Palladium(II) Pyrazolin-4-ylidenes: Remote N-Heterocyclic Carbene Complexes and Their Catalytic Application in Aqueous Suzuki−Miyaura Coupling

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Two monocationic complexes of pyrazole-derived remote carbene ligands of the type *trans*-$[PdI(rNHC)(PPh_3)_2]^+OTf^-$ {rNHC = 2-ethyl-3,5-dimethyl-1-phenylpyrazolin-4-ylidene (**6a**), 1-ethyl-2,3,5-trimethylpyrazolin-4-ylidene (**6b**)} were prepared by oxidative addition of 4-iodo-1,2,3,5-tetrasubstituted pyrazolium triflate salts to $[Pd_2(dba)_3]/PPh_3$ in good yields. Both compounds were fully characterized by multinuclei NMR spectroscopies, electrospray ionization mass spectrometry, and X-ray diffraction analysis. A comparative study on the aqueous Suzuki−Miyaura catalytic activities of these cationic complexes with their previously reported neutral counterparts reveals the superiority of the former.

Introduction

N-Heterocyclic carbenes (NHCs) have become "state of the art" ligands in the area of organometallic chemistry and transition-metal-mediated catalysis.[1] In addition to the classical C2-bound systems ("normal" carbenes, type **A**; Figure 1), NHC chemistry has recently been extended to complexes of "abnormal" carbenes, which contain an unusual C4/C5 coordination (type **B**).[2] The latter contain a carbenoid center that is adjacent to only one N heteroatom. More recently, Raubenheimer and co-workers reported complexes bearing NHC ligands with a 6-membered ring, in which the carbenoid C is distant from the heteroatom (type **C**). Computational studies on these remote NHCs (rNHCs) derived from pyridine or quinoline suggested an even stronger σ-donor ability compared to their well-known normal NHC counterparts, which may be beneficial for certain types of catalytic reactions.[3] Indeed, preliminary catalytic studies have shown that palladium(II) complexes with rNHC ligands give rise to more active catalysts for some C−C coupling reactions than precatalysts derived from standard NHCs.[3a] Despite these promising properties, rNHCs have not attracted the same degree of attention as common NHCs yet. As a contribution to this little-explored field, we have recently communicated the synthesis of the first neutral pyrazole-derived rNHC (type **D**) complexes of palladium(II).[4] Herein, we report on the preparation, properties, and structural characterizations of their monocationic counterparts. An initial study comparing the catalytic activities of neutral and ionic palladium(II) pyrazolin-4-ylidene complexes in the aqueous Suzuki−Miyaura coupling reaction is included as well.

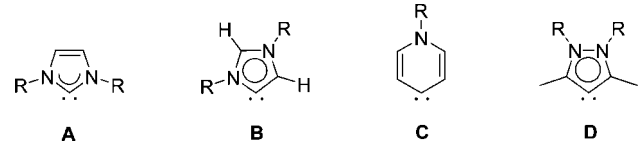

Figure 1. Different types of NHCs: "normal" NHC (**A**); "abnormal" NHC (**B**); rNHCs (**C** and **D**).

Results and Discussion

Palladium(II) Pyrazolin-4-ylidene Complexes. The synthesis of suitable azolium precursors and the corresponding neutral palladium(II) pyrazolin-4-ylidene complexes was communicated earlier.[4] The ligand precursors **3a/b** were prepared in a short reaction sequence and transformed into the neutral $Pd^{II}(rNHC)$ complexes **4a/b** by oxidative addition to $[Pd_2(dba)_3]/PPh_3$ (dba = dibenzylideneacetone), as outlined in Scheme 1. It is important to note that the in situ deprotonation of 1,2,3,5-tetrasubstituted pyrazolium salts with basic metal precursors such as $Pd(OAc)_2$ or Ag_2O was unsuccessful, probably because of the low acidity of the pyrazolium C4 proton. Furthermore, it is worth mentioning that premixing of $[Pd_2(dba)_3]$ with PPh_3 before the addition of the ligand precursors is important for obtaining good yields of the complexes. For instance, complex **4b** was obtained in a yield of only 45% when **3b**, $[Pd_2(dba)_3]$, and PPh_3 were added in a fast sequence.[4] However, the yield could be increased to 60% when the ligand precursor **3b** was added only after having mixed $[Pd_2(dba)_3]$ and PPh_3 in CH_2Cl_2 at ambient temperature for 10 min.

