EurJIC

European Journal of Inorganic Chemistry

Chemistry Europe

European Chemical Societies Publishing

Accepted Article

Title: Easily prepared mono(N,N-dialkylamino)phosphine palladium(II) complexes: Structural and catalytic evaluation

Authors: Jairus L. Lamola, Joy C. Shilubana, Lonwabo Ngodwana, Banele Vatsha, Adedapo S. Adeyinka, Munaka C. Maumela, Cedric H. Holzapfel, and Edwin Mpho Mmutlane

To be cited as: *Eur. J. Inorg. Chem.* 10.1002/ejic.202100232

Link to VoR: https://doi.org/10.1002/ejic.202100232

WILEY-VCH

WILEY-VCH

COMMUNICATION

Easily prepared mono(*N,N*-dialkylamino)phosphine palladium(II) complexes: Structural and catalytic evaluation

Jairus L. Lamola,[a] Joy C. Shilubana,[a] Lonwabo Ngodwana,[a] Banele Vatsha,[a] Adedapo S. Adeyinka,[a] Munaka C. Maumela,[a,b] Cedric W. Holzapfel,[a] and Edwin M. Mmutlane*[a]

[a] Jairus L. Lamola, Joy C. Shilubana, Dr. Lonwabo Ngodwana, Dr. Banele Vatsha, Dr. Adedapo S. Adeyinka, Prof. Dr. Cedric W. Holzapfel,
* Dr. Edwin M. Mmutlane
Research Centre for Synthesis and Catalysis
Department of Chemical Sciences
University of Johannesburg, Kingsway Campus
P.O. Box 123, Auckland Park, 2006, South Africa
E-mail: edwinm@uj.ac.za
[b] Prof. Dr. Munaka C. Maumela
Sasol (Pty) Ltd, Research & Technology (R & T), 1 Klasie Havenga Rd
Sasolburg 1947, South Africa.

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

Abstract: The search for efficient, active and universal catalyst systems for transition-metal catalyzed cross-coupling reactions, continues to be of interest to researchers world-wide. Herein, we report two new Pd(II) complexes, effortlessly prepared from *N,N*-dialkylamino-phosphines for Suzuki-Miyaura cross-coupling reactions. These sufficiently hindered (% V_{Bur} = 30.0 – 31.5%) and electron rich (ν_{CO} = 1947.41 - 1946.29 cm^{-1}) aminophosphines formed active catalysts for Suzuki-Miyaura coupling of aryl bromides and chlorides.

Palladium-catalyzed cross-coupling reactions are indispensable tools in synthesis, providing easy access to C-C and C-X (X = N, O, S, F, Si, and B) bonds.[1,2] Among them is the Suzuki-Miyaura reaction, widely used in pharmaceuticals[3], agrochemicals[4], natural products[5], materials science[6] and process chemistry[7]. As the application of this versatile reaction broadens, the need for robust, highly active catalyst systems increases. Pioneering contributions in this regard have been trialkyl-, biaryl-, ferrocenyl- and adamantyl-based phosphines developed by Fu[8], Buchwald[9], Hartwig[10] and Beller[11], respectively. Notable contributions have subsequently been made by Kwong[12], Verkade[13], Reetz[14], Stradiotto[15], Hong[16], and many more.

