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Water-soluble phosphines[☆]
Part XII. Pd catalyzed P–C coupling reactions: a novel synthetic route to cationic phosphines with *para*- and *meta*-guanidiniumphenyl moieties

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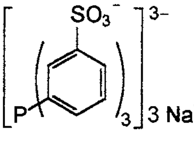
Abstract

Mono- and bifunctional guanidinium phosphines (**3c**, **4a**, **4b**, **5a**–**5d**, **5f**) containing *para*-and *meta*-guanidiniumphenyl moieties $-C_6H_4-NH-C(NH_2)(NR_2)^+$ (R = H, Me) are accessible in high yields by Pd catalyzed P–C coupling reactions between iodophenyl guanidines $I-C_6H_4-NH-C(NH)NR_2$ (*meta*-, *para*-isomers; R = H, Me) and phenyl- or diphenylphosphine. The X-ray structure of **3c**·MeOH (space group $P2_12_12_1$) has been determined, showing a planar guanidinium group in a NH–O and NH–Cl hydrogen bridged arrangement. Pd(II) and Mo(0) complexes of **5c** have been synthesized. The influence of the cationic guanidinium group on the electronic and steric parameters of **5c** is discussed. A comparative study of **5c**, phosphonated and sulfonated phosphine ligands in the biphasic Pd catalyzed Suzuki-type coupling between *m*-bromophenyldiphenyl phosphine oxide and *para*-tolylboronic acid shows **5c** to be less active than $Ph_2P-C_6H_4-4-PO_3Na_2$. © 2000 Published by Elsevier Science S.A. All rights reserved.

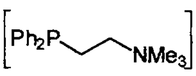
Keywords: meta-, *para*-Guanidiniumphenyl phosphines; Pd catalyzed P–C coupling; X-ray structure; Ligand properties; Suzuki coupling

1. Introduction

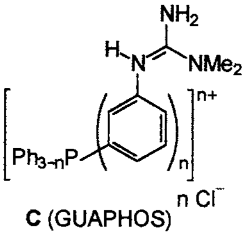
Recently there has been an increasing interest in aqueous biphasic catalysis for the syntheses of organic compounds on industrial and laboratory scales [2]. This is mainly due to the environmental benefits of using water as a solvent and the ease by which the catalysts can be recycled. The complexes applied as catalysts gain their water-solubility by incorporation of strongly hydrophilic phosphine ligands. The most widely studied complex catalysts are those of tris-*meta*-sulfonatophenylphosphine (TPPTS, **A**) [3], the prototype of anionic phosphine ligands. In contrast, cationic phosphines have, until recently [4], received only little attention as ligands in catalytically active transition metal complexes, although some of them (e.g. AMPHOS, **B**) have been known for more then two decades [5].



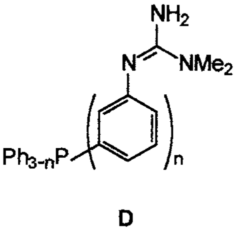
A (TPPTS)



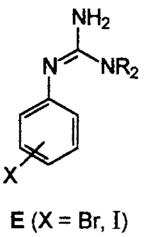
B (AMPHOS)



C (GUAPHOS)



D



E (X = Br, I)

[☆] For Part XI see Ref. [1].

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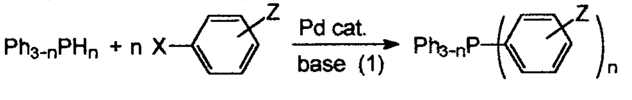
Cationic phosphines **C** (GUAPHOS) containing *meta*-guanidiniumphenyl moieties have been obtained by us very recently in moderate overall yields using a multistage synthesis [6a]. Due to the highly polar functions these ligands show a pronounced solubility in water. The anion binding capacity of the guanidinium groups [7a,8] should exert some precoordination and preorientation of anionic substrates in the periphery of catalyst complexes containing these ligands. They were shown to be very active in Pd mediated C–C coupling reactions between aryl iodides and alkynes [6a,b] (Castro–Stephens–Sonogashira reaction [6c]) and Rh catalyzed hydroformylation of olefins in two-phase systems [9]. Due to their potential as catalyst ligands a single stage high yield synthesis for the *meta*- and *para*-isomers of these cationic phosphines was therefore highly desirable.

In contrast to the cationic phosphines of the AMPHOS type, guanidinium phosphines are stable even in strongly basic media and may therefore be employed as catalyst components in Heck type and Suzuki type coupling reactions [10]. Deprotonation of the guanidinium group in type **C** ligands affords the neutral guanidino phosphines **D** which are soluble in the organic substrate phase of aqueous two-phase systems where they effect the catalytic conversion. Recovery of the catalyst and its separation from the products is simply achieved by acidification of the aqueous phase, the cationic water-soluble ligands **C** and their complexes being formed back again.

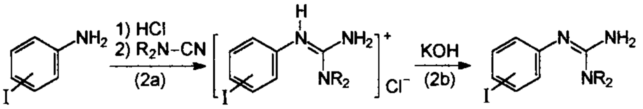


n = 1, 2; X = Br, I
Z = OH, NH$_2$, COOH, SO$_3$Na, PO$_3$Et$_2$
ortho, meta, para

Palladium catalyzed P–C coupling of primary and secondary phosphines with mono and multiply functionalized bromo- or iodobenzenes as developed by us has shown to provide a straightforward synthetic approach to an extended range of tailor-made hydrophilic phosphine ligands (Eq. (1)) [11]. Using this synthetic strategy *para*- and *meta*-isomers of type **C** ligands should be accessible by a single stage P–C coupling reaction between Ph$_2$PH or PhPH$_2$ and iodo- or bromophenylguanidines **E** which function as eletrophiles and bases due to the strongly basic guanidino group. Preliminary work has been published by us elsewhere [12].

2. Syntheses of monocationic *para*-guanidiniumphenylphosphines

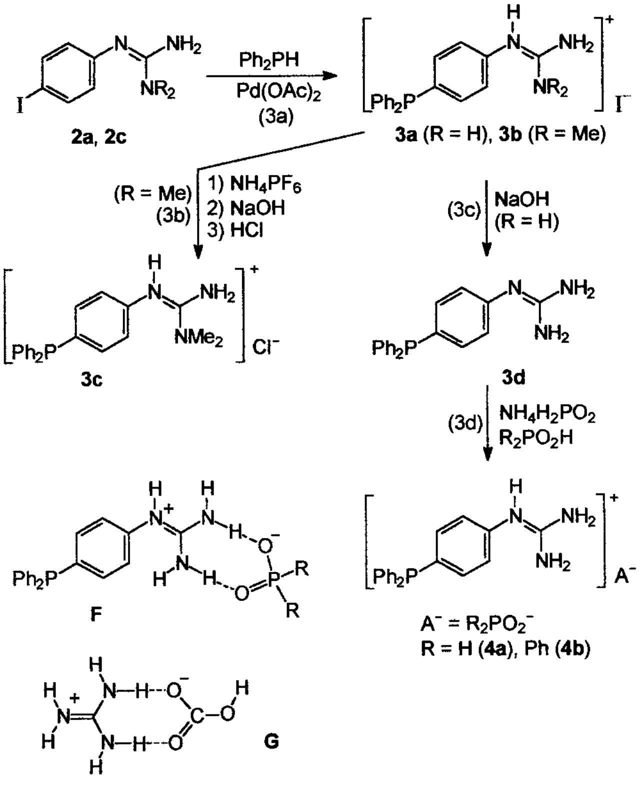
The *para*-iodophenylguanidines **2a** and **2c** may be obtained in a straightforward manner by reaction of the cyanamides R$_2$N–CN (R = H, Me) with the corresponding iodoanilinium chlorides and subsequent deprotonation of the resulting guanidinium salts **1a** and **1c** with KOH (Eqs. (2a) and (2b)).