In an attempt to extend our research on pyrazolin-4-ylidenes, we have also synthesized the monocationic $Pd^{II}(rNHC)$ complexes **6a/b** according to Scheme 2. The 4-iodopyrazolium triflate salt precursors **5a/b** were easily obtained in quantitative yields by reacting **3a/b** with silver triflate. In a preparative manner similar to that of **4a/b**, treatment of **5a/b** with premixed $[Pd_2(dba)_3]$ and PPh_3 in CH_2Cl_2 under reflux conditions led to the formation of the monocationic bis(phosphine) complexes **6a/b** in good yields of 80 and 73%, respectively. Complexes

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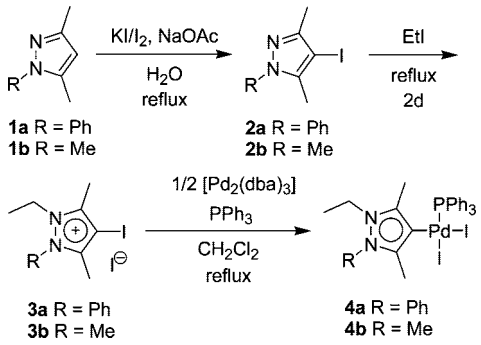
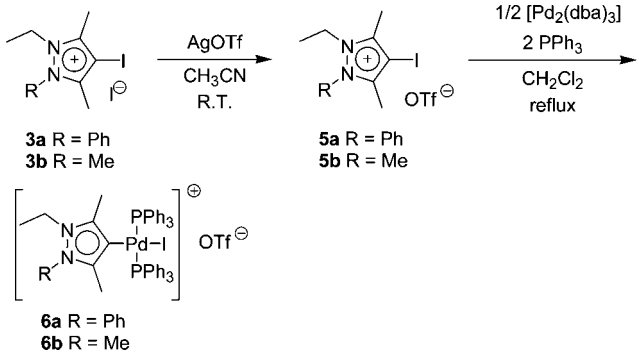
Scheme 1. Synthetic Pathway to Neutral Pd^{II}(rNHC) Complexes



Scheme 2. Synthesis of the Ionic Pd^{II}(rNHC) Complexes



6a/b are stable in air and moisture. They are insoluble in nonpolar solvents such as hexane, diethyl ether, and toluene but generally more soluble than the neutral complexes **4a/b** in most polar solvents such as $CHCl_3$, CH_2Cl_2, CH_3CN, and dimethyl sulfoxide (DMSO). The improved solubilities of **6a/b** allow for an identification of their carbene signals by ^{13}C NMR spectroscopy (vide infra).

The formation of complexes **6a/b** was confirmed by electrospray ionization mass spectrometry (ESIMS), which shows base peaks at *m/z* 957 (**6a**) and *m/z* 895 (**6b**) in their positive-mode spectra, corresponding to the cationic complex $[M-CF_3SO_3]^+$. In the ^{31}P NMR spectra, the phosphine donors in both complexes give rise to very similar chemical shifts with values of 23.0 (**6a**) and 22.8 ppm (**6b**). The fact that only one ^{31}P NMR signal was observed for each complex indicates two equivalent phosphine ligands and therefore a trans configuration of the complex. The triflate ^{19}F NMR resonances in **6a/b** found in a narrow range of −2.2 to −2.3 ppm remain largely unchanged compared to those of the ligand precursors **5a/b**, which is in line with a noncoordinating triflate counteranion. In general, the ^1H NMR resonances of both complexes are shifted upfield with respect to the corresponding signals of their ligand precursors. More importantly, the ^{13}C NMR signals for the carbenoid C atoms in complexes **6a/b** are observed at 128.2 and 127.8 ppm, respectively. Both signals appear as triplets because of heteronuclear coupling with constants of $^2J(C,P) = 7.3$ Hz, again corroborating the trans arrangement of the two phosphine ligands. Although these carbenoid resonances are more upfield than the values commonly observed for analogous palladium(II) complexes of other rNHCs[5] or standard NHCs,[3a,6] they are still significantly downfield-shifted by $\Delta\delta = 60.4$ (**6a**) and 61.0 ppm (**6b**) compared to the C4 carbon resonances in their ligand precursors.

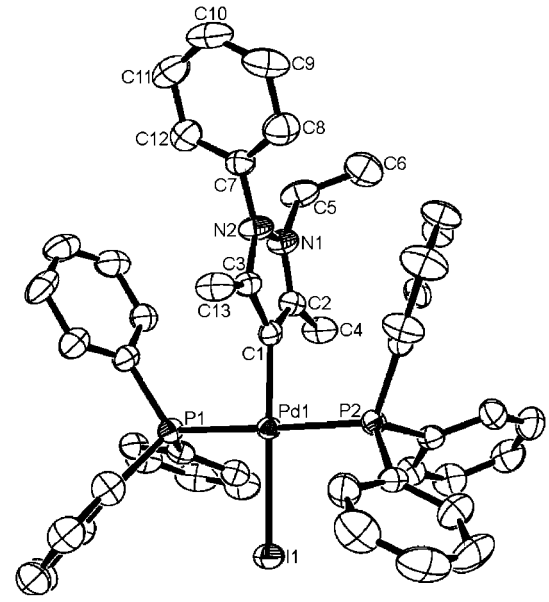


Figure 2. Molecular structure of the complex cation of **6a**·CH_2Cl_2·H_2O showing 50% probability ellipsoids. The triflate counterion, solvent molecules, and H atoms are omitted for clarity.