Our focus is on aminophosphines,[17,18] pioneered as ligands in Suzuki-Miyaura coupling by Woolins[19] and now applicable in other catalyst systems such as intermolecular hydroamination of alkenes[20], alkylation of amines by alcohols[21], and amination of aryl-substituted allylic alcohols[22]. This class of ligands allows for easy tuning of donor and steric capacities by varying substituents on the *N*-(abundance of amines, including easily accessible imidazol-2-ylidene- and pyridinylide amines), the *P*-center or both.[23–29] Arylamino groups attenuate the basicity of the *P*-donor atom through resonance and *σ*-electron withdrawal, while aliphatic amino groups increase the basicity due to the absence of the *π*-system.[30] This was independently demonstrated by Ziółkowski[31] and Woollins[32], studying the electronic properties of *N*-pyrrolyl- and *N*-pyrrolidinyl-phosphines employing ν_{CO} of *trans*-[RhCl(CO)L$_2$], respectively. Their studies also revealed the alkyl-based [P(NC$_4$H$_8$)$_3$] (1951 cm^{-1}) as a better donor compared to its aromatic counterpart [P(NC$_4$H$_4$)$_3$] (2012 cm^{-1}) (Table 1, entries 9 and 2). Most notable was the finding that *P*-basicity increases with decrease of amino-substituents, $Ph_2P(NR_2)$ > $PhP(NR_2)_2$ > $P(NR_2)_3$. This trend was further confirmed by Burrows and co-workers[33], in their parameterization studies of *N*-carbazolyl phosphines which showed a decrease in donor character with increase in number of *N*-carbazolyl substituents in the order [PPh$_2$(NC$_{12}$H$_8$)] < [PPh(NC$_{12}$H$_8$)$_2$] < [P(NC$_{12}$H$_8$)$_3$] (Table 1). Furthermore, Singh and co-workers identified [PPh(NEt$_2$)$_2$)] as a poor donor than [PPh$_2$(NEt$_2$)], with electron descriptors of ν_{CO} = 2007 cm^{-1} and 1974 cm^{-1}, and $^1J_{PSe}$ = 761 Hz and 746 Hz, respectively.[29]

Table 1. Electronic descriptors derived from ν_{CO} of *trans*-[RhCl(CO)L$_2$], complexes.

Entry	Ligand	ν_{CO} (cm^{-1})	Ref
1	P(OPh)$_3$[a]	2016	[34]
2	P(Pyrrolyl)$_3$[a]	2012	[31]
3	P(Carbazolyl)$_3$[b]	2012	[33]
4	PhP(Pyrrolyl)$_2$[a]	2009	[31]
5	Ph$_2$P(Pyrrolyl)[a]	2000	[31]
6	PPh(Carbazolyl)$_2$[b]	1997	[33]
7	PPh$_2$(Carbazolyl)[b]	1990	[33]
8	PPh$_3$[a]	1965	[34]
9	P(Pyrrolidinyl)$_3$[a]	1951	[32]
10	PhP(Pyrrolidinyl)$_2$[a]	1949	[32]
11	Ph$_2$P(di-*n*-butylamino)[c]	1947	*this work*
12	Ph$_2$P(di-*iso*-butylamino)[c]	1946	*this work*

[a]KBr. [b]CH_2Cl_2. [c]WB97XD/LANL2DZ.

Following these precedents, we report the use of novel Pd(II) complexes comprising strongly basic mono-(*N*,*N*-dialkylamino)diphenylphosphines of general formular $PPh_2(NR_2)$ (Scheme 1), for Suzuki-Miyaura cross-coupling. Previously demonstrated to be good donors, the catalytic efficiency of this family of aminophosphine ligands was evaluated parallel to triphenylphosphine (PPh_3) and 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (SPhos) as the benchmark and gold standard, respectively.

Diphenylphosphino-*N,N*-di-*n*-butylamine (**L1**) and diphenylphosphino-*N,N*-di-isobutylamine (**L2**) were prepared by condensation of chlorodiphenylphosphine with the corresponding secondary amine in anhydrous diethyl ether or THF at room temperature (Scheme 1 (i)).[30]

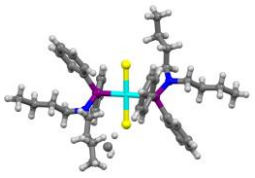
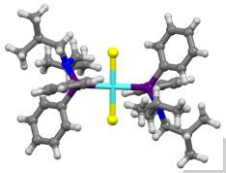
$$Ph_2PCl \xrightarrow{(i)} Ph_2PNR_2 \xrightarrow{(ii)} [PdCl_2(Ph_2PNR_2)_2]$$