1a (R = H, *para*)
1b (R = H, *meta*)
1c (R = Me, *para*)
1d (R = Me, *meta*)

2a (R = H, *para*)
2b (R = H, *meta*)
2c (R = Me, *para*)
2d (R = Me, *meta*)

Reaction of **2a** and **2c** with Ph$_2$PH in presence of a catalytic amount of palladium(II) acetate affords **3a** and **3b** in high yields (Eq. (3a)). Due to strongly basic character of the guanidino groups in **2a** and **2c** no extra base has to be added as in case of the P–C coupling reactions depicted in Eq. (1). For phenylguanidine a pK_a value of 10.77 has been reported in the literature [7]. In order to get analytically pure samples of the *para*-guanidiniumphenylphosphines the hexafluorophosphate of the cation in **3b** was precipitated from the reaction mixture. Deprotonation of the guanidinium group with NaOH and subsequent addition of HCl yields the chloride **3c** (Eq. (3b)). Deprotonation of **3a** with NaOH yields the guanidinophosphine **3d** (Eq. (3c)). On reaction of **3d** with ammonium hypophosphite or diphenylphosphinic acid in methanol, ethanol or glyme the phosphinates **4a** and **4b** are formed as colorless precipitates in high yields (Eq. (3d)).



In the $^{31}P\{^1H\}$-NMR spectra **3a**–**3d**, **4a** and **4b** show singlets in the range between $\delta = -1$ and -6 for the Ph_2P group. The δP values for the hypophosphite and diphenylphosphinate anions in **4a** and **4b** are shifted to high field compared with the corresponding values of the hydrophosphorous acid and diphenylphosphinic acid [13] indicating the proton transfer to the basic guanidino group on their formation according to Eq. (3d). The bidentate anions $R_2PO_2^-$ (R = H, Ph) in **4a** and **4b** are capable of forming hydrogen bridged ion pairs **F** with the guanidinium moieties in the solid state or possibly even in low dielectric environment. The prototype of this interaction is represented by the structure of guanidinium bicarbonate, which has been considered as a model for the bicarbonate anion binding site of the transferrines [14a]. According to an X-ray structural analysis the two oxygen atoms of the planar bicarbonate form hydrogen bonds with different nitrogen atoms of the guanidinium cation (**G**) [14b].

The $^{13}C\{^1H\}$-NMR spectra of **3a**–**3d**, **4a** and **4b** show eight signals for the aromatic carbon atoms which could be assigned using DEPT experiments [15] and by comparison with pertinent data of triphenylphosphine [16a] and related phenylguanidines [16b]. For **3c**, **4a** and **4b** ^{13}C-NMR resonances ($\delta C = 155.5$–157.8) are observed in the range typical for guanidinium carbon atoms [17]. The $^{15}N\{^1H\}$-NMR spectrum of **3c** shows three well-separated resonances at $\delta^{15}N = -299.3$, -281.4 and -303.8 which may be assigned to the NH, NH_2 and NMe_2 groups, respectively [18]. For **4a** two ^{15}N-NMR signals at $\delta^{15}N = -282.2$ (NH, $^1J(NH) = 92.5$ Hz) and -305.7 (NH_2, $^1J(NH) = 91.8$ Hz) are observed showing doublet or triplet fine structure, respectively.

3. X-ray structure of 3c·CH_3OH

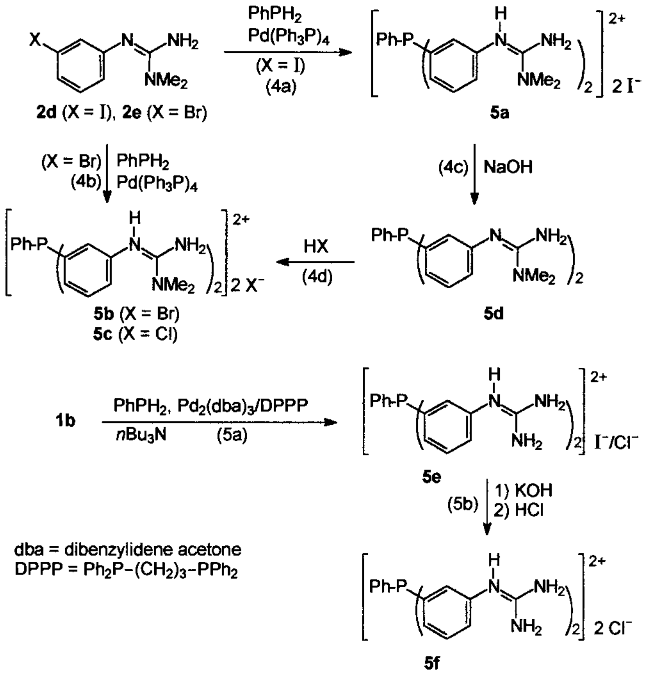
So far there are no reports in the literature on the structure of phosphines containing peripheral guanidinium moieties. In order to gain detailed information about the geometry of the $NH–C(NH_2)(NMe_2)$ group and its orientation with respect to the plane of the *p*-phenylene spacer unit in **3c** a structure determination has been performed. On recrystallization of **3c** from methanol crystals of composition **3c**·CH_3OH were obtained. In the unit cell the cations of **3c** are interconnected by hydrogen bridges between NH(1) and NH(2) and the chloride ions (N(1)···Cl 3.220(4) Å, N(2)···Cl 3.222(5) Å) forming chains parallel to the *a*-axis. They are coupled by methanol molecules via OH···Cl and NH···O bridges (N(2)···O 2.804(7) Å, O···Cl 3.047(5) Å) to give double strands.

The molecular structure of the cationic part of **3c**·CH_3OH is shown in Fig. 1. Selected bond distances, angles and contact distances are listed in Table 1, while crystallographic details are given in Table 3. The N atoms N(1), N(2), N(3) and the carbon atom C(1) of the guanidinium group in **3c** lie almost in the same plane, the sum of the N–C–N bond angles being close to 360°. The carbon nitrogen bond lengths (C(1)–N(1) 1.337(6), C(1)–N(2) 1.329(7), C(1)–N(3) 1.326(7) Å) are halfway between the normal C–N single bond length (1.47 Å) and the pure double bond lengths (1.24 Å) [19] in a range typical for carbon substituted guanidinium ions [20] and the parent guanidinium ion [21]. The NMe_2 substituent with a planar geometry at N(3) is rotated counter clockwise around the C(1)–N(3) axis (dihedral angle C(2)–N(3)–C(1)–N(1) = −16.8(7)°) thus lowering the steric repulsion between N(1)H and $N(2)H_2$ and the two methyl groups. The plane defined by the guanidinium system and that of the *p*-phenylene spacer are rotated against each other as indicated by the dihedral angle C(1)–N(1)–C(14)–C(13) = −51.9(7)°. While the P–C bond lengths between P and C(21) and C(31) are in the typical range [22], the distance P–C(11) (1.817(4) Å) is somewhat shortened.

4. Syntheses of dicationic *meta*-guanidiniumphenylphosphines

For the syntheses of the dicationic *meta*-guanidiniumphenylphosphines the *meta*-iodophenyl guanidines **2b** and **2d** have been employed as starting materials. The guanidinium salts **1b** and **1d** may be obtained in an analogous manner as **1a** and **1c** by reaction of the cyanamides $R_2N–CN$ (R = H, Me) with the corresponding iodoanilinium salts (Eq. (2a)). They were deprotonated with KOH to give **2b** or **2d**, respectively, in high yields (Eqs. (2a) and (2b)).

On reaction of the *meta*-iodophenylguanidine **2d** with $PhPH_2$ using $Pd(PPh_3)_4$ [23] as catalyst, the iodide of the guanidiniumphosphine **5a** [6a] was obtained in almost quantitative yield (Eq. (4a)). If the *meta*-bromophenylguanidine **2e** was employed instead of its iodo analog **2d**, the P–C coupling reaction (Eq. (4b)) proceeds much slower, the phosphinophenyl guanidinium bromide **5b** being formed in small yields only. **5b** and **5c** are accessible by deprotonation of **5a** (Eq. (4c)) in a two-phase system (CH_2Cl_2/H_2O) and subsequent reprotonation of the intermediate guanidino phenylphosphine **5d** with HBr or HCl, respectively (Eq. (4d)).



Iodophenyl guanidinium salts may be employed as starting materials instead of the corresponding iodophenyl guanidines for the syntheses of the dicationic phosphino guanidiniumphenyl halides. In this case extra base had to be added, however, in order to bind the HI formed during the reaction. Thus P–C coupling of the iodophenyl guanidinium chloride **1b** with $PhPH_2$ was achieved using a 1:2 mixture of dipalladium trisbenzylideneacetone and 1,3-bisdiphenylphosphinopropane as the catalyst. Tri-*n*-butylamine was added as the base. In order to yield a product **5f** with a uniform anion the primary reaction product **5e** was deprotonated with KOH to give the guanidinophosphine which on reprotonation with HCl affords the phosphinoguanidiniumphenyl chloride **5f** (Eqs. (5a) and (5b)).

