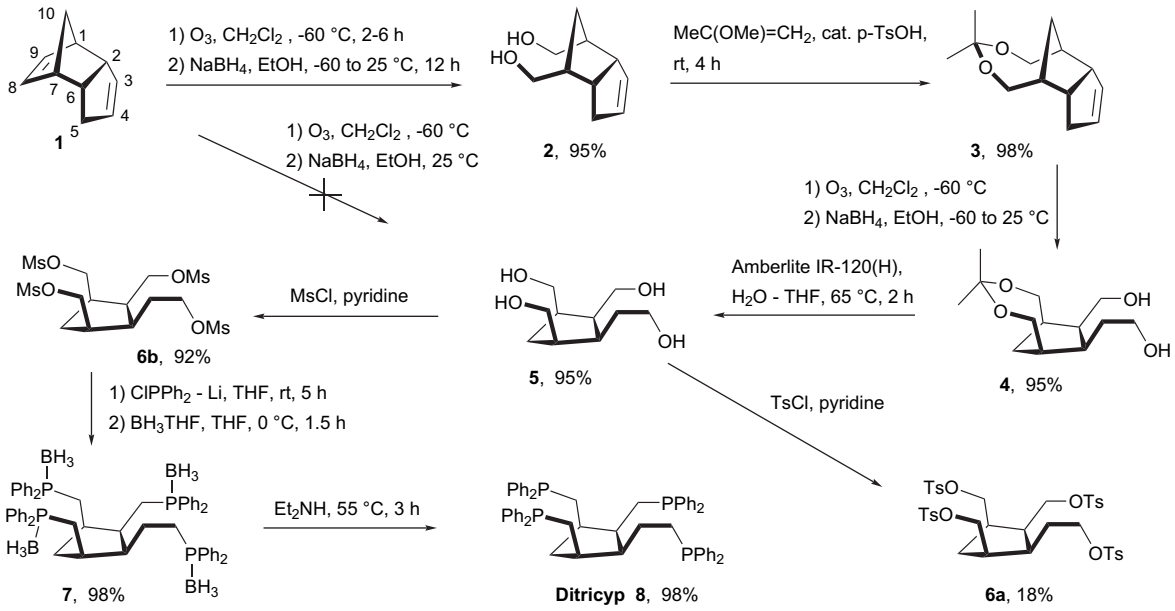


Scheme 2.

confirmed by COSY and HMBC experiments. This result was expected, as the 1,3-dipolar cycloadditions of nitrile oxides to *endo*-dicyclopentadiene take place exclusively from the *exo*-face of the bicycloheptene moiety.[16] The same chemoselectivity was observed for many other reactions: cycloaddition of 2-(oxy-phenyl-imino)-1-phenyl-ethanone or arylazides,[17] alkylazide,[18] tributyl-dithiocarboxy-phosphonium betaine,[19] dinitrogen trioxide,[20] sulfur,[21] Diels–Alder reaction with cyclopentadiene,[22] oxidation with CrO_3,[23] hydratation[24] and also oxidative photoaddition of *N*-nitrodimethylamine.[15] In contrast, the two double bonds are of equal reactivity concerning the epoxidation with sodium perborate[25] or with hydroperoxides.[26,27] Interestingly, calculations at B3LYP/6-311G++(d,p) level showed that the HOMO was centred on the double bond of the cyclopentene moiety (HOMO: OM 136, E=6.588 eV; Σ 2p coeff. C(3), 0.22; C(4), 0.22; C(8), 0.02; C(9) 0.025) while the HOMO-1 corresponded to the norbornene moiety (HOMO-1: OM 135, E=6.600 eV; Σ 2p coeff. C(3), 0.017; C(4), 0.025; C(8), 0.18; C(9), 0.18). Consequently, a soft electrophilic reagent should preferentially attack the C(3)–C(4) double bond, but the HOMO and HOMO-1 energies are very close.

Treatment of **2** with 2-methoxypropene affords, in 98% yield, the tricyclic compound **3**. A COSY gradient experiment on acetonide **3** confirmed the structure. Curiously, the rate of ozonolysis depends on the structure of the bicyclo derivative. No ozonolysis occurred after 6 h at −60 °C in the presence of the diol **2**, while protected diol **3** was cleaved to give **4** only after 2 h of reaction at this temperature. Exposure of **4** to water in THF in the presence of an acidic cation exchange resin led to tetraol **5**.[28] Treatment of **5** with an excess of mesyl chloride in pyridine afforded the expected tetramesylate **6b** in 92% yield.[29] It should be noted that using tosyl chloride, the tetratosylate **6a** was obtained in a low 18% yield. Addition of Ph_2PLi to **6b** at room temperature affords **8**. However, this tetraphosphine is air-sensitive and requires protection for handling and storage. For this reason, borane was added before work-up to give **7** in 98% yield.[30] Ligand **8** was obtained by treatment with diethylamine followed by chromatography on silica gel.[31]

Then, the efficiency of ligand **8** for Suzuki, Negishi and Sonogashira coupling, for Heck vinylation and for allylic alkylation was studied. The results are summarised in Table 1. For this study, based on previous results,[8–12] the Suzuki, Sonogashira and Heck reactions were performed with xylene or DMF as the solvents and K_2CO_3 as the base at 130 °C under argon in the presence of 1:2 ratio of $[Pd(C_3H_5)Cl]_2$/**8** as catalyst (Scheme 2). The Negishi couplings were performed in THF at a lower temperature: 70 °C.[10b]

First, we examined the efficiency of this ligand associated to palladium for Suzuki coupling. Three aryl bromides have been employed, but in all cases the reaction rates were lower than those observed with the Tedicyp ligand (Table 1, entries 1–8).[11,12] With the electron-poor 4-bromoacetophenone and phenylboronic acid, **10** was obtained in a turnover number (TON) of 710,000. On the other hand, with electron-rich 4-bromoanisole or sterically congested 2,4,6-trimethylbromobenzene, **9** and **11** were obtained in lower TONs of 10,000 and 14,000, respectively. These results were relatively disappointing, so we turned our attention on Heck vinylation (Table 1, entries 9–17). A relatively high TON was obtained for the coupling of 4-bromobenzophenone with *n*-butyl acrylate (100,000). However, using similar reaction conditions, Tedicyp ligand led to a TON of 970,000 for this reaction.[9,12] Using 4-bromoanisole a similar difference of reactivity was observed. TONs of 8400 and 82,000 were obtained using Ditricyp and Tedicyp, respectively (Table 1, entries 9–11). On the other hand, using the sterically congested 2-bromotoluene, Ditricyp gave a slightly higher TON than Tedicyp (Table 1, entries 15–17). A similar tendency was observed for Sonogashira alkynylation with phenylacetylene (Table 1, entries 18–26). In the presence of *para*-substituted 4-bromoacetophenone or 4-bromoanisole,