R = *n*-butyl **L1** (88%), **C1** (92%)
= *iso*-butyl **L2** (90%), **C2** (89%)

Scheme 1. Synthesis of mono-(*N,N*-dialkylamino)phosphine ligands through condensation and complexation to Pd(II); (i) 1 equiv. NR_2, 1 equiv. Et_3N, and 0.5 equiv. PPh_2Cl, rt, 3 h, N_2, THF (**L1**, 88%) or Et_2O (**L2**, 90%); (ii) 1 equiv. $(CH_3CN)PdCl_2$, 2 equiv. **L**, rt, 24 h, N_2, DCM, affording **C1** (92%) and **C2** (89%).

The desired aminophosphine products were isolated in yields of 88% (**L1**, viscous oil) and 90% (**L2**, white powdery solid, after recrytallization from absolute ethanol) in 3 h. The novel Pd(II) complexes **C1** and **C2** were prepared through the reaction of the free ligands with bis(acetonitrile)dichloropalladium(II) in CH_2Cl_2 for 24 h at 25 °C (Scheme 1 (ii) and Table 2). ^{31}P NMR showed shifts 61.9 to 70.1 ppm (**L1** → **C1)** and 64.3 – 68.7 ppm (**L2** → **C2**).

Table 2: Selected crystallographic and refinement parameters of **C1** and **C2**.[a]

Crystal structure		
CCDC #	2064686	2064689
Complex	**C1**	**C2**
Empirical formula	$C_{40}H_{56}Cl_2N_2P_2Pd$	$C_{40}H_{56}Cl_2N_2P_2Pd$
Formula weight	804.10	804.10
Temperature/K	100	100
Crystal system	Monoclinic	Triclinic
Space group, Z	$P2_1/c$, 4	P-1, 1
a/Å	14.952(8)	8.9283(10)
b/Å	9.929(5)	8.9344(9)
c/Å	26.495(14)	13.2260(14)
α/°	90	109.168(2)
β/°	103.283(14)	103.863(3)
γ/°	90	90.467(3)
Volume/Å^3	3828(3)	963.16(18)
Final R indexes [I>=2σ (I)]	R_1 = 0.0542, wR_2 = 0.1361	R_1 = 0.0365, wR_2 = 0.1002

[a]Complete crystal data can be retrieved from Table S1 and S2. Selected bond lengths and angles are included in Table 3.

To get an indication of the robustness of the free ligands, simple stability tests were conducted, where the rate of their oxidation was monitored in isolated forms and solution (SI). ^{31}P NMR experiments revealed that in their isolated forms, **L1** and **L2** are stable to atmospheric air and moisture for the duration of the study (6 days)**.** Exposed to air and moisture whilst in solution, they are only stable for 12 h, with increased oxidation over 24 h (particularly **L2**), and full oxidation in 48 h. Additional stability tests included base and elevated temperature exposure, to which they were relatively stable (SI). Trace amounts of other phosphine oxides were noticeable on the NMR spectra suggesting some decomposition or possibly the oxide of 1,1,2,2-tetraphenyldiphosphine, the insidious homo-coupling product of diphenylchlorophosphine[35–37] which would have escaped recrystallization after the ligand synthesis. This we are currently investigating further.

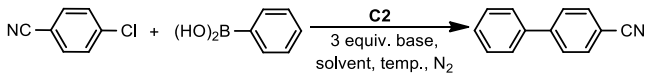
Table 3: Selected bond lengths and angles of complexes **C1** and **C2**.[a]