The *meta*-guanidiniumphenyl phosphines **5a**–**5c**, **5f** and the *meta*-phenylguanidino phosphine **5d** show singlets at δP of about -5.0 in the $^{31}P\{^1H\}$-NMR spectra. Assignments of the resonances in the $^{13}C\{^1H\}$-NMR spectra could be achieved at least in

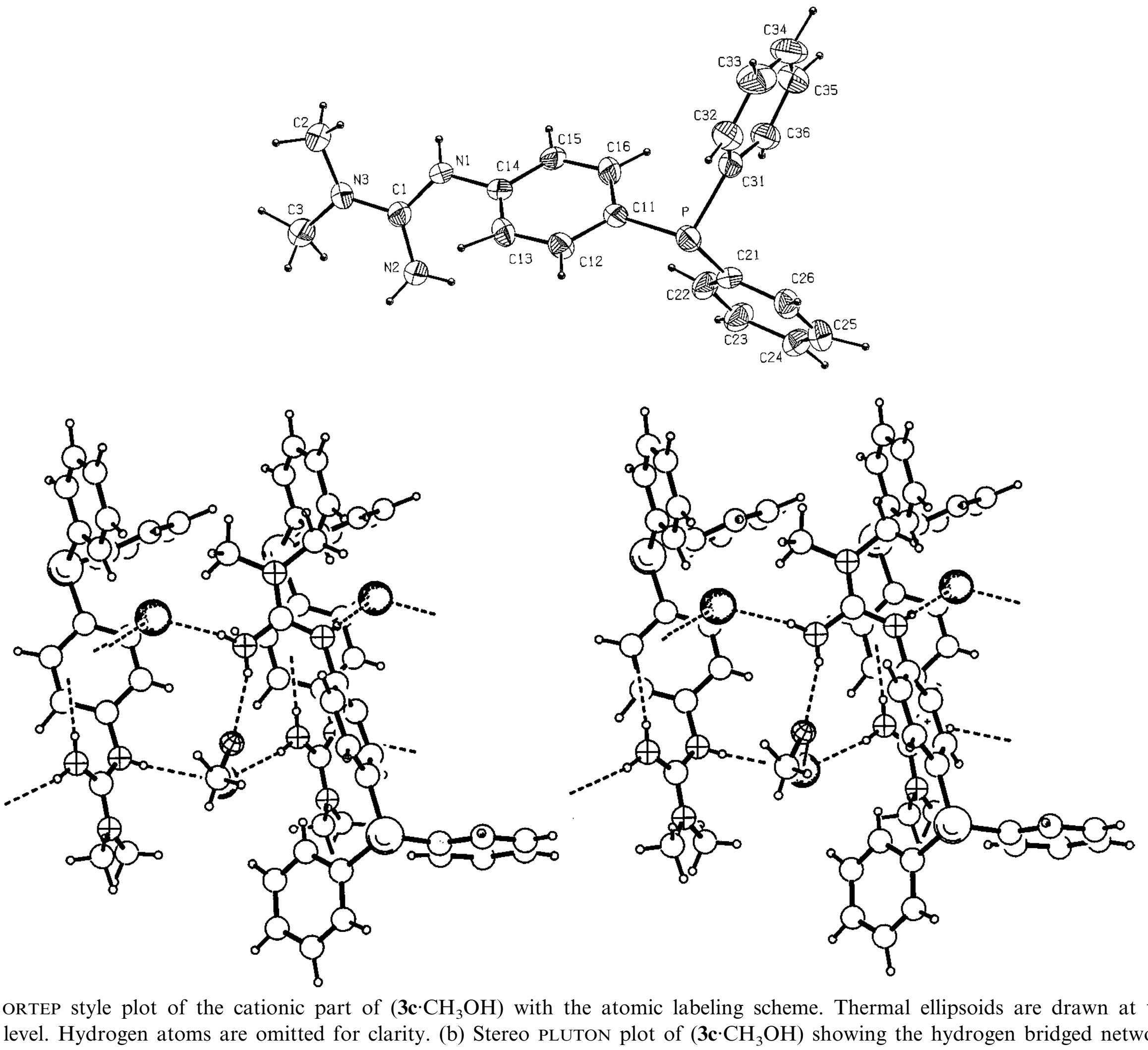


Fig. 1. (a) ORTEP style plot of the cationic part of (3c·CH_3OH) with the atomic labeling scheme. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. (b) Stereo PLUTON plot of (3c·CH_3OH) showing the hydrogen bridged network.

Table 1
Selected interatomic distances (Å) and angles (°) for **3c**·CH_3OH

Bond lengths			
P–C(11)	1.817(4)	C(14)–C(15)	1.389(7)
P–C(21)	1.848(5)	C(15)–C(16)	1.374(7)
P–C(31)	1.836(5)	C(21)–C(26)	1.386(8)
O–C	1.358(10)	C(21)–C(22)	1.395(8)
N(1)–C(1)	1.337(6)	C(22)–C(23)	1.376(8)
N(1)–C(14)	1.432(7)	C(23)–C(24)	1.394(8)
N(2)–C(1)	1.329(7)	C(24)–C(25)	1.397(8)
N(3)–C(2)	1.465(8)	C(25)–C(26)	1.373(8)
N(3)–C(3)	1.456(7)	C(31)–C(36)	1.407(7)
N(3)–C(1)	1.326(7)	C(31)–C(32)	1.380(8)
C(11)–C(12)	1.408(7)	C(32)–C(33)	1.392(9)
C(11)–C(16)	1.391(7)	C(33)–C(34)	1.354(10)
C(12)–C(13)	1.396(7)	C(34)–C(35)	1.364(10)
C(13)–C(14)	1.366(7)	C(35)–C(36)	1.390(8)
Bond angles			
C(11)–P–C(21)	102.0(2)	N(1)–C(1)–N(3)	119.6(4)
C(11)–P–C(31)	102.7(2)	P–C(11)–C(12)	117.0(3)
C(21)–P–C(31)	103.1(2)	P–C(11)–C(16)	126.0(4)
C(1)–N(1)–C(14)	124.3(4)	N(1)–C(14)–C(15)	118.6(5)
C(1)–N(3)–C(3)	121.1(5)	N(1)–C(14)–C(13)	120.9(4)
C(2)–N(3)–C(3)	117.7(5)	P–C(21)–C(26)	116.7(4)
C(1)–N(3)–C(2)	121.2(4)	P–C(21)–C(22)	124.5(4)
N(2)–C(1)–N(3)	120.0(5)	P–C(31)–C(32)	116.5(4)
N(1)–C(1)–N(2)	120.3(5)	P–C(31)–C(36)	125.0(4)

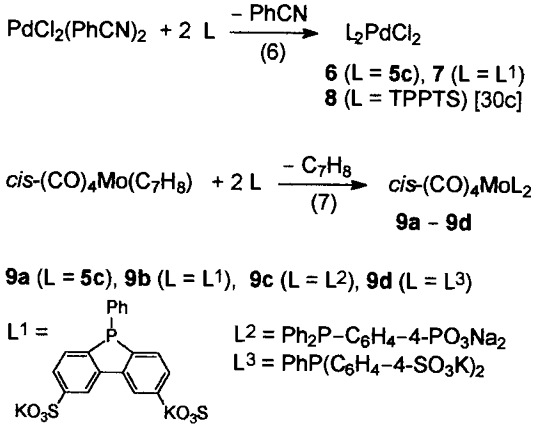
D H A	D–H	H···A	D···A	D–H···A
[i] N(1)–H(1)···Cl_a	0.78(5)	2.45(5)	3.220(4)	173(4)
N(2)–H(2)···O	0.78(5)	2.05(5)	2.804(7)	161(5)
[i] N(2)–H(3)···Cl_b	0.83(6)	2.40(6)	3.222(5)	169(5)
O–H(7)···Cl	0.84(4)	2.23(4)	3.047(5)	168(4)
C(23)–H(231)···Cl	0.97(7)	2.69(7)	3.520(6)	144(5)