Table 1. Catalysed reaction with the Ditricyp/Pd complex (Scheme 3)

Entry	Aryl halide	Arylboronic acid or alkene or alkyne or alkylzinc halide	Ligand	Substrate/catalyst ratio	Product	Yield (%)[a]
1	4-Bromoanisole	Benzeneboronic acid	**8**	10,000	**9**	97 (100)[b]
2	4-Bromoanisole	Benzeneboronic acid	**8**	100,000	**9**	(3)[b]
3	4-Bromoanisole	Benzeneboronic acid	Tedicyp	100,000	**9**	93[b]
4	4-Bromoacetophenone	Benzeneboronic acid	**8**	100,000	**10**	95 (100)[b]
5	4-Bromoacetophenone	Benzeneboronic acid	**8**	1,000,000	**10**	(71)[b]
6	4-Bromoacetophenone	Benzeneboronic acid	Tedicyp	100,000,000	**10**	(97)[b]
7	2,4,6-Trimethylbromobenzene	Benzeneboronic acid	**8**	10,000	**11**	70 (78)[b]
8	2,4,6-Trimethylbromobenzene	Benzeneboronic acid	**8**	100,000	**11**	(14)[b]
9	4-Bromoanisole	*n*-Butyl acrylate	**8**	1000	**12**	96 (100)
10	4-Bromoanisole	*n*-Butyl acrylate	**8**	10,000	**12**	(84)
11	4-Bromoanisole	*n*-Butyl acrylate	Tedicyp	100,000	**12**	(82)[c]
12	4-Bromobenzophenone	*n*-Butyl acrylate	**8**	100,000	**13**	95 (100)
13	4-Bromobenzophenone	*n*-Butyl acrylate	**8**	1,000,000	**13**	(2)
14	4-Bromobenzophenone	*n*-Butyl acrylate	Tedicyp	1,000,000	**13**	(97)
15	2-Bromotoluene	*n*-Butyl acrylate	**8**	1000	**14**	82 (90)
16	2-Bromotoluene	*n*-Butyl acrylate	**8**	10,000	**14**	(34)
17	2-Bromotoluene	*n*-Butyl acrylate	Tedicyp	1000	**14**	(75)
18	4-Bromoanisole	Phenylacetylene	**8**	1000	**15**	96 (100)[d]
19	4-Bromoanisole	Phenylacetylene	**8**	10,000	**15**	(0)[d]
20	4-Bromoanisole	Phenylacetylene	Tedicyp	10,000	**15**	(38)[d]
21	4-Bromoacetophenone	Phenylacetylene	**8**	1000	**16**	95 (100)[d]
22	4-Bromoacetophenone	Phenylacetylene	**8**	10,000	**16**	(56)[d]
23	4-Bromoacetophenone	Phenylacetylene	Tedicyp	1,000,000	**16**	70[d]
24	2-Bromotoluene	Phenylacetylene	**8**	1000	**17**	93 (100)[d]
25	2-Bromotoluene	Phenylacetylene	**8**	10,000	**17**	(0)[d]
26	2-Bromotoluene	Phenylacetylene	Tedicyp	1000	**17**	(47)[d]
27	4-Bromoanisole	*n*-Butylzinc bromide	**8**	1000	**18**	96 (100)[e]
28	4-Bromoanisole	*n*-Butylzinc bromide	**8**	10,000	**18**	(0)[e]
29	4-Bromoanisole	*n*-Butylzinc bromide	Tedicyp	1000	**18**	85 (100)[e]
30	4-Bromobenzonitrile	*n*-Butylzinc bromide	**8**	10,000	**19**	95 (100)[e]
31	4-Bromobenzonitrile	*n*-Butylzinc bromide	**8**	100,000	**19**	(99)[e]
32	4-Bromobenzonitrile	*n*-Butylzinc bromide	Tedicyp	100,000	**19**	(88)[e]
33	1-Bromonaphthalene	*n*-Butylzinc bromide	**8**	1000	**20**	94 (100)[e]
34	1-Bromonaphthalene	*n*-Butylzinc bromide	**8**	10,000	**20**	(100)[e]
35	1-Bromonaphthalene	*n*-Butylzinc bromide	Tedicyp	10,000	**20**	(38)[e]
36	2-Bromotoluene	*n*-Butylzinc bromide	**8**	1000	**21**	84 (100)[e]
37	2-Bromotoluene	*n*-Butylzinc bromide	**8**	10,000	**21**	(0)[e]
38	3-Bromoquinoline	*n*-Butylzinc bromide	**8**	1000	**22**	92 (100)[e]
39	3-Bromoquinoline	*n*-Butylzinc bromide	**8**	10,000	**22**	(86)[e]

Conditions: catalyst $[Pd(C_3H_5)Cl]_2$/**8** (1:2), ArBr (1 equiv), benzeneboronic acid (2 equiv) or *n*-butyl acrylate (2 equiv) or phenylacetylene (2 equiv) or *n*-butylzinc bromide (3 equiv), K_2CO_3 for entries 1–26 (2 equiv), DMF, 20 h, 130 °C, under argon, isolated yields, substrate/catalyst ratio based on the aryl halide.

[a] Yields in parenthesis correspond to GC and NMR yields.

[b] Solvent: xylene.

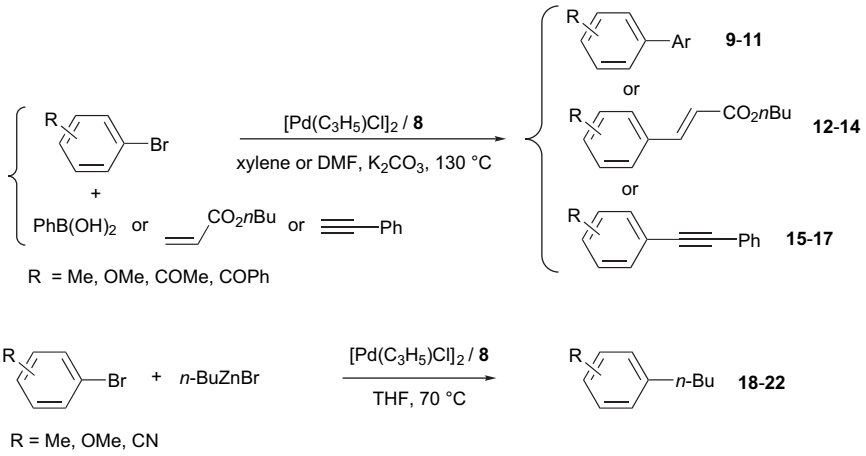
[c] 72 h.

[d] 5 mol % of CuI was added.