Complex	Bond	Length	Bond	Angle
C1	Pd-Cl1	2.2774(15)	P1-Pd-Cl1	91.07(6)
	Pd-P1	2.2989(16)	P2-Pd-Cl1	88.23(6)
	Pd-P2	2.2907(15)	Cl2-Pd-P1	89.41(6)
	Pd-Cl2	2.2737(15)	Cl2-Pd-P2	91.25(6)
	P1-N1	1.640(4)	N1-P1-Pd	117.73(15)
C2	Pd-Cl1	2.3084(7)	Cl1^1-Pd-P1^1	93.92(2)
	Pd-Cl1^1	2.3084(7)	Cl1^1-Pd- P1	86.08(2)
	Pd-P1	2.3533(6)	Cl1-Pd- P1^1	86.08(2)
	Pd-P1^1	2.3533(6)	Cl1-Pd- P1	93.92(2)
	P1-N1	1.690(2)	N1-P1-Pd	113.83(8)

[a]The complete list of bond lengths and angles can be retrieved in the **SI**. Both complexes share similar bond lengths and angles around the Pd center, i.e., Pd-Cl (2.2774 and 2.3089 Å); Pd-P (2.2989 and 2.3533 Å); and Pd-P-N (113.09 and 113.83°), for **C1** and **C2**, respectively. These are comparable to those previously reported by Jin[38] (Pd-Cl = 2.2772 Å) and Jambor[39] (Pd-P = 2.3124 Å and P-N = 1.6901 Å).

Though not ideal substrates to model Suzuki-Miyaura coupling, we could easily access 4-chlorobenzonitrile and phenylboronic acid and used them to screen suitable reaction conditions using **C2** (Table 4). Optimal conditions were found to be 3 mol % **C2** and 3 equiv. of K_3PO_4 in toluene at 100 °C for 5 h, affording the biaryl product in 82% yield (entry 10, Table 4). Yields with K_2CO_3[40] (entries 1 – 4) and Cs_2CO_3[41] (entry 5) were poor (Table 4). Similarly, the use of conventional solvents THF, DMF, and CH_2Cl_2 gave poor yields (Table S3). With optimum conditions determined[42–44], the catalytic efficacies of **C1** and **C2** were compared using electronically

Table 4: Optimization of Suzuki-Miyaura cross-coupling using **C2**.[a]



Entry	Solvent	Base	Catalyst mol %	Temperature (°C)	Time (h)	GC yield (%)
1	THF	K_2CO_3	1	reflux	24	9
2	DCM	K_2CO_3	1	reflux	24	11
3	DMF	K_2CO_3	1	140	24	34
4	Toluene	K_2CO_3	1	100	24	43
5	Toluene	Cs_2CO_3	1	100	24	54
6	Toluene	K_3PO_4	1	100	24	59
7	Toluene	K_3PO_4	2	100	24	70
8	Toluene	K_3PO_4	3	100	24	83
9	Toluene	K_3PO_4	3	100	12	81
10	**Toluene**	**K_3PO_4**	**3**	**100**	**5**	**82**
11	Toluene	K_3PO_4	3	100	1	51

[a]Reaction conditions: ArCl, 1.2 equiv. $PhB(OH)_2$, 3 equiv. base, 1 – 3 mol % **C2**, solvent, 1 – 24 h, N_2. GC yield (%) as an average of two experiments. Full optimization table given in the SI.

diverse aryl bromides and chlorides (entries 1 – 6. **Table 5**). Catalytic efficacies of **C1** and **C2** were comparable in the parallel screening of aryl bromides (entries 1 – 3, **Table 5**), with average product yields of 76 and 78%, respectively. Differences were observed in couplings of aryl chlorides (entries 4 – 6), with **C2** marginally superior to **C1**, giving average yields of 74 and 68%, respectively. The efficiency of **C2** prompted its benchmarking against SPhos and PPh_3 (entry 7 – 14, Table 5). Prior to this, a comparison between *in-situ* and pre-formed complexes of **L2**, permitted the subsequent examination of **L2** as a free ligand (entries 6 – 7, Table 5). **L2** and SPhos formed effective catalysts for cross-coupling of activated aryl chlorides (7 – 11), with average yields of 83 and 89%, respectively.