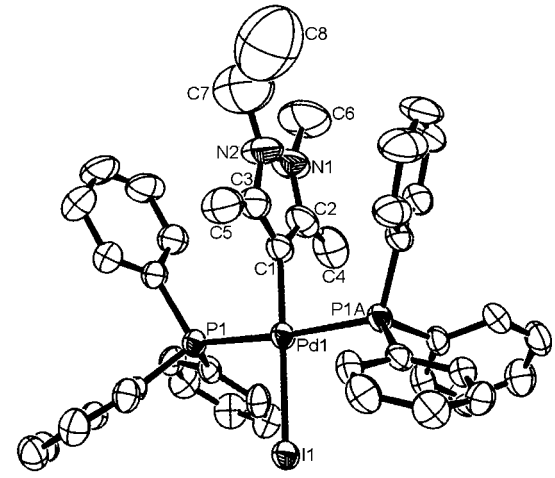


Figure 3. Molecular structure of the complex cation of **6b**·CH_2Cl_2 showing 50% probability ellipsoids. The triflate counterion, solvent molecules, H atoms, and one of the disordered C8 atoms are omitted for clarity.

The identities of complexes **6a/b** were further confirmed by X-ray diffraction analyses on single crystals obtained from concentrated CH_2Cl_2/Et_2O solutions. The molecular structures of the complex cations are depicted in Figures 2 and 3, selected bond parameters are summarized in Table 1, and crystallographic data are listed in Table 2. Both complexes crystallized as solvates **6a**·CH_2Cl_2·H_2O and **6b**·CH_2Cl_2, respectively. As found in solution NMR studies, both complexes exhibit the expected trans configuration of the phosphine ligands in an essentially square-planar geometry around the palladium center. The carbene ring plane of the rNHC ligand in each complex is situated almost perpendicularly to the $PdICP_2$ coordination plane with a torsion angle of 89.91° (**6a**) or 90.00° (**6b**) to relieve steric congestion. These angles are bigger than those in the less

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Table 1. Selected Bond Lengths [Å] and Angles [deg] for Complexes 6a/b

	6a · CH_2Cl_2 · H_2O	**6b** · CH_2Cl_2
Pd1−C1	2.020(5)	2.004(9)
Pd1−I1	2.6727(5)	2.6685(9)
Pd1−P1	2.3270(13)	2.3375(15)
Pd1−P2	2.3299(13)	-
C1−C2	1.391(7)	1.422(14)
C1−C3	1.396(6)	1.374(15)
N1−C2	1.351(6)	1.340(15)
N2−C3	1.357(6)	1.379(15)
N1−N2	1.369(6)	1.351(15)
C1−Pd1−P1	88.72(13)	86.84(5)
C1−Pd1−P2	89.37(13)	
P1−Pd1−I1	90.46(3)	93.20(4)
P2−Pd1−I1	91.27(3)	
C2−C1−C3	105.9(4)	107.4(10)
coordination plane/ carbene ring dihedral angle	89.91	90.00

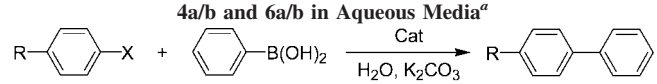
Table 2. Selected X-ray Crystallographic Data for Complexes 6a · CH_2Cl_2 · H_2O and 6b · CH_2Cl_2

	6a · CH_2Cl_2 · H_2O	**6b** · CH_2Cl_2
formula	$C_{51}H_{50}Cl_2F_3IN_2O_4P_2PdS$	$C_{46}H_{46}Cl_2F_3IN_2O_3P_2PdS$
fw	1210.13	1130.05
color, habit	yellow, thin plate	colorless, plate
cryst size [mm]	0.24 × 0.14 × 0.04	0.26 × 0.10 × 0.06
T [K]	293(2)	223(2)
cryst syst	monoclinic	orthorhombic
space group	*P*2(1)/*c*	*Pnma*
a [Å]	12.0615(5)	10.0914(5)
b [Å]	39.2897(18)	22.4737(11)
c [Å]	11.1728(5)	20.9892(11)
α [deg]	90	90
β [deg]	100.8010(10)	90
γ [deg]	90	90
V [Å^3]	5200.9(4)	4760.2(4)
Z	4	4
D_c [g cm^{-3}]	1.545	1.577
radiation used	Mo Kα	Mo Kα
μ [mm^{-1}]	1.211	1.315
θ range [deg]	1.72–27.50	1.81–27.50
unique data	37279	32206
max, min transmn	0.9532, 0.7599	0.9253, 0.7262
final *R* indices [$I > 2\sigma(I)$]	R1 = 0.0607, wR2 = 0.1231	R1 = 0.0705, wR2 = 0.1551
R indices (all data)	R1 = 0.0962, wR2 = 0.1356	R1 = 0.1000, wR2 = 0.1674
GOF on F^2	1.038	1.079
peak/hole [e Å^{-3}]	+1.558/−0.685	+1.245/−0.793