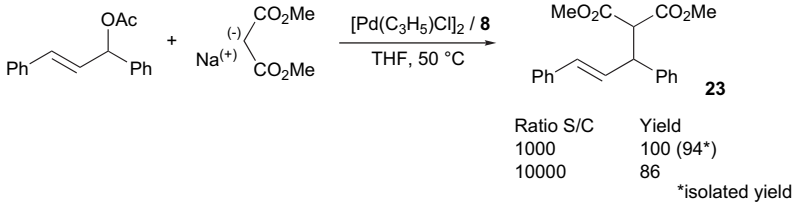
[e] Solvent: THF, temp 70 °C.

15 and **16** were obtained in 5600 and 1000 TONs using Ditricyp. With Tedicyp, the TONs for these reactions were higher (700,000 and 3800).[10a,12] Using the sterically congested 2-bromotoluene, Ditricyp and Tedicyp led to TONs of 1000 and 470, respectively (Table 1, entries 24 and 26). With Ditricyp ligand, the best results were obtained for Negishi cross-coupling using *n*-butylzinc bromide (Table 1, entries 27 and 39). In the presence of the electron-poor 4-bromobenzonitrile, using Ditricyp and Tedicyp, **19** was obtained in relatively similar TONs of 99,000 and 88,000.[10b] With 4-bromoanisole, both ligands led to complete conversions and high yields of product **18** using as little as 0.1 mol % catalyst (Table 1, entries 27 and 29). Employing congested 1-bromonaphthalene gave **20** in a higher TON of 10,000 using Ditricyp than with Tedicyp (TON: 3800). Then, we studied the reactivity of 2-bromotoluene and 3-bromoquinoline. With both substrates the coupling products **21** and **22** were obtained in high yields using as little as 0.1–0.01 mol % catalyst (Table 1, entries 36 and 39).

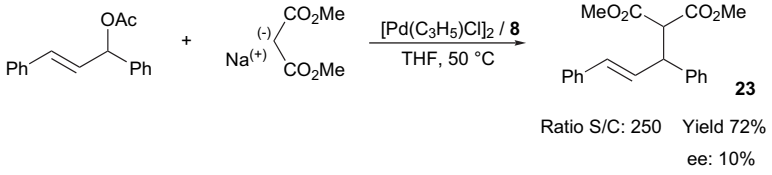
In summary, Ditricyp ligand associated to palladium is generally less efficient than Tedicyp. However, for sterically congested substrates or for Negishi coupling, satisfactory results were achieved, and in a few cases, higher TONs were obtained using Ditricyp as ligand. The difference of efficiency between these two ligands might come from a more stable and more hindered complex formed with Ditricyp, which slows down the oxidative addition of the aryl bromides to palladium. The formation of this stable and hindered complex could explain the lower reactivity of electron-deficient aryl bromides. For the reactions with sterically congested aryl bromides, the rate-limiting step of the catalytic cycle is probably not the oxidative addition, but might be the insertion of the alkene for Heck reaction or the reductive elimination for Suzuki, Negishi or Sonogashira coupling. This might explain the satisfactory results obtained in several cases in the presence of the congested substrates with the Ditricyp/Pd complex (Scheme 3).



Scheme 3.



Scheme 4.



Scheme 5.

Then, we examined the efficiency of this ligand for palladium-catalysed allylic alkylation (Scheme 4). The reaction of 1,3-diphenylpropenyl acetate with sodium dimethyl malonate gave the expected product **23** in good yield and in a very high TON of 8600.

The separation of the two enantiomers of Ditricyp was possible by semi-preparative HPLC. Using one of these enantiomers associated to palladium the alkylation of 1,3-diphenylpropenyl acetate gave **23** in 72% yield and 10% enantiomeric excess (Scheme 5). Due to the relatively 'low asymmetry' of this ligand such low enantiomeric excess was expected. However, this result indicates that enantioselective reaction can be performed even with chiral tetradentate phosphine ligands. Using other chiral tetraphosphine ligands, for example, bearing the chirality on the phosphorus atom might lead to better results.

3. Conclusion

In summary, we have prepared a new tetraphosphine, Ditricyp in seven steps and good overall yield from dicyclopentadiene. The efficiency of this new tetraphosphine ligand for palladium-catalysed coupling reactions gave satisfactory results in terms of substrate/catalyst ratio for Suzuki, Negishi and Sonogashira couplings, for Heck vinylation and also for allylic substitution reaction. The best results were obtained with sterically congested aryl bromides or for Negishi cross-coupling reaction.

4. Experimental section

4.1. General

TLC was performed on silica gel 60 F254. Flash chromatographies were performed on silica gel (230–400 mesh) obtained from Macherey-Nagel and Co. CH_2Cl_2 was distilled before use from calcium hydride and THF was distilled from sodium benzophenone. DMF and xylene of analytical grade were used without drying. Commercial aryl bromides, *n*-butyl acrylate, phenylacetylene and phenylboronic acid were used without purification. All palladium-catalysed reactions were run under argon using vacuum lines in Schlenk tubes in oven-dried glassware. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ solutions at 300 and 75 MHz, respectively. Chemical shifts are reported in parts per million relative to $CDCl_3$ (signals for residual $CHCl_3$ in the $CDCl_3$: 7.24 for ^1H NMR and 77.16 (central) for ^{13}C NMR).

Carbon–proton couplings were determined by DEPT sequence experiments.

4.2. (1*S**,2*R**,4*S**,5*R**)-2,4-Dihydroxymethylbicyclo-[3.3.0]oct-6-ene (2)

Ozone in oxygen was bubbled through a stirred solution of commercial *endo*-dicyclopentadiene **1** (20 g, 150 mmol) in CH_2Cl_2 (300 mL) containing three drops of an ethanolic solution of 'Sudan III' (Eastman Kodak) (ozonizable red dye as internal standard)[32] at −60 °C until the red colour has disappeared. The mixture was flushed with argon and cooled to −80 °C. A suspension of $NaBH_4$ (11.4 g, 0.30 mol) in EtOH was slowly added. The mixture was stirred at room temperature overnight. Tartaric acid (67.5 g, 0.45 mol) was added and the pasty mixture was stirred for 2 h and then filtered. The solution was dried over $MgSO_4$. After filtration, the solvent was removed in vacuo, yielding **2** as a yellow oil (23.9 g, 95%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.70 (dd, J=5.5, 1.9 Hz, 1H, H^6), 5.56 (dt, J=5.5, 2.4 Hz, 1H, H^7), 3.63 (d, J=7.4 Hz, 2H, CH_2OH), 3.56 (dd, J=7.2, 5.0 Hz, 2H, CH_2OH), 3.25 (br t, J=7.7 Hz, 1H, H^5), 2.87 (qd, J=8.4, 5.4 Hz, 1H, H^1), 2.35–2.15 (m, 4H, $2H^8$, H^2, H^4), 1.70 (quint., J=5.6 Hz, 1H, H^3), 0.84 (q, J=12.2 Hz, 1H, H^3); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 132.7 (d, C^6), 130.2 (d, C^7), 64.7 (t), 64.5 (t), 52.3 (d, C^5), 46.4 (d, C^{2*}), 45.7 (d, C^{4*}), 42.4 (d, C^1), 33.5 (t, C^8), 31.3 (t, C^3).