Table 5: Suzuki-Miyaura cross-coupling of aryl bromides and chlorides using **C1**, **C2**, PPh_3 and SPhos.[a]

$Ar^1X + Ar^2B(OH)_2$ — 3 mol % catalyst; 3 equiv. K_3PO_4, toluene; 100 °C, 5 h, N_2 → $Ar^1—Ar^2$

Entry	Ar^1X	$Ar^2B(OH)_2$	Catalyst	%: GC/ (*isolated*)
1	4-$MeOC_6H_4Br$	$PhB(OH)_2$	**C1**	71 (*68*)
			C2	73 (*69*)
2	4-CNC_6H_4Br	$PhB(OH)_2$	**C1**	81 (*79*)
			C2	84 (*81*)
3	C_6H_5Br	4-$MeC_6H_4B(OH)_2$	**C1**	75 (*70*)
			C2	78 (*73*)
4	C_6H_5Cl	4-$MeC_6H_4B(OH)_2$	**C1**	56 (*51*)
			C2	64 (*60*)
5	4-MeC_6H_4Cl	$PhB(OH)_2$	**C1**	53 (*50*)
			C2	61 (*58*)
6	4-CNC_6H_4Cl	$PhB(OH)_2$	**C1**	69 (*65*)
			C2	82 (*79*)
7	4-CNC_6H_4Cl	$PhB(OH)_2$	**L2/Pd**	84 (*80*)
			PPh_3/Pd	50
			SPhos/Pd	90
8	4-CNC_6H_4Cl	4-$MeC_6H_4B(OH)_2$	**L2/Pd**	86 (*82*)
			PPh_3/Pd	56
			SPhos/Pd	91
9	4-$CF_3C_6H_4Cl$	$PhB(OH)_2$	**L2/Pd**	77 (*71*)
			PPh_3/Pd	42
			SPhos/Pd	89
10	4-$CF_3C_6H_4Cl$	2,5-$Me_2C_6H_3B(OH)_2$	**L2/Pd**	79 (*73*)
			PPh_3/Pd	44
			SPhos/Pd	81
11	4-$NO_2C_6H_4Cl$	$PhB(OH)_2$	**L2/Pd**	88 (*82*)
			PPh_3/Pd	71
			SPhos/Pd	95
12[b]	4-MeC_6H_4Cl	$PhB(OH)_2$	**L2/Pd**	80 (*71*)
			PPh_3/Pd	0
			SPhos/Pd	90
13[b]	1,2-$Me_2C_6H_4Cl$	$PhB(OH)_2$	**L2/Pd**	59 (*51*)
			PPh_3/Pd	0
			SPhos/Pd	79
14[b]	4-$MeOC_6H_4Cl$	$PhB(OH)_2$	**L2/Pd**	69 (*60*)
			PPh_3/Pd	0
			SPhos/Pd	88

[a]Reaction conditions: ArX, 1.2 equiv. $ArB(OH)_2$, 3 equiv. K_3PO_4, 3 mol % **catalyst**, Toluene, 5 h, N_2. GC yield (%) as average of two experiments, (*isolated* yields). [b]Reaction ran for 24 h.

For deactivated chlorides (entries 12-14), SPhos gave consistently high yields whilst yields with **L2** were moderate. PPh_3 gave no product at all, which is consistent with reports by Beller[11] and Fu[8]. The superiority of SPhos, able to provide a catalyst system that effects Suzuki-Miyaura coupling of even sterically demanding aryl chlorides and boronic acids at room temperature using 0.05-0.1% Pd, has been ascribed to the hemilabile methoxy group(s) on a phenyl ring bearing these.[45] Besides the Buchwald ligands,[9,43,46] other highly efficient catalyst systems for coupling of deactivated aryl chlorides include those reported by Beller[11], Fu[8] and Hartwig[10]. The group of Frech showed that palladium nanoparticles are the catalytically active form when using dichloro-*bis*(aminophosphine) complexes.[27] In our case, adding excess elemental mercury at the beginning of the reaction (4-chlorotoluene and phenylboronic acid) did not retard the reaction at all; the same result as in Table 5, entry 5, was obtained, indicative of the homogeneity of the reaction.