crowded complexes **4a/b** (89.40° and 85.98°, respectively) for obvious reasons. The Pd−P bonds amounting to 2.3270(13) and 2.3299(13) Å in **6a** and 2.3375(15) Å in **6b** are comparable to those in analogous complexes containing other rNHCs.[5] Furthermore, both Pd−$C_{carbene}$ bond lengths of 2.020(5) Å (**6a**) and 2.004(9) Å (**6b**) fall within the normal range, with the former slightly longer than the latter. The same trend was also observed in the comparison of **4a** [2.012(8) Å] with **4b** [1.996(7) Å]. These observations suggest that 2-ethyl-3,5-dimethyl-1-phenylpyrazolin-4-ylidene in **6a** and **4a** is a weaker ligand than 1-ethyl-2,3,5-trimethylpyrazolin-4 **-**ylidene in **6b** and **4b** because of the less electron-donating *N*-phenyl substituent compared to the *N*-methyl substituent as a consequence of different inductive effects. However, the existence of such substituent effects in pyrazole-based rNHCs remains to be investigated in more detail.

Catalysis. All pyrazolin-4-ylidene complexes discussed here were subjected to Suzuki−Miyaura coupling reactions to test their catalytic activities. The coupling of simple aryl bromides and chlorides with phenylboronic acid in water under aerobic conditions with 1 mol % catalyst loading was chosen as a standard test reaction, and the results are presented in Table 3. We have chosen water as the reaction media because it is economically and environmentally benign. In addition, it has been shown that water can be a good solvent for the Suzuki−Miyaura coupling reaction.[7]

Table 3. Suzuki−Miyaura Cross-coupling Reactions Catalyzed by 4a/b and 6a/b in Aqueous Media[a]



X = Br, Cl
R = $COCH_3$, CHO, OCH_3

entry	catalyst	aryl halide	*t* [h]	*T* [°C]	yield [%][b]
1	**4a**	4-bromobenzaldehyde	19	RT	80
2	**4b**	4-bromobenzaldehyde	19	RT	82
3	**6a**	4-bromobenzaldehyde	19	RT	93
4	**6b**	4-bromobenzaldehyde	19	RT	92
5	**4a**	4-bromoacetophenone	19	RT	80
6	**4b**	4-bromoacetophenone	19	RT	67
7	**6a**	4-bromoacetophenone	19	RT	95
8	**6b**	4-bromoacetophenone	19	RT	91
9	**4a**	4-bromoanisole	21	80	82[c]
10	**4b**	4-bromoanisole	21	80	90[c]
11	**6a**	4-bromoanisole	21	80	96[c]
12	**6b**	4-bromoanisole	21	80	92[c]
13	**4a**	4-chlorobenzaldehyde	21	80	20[c]
14	**4b**	4-chlorobenzaldehyde	21	80	14[c]
15	**6a**	4-chlorobenzaldehyde	21	80	37[c]
16	**6b**	4-chlorobenzaldehyde	21	80	39[c]

[a] Reaction conditions: 1 mmol of aryl halide; 1.2 mmol of phenylboronic acid; 3 mL of water; 1.5 equiv of K_2CO_3; 1 mol % of catalyst. [b] Yields were determined by ^{1}H NMR spectroscopy for an average of two runs. [c] With the addition of 1.5 equiv of [N(*n*-C_4H_9)$_4$]Br.

From entries 1–8, it can be seen that all four complexes give rise to catalysts that are able to couple the activated substrates 4-bromobenzaldehyde and 4-bromoacetophenone at ambient temperature in moderate to very good yields. As for the nonactivated substrate 4-bromoanisole, good conversions could only be obtained at elevated temperatures and with the addition of [N(*n*-C_4H_9)$_4$]Br (TBAB) (entries 9–12). However, even under such conditions, the coupling of the more difficult substrate 4-chlorobenzaldehyde afforded only low yields ranging from 14 to 39% (entries 13–16). Overall, reactions using the ionic precatalysts **6a** and **6b** generally show remarkably better conversions than those of their corresponding neutral counterparts **4a** and **4b**. This finding is consistent with the result reported by Raubenheimer and co-workers, where the superiority of the simple cationic NHC complex *trans*-[PdCl(Me_2-imy)(PPh_3)$_2$]$^+$ over its corresponding neutral complex *trans*-[PdI_2(Me_2-imy)(PPh_3)] was observed in both Mizoroki−Heck and Suzuki−Miyaura reactions.[3a] The catalyst derived from complex **6a** exhibits the best catalytic activity in the reactions with aryl bromides. However, in the coupling of 4-chlorobenzaldehyde, **6b** performs slightly better.