4.3. (1*R**,7*S**,8*R**,12*S**)-4,4-Dimethyl-3,5-dioxatricyclo[5.5.1.0]tridec-9-ene (3)

To a solution of **2** (6.0 g, 35.7 mmol) in CH_2Cl_2 (250 mL) containing some crystals of *p*-TsOH was slowly added 2-methoxypropene (1.03 mL, 107.1 mmol) at room temperature. After 2 h of stirring at 25 °C, K_2CO_3 was added and the solution was stirred for 1 h. The solution was filtered and the solvent was removed in vacuo, yielding **3** as a yellow oil (7.4 g, 98%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.60 (m, 1H), 5.47 (m, 1H), 3.63 (m, 2H), 3.21 (m, 2H), 2.79 (m, 1H), 2.25–2.05 (m, 4H), 1.68 (m, 1H), 1.25 (s, 6H), 0.76 (t, J=6.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 131.9 (d, C^9), 130.1 (d, C^{10}), 99.7 (s, C), 62.4 (t, C^{2*}), 62.1 (t, C^{6*}), 52.0 (d, C^8), 43.7 (d), 43.0 (d), 42.1 (d), 33.5 (t, C^{11}), 32.5 (t, C^{13}), 24.5 (q), 24.4 (q).

4.4. (1*S**,7*R**,8*R**,9*R**)-4,4-Dimethyl-8-(2-hydroxyethyl)-9-hydroxymethyl-3,5-dioxabicyclo[5.2.1]decane (4)

Following the procedure previously described for the ozonolysis of dicyclopentadiene, from **3** (7.4 g, 35 mmol), **4** was obtained as a yellow solid (8.12 g, 95%), mp 102 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.04–3.83 (m, 8H), 2.52 (m, 4H), 1.94 (m, 2H), 1.70–1.60 (m, 2H), 1.63 (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 101.3 (s), 63.8 (t), 63.5 (t), 63.0 (t), 60.4 (t), 48.2 (d), 42.3 (d), 41.7 (d), 41.1 (d), 33.5 (t), 30.1 (t), 24.8 (q, 2C). Anal. Calcd for $C_{13}H_{24}O_4$: C, 63.91; H, 9.90. Found: C, 63.71; H, 9.91.

4.5. *cis*,*cis*,*cis*-3-(2-Hydroxyethyl)-1,2,4-tri(hydroxymethyl)cyclopentane (5)

To a solution of **4** (6.0 g, 24 mmol) in THF (100 mL) were added water (6 mL) and ion exchange resin Amberlite® IR 120 hydrogen form (4 g). After refluxing and stirring for 4 h, the solution was cooled to room temperature and filtered. After filtration, the product was concentrated in vacuo. Water was removed in vacuo by rotary evaporation distillations using toluene. This operation was repeated twice. The crude product **5** appeared as a yellow oil, which was used for the following tosylation step without further purification. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.68–3.50 (m, 8H), 2.2 (m, 4H), 1.94 (m, 1H), 1.57 (m, 2H), 1.15 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 65.0 (t), 64.7 (t), 62.8 (t), 60.0 (t), 47.8 (d), 44.7 (d), 43.5 (d), 41.0 (d), 32.1 (t), 29.9 (t).

4.6. *cis*,*cis*,*cis*-3-(((Tolyl-4-sulfonyl)oxy)ethyl)-1,2,4-tris(((tolyl-4-sulfonyl)oxy)methyl)cyclopentane (6a)

A solution of **5** (14 g, 68 mmol) in anhydrous pyridine (250 mL) was cooled to −20 °C. Tosyl chloride (106.4 g, 560 mmol) was added and the mixture was stirred at −20 °C for 5 h. The mixture was poured on ice and acidified (pH∼1) by addition of HCl followed by extraction with CH_2Cl_2. The organic layers were dried on $MgSO_4$ and evaporated. The purified product **6a** was obtained by chromatography on silica gel (CH_2Cl_2) (10.1 g, 18%) as an oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.71 (d, J=8.1 Hz, 8H), 7.33 (d, J=8.1 Hz, 8H), 3.96–3.69 (m, 8H), 2.42 (s, 12H), 2.18 (m, 4H), 1.89 (m, 1H), 1.41 (m, 1H), 1.21 (m, 1H), 0.97 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 145.3, 145.1, 145.0, 145.0, 132.6, 132.5, 132.3, 132.0, 130.1 (2C), 130.0 (2C), 129.9 (2C), 129.8 (2C), 127.8 (4C), 127.7 (4C), 70.5, 70.1, 68.9, 66.3, 42.0, 40.4, 38.9, 37.9, 30.3, 25.0, 21.6. Anal. Calcd for $C_{38}H_{44}O_{12}S_4$: C, 55.59; H, 5.40. Found: C, 55.42; H, 5.32.

4.7. *cis*,*cis*,*cis*-3-((Mesyloxy)ethyl)-1,2,4-tri((mesyloxy)-methyl)cyclopentane (6b)

A solution of **5** (4.2 g, 20 mmol) in anhydrous pyridine (100 mL) was cooled to −20 °C. Mesyl chloride (15.9 mL, 200 mmol) was added and the mixture was stirred at 25 °C for 4 h. The mixture was poured on ice and acidified (pH∼1) by addition of HCl followed by extraction with CH_2Cl_2. The organic layers were dried on $MgSO_4$ and evaporated. The purified product **6b** was obtained by chromatography on silica gel (CH_2Cl_2) (9.6 g, 92%) as an oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.11–4.30 (m, 8H), 3.05 (s, 3H), 3.03 (s, 9H), 2.41–2.65 (m, 4H), 2.14 (m, 1H), 1.92 (m, 2H), 1.37 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 70.1, 69.4, 68.9, 66.2, 42.4, 40.4, 39.2, 38.3, 37.2, 37.2 (3C), 29.9, 25.5; MS (EI, 70 eV): m/z (%)=516 (100). Anal. Calcd for $C_{14}H_{28}O_{12}S_4$: C, 32.55; H, 5.46. Found: C, 32.70; H, 5.73.