A study to quantify the ligand electronic and steric descriptors was also performed (Table 6). The carbonyl strecthing frequencies (ν_{CO}) were accessed from computational models of *trans*-$RhCOCl(L)_2$. This study revealed the strong donor character of the described P-N ligands compared to PPh_3, due to the strongly basic amine groups, as previously demonstrated by Ziółkowski[31] and Woollins[32]. However, SPhos, comprising two Cy groups, proved to be the best donor (Table 6).

Computational calculations of the overall electronic density (ρ) donated by the *P*-ligands to the Rh-center further confirmed the observed ν_{CO} (cm^{-1}) trend (Table 6). Thus, the poor catalytic performance of PPh_3 based catalysts is ascribed to the overall poor donor character of PPh_3, in contrast to the more electron rich SPhos and aminophosphines **L1** and **L2**. The inherent role of electron rich ligands towards facile oxidative addition is well known.[43,47]

Table 6: Parameterization of ligands.

Entry	Ligand	ν_{CO} (cm^{-1})[a]	Electron density, ρ (a.u.)[a]	% V_{Bur}[b]
1	PPh_3	1952.69[c]	0.0008	29.2
2	**L1**	1947.41	0.0012	30.0
3	**L2**	1946.29	0.0015	31.5
4	SPhos	1937.83	0.0030	32.7

[a]Determined from WB97XD/LANL2DZ *trans*-$RhCOCl(L)_2$ at DFT. [b]Determined from crystallographic data of $PdCl_2L_2$ (Table S1 and S4). [c]With a 0.66% deviation, which is within 0.05 and 3.71% deviation reported by Kohls and Stein[48], at BP86/def2-TZVP and B3LYP/def2-TZVP, respevtively.

Steric effects, also important for efficient catalytic activity, were quantified from the percent buried volume (% V_{Bur}) of $PdCl_2L_2$ complexes (Table 6). Clavier and Nolan[49] found the % V_{Bur} of SPhos and PPh_3 to be 29.3- and 32.7%, and ours are almost the same (29.2 and 32.7%, Table 6). Steric bulk is believed to facilitate reductive elimination[43,47] which also explains the catalytic outcomes of the more hindered **L1**, **L2**, and SPhos, contrary to PPh_3.

In conclusion, Pd(II) monoaminophosphine complexes assembled from inexpensive and easily prepared air and moisture stable ligands, formed promising catalyst systems for Suzuki-Miyaura coupling of aryl bromides and chlorides. Through ligand parameterization, we found sufficient steric bulk and electronic density, $\nu_{CO} \leq 1947.41$ cm^{-1} and % $V_{Bur} \geq 30.0$ % (**L1** and **L2**), to yield active catalysts for the described substrate scope. Whilst

SPhos and other literature reported ligands are, on the basis of our small data set far superior, we are currently exploring the utility of the aminophosphine ligands [$PAr_2(NR_2$, with R = alkyl or aryl)] in terms of substrate scope and optimal catalyst loading and reaction conditions in Suzuki-Miyaura and other cross coupling reactions. The results will be disclosed in due course.

Acknowledgements

This work was funded through the NRF's Thuthuka Program (EMM, Grant no 107406: 2017-2019). Jairus Lamola is grateful for a scholarship by SASOL. We thank Mr Mutsinyalo Nwamadi (SPECTRUM) for assistance with NMR analyses. The authors acknowledge the Centre for High Performance Computing (CHPC), South Africa for providing computational resources to this research project.

Keywords: aminophosphines • biaryl • cross-coupling • ligand parameters • Suzuki-Miyaura

[1] T. J. Colacot, *New Trends in Cross-Coupling Theory and Applications.*, The Royal Society Of Chemistry, Cambridge, **2015**.

[2] A. Biffis, P. Centomo, A. Del Zotto, M. Zecca, *Chem. Rev.* **2018**, *118*, 2249–2295.

[3] C. Torborg, M. Beller, *Adv. Synth. Catal.* **2009**, *351*, 3027–3043.