Conclusion

In conclusion, we have presented a straightforward synthetic pathway to monocationic palladium(II) complexes containing new pyrazole-derived rNHC ligands as an extension of NHC chemistry. A preliminary study on rNHC-assisted palladium-

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catalyzed aqueous Suzuki−Miyaura coupling showed that the novel cationic complexes give rise to more active catalysts than their corresponding neutral counterparts. Research in our laboratories is underway to extend the synthetic methodology to other transition metals as well as to widen the scope of rNHC complexes in catalysis.

Experimental Section

General Considerations. Unless otherwise noted, all operations were performed without taking precautions to exclude air and moisture. All solvents and chemicals were used as received without any further treatment if not noted otherwise. 1,3,5-Trimethylpyrazole was purchased from Sigma-Aldrich. Tris(dibenzylideneacetone)dipalladium(0) was received from Alfa Aesar. ^{1}H, ^{13}C, ^{31}P, and ^{19}F NMR spectra were recorded on Bruker ACF 300 and AMX 500 spectrometers, and the chemical shifts (δ) were internally referenced to the residual solvent signals relative to tetramethylsilane (^{1}H and ^{13}C NMR) or externally to 85% H_3PO_4 (^{31}P NMR) and CF_3CO_2H (^{19}F NMR). Mass spectra were measured using a Finnigan MAT LCQ (ESI) spectrometer. Elemental analyses were performed on a Perkin-Elmer PE 2400 elemental analyzer at the Department of Chemistry, National University of Singapore.

4-Iodo-3,5-dimethyl-1-phenylpyrazole (2a). An aqueous solution of KI_3 [prepared by dissolving I_2 (1505 mg, 5.95 mmol) and KI (2955 mg, 17.8 mmol) in H_2O (20 mL)] was added dropwise to a solution of 3,5-dimethyl-1-phenylpyrazole (520 mg, 3 mmol) and NaOAc (535 mg, 5.65 mmol) in H_2O (12 mL) under reflux. The resulting dark-brown solution was kept under reflux for another 7 h and then cooled to ambient temperature. Subsequently, an aqueous solution of $Na_2S_2O_3$ was added dropwise until the reaction mixture was decolored. The product was extracted with diethyl ether (4 × 30 mL). The combined organic layer was washed with $NaHCO_3$ (2 × 40 mL) and brine (2 × 40 mL). Drying over $MgSO_4$ followed by removal of the solvent in vacuo afforded the product as a brown oil (827 mg, 2.8 mmol, 93%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.48–7.33 (m, 5 H, Ar−H), 2.32 (s, 3 H, CH_3), 2.30 (s, 3 H, CH_3). ^{13}C{^{1}H} NMR (75.47 MHz, $CDCl_3$): δ 150.8 (s, *C*CH_3), 140.9, 140.0 (s, *C*CH_3/Ar−C), 129.2, 128.0, 124.9 (s, Ar−C), 65.4 (s, CI), 14.2, 13.5 (s, CH_3). Anal. Calcd for $C_{11}H_{11}IN_2$: C, 44.32; H, 3.72; N, 9.40. Found: C, 44.78; H, 3.78; N, 9.45. MS (ESI): *m*/*z* 299 $[M + H]^+$.

4-Iodo-1,3,5-trimethylpyrazole (2b). 2b was prepared analogously to **2a** from 1,3,5-trimethylpyrazole (441 mg, 4 mmol). The product was purified by chromatography on silica using diethyl ether. Yield: 637 mg, 2.7 mmol, 67%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.77 (s, 3 H, NCH_3), 2.24 (s, 3 H, CH_3), 2.19 (s, 3 H, CH_3). ^{13}C{^{1}H} NMR (75.47 MHz, $CDCl_3$): δ 149.0 (s, *C*CH_3), 140.7 (s, *C*CH_3), 62.2 (s, CI), 37.1 (s, NCH_3), 14.0, 12.0 (s, CH_3). Anal. Calcd for $C_6H_9IN_2$: C, 30.53; H, 3.84; N, 11.87. Found: C, 30.89; H, 3.76; N, 11.60. MS (ESI): *m*/*z* 237 $[M + H]^+$.

2-Ethyl-4-iodo-3,5-dimethyl-1-phenylpyrazolium Iodide (3a). 2a (713 mg, 2.4 mmol) was dissolved in iodoethane (2 mL) and heated under reflux for 2 days shielded from light. The reaction mixture was cooled to ambient temperature, and all volatiles were removed under reduced pressure. The residue was washed with diethyl ether and dried in vacuo to give the product as an off-white powder (545 mg, 1.2 mmol, 50%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.81–7.65 (m, 5 H, Ar−H), 4.39 (m, ^{3}J(H,H) = 7.3 Hz, 2 H, CH_2), 2.70 (s, 3 H, CH_3), 2.25 (s, 3 H, CH_3), 1.22 (t, ^{3}J(H,H) = 7.3 Hz, 3 H, CH_2CH_3). ^{13}C{^{1}H} NMR (75.47 MHz, $CDCl_3$): δ 149.9, 149.8 (s, *C*CH_3), 133.6, 131.8, 131.6, 129.8 (s, Ar−C), 72.6 (s, CI), 46.7 (s, CH_2), 15.4 (s, C *C*H_3), 15.0 (s, CH_2CH_3). Anal. Calcd for $C_{13}H_{16}I_2N_2$: C, 34.39; H, 3.55; N, 6.17. Found: C, 34.78; H, 3.45; N, 6.19. MS (ESI): *m*/*z* 327 $[M - I]^+$.