4.8. *cis*,*cis*,*cis*-3-((2-Boranatodiphenylphosphanyl)-ethyl)-1,2,4-tris((boranatodiphenylphosphanyl)-methyl)cyclopentane (7)

Compound **6b** (5.0 g, 9.69 mmol) was added to THF (100 mL) under argon. The solution was stirred at 0 °C and 94 mL (10 equiv) of a solution of phosphide lithium (1.03 mmol/mL) was slowly added. The solution was heated at 35 °C, stirred for 5 h and then cooled to 0 °C. A solution of borane/THF (1 M, 213 mL) was slowly added via cannula. The reaction mixture was poured on ice and extracted with

CH_2Cl_2 (3×200 mL). The combined organic layers were dried on $MgSO_4$ and evaporated. The crude oil was chromatographed on silica gel (pentane/ether, 1:1) to give white crystals (8.9 g, 98%) of **7**, mp 99 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.72–7.53 (m, 16H), 7.53–7.28 (m, 24H), 2.44 (t, J=12.9 Hz, 1H), 2.33–1.94 (m, 9H), 1.91–1.74 (m, 3H), 1.56–0.50 (m, 15H); ^{31}P NMR (121 MHz, $CDCl_3$) δ 15.31 and 16.37 (broad peaks); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 132.9, 132.8, 132.3–131.6 (14C), 131.4–130.9 (10C), 130.2–129.0 (12C), 128.9–128.5 (8C), 128.3, 128.1, 47.1 (dd, $J_{(C-P)}$=8.0, 4.7 Hz), 42.1 (d, $J_{(C-P)}$=12.2 Hz), 39.9 (d, $J_{(C-P)}$=3.7 Hz), 36.9, 36.2 (d, $J_{(C-P)}$=8.4 Hz), 29.5 (d, $J_{(C-P)}$=35.3 Hz), 28.0 (d, $J_{(C-P)}$=34.8 Hz), 24.3 (d, $J_{(C-P)}$=36.7 Hz), 22.8 (d, $J_{(C-P)}$=34.8 Hz), 19.0. Anal. Calcd for $C_{58}H_{68}B_4P_4$: C, 74.72; H, 7.35. Found: C, 74.87; H, 7.51.

4.9. *cis*,*cis*,*cis*-3-((Diphenylphosphanyl)ethyl)-1,2,4-tris((diphenylphosphanyl)methyl)cyclopentane (8)

Compound **7** (0.1 g, 0.107 mmol) was added to anhydrous diethylamine (3 mL) and the solution was heated at 60 °C for 2 h. The amine was removed in vacuo. The crude product was chromatographed on silica gel (pentane/ether, 5:1) to give **8** as white crystals (0.92 g, 98%), mp 63 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55–7.19 (m, 40H), 2.45 (m, 1H), 2.31–2.08 (m, 3H), 2.04–1.67 (m, 8H), 1.53 (m, 2H), 1.56 (m, 2H), 1.40–1.29 (m, 2H); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ −14.8 (s), −17.2 (d, $J_{(P-P)}$=7.4 Hz), −18.2 (d, $J_{(P-P)}$=7.4 Hz), −19.2 (s); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 139.9–137.8 (8C), 133.6–132.2 (24C), 128.7–128.1 (16C), 48.5 (dd, J=13.7, 6.5 Hz), 43.1 (dd, J=12.6, 8.2 Hz), 39.7 (t, J=9.1 Hz), 38.1 (t, J=13.2 Hz), 37.9, 31.8 (d, J=13.2 Hz), 29.7, 28.2 (d, J=11.5 Hz), 25.7 (d, J=13.7 Hz), 22.5 (d, J=13.2 Hz); MS (EI, 70 eV): m/z (%)=876 (100) [M^+].

4.10. Separation of the two enantiomers of Ditricyp

The two enantiomers of Ditricyp were separated using semi-preparative HPLC chromatography (Merck D-7000 HPLC with Merck-Hitachi L-4000 UV detector) with a Whelk-01 (*R*,*R*) (250×4.6 mm) column, using hexane/chloroform as an eluent (7:3). Semi-preparative separation was performed under the same conditions by successive injection of 100 μL of a 10 mg/mL solution of racemate every 3 min. We collected 18 mg of the first eluted enantiomer with an enantiomeric excess of 94% and 20 mg of the second one with an enantiomeric excess of 96%. First eluted enantiomer: $[\alpha]_D^{25}$ −5.3 (*c* 1, $CHCl_3$). Second eluted enantiomer: α_D^{25} +5.2 (*c* 1, $CHCl_3$).

4.11. Preparation of the Ditricyp/Pd catalyst

$[Pd(C_3H_5)Cl]_2$ (18 mg, 0.05 mmol) and **8** (88 mg, 0.1 mmol) in 2 mL of anhydrous DMF under argon were stirred at room temperature for 10 min. The appropriate amount of this solution was used directly for catalysing the reactions.

4.12. Typical procedure for Suzuki, Heck, Sonogashira and Negishi catalysed reactions

As a typical experiment (Table 1), the reaction of the aryl bromide (1 mmol), benzeneboronic acid (2 mmol) (Table 1, entries 1–8) or *n*-butyl acrylate (2 mmol) (Table 1, entries 9–17) or phenylacetylene (2 mmol) (Table 1, entries 18–26) or *n*-butylzinc bromide (3 mmol) (Table 1, entries 27–39), K_2CO_3 (0.276 g, 2 mmol) for Suzuki, Heck and Sonogashira (Table 1, entries 1–26), CuI (0.05 mmol) for Sonogashira reactions (Table 1, entries 18–26) at 130 °C (Table 1, entries 1–26) or 70 °C (Table 1, entries 27–39) over 20 h in xylene (Table 1, entries 1–8), DMF (Table 1, entries 9–26) or THF (Table 1, entries 27–39) (3 mL) in the presence of the appropriate amount of $[PdCl(C_3H_5)]_2$/**8** complex under argon afforded the products **9**–**22** after evaporation and filtration on silica gel.

4.12.1. 4-Methoxybiphenyl (9). From 4-bromoanisole (187 mg, 1 mmol) and benzeneboronic acid (244 mg, 2 mmol), **9** was obtained in 97% yield (179 mg).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54 (d, J=7.4 Hz, 2H), 7.52 (d, J=8.6 Hz, 2H), 7.40 (dd, J=7.4, 7.2 Hz, 2H), 7.29 (t, J=7.4 Hz, 1H), 6.96 (d, J=8.6 Hz, 2H), 3.82 (s, 3H).

4.12.2. 4-Phenylacetophenone (10). From 4-bromoacetophenone (199 mg, 1 mmol) and benzeneboronic acid (244 mg, 2 mmol), **10** was obtained in 95% yield (186 mg).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.0 (d, J=8.5 Hz, 2H), 7.67 (d, J=8.5 Hz, 2H), 7.61 (d, J=7.0 Hz, 2H), 7.45 (dd, J=7.5, 7.0 Hz, 2H), 7.37 (t, J=7.5 Hz, 1H), 2.60 (s, 3H).