[4] P. Devendar, R. Qu, W. Kang, B. He, G. Yang, *J. Agric. Food Chem.* **2018**, *66*, 8914–8934.

[5] A. Taheri Kal Koshvandi, M. M. Heravi, T. Momeni, *Appl. Organomet. Chem.* **2018**, *32*, 1–59.

[6] S. Xu, E. H. Kim, A. Wei, E. Negishi, *Sci. Technol. Adv. Mater.* **2014**, *15*, 1–23.

[7] B. J. Reizman, Y. M. Wang, S. L. Buchwald, K. F. Jensen, *React. Chem. Eng.* **2016**, *1*, 658–666.

[8] A. F. Littke, G. C. Fu, *Angew. Chem. Int. Ed.* **1999**, *37*, 3387–3388.

[9] D. W. Old, J. P. Wolfe, S. L. Buchwald, *J. Am. Chem. Soc.* **1998**, *120*, 9722–9723.

[10] N. Kataoka, Q. Shelby, J. P. Stambuli, J. F. Hartwig, *J. Org. Chem.* **2002**, *8107*, 5553–5566.

[11] A. Zapf, A. Ehrentraut, M. Beller, *Angew. Chem. Int. Ed.* **2000**, *39*, 4153–4155.

[12] K. H. Chung, C. M. So, S. M. Wong, C. H. Luk, Z. Zhou, C. P. Lau, F. Y. Kwong, *Chem. Commun.* **2012**, *48*, 1967–1969.

[13] J. V Kingston, J. G. Verkade, *J. Org. Chem.* **2007**, *72*, 2816–2822.

[14] G. D. Roiban, G. Mehler, M. T. Reetz, *Eur. J. Org. Chem.* **2014**, 2070–2076.

[15] C. A. Wheaton, J. P. J. Bow, M. Stradiotto, *Organometallics* **2013**, *32*, 6148–6161.

[16] Y. Chang, F. Hong, *Tetrahedron* **2013**, *69*, 2327–2335.

[17] C. Kayan, N. Biricik, M. Aydemir, *Transit. Met. Chem.* **2011**, *36*, 513–520.

[18] M. Aydemir, A. Baysal, E. Sahin, B. Gumgum, S. Ozkar, *Inorganica Chim. Acta* **2011**, *378*, 10–18.

[19] M. L. Clarke, D. J. Cole-Hamilton, J. D. Woollins, *J. Chem. Soc. Dalton Trans.* **2001**, 2721–2723.

[20] Z. Liu, J. F. Hartwig, *J. Am. Chem. Soc.* **2008**, *23*, 1–7.

[21] L. M. Broomfield, Y. Wu, E. Martin, A. Shafir, *Adv. Synth. Catal.* **2015**, *357*, 3538–3548.

[22] R. Ghosh, A. Sarkar, *J. Org. Chem.* **2011**, *76*, 8508–8512.

[23] P. Rotering, L. F. B. Wilm, J. A. Werra, F. Dielmann, *Chem. Eur. J.* **2020**, *26*, 406–411.

[24] M. A. Wünsche, P. Mehlmann, T. Witteler, F. Buß, P. Rathmann, F. Dielmann, *Angew. Chem. Int. Ed.* **2015**, *54*, 11857–11860.

[25] A. P. Mehlmann, C. Mück-lichtenfeld, T. Y. Tristan, F. Dielmann, P. Mehlmann, C. Mück-lichtenfeld, T. T. Y. Tan, F. Dielmann, *Chem. Eur. J.* **2016**.

[26] J. L. Bolliger, O. Blacque, C. M. Frech, *Angew. Chem. Int. Ed.* **2007**, *46*, 6514–6517.

[27] M. Oberholzer, C. M. Frech, *Green Chem.* **2013**, *15*, 1678–1686.

[28] J. Cheng, F. Wang, J. H. Xu, Y. Pan, Z. Zhang, *Tetrahedron Lett.* **2003**, *44*, 7095–7098.