[i] Symmetry code for equivalent atoms: _a ($x-0.5$, $-y+0.5$, $-z+1$); _b ($x+0.5$, $-y+0.5$, $-z+1$).

part by comparison with relevant data of Ph_3P and with the aid of DEPT ^{13}C-NMR spectra. ^{13}C-NMR signals at $\delta = 157.8$, 152.7 and 155.2 may be assigned to the guanidinium carbon atoms of **5c**, **5d** or **5f**, respectively. In case of the neutral guanidino phosphine **5d** the ^{13}C-NMR signal of the *ipso*-carbon atom attached to nitrogen is shifted downfield to $\delta = 150.8$ ($^3J(PC) = 7.1$ Hz). The same applies for the chemical shift of the *ipso*-carbon atom in **3d** ($\delta = 151.3$) as compared with that of **4a** ($\delta = 137.0$) or **4b** ($\delta = 137.0$), respectively. A similar lowfield shift is observed for the ^{13}C-NMR resonance of the *ipso*-carbon on going from the anilinium cation ($\delta = 128.6$) to aniline ($\delta = 147.0$) [16a]. The $^{15}N\{^1H\}$-NMR spectrum of **5f** reveals two resonances at $\delta = -283.7$ and -306.4 which correspond to the NH and the NH_2 groups. The resonance at $\delta = -283.7$ shows a doublet fine structure ($^4J(^{15}N^{31}P) = 2.1$ Hz). In the ^{15}N-NMR spectrum the signal at $\delta = -283.7$ appears as a doublet ($^1J(^{15}N^1H) = 91.8$ Hz) while the resonance at $\delta = -306.4$ is split into a triplet ($^1J(^{15}N^1H) = 92.0$ Hz). This is in line with the results obtained for **4a** (see above). In analogy with the situation in the guanidinium form of L-arginine [18] the rotation about the C–N(H,Ph) bond is fast on the NMR time scale, so that averaged peaks for the NH_2 groups are observed in both cases.

5. Ligand properties and coordination chemistry of 5c

In order to get information about the influence of the positive charge of the guanidinium groups on the ligand properties of guanidinium phosphines a comparative study of the Pd(II) complexes and tetracarbonyl molybdenum(0) complexes of dicationic **5c** and dianionic phosphines (disulfonated dibenzophosphole [24a], monophosphonated $Ph_2P–C_6H_4–4-PO_3Na_2$ [24b] and *para*-TPPDS [24c]) with a common skeleton was undertaken. The tetracarbonyl molybdenum(0) complexes of Ph_3P [25a] and TPPTS [25b] were included into these studies for sake of comparison.



On reaction of the highly water-soluble dicationic phosphine **5c** (L) with bisbenzonitrile palladium(II) chloride in an aqueous suspension a Pd(II) complex **6** of composition Cl_2PdL_2 is formed (Eq. (6)). While in methanol (dielectric constant 32.3 [26a], dipole moment 69 D [26b]) the *trans*-isomer of **6** predominates (the *trans*:*cis* ratio being about 95:5) in aqueous solution (dielectric constant 80.4 [26a], dipole moment 1.83 D [26b]) the *cis*-isomer is found exclusively.

This is consistent with the observation that the amount of the *cis* isomers of Cl_2PdL_2 complexes generally increases as the dielectric constant or the dipole moment of the solvent increases [27]. The assignment of the *cis*- or *trans*-structure of **6** is based on the analysis of the $^{13}C\{^1H\}$-NMR spectra, which for the *ipso*-, *ortho*- and *meta*-carbon atoms show triplet fine structure in case of the *trans*-isomer, while five or six line patterns are observed for the *cis*-isomer [28]. The quaternary guanidinium carbon atoms give rise to singlets in both isomers. The general observation that for a particular phosphine ligand the δP value of the *cis*-isomer is downfield from that of the *trans* isomer [29] provides further support of the assignments given.

The disulfonated dibenzophosphole [24a] (L^1) reacts with bisbenzonitrile palladium(II) chloride in an analogous way as **5c**, a complex of composition Cl_2PdL_2 being formed. In aqueous solution only the *cis*-isomer of **7** is present as indicated by the 'filled in doublet' fine structure of the signals in the $^{13}C\{^1H\}$-NMR spectrum. For the Pd(II) complex of TPPTS (**8**) [30c] two ^{31}P-NMR resonances ($\delta = 34.3$ and 25.3) are observed, which may be assigned to the *cis* and *trans*-isomer. Using the correlation between the δP chemical shift of complexes *trans*-Cl_2PdL_2 and the sterical parameter θ_{Tol} [31] of the ligands L a value of ca. 148° can be estimated for **5c** [30a,b]. This value compares well with that of the parent phosphine Ph_3P (δP(*trans*-L_2PdCl_2) = 13.3 [30a], $\theta = 145°$ [31]) characterizing **5c** as somewhat less bulky than TPPTS ($\theta_{Tol} = 166°$) [30b].

The cationic molybdenum complex **9a** has been obtained by reaction of norbornadiene tetracarbonyl molybdenum(0) with the aqueous solutions of **5c**. The anionic Mo(0) complexes of disulfonated dibenzophosphole, phosphonated and disulfonated phosphine are accessible in an analogous way [24a] (Eq. (7)).

$$v(CO)A_1(1) = 2005 + \sum_{i=1}^{3} \chi_i^{Mo} \qquad (8)$$

The $v(CO)A_1(1)$ stretching frequency of the complexes *cis*-$(CO)_4Mo(R^1R^2R^3P)_2$ has been proposed as measure for the electronic donor–acceptor character of the phosphorus ligands L. The definition of the individual electronic parameters of the substituents R^i at phosphorus is given in Eq. (8) using the bulky tBu_3P as standard [32]. The χ_i^{Mo} parameters thus obtained correlate very well [33] (correlation coefficient $R = 0.9943$) with the corresponding values χ_i^{Ni} derived by Tolman form the $v(CO)A_1$ stretching frequency of $R^1R^2R^3P$–$Ni(CO)_3$ complexes [31].

The $\Sigma\chi_i^{Mo}$ values obtained according to Eq. (8) for **5c** and the anionic phosphine ligands with *para*-sulfonated and phosphonated aromatic substituents are collected in Table 2. For comparison purposes the corresponding values of Ph_3P [25a] and TPPTS [25b] have been included. The $\Sigma\chi_i^{Mo}$ values of the ligands **5c**, L^1–L^3, Ph_3P and TPPTS do not differ significantly. The coordination shifts of the ^{31}P resonances and the coupling constants $^2J(PP)$ are also quite similar. These results indicate, that the donor properties are not greatly changed by introduction of the charged functionalities $[NH–C(NH_2)(NMe_2)]^+$ or PO_3^{2-}, SO_3^- into the skeleton of Ph_3P. Similar results have been obtained for AMPHOS [5], its electron donor properties in $Fe(CO)_4L$, $W(CO)_5L$ and $Mo(CO)_5L$ complexes being only slightly lower than those of Ph_3P and Ph_2MeP.

6. Suzuki aryl coupling mediated by Pd complexes of cationic and anionic phosphines

Palladium mediated cross coupling of aryl halides and aryl boronic acids (Suzuki coupling [10]) is a versatile method for the synthesis of functionalized unsymmetrical biaryls. These compounds are of potential use in pharmaceutical chemistry and for the preparation of liquid crystalline materials [34]. To examine the effect of the catalyst ligand, we studied the cross coupling reaction of *meta*-bromophenyl diphenylphosphine oxide **10** [35] with *para*-tolylboronic acid to yield the 4-methyl-1,1′-biphenyl substituted phosphine oxide **11** (Eq. (9)). The reaction was performed in a two-phase system using a 1:1 mixture of ethyleneglycol–water as the polar phase and toluene as the organic phase. Potassium carbonate was employed as the base.