4.12.3. 2,4,6-Trimethylbiphenyl (11). From 2,4,6-trimethylbromobenzene (199 mg, 1 mmol) and benzeneboronic acid (244 mg, 2 mmol), **11** was obtained in 70% yield (137 mg).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47 (d, J=7.0 Hz, 2H), 7.39 (t, J=7.0 Hz, 1H), 7.22 (t, J=7.0 Hz, 2H), 7.03 (s, 2H), 2.41 (s, 3H), 2.09 (s, 6H).

4.12.4. Butyl (*E*)-3-(4-methoxyphenyl)acrylate (12). From 4-bromoanisole (187 mg, 1 mmol) and *n*-butyl acrylate (256 mg, 2 mmol), **12** was obtained in 96% yield (225 mg).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55 (d, J=16.0 Hz, 1H), 7.37 (d, J=8.7 Hz, 2H), 6.80 (d, J=8.7 Hz, 2H), 6.21 (d, J=16.0 Hz, 1H), 4.12 (t, J=6.6 Hz, 2H), 3.69 (s, 3H), 1.60 (tt, J=6.8, 6.6 Hz, 2H), 1.33 (qt, J=7.3, 6.8 Hz, 2H), 0.87 (q, J=7.3 Hz, 3H).

4.12.5. Butyl (*E*)-3-(4-benzoylphenyl)acrylate (13). From 4-bromobenzophenone (261 mg, 1 mmol) and *n*-butyl acrylate (256 mg, 2 mmol), **13** was obtained in 95% yield (293 mg).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78 (m, 4H), 7.70 (d, J=16.0 Hz, 1H), 7.58 (m, 3H), 7.46 (m, 2H), 6.52 (d, J=16.0 Hz, 1H), 4.20 (t, J=6.6 Hz, 2H), 1.68 (tt, J=6.8, 6.6 Hz, 2H), 1.40 (qt, J=7.3, 6.8 Hz, 2H), 0.94 (q, J=7.3 Hz, 3H).

4.12.6. Butyl (*E*)-3-(2-methylphenyl)acrylate (14). From 2-bromotoluene (171 mg, 1 mmol) and *n*-butyl acrylate (256 mg, 2 mmol), **14** was obtained in 82% yield (179 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J=16.1 Hz, 1H), 7.47 (d, J=7.1 Hz, 1H), 7.15 (m, 3H), 6.26 (d, J=16.1 Hz, 1H), 4.13 (t, J=6.7 Hz, 2H), 2.35 (s, 3H), 1.62 (tt, J=6.8, 6.7 Hz, 2H), 1.36 (qt, J=7.3, 6.8 Hz, 2H), 0.89 (q, J=7.3 Hz, 3H).

4.12.7. 4-(Phenylethynyl)anisole (15). From 4-bromoanisole (187 mg, 1 mmol) and phenylacetylene (204 mg, 2 mmol), **15** was obtained in 96% yield (200 mg).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56 (d, J=7.5 Hz, 2H), 7.52 (d, J=8.8 Hz, 2H), 7.40–7.33 (m, 3H), 6.92 (d, J=8.8 Hz, 2H), 3.85 (s, 3H).

4.12.8. 4-(Phenylethynyl)acetophenone (16). From 4-bromoacetophenone (199 mg, 1 mmol) and phenylacetylene (204 mg, 2 mmol), **16** was obtained in 95% yield (209 mg).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92 (d, J=8.1 Hz, 2H), 7.59 (d, J=8.1 Hz, 2H), 7.53 (d, J=7.5 Hz, 2H), 7.35 (m, 3H), 2.58 (s, 3H).

4.12.9. 2-(Phenylethynyl)toluene (17). From 2-bromotoluene (171 mg, 1 mmol) and phenylacetylene (204 mg, 2 mmol), **17** was obtained in 93% yield (179 mg).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63–7.57 (m, 3H), 7.45–7.38 (m, 3H), 7.30–7.20 (m, 3H), 2.60 (s, 3H).

4.12.10. 4-*n*-Butylanisole (18). From 4-bromoanisole (187 mg, 1 mmol) and *n*-butylzinc bromide (3 mL, 1.0 M in THF, 3 mmol), **18** was obtained in 96% yield (158 mg).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.11 (d, J=8.7 Hz, 2H), 6.83 (d, J=8.7 Hz, 2H), 3.79 (s, 3H), 2.56 (t, J=7.6 Hz, 2H), 1.58 (quint., J=7.6 Hz, 2H), 1.34 (sext., J=7.6 Hz, 2H), 0.93 (t, J=7.6 Hz, 3H).

4.12.11. 4-*n*-Butylbenzonitrile (19). From 4-bromobenzonitrile (182 mg, 1 mmol) and *n*-butylzinc bromide (3 mL, 1.0 M in THF, 3 mmol), **19** was obtained in 95% yield (151 mg).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52 (d, J=8.3 Hz, 2H), 7.24 (d, J=8.3 Hz, 2H), 2.63 (t, J=7.4 Hz, 2H), 1.57 (quint., J=7.4 Hz, 2H), 1.32 (sext., J=7.4 Hz, 2H), 0.89 (t, J=7.4 Hz, 3H).

4.12.12. 1-*n*-Butylnaphthalene (20). From 1-bromonaphthalene (207 mg, 1 mmol) and *n*-butylzinc bromide (3 mL, 1.0 M in THF, 3 mmol), **20** was obtained in 94% yield (173 mg).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.12 (d, J=8.0 Hz, 1H), 7.92 (dd, J=7.5, 1.8 Hz, 1H), 7.77 (d, J=8.0 Hz, 1H), 7.56 (t, J=8.0 Hz, 1H), 7.53 (t, J=8.0 Hz, 1H), 7.46 (t, J=7.5 Hz, 1H), 7.38 (d, J=7.5 Hz, 1H), 3.15 (t, J=7.6 Hz, 2H), 1.81 (quint., J=7.6 Hz, 2H), 1.56 (sext., J=7.6 Hz, 2H), 1.06 (t, J=7.6 Hz, 3H).

4.12.13. 2-*n*-Butyltoluene (21). From 2-bromotoluene (171 mg, 1 mmol) and *n*-butylzinc bromide (3 mL, 1.0 M in THF, 3 mmol), **21** was obtained in 84% yield (124 mg).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.15–7.07 (m, 4H), 2.57 (t, J=7.5 Hz, 2H), 1.53 (quint., J=7.5 Hz, 2H), 1.37 (sext., J=7.5 Hz, 2H), 0.92 (t, J=7.5 Hz, 3H).