1-Ethyl-4-iodo-2,3,5-trimethylpyrazolium Iodide (3b). 3b was prepared analogously to **3a** from **2b** (283 mg, 1.2 mmol). Yield: 153 mg, 0.39 mmol, 33%. ^{1}H NMR (300 MHz, DMSO-d_6): δ 4.54 (m, ^{3}J(H,H) = 7.2 Hz, 2 H, CH_2), 4.03 (s, 3 H, NCH_3), 2.49 (s, 3 H, CH_3), 2.45 (s, 3 H, CH_3), 1.30 (t, ^{3}J(H,H) = 7.2 Hz, 3 H, CH_2CH_3). ^{13}C{^{1}H} NMR (75.47 MHz, DMSO-d_6): δ 147.9, 146.8 (s, *C*CH_3), 69.3 (s, CI), 43.2 (s, CH_2), 35.1 (s, NCH_3), 13.7, 13.2, 12.8 (s, CH_3). Anal. Calcd for $C_8H_{14}I_2N_2$: C, 24.51; H, 3.60; N, 7.15. Found: C, 24.76; H, 3.80; N, 7.06. MS (ESI): *m*/*z* 265 $[M - I]^+$.

***cis*-(2-Ethyl-3,5-dimethyl-1-phenylpyrazolin-4-ylidene)diiodo (triphenylphosphine)palladium(II)(4a).** Tris(dibenzylideneacetone) dipalladium(0) (229 mg, 0.25 mmol) and triphenylphosphine (131 mg, 0.50 mmol) were dissolved in dry CH_2Cl_2 (30 mL) and stirred at ambient temperature for 10 min under nitrogen. The resulting dark-red solution was transferred to a suspension of **3a** (227 mg, 0.5 mmol) in dry CH_2Cl_2 (20 mL) via cannula. The reaction mixture was heated under reflux for 4 h in an inert nitrogen atmosphere and then cooled to ambient temperature. The resulting mixture was filtered through Celite, and the filtrate was extracted with H_2O (4 × 30 mL). The CH_2Cl_2 layer was dried over $MgSO_4$, and the solvent was removed under reduced pressure. The residue was washed with diethyl ether (2 × 30 mL) and dried in vacuo to give the crude product as a yellow powder. Slow evaporation of a concentrated CH_2Cl_2 solution at ambient temperature afforded the pure product as yellow crystals (290 mg, 0.35 mmol, 70%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.78–6.87 (m, 20 H, Ar−H), 3.78 (m, ^{2}J(H,H) = 15.4 Hz, ^{3}J(H,H) = 7.2 Hz, 1 H, CH_2), 3.63 (m, ^{2}J(H,H) = 15.4 Hz, ^{3}J(H,H) = 7.2 Hz, 1 H, CH_2), 2.36 (s, 3 H, CH_3), 1.99 (s, 3 H, CH_3), 0.95 (m, ^{3}J(H,H) = 7.2 Hz, 3 H, CH_2CH_3). ^{31}P{^{1}H} NMR (121 MHz, CD_2Cl_2): δ 29.4 (s, 1 P, PPh_3). ^{13}C{^{1}H} NMR (75.47 MHz, CD_2Cl_2): δ 147.2 (d, ^{3}J(P,C) = 3.8 Hz, *C*CH_3), 146.9 (d, ^{3}J(P,C) = 2.7 Hz, *C*CH_3), 134.9 (d, $^{2/3}J$(P,C) = 11.0 Hz, Ar−C), 132.9 (d, ^{1}J(P,C) = 48.3 Hz, Ar−C), 132.3, 131.6, 130.5 (s, Ar−C), 130.2 (d, ^{4}J(P,C) = 2.2 Hz, Ar−C), 130.1, 128.7, 127.8 (s, Ar−C), 127.7 (d, $^{2/3}J$(P,C) = 11.0 Hz, Ar−C), 41.9 (s, CH_2), 15.3, 15.1, 14.7(s, CH_3), carbene signal not detected. Anal. Calcd for $C_{31}H_{31}I_2N_2PPd$: C, 45.25; H, 3.80; N, 3.40. Found: C, 45.03; H, 4.28; N, 3.18. MS (ESI): *m*/*z* 695 $[M - I]^+$.