Table 2
v(CO) carbonyl stretching frequencies (cm^{-1}), $\Sigma\chi_i^{Mo}$ parameters and coordination chemical shift values $\Delta\delta P$ for the complexes *cis*-$Mo(CO)_4L_2$ (L = **5c**, L^1–L^3 [24a], Ph_3P, TPPTS) (see Eq. (7) for the definition of L^1–L^3)

L	$A_1^{(2)}$	$A_1^{(1)}$	B_1	B_2	$\Sigma\chi_i^{Mo}$	$\Delta\delta P$ [d]	$^2J(PP)$ [e]
5c	2020 [a]	1922	1907	1884	15	44.5 [f]	26
L^1	2016 [a]	1918	1901	1886	13	43.8 [h]	23
L^2	2018 [a]	1917	1903	1882	11	47.2 [g]	19
L^3	2021 [a]	1921	1908	1887	16	45.4 [i]	
Ph_3P	2023 [b]	1929	1911	1899 [25a]	18		
TPPTS	2025 [a]	1931	1914	1898 [25b]	20		
	2023 [c]	1911	1909	1859 [25b]	18		

[a] 2-Methoxyethanol.

[b] *n*-Hexane.

[c] CH_3CN, [Na-kryptofix-221]$_6$[*cis*-$(CO)_4Mo\{P(C_6H_4$–*m*-$SO_3)_3\}_2$].

[d] $\Delta\delta P = \delta P_{complex} - \delta P_{ligand}$.

[e] In Hz, determined from the *CO*-$^{13}C\{^1H\}$-NMR spectra (X parts of ABX spectra).

[f] D_2O.

[g] H_2O/d^6-DMSO.

[h] CD_3OD.

[i] D_2O/isopropanol.

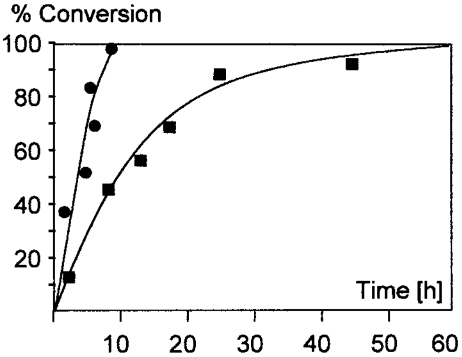
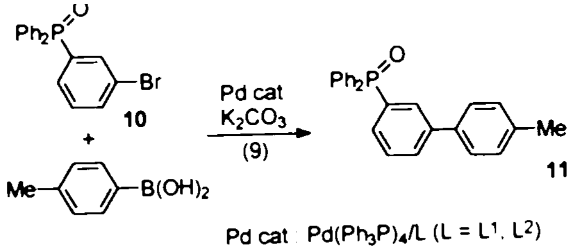


Fig. 2. Conversion vs. time diagram for the two-phase Suzuki-coupling of **10** with *p*-toluene boronic acid (■: **5c**, ●: $Ph_2P–C_6H_4$-4-PO_3Na_2).



The catalysts were formed in situ by an exchange reaction between Pd($Ph_3P)_4$ [23] and the water-soluble ligands (employed in a 1:20 molar ratio) in a two-phase system (dichloromethane–water). In order to elaborate the influence of the ligand charge on the catalytical activity of their Pd(0) complexes the phosphines L^1 [24a] and L^2 [24b] were studied in addition to the cationic phosphine **5c**. Using the $Ph_2P(O)$ groups in **10** ($\delta P = 29.2$) and **11** ($\delta P = 30.6$) as a probe the conversion rate could be determined quite conveniently by $^{31}P\{^1H\}$-NMR spectroscopy. The results for **5c** and $Ph_2P–C_6H_4$-4-PO_3Na_2 are collected in Fig. 2.

The anionic ligand $Ph_2P–C_6H_4$-4-PO_3Na_2 [24b] is significantly more efficient in this C–C coupling reaction compared with the cationic **5c**, both forming a homogeneous catalyst system. The anionic dibenzophosphole L^1 was inactive as catalyst ligand. In the case of **5c** deprotonation of the guanidinium group by K_2CO_3 occured, the neutral ligand **5d** and its Pd complex were dissolved in the organic phase as indicated by the yellow color and the signal at $\delta P = -5.7$ in the $^{31}P\{^1H\}$-NMR. Before work-up the reaction mixture the guanidinium phosphine was extracted into the aqueous solution with dilute hydrochloric acid.

7. Experimental

For experimental details, see Part XI of this series [1]. Diphenylphosphine [36a], phenylphosphine [36b], $Ph_2P(O)(OH)$ [37], $Pd(Ph_3P)_4$ [23], $PdCl_2(PhCN)_2$ [38], $C_7H_8Mo(CO)_4$ [39], and $Ph_2P(O)–C_6H_4$-4-Br [35] were prepared according to literature methods. Cyanamide, dimethylcyanamide, ammonium hypophosphite, *p*-tolylboronic acid, and 1,3-bisdiphenylphosphinopropane were purchased from Aldrich GmbH or Strem Chemicals. Starting materials were characterized by ^1H-, $^{13}C\{^1H\}$- and $^{31}P\{^1H\}$-NMR spectroscopy and mass spectrometry. ^1H-, $^{13}C\{^1H\}$-, and $^{31}P\{^1H\}$-NMR spectra were recorded on a Bruker AC 400 or AM 250 and a Jeol FX90 Q Fourier transform spectrometer. Mass spectra were obtained on a Varian MAT 311A spectrometer.

7.1. Synthesis of the 4-iodophenyl guanidines 2a and 2c

A total of 40.0 g (156.6 mmol) or 70.0 g (274.0 mmol) of finely grounded 4-iodophenylammonium chloride and 6.3 g (150.0 mmol) of cyanamide or 21.1 g (301.0 mmol) of dimethylcyanamide was mixed together and the mixture was heated to 160°C for 10 min. The solution obtained after addition of 500 ml of water was extracted with three aliquots of 100 ml of ether. The aqueous phase was separated and evacuated at 1 mbar in order to remove the ether dissolved in the solution. Thereafter conc. aqueous NaOH solution was added until a pH value of 12 was reached. The precipitate formed was collected by filtration on a Buchner funnel and washed with water until the filtrate showed no alkaline reaction. The precipitate was dried in vacuo (20°C, 0.1 mbar). Yields: 28.1 g (72%) **2a**, 54.6 g (69%) **2c**.

2a. Anal. Found: C, 32.50; H, 3.10; N, 16.0. $C_7H_8IN_3$ (261.1). Calc.: C, 32.21; H, 3.09; N, 16.09%. M.p. = 155°C; ^1H-NMR (CD_3CN, δ): 4.60 (NH_2), 6.60–6.63, 7.50–7.60 (arom. H); $^{13}C\{^1H\}$-NMR (d^6-acetone, δ): 154.3; 152.4; 139.1, 127.3, 84.1; $^{15}N\{^1H\}$-NMR (d^6-DMSO, δ): -307.3 (NH_2).

2c. Anal. Found: C, 37.70; H, 4.20; N, 14.60. $C_9H_{12}IN_3$ (289.1). Calc.: C, 37.39; H, 4.18; N, 14.53%. M.p. = 101°C; ^1H-NMR (CD_3CN, δ): 2.88 (CH_3), 4.30 (NH_2), 6.5–6.6, 7.4–7.5 (arom. H); $^{13}C\{^1H\}$-NMR (CD_3CN, δ): 153.9, 152.7, 138.9, 126.6, 88.3, 37.8 (CH_3).

7.2. Synthesis of the 3-iodophenyl guanidines 2b and 2d

The mixtures of 58.2 g (228.0 mmol) or 52.6 g (205.9 mmol) of 3-iodophenylammonium chloride and 9.15 g (232.0 mmol) of cyanamide or 14.4 g (205.9 mmol) of dimethylcyanamide were heated to 130°C for 10 min. After the reaction was completed 150 ml of water was added to the reaction mixtures. The solutions obtained were extracted with three aliquots of 100 ml of diethyl ether. To the aqueous phase conc. KOH was added until a pH value of 12 was reached and the solution was extracted with three aliquots of dichloromethane. The collected organic phases were dried over magnesium sulfate. After evaporation of all volatiles in vacuo **2b** and **2d** were obtained as pale yellow crystals. Yields: 47.6 g (80%) **2b**, 48.2 g (81%) **2d**.

2b. Anal. Found: C, 32.50; H, 3.20; N, 16.1. $C_7H_8IN_3$ (261.1). Calc.: C, 32.21; H, 3.09; N, 16.09%. M.p. = 125°C; ^{1}H-NMR (CD_3CN, δ): 4.98 (NH_2), 6.8–7.3 (arom. H); $^{13}C\{^1H\}$-NMR (CD_3CN, δ): 154.8, 153.9, 133.6, 132.1, 131.0, 124.3, 95.8.