[29] P. W. Dyer, J. Fawcett, M. J. Hanton, R. D. W. Kemmitt, R. Padda, N. Singh, *J. Chem. Soc., Dalton Trans.* **2003**, 104–113.

[30] J. Gopalakrishnan, *Appl. Organomet. Chem.* **2009**, *23*, 291–318.

[31] A. M. Trzeciak, T. Głowiak, J. J. Ziółkowski, *J. Chem. Soc., Dalton. Trans.* **1997**, 1831–1837.

[32] M. L. Clarke, G. L. Holliday, A. M. Z. Slawin, J. D. Woollins, *J. Chem. Soc., Dalton Trans.* **2002**, 1093–1103.

[33] A. D. Burrows, M. F. Mahon, M. Varrone, *J. Chem. Soc., Dalton Trans.* **2004**, 3321–3330.

[34] K. G. Moloy, J. L. Petersen, W. Virginia, W. V. Unigersity, *J. Am. Chem. Soc.* **1995**, *117*, 7696–7710.

[35] L. Wu, V. T. Annibale, H. Jiao, A. Brookfield, D. Collison, I. Manners, *Nat. Commun.* **2019**, *10*, 1–10.

[36] Y. Sato, S. ichi Kawaguchi, A. Nomoto, A. Ogawa, *Chem. Eur. J.* **2019**, *25*, 2295–2302.

[37] Y. Yamamoto, R. Tanaka, M. Ota, M. Nishimura, C. C. Tran, S. I. Kawaguchi, S. Kodama, A. Nomoto, A. Ogawa, *J. Org. Chem.* **2020**, *85*, 14708–14719.

[38] Y. Lai, Z. Zong, Y. Tang, W. Mo, N. Sun, B. Hu, Z. Shen, L. Jin, W. H. Sun, X. Hu, *Beilstein J. Org. Chem.* **2017**, *13*, 213–221.

[39] J. Jansa, T. Řezníček, L. Dostál, Z. Růžičková, F. Bureš, R. Jambor, *Appl. Organomet. Chem.* **2016**, *30*, 1036–1042.

[40] S. Vuoti, J. Autio, M. Laitila, M. Haukka, J. Pursiainen, *Eur. J. Inorg. Chem.* **2008**, *1*, 397–407.

[41] R. Rabie, M. M. Hammouda, K. M. Elattar, *Res. Chem. Intermed.* **2017**, *43*, 1979–2015.

[42] S. Kotha, K. Lahiri, D. Kashinath, *Tetrahedron* **2002**, *58*, 9633–9695.

[43] R. Martin, S. L. Buchwald, *Acc. Chem. Res.* **2008**, *41*, 1461–1473.

[44] J. El-maiss, T. Mohy, E. Dine, C. Lu, I. Karam, A. Kanj, K. Polychronopoulou, J. Shaya, *Catalysts* **2020**, *10*, 296.

[45] K. L. Billingsley, K. W. Anderson, S. L. Buchwald, *Angew. Chem. Int. Ed.* **2006**, *45*, 3484–3488.

[46] S. D. Walker, T. E. Barder, J. R. Martinelli, S. L. Buchwald,

Angew. Chem. Int. Ed. **2004**, *43*, 1871–1876.

[47] M. L. Clarke, J. J. R. Frew, *Organomet. Chem.* **2009**, *44*, 19–46, and references therein.

[48] E. Kohls, M. Stein, *Contrib. Sect. Nat. Math. Biotech. Sci.* **2017**, *38*, 43–56.

[49] H. Clavier, S. P. Nolan, *Chem. Commun.* **2010**, *46*, 841–861.

…

TOC

New mono-(*N*,*N*-dialkylamino)phosphine based palladium (II) complexes were successfully prepared and their crystal structures determined. The complexes showed moderate to high catalytic performance in Suzuki-Miyaura cross-coupling of aryl-bromides and chlorides which could be ascribed to their structural features.