4.12.14. 3-*n*-Butylquinoline (22). From 3-bromoquinoline (208 mg, 1 mmol) and *n*-butylzinc bromide (3 mL, 1.0 M in THF, 3 mmol), **22** was obtained in 92% yield (170 mg).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.98 (s, 1H), 8.30 (d, J=7.9 Hz, 1H), 8.06 (s, 1H), 7.79 (d, J=8.1 Hz, 1H), 7.64 (td, J=8.1, 1.4 Hz, 1H), 7.52 (t, J=8.1 Hz, 1H), 2.78 (t, J=7.4 Hz, 2H), 1.66 (quint., J=7.4 Hz, 2H), 1.36 (sext., J=7.4 Hz, 2H), 0.91 (t, J=7.4 Hz, 3H).

4.13. Dimethyl (1,3-diphenylprop-2-en-1-yl)malonate (23) (Scheme 4)

The reaction of 1,3-diphenylpropenyl acetate (252 mg, 1 mmol), sodium dimethyl malonate (2 mmol), THF (10 mL) at 50 °C over 20 h in xylene in the presence of $[PdCl(C_3H_5)]_2$/**8** complex (0.001 mmol) under argon afforded the corresponding product **23** after hydrolysis, extraction, drying, evaporation and filtration on silica gel in 94% yield (305 mg).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33–7.20 (m, 10H), 6.48 (d, J=15.7 Hz, 1H), 6.34 (dd, J=15.7, 8.4 Hz, 1H), 4.27 (dd, J=10.8, 8.4 Hz, 1H), 3.95 (d, J=10.8 Hz, 1H), 3.70 (s, 3H), 3.52 (s, 3H).

4.14. Enantioselective allylic alkylation (23) (Scheme 5)

Using the previously described procedure with one enantiomer of the Ditricyp ligand (0.004 mmol), the product **23** was obtained in 72% yield (233 mg) with an enantiomeric excess of 10%. The chiral HPLC experiments were performed in an unit composed of Merck D-7000 system manager, Merck-Hitachi L-6000 pump, Rheodyne valve and a Merck-Hitachi L-4000 UV-detector. Retention times Rt in minutes, retention factors k_i=(Rt$_i$−Rt$_0$)/Rt$_0$ and enantioselectivity factor α=k_2/k_1 are given. Rt$_0$ was determined by injection of tri-*tert*-butyl benzene. The product was separated on Whelk-O1 (*R*,*R*) (250×4.6 mm, from Regis, Morton Grove, USA) in a mixture of hexane/chloroform (7:3): flow rate=2 mL/min, UV detection at 254 nm, Rt(−)=9.79, Rt(+)=10.83, k(−)=6.00, k(+)=6.73, α=1.12 and Rs=1.38. Semi-preparative separation was performed under the same conditions by injection of 100 μL of a 10 mg/mL solution of racemate every 3 min.

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References and notes

1. For reviews on palladium-catalysed Suzuki coupling reactions, see: (a) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457;