2d. Anal. Found: C, 37.21; H, 4.13; N, 14.25. $C_9H_{12}IN_3$ (289.1). Calc.: C, 37.39; H, 4.18; N, 14.53%. ^{1}H-NMR ($CDCl_3$, δ): 2.99 (CH_3), 6.85–7.30 (arom. H); $^{13}C\{^1H\}$-NMR ($CDCl_3$, δ): 152.7, 152.6, 132.6, 130.9, 130.5, 123.0, 95.0, 37.7 (CH_3).

*7.3. Synthesis of 4-diphenylphosphinophenyl guanidine (**3d**) and the 4-diphenylphosphinophenyl guanidinium salts **4a** and **4b***

*7.3.1. Synthesis of **3d***

A total of 6.92 g (37.2 mmol) of diphenylphosphine and 9.70 g (37.2 mmol) of **2a** was dissolved in 100 ml of dimethylacetamide. Oxygen dissolved in this solution was thoroughly removed by repeated freeze–thaw cycles. After addition of 4.2 mg (0.05 mol.%) of $Pd(OAc)_2$ the reaction mixture was heated to 130°C for 12 h. All volatiles were then removed in vacuo and the residue obtained was dissolved in 200 ml of a 1:1 ethanol–water mixture. To this solution concentrated aqueous solution of sodium hydroxide was added until the pH value reached 12. The reaction mixture was extracted with 100 ml of CH_2Cl_2 and the collected extracts were washed with three aliquots of 10 ml of water. After drying the organic phase over magnesium sulfate, the solvent was evaporated in vacuo leaving **3d** as a pale yellow solid, which was dried at 20°C, 0.02 mbar. Due to variable content of water no satisfying analytical data could be obtained from **3d**. Yield: 11.50 g (97%).

^{1}H-NMR (d^6-DMSO, δ): 5.46 (NH_2), 6.8–7.4 (arom. H); $^{13}C\{^1H\}$-NMR (d^6-DMSO, δ): 152.8; 151.3; 137.9 (J = 11.2 Hz), 134.6 (J = 21.4 Hz), 132.9 (J = 19.3 Hz), 128.5, 128.4 (J = 6.1 Hz), 125.6 (J = 7.1 Hz), 123.3 (J = 8.1 Hz); $^{31}P\{^1H\}$-NMR (d^6-DMSO, δ): −6.1.

*7.3.2. Preparation of **4a** and **4b***

A total of 1.59 g (5.00 mmol) or 1.00 g (3.13 mmol) of 4-diphenylphosphinophenyl guanidine **3d** was dissolved in 10 ml of methanol or 5 ml of ethanol, respectively. 0.415 g (5.00 mmol) of $NH_4H_2PO_2$ or 0.683 g (3.13 mmol) of $Ph_2P(O)OH$ was added to these solutions. On concentration of these solutions to about half of their volume by evaporation of the solvent in vacuo (and addition of 3 ml of ether in case of **4b**) the phosphines **4a** and **4b** precipitated out as colorless solids, which were collected by filtration. **4a** was further purified by recrystallization from methanol. Yields: 1.72 g (89%) **4a**, 1.32 g (78%) **4b**.

4a. Anal. Found: C, 59.18; H, 5.55; N, 10.78. $C_{19}H_{21}N_3O_2P_2$ (385.3). Calc.: C, 59.22; H, 5.49; N, 10.90%. ^{1}H-NMR (CD_3OD, δ): 7.14 (^1J(PH) = 502.8, $H_2PO_2^-$), 7.2–7.6 (arom. H). $^{13}C\{^1H\}$-NMR (CD_3OD, δ): 157.8, 138.1 (J = 10.9 Hz), 137.8 (J = 12.7 Hz), 137.0, 136.2 (J = 20.3 Hz), 134.8 (J = 19.9 Hz), 130.1, 129.7 (J = 6.9 Hz), 125.8 (J = 7.1 Hz); $^{31}P\{^1H\}$-NMR (CD_3OD, δ): −1.0 (σ^3-P), 8.3 (^1J(PH) = 503.1 Hz, t, H_2PO_2); $^{15}N\{^1H\}$-NMR (CH_3OH, CD_3OD, δ): −282.2 (J = 92.5 Hz, NH), −305.7 (J = 91.8, NH_2).

4b. Anal. Found: C, 69.22; H, 5.40; N, 7.80. $C_{31}H_{29}N_3O_2P_2$ (537.5). Calc.: C, 69.27; H, 5.44; N, 7.82%. $^{13}C\{^1H\}$-NMR (CD_3OD, δ): 157.6, 140.2 (J = 131.4 Hz), 138.1 (J = 10.9 Hz), 137.4 (J = 12.6 Hz), 137.0, 136.1 (J = 20.4 Hz), 134.7 (J = 19.8 Hz), 132.0 (J = 9.5 Hz), 131.1 (J = 2.6 Hz), 130.3, 129.7 (J = 7.0 Hz), 128.9 (J = 12.1 Hz), 125.7 (J = 7.1 Hz); $^{31}P\{^1H\}$-NMR (CD_3OD, δ): −1.2 (σ^3-P), 26.6 ($Ph_2PO_2^-$).

*7.4. Synthesis of N,N-dimethyl-N′-(4-diphenylphosphino)phenyl guanidinium chloride (**3c**)*

A total of 8.0 g (27.6 mmol) of **2c** and 5.14 g (27.6 mmol) of diphenylphosphine was dissolved in 50 ml of dimethylacetamide. Molecular oxygen dissolved in this solution was thoroughly removed by repeated freeze–thaw cycles. After addition of 6.2 mg (0.1 mol.%) of $Pd(OAc)_2$ the solution was heated to 130°C and stirred for 12 h. Thereafter the reaction mixture was poured into a solution of 5.70 g (35.0 mmol) of NH_4PF_6 in 300 ml of water. The precipitate formed was collected by filtration on a Buchner funnel, washed with 50 ml of water and dried in vacuo (20°C, 0.01 mbar). Yield: 13.1 g (96%) of the hexafluorophosphate of the cation in **3c**.

A total of 5.0 g (10.1 mmol) of the hexafluorophosphate of the cation in **3c** was dissolved in 20 ml of ethanol. To this solution conc. aqueous NaOH was added at 0°C until a pH value of about 12 was reached. After addition of 10 ml of water the aqueous phase was extracted with 50 ml of CH_2Cl_2, the organic phase was separated and washed with five aliqots of 10 ml of water. After addition of 11 ml of 1 N HCl to the organic phase all volatiles were removed in vacuo (20°C, 0.01 mbar). Yield: 3.35 g (80%) **3c**. Crystals of **3c**·CH_3OH were precipitated on slow evaporation of a methanolic solution of **3c**.

3c. Anal. Found: C, 63.51; H, 6.89. $C_{21}H_{23}ClN_3P{\cdot}CH_3OH$ (415.9). Calc.: C, 63.53; H, 6.54%. ^{1}H-NMR (CD_3OD, δ): 7.82 (NH_2), 9.52 (NH), 3.12 (NMe_2), 7.1–7.6 (arom. H); $^{13}C\{^1H\}$-NMR (CD_3OD, δ): 155.5, 138.2, 137.0 (J = 10.8 Hz), 135.1 (J = 20.4 Hz), 133.8 (J = 11.5 Hz), 133.7 (J = 19.5 Hz), 129.6, 129.3 (J = 6.9 Hz), 124.0 (J = 7.4 Hz), 39.0 (CH_3); $^{31}P\{^1H\}$-NMR (CD_3OD, δ): −3.6; $^{15}N\{^1H\}$-NMR (CH_3OH, CD_3OD, δ): −299.3 (NH), −281.4 (NH_2), −303.8 (NMe_2).

7.5. Synthesis of **5a**–**5d**

7.5.1. Preparation of **5a**

To the solution of 6.12 g (55.6 mmol) of phenylphosphine and 32.14 g (111.2 mmol) of **2d** in 100 ml of acetonitrile 0.26 g (0.2 mol.%) of $Pd(PPh_3)_4$ were added after removal of molecular oxygen dissolved in this solution by repeated freeze–thaw cycles. The reaction mixture was heated under reflux for 40 h. After removal of all volatiles in vacuo (60°C, 0.01 mbar) **5a** was obtained as pale yellow crystals. Yield: 37.7 g (98%).