***cis*-(1-Ethyl-2,3,5-trimethylpyrazolin-4-ylidene)diiodo(triphenylphosphine)palladium(II) (4b). 4b** was prepared analogously to **4a** from **3b** (196 mg, 0.5 mmol), tris(dibenzylideneacetone)dipalladium(0) (229 mg, 0.25 mmol), and triphenylphosphine (131 mg, 0.50 mmol). Yield: 228 mg, 0.30 mmol, 60%. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.67–7.31 (m, 15 H, Ar−H), 3.86 (m, ^{3}J(H,H) = 7.3 Hz, 2 H, CH_2), 3.43 (s, 3 H, NCH_3), 2.21 (s, 3 H, CH_3), 2.13 (s, 3 H, CH_3), 1.15 (m, ^{3}J(H,H) = 7.3 Hz, 3 H, CH_2CH_3). ^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2): δ 29.3 (s, 1 P, PPh_3). ^{13}C{^{1}H} NMR (125.76 MHz, CD_2Cl_2): δ 145.9 (d, ^{3}J(P,C) = 4.6 Hz, *C*CH_3), 145.4 (d, ^{3}J(P,C) = 3.7 Hz, *C*CH_3), 135.0 (d, $^{2/3}J$(P,C) = 11.0 Hz, Ar−C), 132.7 (d, ^{1}J(P,C) = 48.6 Hz, Ar−C), 130.2 (d, ^{4}J(P,C) = 1.8 Hz, Ar−C), 127.7 (d, $^{2/3}J$(P,C) = 11.0 Hz, Ar−C), 41.6 (s, CH_2), 33.2 (s, NCH_3), 15.0, (s, CH_3), 14.9 (s, CH_3), 14.7 (s, CH_3), carbene signal not detected. Anal. Calcd for $C_{26}H_{29}I_2N_2PPd \cdot CH_2Cl_2$: C, 38.35; H, 3.69; N, 3.31. Found: C, 38.47; H, 3.85; N, 3.22. MS (ESI): *m*/*z* 633 $[M - I]^+$.

2-Ethyl-4-iodo-3,5-dimethyl-1-phenylpyrazolium Triflate (5a). 3a (197 mg, 0.43 mmol) and silver triflate (118 mg, 0.46 mmol) were suspended in CH_3CN (5 mL) and stirred at ambient temperature for 30 min shielded from light. The reaction mixture was filtered through Celite, and the solvent of the filtrate was evaporated off. To the residue was added CH_2Cl_2 (15 mL), and the resulting mixture was filtered through Celite. Removal of the solvent in vacuo afforded the product as an off-white powder (201 mg, 0.42 mmol, 98%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.74–7.62 (m, 5 H, Ar−H), 4.29 (m, ^{3}J(H,H) = 7.3 Hz, 2 H, CH_2), 2.62 (s, 3 H, CH_3), 2.24 (s, 3 H, CH_3), 1.20 (t, ^{3}J(H,H) = 7.3 Hz, 3 H, CH_2CH_3). ^{19}F{^{1}H} NMR (282 MHz, $CDCl_3$): δ −2.3 (s, 3 F, CF_3). ^{13}C{^{1}H} NMR (75.47 MHz, $CDCl_3$): δ 149.6, 149.5 (s, *C*CH_3), 133.2, 131.5, 131.2, 129.0 (s, Ar−C), 120.8 (m, ^{1}J(C,F) = 320.7 Hz, CF_3), 67.8 (s,

CI), 44.9 (s, CH_2), 14.5, 14.2, 13.9 (s, CH_3). Anal. Calcd for $C_{14}H_{16}F_3IN_2O_3S$: C, 35.31; H, 3.39; N, 5.88. Found: C, 35.16; H, 3.13; N, 5.71. MS (ESI): *m*/*z* 327 $[M - CF_3SO_3]^+$.

1-Ethyl-4-iodo-2,3,5-trimethylpyrazolium Triflate (5b). 5b was prepared analogously to **5a** from **3b** (169 mg, 0.43 mmol) and silver triflate (118 mg, 0.46 mmol). Yield: 174 mg, 0.42 mmol, 98%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.54 (m, ^3J(H,H) = 7.3 Hz, 2 H, CH_2), 4.09 (s, 3 H, NCH_3), 2.50 (s, 3 H, CH_3), 2.49 (s, 3 H, CH_3), 1.42 (t, ^3J(H,H) = 7.3 Hz, 3 H, CH_2CH_3). ^{19}F{^{1}H} NMR (282 MHz, $CDCl_3$): δ −2.5 (s, 3 F, CF_3). ^{13}C{^{1}H} NMR (75.47 MHz, $CDCl_3$): δ 148.7, 147.5 (s, CCH_3), 120.7 (m, ^1J(C,F) = 320.2 Hz, CF_3), 66.8 (s, CI), 44.4 (s, CH_2), 35.7 (s, NCH_3), 14.3 (s, CH_3), 13.8 (s, CH_3), 13.5 (s, CH_3). Anal. Calcd for $C_9H_{14}F_3IN_2O_3S$: C, 26.10; H, 3.41; N, 6.76. Found: C, 26.08; H, 2.94; N, 6.62. MS (ESI): *m*/*z* 265 $[M - CF_3SO_3]^+$.