(b) Suzuki, A. *J. Organomet. Chem.* **1999**, *576*, 147; (c) Beletskaya, I. P.; Cheprakov, A. V. *Chem. Rev.* **2000**, *100*, 3009; (d) Suzuki, A. *J. Organomet. Chem.* **2002**, *653*, 83; (e) Littke, A. F.; Fu, G. C. *Angew. Chem., Int. Ed.* **2002**, *41*, 4177.
2. For reviews on palladium-catalysed Sonogashira coupling reactions, see: (a) Sonogashira, K. *Metal-Catalyzed Cross-Coupling Reactions*; Diederich, F., Stang, P. J., Eds.; Wiley: New York, NY, 1998; (b) Sonogashira, K. *J. Organomet. Chem.* **2002**, *653*, 46; (c) Brandsma, L.; Vasilevsky, S. F.; Verkruijsse, H. D. *Application of Transition Metal Catalysts in Organic Synthesis*; Springer: Berlin, 1998; (d) Doucet, H.; Hierso, J. C. *Angew. Chem., Int. Ed.* **2007**, *46*, 834.
3. For reviews on palladium-catalysed Heck vinylation reactions, see: (a) de Meijere, A.; Meyer, F. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2379; (b) Reetz, M. T. *Transition Metal Catalysed Reactions*; Davies, S. G., Murahashi, S.-I., Eds.; Blackwell Science: Oxford, 1999; (c) See Ref. 1c; (d) Whitcombe, N.; Hii (Mimi), K. K.; Gibson, S. *Tetrahedron* **2001**, *57*, 7449; (e) Farina, V. *Adv. Synth. Catal.* **2004**, *346*, 1553.
4. For a review on the polypodal diphenylphosphine ligands, see: Laurenti, D.; Santelli, M. *Org. Prep. Proced. Int.* **1999**, *31*, 245.
5. (a) Ghilardi, C. A.; Midollini, S.; Sacconi, L. *Inorg. Chem.* **1975**, *14*, 1790; (b) Cecconi, F.; Ghilardi, C. A.; Midollini, S.; Moneti, S.; Orlandini, A.; Scapacci, G. *J. Chem. Soc., Dalton Trans.* **1989**, 211; (c) Bianchini, C.; Meli, A.; Peruzzini, M.; Vizza, F.; Frediani, P.; Ramirez, J. A. *Organometallics* **1990**, *9*, 226; (d) Grévin, J.; Kalck, P.; Dran, J. C.; Vaissermann, J.; Bianchini, C. *Inorg. Chem.* **1993**, *32*, 4965; (e) Seitz, T.; Asam, A.; Huttner, G.; Walter, O.; Zsolnai, L. *Z. Naturforsch.* **1995**, *50b*, 1287; (f) Barbaro, P.; Bianchini, C.; Giambastiani, G.; Togni, A. *Eur. J. Inorg. Chem.* **2003**, 4166; (g) Hierso, J.-C.; Fihri, A.; Amardeil, R.; Meunier, P.; Doucet, H.; Santelli, M.; Ivanov, V. V. *Org. Lett.* **2004**, *6*, 3473; (h) Boardman, B.; Hanton, M. J.; Van Rensburg, H.; Tooze, R. P. *Chem. Commun.* **2006**, 2289; (i) Ciclosi, M.; Lloret, J.; Estevan, F.; Lahuerta, P.; Sanau, M.; Perez-Prieto, J. *Angew. Chem., Int. Ed.* **2006**, *45*, 6741.
6. For tetrapodal ligands, see: (a) Nagel, U.; Kinzel, E.; Andrade, J.; Prescher, G. *Chem. Ber.* **1986**, *119*, 3326; (b) Khan, M. T. T.; Paul, P.; Venkatasubramanian, K.; Purohit, S. *J. Chem. Soc., Dalton Trans.* **1991**, 3405; (c) Schmidbaur, H.; Stützer, A.; Bissinger, P. *Z. Naturforsch.* **1992**, *47b*, 640; (d) Mason, M. R.; Duff, C. M.; Miller, L. L.; Jacobson, R. A.; Verkade, J. G. *Inorg. Chem.* **1992**, *31*, 2746; (e) Steewinkel, P.; Kolmshot, S.; Gossage, R. A.; Dani, P.; Veldman, N.; Spek, A. L.; van Koten, G. *Eur. J. Inorg. Chem.* **1998**, 477; (f) Bianchini, C.; Lee, H. M.; Meli, A.; Oberhauser, W.; Vizza, F.; Brüggeller, P.; Haid, R.; Langes, C. *Chem. Commun.* **2000**, 777; (g) Oberhauser, W.; Stampfl, T.; Bachmann, C.; Haid, R.; Langes, C.; Kopacka, H.; Ongania, H. K.; Brüggeller, P. *Polyhedron* **2000**, *19*, 913; (h) Nair, P.; Anderson, G. K.; Rath, N. P. *Inorg. Chem. Commun.* **2003**, *6*, 1307; (i) Nair, P.; Anderson, G. K.; Rath, N. P. *Organometallics* **2003**, *22*, 1494; (j) Imamoto, T.; Yashio, K.; Crepy, K. V. L.; Katagiri, K.; Takahashi, H.; Kouchi, M.; Gridnev, I. D. *Organometallics* **2006**, *25*, 908.
7. Hierso, J.-C.; Fihri, A.; Amardeil, R.; Meunier, P.; Doucet, H.; Santelli, M. *Organometallics* **2003**, *22*, 4490.
8. Laurenti, D.; Feuerstein, M.; Pèpe, G.; Doucet, H.; Santelli, M. *J. Org. Chem.* **2001**, *66*, 1633.
9. For examples of Heck reactions or C–H functionalisations with Tedicyp ligand: (a) Feuerstein, M.; Doucet, H.; Santelli, M. *J. Org. Chem.* **2001**, *66*, 5923; (b) Berthiol, F.; Doucet, H.; Santelli, M. *Appl. Organomet. Chem.* **2006**, *20*, 855; (c) Battace, A.; Zair, T.; Doucet, H.; Santelli, M. *Synthesis* **2006**, 3495; (d) Lemhadri, M.; Doucet, H.; Santelli, M. *Synlett* **2006**, 2935; (e) Lemhadri, M.; Battace, A.; Zair, T.; Doucet, H.; Santelli, M. *J. Organomet. Chem.* **2007**, *692*, 2270; (f) Battace, A.; Lemhadri, M.; Zair, T.; Doucet, H.; Santelli, M. *Organometallics* **2007**, *26*, 472.
10. For examples of Sonogashira and Negishi reactions with Tedicyp ligand: (a) Feuerstein, M.; Berthiol, F.; Doucet, H.; Santelli, M. *Org. Biomol. Chem.* **2003**, 2235; (b) Kondolff, I.; Doucet, H.; Santelli, M. *Organometallics* **2006**, *25*, 5219.
11. For examples of Suzuki reactions with Tedicyp ligand: (a) Feuerstein, M.; Laurenti, D.; Bougeant, C.; Doucet, H.; Santelli, M. *Chem. Commun.* **2001**, 325; (b) Kondolff, I.; Doucet, H.; Santelli, M. *J. Mol. Catal. A: Chem.* **2007**, *269*, 110.
12. For an account on Tedicyp ligand: Doucet, H.; Santelli, M. *Synlett* **2006**, 2001.
13. Mori, K.; Murata, N. *Liebigs Ann.* **1995**, 2089.
14. (a) Fremery, M. I.; Fields, E. K. *J. Org. Chem.* **1963**, *28*, 2537; (b) Tolstikov, G. A.; Miftakhov, M. S.; Danilova, N. A.; Shitikova, O. V. *Zh. Org. Khim.* **1985**, *21*, 675.
15. Chow, Y. L.; Richard, H. *J. Chem. Soc., Perkin Trans. 1* **1982**, 1405.
16. Namboothiri, I. N. N.; Rastogi, N.; Ganguly, B.; Mobin, S. M.; Cojocaru, M. *Tetrahedron* **2004**, *60*, 1453.
17. Samuilov, Y. D.; Movchan, A. I.; Solov'eva, S. E.; Konovalov, A. I. *J. Org. Chem. USSR (Engl. Transl.)* **1985**, *21*, 1618.
18. Laatsch, H.; Ernst, B. P.; Hoffmann, D. *Liebigs Ann.* **1995**, 1773.
19. Aitken, R. A.; Hill, L.; Massil, T. *Phosphorus Sulfur Silicon Relat. Elem.* **1996**, *109*, 593.
20. Barnes, J. F.; Barrow, M. J.; Harding, M. M.; Paton, R. M.; Sillitoe, A.; Ashcroft, P. L.; Bradbury, R.; Cosby, J.; Joyce, C. L.; Holmes, D. R.; Milner, J. *J. Chem. Soc., Perkin Trans. 1* **1983**, 293.
21. (a) Bartlett, P. D.; Ghosh, T. *J. Org. Chem.* **1987**, *52*, 4937; (b) Kustos, M.; Steudel, R. *J. Org. Chem.* **1995**, *60*, 8056.
22. Kolesnikov, R. V.; Grigo'rev, A. A.; Vinberg, L. B.; Yampol'skii, Y.; Zhavoronkov, I. P. *J. Org. Chem. USSR (Engl. Transl.)* **1986**, *22*, 901.
23. Pandey, P. N.; Purkayastha, M. L. *Indian J. Chem., Sect. B* **1984**, *23B*, 717.
24. Okazaki, S.; Harada, H. *Chem. Lett.* **1988**, 1313.
25. Xie, G.; Xu, L.; Hu, J.; Ma, S.; Hou, W.; Tao, F. *Tetrahedron Lett.* **1988**, *29*, 2967.
26. Sheng, M. N.; Zajacek, J. G. *J. Org. Chem.* **1970**, *35*, 1839.
27. Ozonolysis of the diol, *endo*,*endo*-2,3-dihydroxymethyl-7-isopropylidenebicyclo[2.2.1]hept-5-ene, with controlled amount of ozone, occurred on the norbornene moiety, see: Wu, C.-Y.; Lin, H.-C.; Wang, Z.; Wu, H.-J. *J. Org. Chem.* **2001**, *66*, 4610.
28. Böhme, H.; Seitz, G. *Chem. Ber.* **1968**, *101*, 1689.
29. Alder, K.; Roth, W. *Chem. Ber.* **1955**, *88*, 407.
30. Börner, A.; Ward, J.; Ruth, W.; Holz, J.; Kless, A.; Heller, D.; Kagan, H. B. *Tetrahedron* **1994**, *50*, 10409.
31. Ohff, M.; Holz, J.; Quirmbach, M.; Börner, A. *Synthesis* **1998**, 1391.
32. Veysoglu, T.; Mitscher, L. A.; Swayze, J. K. *Synthesis* **1980**, 807.