Anal. Found: C, 41.94; H, 4.60; N, 12.36. $C_{24}H_{31}I_2N_6P$ (688.3). Calc.: C, 41.88; H, 4.54; N, 12.21%. ^{1}H-NMR (d^6-DMSO, δ): 3.04 (NMe_2), 7.11–7.51 (arom. H); $^{13}C\{^1H\}$-NMR (d^6-DMSO, δ): 155.8, 138.6 ($J = 13.2$ Hz), 137.9 ($J = 9.2$ Hz), 136.3 ($J = 11.2$ Hz), 134.3 ($J = 20.1$ Hz), 131.0 ($J = 18.3$ Hz), 130.6 ($J = 6.1$ Hz); 130.0, 129.6 ($J = 7.1$ Hz), 128.9 ($J = 22.4$ Hz), 125.2, 39.4 (NMe_2); $^{31}P\{^1H\}$-NMR (d^6-DMSO, δ): −4.0.

7.5.2. Preparation of **5d**

To the solution of 37.8 g (54.9 mmol) **5a** in 120 ml of water at 60°C conc. aqueous NaOH (4.40 g in 10 ml of water) was added. The precipitate formed was dissolved in 100 ml of CH_2Cl_2 and the aqueous phase was extracted with a further aliquot of 100 ml of CH_2Cl_2. The collected extractands were dried over $MgSO_4$. After evaporation of the solvents in vacuo (20°C, 20 mbar) **5d** was obtained as a yellow powder. Yield: 21.9 g (84%).

Anal. Found: C, 60.88; H, 6.48. $C_{24}H_{29}N_6P \cdot 2.5H_2O$ (477.5). Calc.: C, 60.36; H, 7.17%. ^{1}H-NMR ($CDCl_3$, δ): 2.95 (NMe_2), 4.1 (NH), 6.85–7.37 (arom. H); $^{13}C\{^1H\}$-NMR ($CDCl_3$ δ): 152.7, 150.8 ($J = 7.1$ Hz), 138.5 ($J = 11.2$ Hz), 137.9 ($J = 11.2$ Hz), 133.9 ($J = 19.3$ Hz), 129.5 ($J = 8.1$ Hz), 128.6 ($J = 20.2$ Hz), 128.5 ($J = 12.2$ Hz), 128.5, 128.5, 127.3 ($J = 19.3$ Hz), 37.7 (NMe_2); $^{31}P\{^1H\}$-NMR ($CDCl_3$, δ): −2.9; MS: m/e 432 [M^+].

7.5.3. Preparation of **5b** and **5c**

To 21.9 g (31.8 mmol) of the guanidinium base **5d** suspended in 100 ml of water 15 ml of 48% HBr was added. After all the solid material was dissolved, water and excess HBr were removed in vacuo (20°C, 0.01 mbar). **5b** was obtained as a creme colored hygroscopic powder. Yield: 20.0 g (92%) **5b**. Due to variable content of water no satisfying analytical data could be obtained.

Potassium hydroxide was added to the solution of 43.6 g (63.3 mmol) of **5a** in 350 ml of water. The precipitate formed was dissolved in 100 ml of CH_2Cl_2. The organic phase was separated and the aqueous phase washed with three aliquots of CH_2Cl_2. The collected organic phases were evaporated to dryness and the residue obtained was treated with 127 ml of a 1 N HCl. After removal of the solvent in vacuo **5c** was obtained as a creme colored powder. Yield: 29.2 g (91%). **5c**.

5c. Anal. Found: C, 57.00; H, 6.90; N, 16.40. $C_{24}H_{31}Cl_2N_6P$ (505.4). Calc.: C, 57.03; H, 6.18; N, 16.63%. $^{13}C\{^1H\}$-NMR (D_2O, δ): 157.8, 140.2 ($J = 9.2$ Hz), 138.6 ($J = 8.1$ Hz), 137.1 ($J = 7.2$ Hz), 136.0 ($J = 19.3$ Hz), 133.9 ($J = 20.3$ Hz), 132.6 ($J = 8.2$ Hz), 132.1, 131.3 ($J = 7.1$ Hz), 131.0 ($J = 18.3$ Hz), 127.7, 40.5 (NMe_2); $^{31}P\{^1H\}$-NMR (D_2O, δ): −4.7.

7.6. Synthesis of **5f**

A total of 21.3 g (71.6 mmol) of the 3-iodophenylguanidinium chloride **1b**, 3.9 g (35.8 mmol) of $PhPH_2$ and 13.3 g (71.6 mmol) of $n Bu_3N$ was dissolved in 120 ml of dimethylacetamide. Molecular oxygen dissolved in the solution was removed by repeated freeze–thaw cycles. Thereafter 41.2 mg (0.06 mol.%) of Pd_2dba_3 and 29.5 mg (0.2 mol.%) of DPPP dissolved in dimethylacetamide were added. The reaction mixture was heated at 130°C for 2 days. Thereafter all volatiles were removed in vacuo (100°C, 0.01 mbar), the remaining residue was dissolved in 500 ml of water and the aqueous solution was extracted with two portions of 100 ml of ether. Solid NaOH was added until the solution showed a pH value of about 12. The precipitate formed was extracted with three aliquots of 50 ml of CH_2Cl_2. The collected extracts were washed with 60 ml of water and dried over $MgSO_4$. After removal of the solvent in vacuo a creme colored solid was left which was dissolved in 90 ml of 1 N HCl. The aqueous solution was evaporated to dryness and the solid obtained was dissolved in ethanol and precipitated with acetone. This procedure was repeated three times. Yield: 8.06 g (50%).

Anal. Found: C, 52.45; H, 5.95; N, 15.20. $C_{20}H_{23}Cl_2N_6P \cdot 2C_2H_5OH$ (541.5). Calc.: C, 53.24; H, 6.52; N, 15.52%. ^{1}H-NMR (D_2O, δ): 7.1–7.6, 3.63, 1.16 (C_2H_5OH); $^{13}C\{^1H\}$-NMR (D_2O, δ): 155.2, 137.7 ($J = 10.9$ Hz), 134.3 ($J = 8.2$ Hz), 134.0 ($J = 8.0$ Hz), 133.1 ($J = 20.0$ Hz), 131.8 ($J = 18.7$ Hz), 129.7 ($J = 7.2$ Hz), 129.3, 129.0 ($J = 3.0$ Hz), 128.3 ($J = 7.5$ Hz), 125.5;$^{31}P\{^1H\}$-NMR (D_2O, δ): −5.0; $^{15}N\{^1H\}$-NMR (D_2O, δ): −283.8 (^1J(NH) = 91.8 Hz, NH; ^4J(PN) = 2.1 Hz), 306.4 (^1J(NH) = 92 Hz, NH_2).

7.7. Syntheses of the Pd(II) complexes **6** (cis, trans)

To a suspension of 0.21 g (0.55 mmol) of bis(benzonitrile)palladium dichloride in 20 ml of water 0.56 g (1.11 mmol) of **5c** was added and the reaction mixture was stirred for 1 h. The $^{31}P\{^1H\}$-NMR spectrum of the reaction mixture indicated that the complexes **6** had been formed quantitatively. After filtration of the yellow solution through a fritted glass funnel all volatiles were removed in vacuo (20°C, 0.01 mbar). The yellow solid obtained was washed with 15 ml of toluene and 15 ml of ether. The residue was dissolved in 10 ml of methanol and precipitated by addition of 5 ml of ether. Yield: 1.3 g (99%).

6 (*cis*). Anal. Found: C, 46.97; H, 5.44. $C_{48}H_{62}Cl_6N_{12}P_2Pd\cdot 2H_2O$ (1224.2). Calc.: C, 47.09; H, 5.43%. ^{1}H-NMR (D_2O, δ): 3.1 (NMe_2), 7.2–7.9 (arom. H); $^{13}C\{^1H\}$-NMR (D_2O, δ): 157.5, 138.5 ($N = 14.2$ Hz), 137.7 ($N = 12.7$ Hz), 135.2 ($N = 135.2$ Hz), 134.3 ($N = 10.2$ Hz), 132.8 ($N = 57.5$ Hz), 132.7 ($N = 12.7$ Hz), 131.6 ($N = 13.7$ Hz), 131.5 ($N = 13.2$ Hz), 129.7, 128.6 ($N = 58.0$ Hz), 40.6 (NMe_2); $^{31}P\{^1H\}$-NMR (D_2O, δ): 35.9 (95%, *cis*), 28.8 (5%, *trans*).

6 (*trans*). $^{13}C\{^1H\}$-NMR (CD_3OD, δ): 157.2, 137.9 ($N = 12.2$ Hz), 136.2 ($N = 13.2$ Hz), 134.0 ($N = 13.2$ Hz), 132.8, 132.4 ($N = 48.8$ Hz), 131.3 ($N = 13.2$ Hz), 131.1 ($N = 11.4$ Hz), 129.8 ($N = 12.2$ Hz), 129.4 ($N = 50.9$ Hz), 128.2, 39.3 (NMe_2); $^{31}P\{^1H\}$-NMR (CD_3OD, δ): 25.3.

7.8. Synthesis of the Mo(0) complex **9a**

A total of 0.18 g (0.6 mmol) of a suspension of *cis*-$C_7H_8Mo(CO)_4$ in 10 ml of water was charged with 0.60 g (1.18 mmol) of **5c** and the reaction mixture was stirred at ambient temperature for 15 h. The yellow solution obtained was filtered through a fritted glass funnel and the filtrate was evaporated to dryness in vacuo (20°C, 0.01 mbar). The residue was washed with CH_2Cl_2 and ether and dried in vacuo. Yield: quantitative.

Anal. Found: C, 50.01; H, 5.30. $C_{52}H_{62}Cl_4MoN_{12}O_4P_2\cdot 2H_2O$ (1254.9). Calc.: C, 49.77; H, 5.30%. ^{1}H-NMR (D_2O, δ): 3.00 (NMe_2), 7.1–7.5 (arom. H); $^{13}C\{^1H\}$-NMR (D_2O, δ): 217.4 ($N = 16.3$ Hz), 212.2 ($J = 9.2$ Hz), 157.6, 139.5 ($N = 32.5$ Hz), 138.6 ($N = 11.2$ Hz), 136.4 ($N = 32.6$ Hz), 135.9 ($N = 12.2$ Hz), 133.2 ($N = 9.5$ Hz), 133.1, 132.5 ($N = 8.6$ Hz), 131.0 ($N = 9.5$ Hz), 130.9 ($N = 15.3$ Hz), 128.3, 40.5 (NMe_2); $^{31}P\{^1H\}$-NMR (D_2O, δ): 39.7.

7.9. General procedure for the Suzuki coupling reactions

7.9.1. In situ preparation of the Pd catalysts

To 20.0 mg (0.017 mmol) of $Pd(Ph_3P)_4$ dissolved in 10 ml of CH_2Cl_2 an aqueous solution of each 0.35 mmol of the ligands **5c** (0.177 g), disulfonated dibenzophosphole [24a] (0.174 g) or Ph_2P–C_6H_4–4-PO_3Na_2 [24b] (0.135 g) was added. After stirring the two-phase system for 1 h the yellow color of the organic phase had dissappeared. The yellow aqueous phase was separated and used for the catalysis experiments.

7.9.2. Suzuki coupling reactions

A total of 0.54 g (1.5 mmol) of **10** [35], 0.62 g (4.5 mmol) of potassium carbonate and 0.22 g (1.6 mmol) of *p*-tolueneboronic acid was dissolved in a two-phase system consisting of 15 ml of toluene, 5 ml of ethyleneglycol and 5.7 ml of water. After heating to 90°C, 4.3 ml of the catalyst solution was added. Samples were drawn periodically from the reaction mixture and investigated by $^{31}P\{^1H\}$-NMR spectroscopy.

7.9.3. Isolation of the coupling product **11**

The toluene phases of the Suzuki coupling reactions were collected and dried over magnesium sulfate. After removal of the solvent in vacuo (20°C, 0.01 mbar) the coupling product **11** was obtained as white solid.

11. Anal. Found: C, 81.07; H, 5.73. $C_{25}H_{21}OP$ (368.4). Calc.: C, 81.50; H, 5.74%. ^{1}H-NMR ($CDCl_3$, δ): 2.4 (CH_3), 6.9–8.0 (arom. H); $^{13}C\{^1H\}$-NMR ($CDCl_3$, δ): 141.3 ($J = 11.2$ Hz), 137.5, 136.9, 133.0 ($J = 103.7$ Hz), 132.5 ($J = 103.8$ Hz), 131.9 ($J = 10.3$ Hz), 131.8 ($J = 2.0$ Hz), 130.3 ($J = 18.9$ Hz), 130.3 ($J = 2.0$ Hz), 130.2 ($J = 5.8$ Hz), 129.4, 128.7 ($J = 13.2$ Hz), 128.4 ($J = 12.2$ Hz), 126.9, 20.9 (CH_3); $^{31}P\{^1H\}$-NMR ($CDCl_3$, δ): 30.6; MS: $m/e = 368$ [M^+], 277 [$M^+ - C_6H_4 - CH_3$].

7.10. X-ray structure analysis of **3c**·CH_3OH

Suitable single crystals of **3c**·CH_3OH for the X-ray diffraction studies were grown by standard techniques from a saturated methanolic solution of **3c**. Preliminary examination and data collection were carried out on a Nonius CAD4 four circle diffractometer equipped with a sealed tube (50 kV; 40 mA) and graphite monochromated Mo–K_α radiation. Data collection were performed at 193 K within the θ range of $1.75° < \theta < 24.98°$. The unit cell parameters were obtained by full-matrix least-squares refinements of 25 accurately centered high angle reflections. A total number of 3807 reflections were collected. A total of 36 systematic absent reflections together with 266 negative intensities were rejected from the original data set. After merging ($R_{int} = 0.0471$), a sum of 3251 independent reflections remained and were used for all calculations. Data were corrected for Lorentz and polarization effects. Within the measuring time three check reflections (120 h, monitored every 3600 s) indicated a loss of 48.6% of the initial intensity. A decay correction was applied. The structure was solved by a combination of direct methods and difference Fourier syntheses. All 'heavy atoms' of the asymmetric unit were refined anisotropically. All hydrogen atoms were found and refined with individual isotropic displacement parameters. Full-matrix least-squares refinements were carried out by minimizing $\Sigma w(F_o^2 - F_c^2)^2$ with SHELXL-93 weighting scheme [40] and stopped at $R_1 = 0.0602$,

$wR_2 = 0.1518$, and shift/err < 0.001. The correct enantiomere was confirmed by Flack's parameter $\varepsilon = 0.10(13)$. Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from International Tables for X-ray Crystallograpy [41]. All calculations were performed on a DEC 3000 AXP workstation with the STRUX-V [42] system, including the programs PLATON [43], SHELXS-86 [44], and SHELXL-93 [45]. A summary of the crystal and experimental data is reported in Table 3.

8. Supplementary material

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 143307. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

Table 3
Crystallographic data for **3c**·CH_3OH

Chemical formula	$C_{22}H_{27}ClN_3OP$
F_w	415.89
Color/shape	Colorless/fragment
Crystal size (mm)	$0.50 \times 0.50 \times 0.10$
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
a (Å)	8.103(1)
b (Å)	15.041(2)
c (Å)	18.308(2)
V (Å^3)	2231.3(5)
Z	4
T (K)	193
D_{calc} (g cm^{-3})	1.238
μ (mm^{-1})	0.260
F_{000}	880
λ (Å)	0.71073
Device/scan method	CAD4/ω-scan
θ Range (°)	1.75–24.98
Index ranges	$0 \le h \le 9$, $0 \le k \le 17$, $-21 \le l \le 21$
No. reflections collected	3807
No. independent reflections	3251 ($I > 0$)
No. observed reflections	3251 ($I > 0$)
No. parameters refined	361
R_{int}	0.0471
R_1 [a]	0.0602
wR_2 [b]	0.1518
GOF [c]	1.100
Weights a/b [d]	0.0794/3.0675
Largest difference peak and hole (e Å^{-3})	0.34/−0.39

[a] $R_1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$.

[b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

[c] $\mathrm{GOF} = [\Sigma w(F_o^2 - F_c^2)^2/(N_o - N_v)]^{1/2}$.

[d] $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ with P: $[\max(0 \text{ or } F_o^2) + 2F_c^2]/3$.

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