***trans*-(2-Ethyl-3,5-dimethyl-1-phenylpyrazolin-4-ylidene)iodobis-(triphenylphosphine)palladium(II) Triflate (6a).** Tris(dibenzylideneacetone)dipalladium(0) (92 mg, 0.10 mmol) and triphenylphosphine (105 mg, 0.40 mmol) were dissolved in dry CH_2Cl_2 (20 mL) and stirred at ambient temperature for 10 min under nitrogen. The resulting dark-red solution was transferred to a solution of **5a** (83 mg, 0.20 mmol) in dry CH_2Cl_2 (10 mL) via cannula. The reaction mixture was heated under reflux for 4 h in an inert nitrogen atmosphere and then cooled to ambient temperature. The resulting mixture was filtered through Celite, and the filtrate was extracted with H_2O (4 × 30 mL). The CH_2Cl_2 layer was dried over $MgSO_4$, and the solvent was reduced under vacuum to 1 mL. Adding diethyl ether to the concentrated solution resulted in an off-white precipitate, which was collected and washed with diethyl ether again (2 × 30 mL) to give the product as a light-yellow powder (177 mg, 0.16 mmol, 80%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.62–7.41 (m, 33 H, Ar−H), 6.76–6.75 (m, 2 H, Ar−H), 3.62 (m, ^3J(H,H) = 7.3 Hz, 2 H, CH_2), 2.07 (s, 3 H, CH_3), 1.68 (s, 3 H, CH_3), 0.76 (m, ^3J(H,H) = 7.3 Hz, 3 H, CH_2CH_3). ^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$): δ 23.0 (s, 2 P, PPh_3). ^{19}F{^{1}H} NMR (282 MHz, $CDCl_3$): δ −2.2 (s, 3 F, CF_3). ^{13}C{^{1}H} NMR (125.76 MHz, $CDCl_3$): δ 146.4 (t, ^3J(P,C) = 3.2 Hz, CCH_3), 145.1 (t, ^3J(P,C) = 3.2 Hz, CCH_3), 134.8 (t, $^{2/3}J$(P,C) = 6.0 Hz, Ar−C), 132.3 (s, Ar−C), 131.7 (t, ^1J(P,C) = 24.7 Hz, Ar−C), 131.3, 131.2, 130.8 (s, Ar−C), 128.6 (t, $^{2/3}J$(P,C) = 5.5 Hz, Ar−C), 128.2 (t, ^2J(P,C) = 7.3 Hz, $C_{carbene}$), 127.9 (s, Ar−C), 121.0 (m, ^1J(F,C) = 320.8 Hz, CF_3), 42.8 (s, CH_2), 14.8, 14.7, 14.6 (s, CH_3). Anal. Calcd for $C_{50}H_{46}F_3IN_2O_3P_2PdS$: C, 54.24; H, 4.19; N, 2.53. Found: C, 54.22; H, 4.12; N, 2.53. MS (ESI): *m*/*z* 957 $[M - CF_3SO_3]^+$.

***trans*-(1-Ethyl-2,3,5-trimethylpyrazolin-4-ylidene)iodobis(triphenylphosphine)palladium(II) Triflate (6b). 6b** was prepared analogously to **6a** from **5b** (62 mg, 0.15 mmol), tris(dibenzylideneacetone)dipalladium(0) (69 mg, 0.075 mmol), and triphenylphosphine (79 mg, 0.30 mmol). Yield: 115 mg, 0.11 mmol, 73%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.55–7.36 (m, 30 H, Ar−H), 3.80 (m, ^3J(H,H) = 7.3 Hz, 2 H, CH_2), 3.40 (s, 3 H, NCH_3), 1.77 (s, 3 H, CH_3), 1.73 (s, 3 H, CH_3), 1.03 (t, ^3J(H,H) = 7.3 Hz, 3 H, CH_2CH_3). ^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$): δ 22.8 (s, 2 P, PPh_3). ^{19}F{^{1}H} NMR (282 MHz, $CDCl_3$): δ −2.3 (s, 3 F, CF_3). ^{13}C{^{1}H} NMR (125.76 MHz, $CDCl_3$): δ 144.7 (t, ^3J(P,C) = 3.2 Hz, CCH_3), 143.9 (t, ^3J(P,C) = 3.7 Hz, CCH_3), 134.7 (t, $^{2/3}J$(P,C) = 6.4 Hz, Ar−C), 131.2 (t, ^1J(P,C) = 24.3 Hz, Ar−C), 131.1 (s, Ar−C), 128.4 (t, $^{2/3}J$(P,C) = 5.1 Hz, Ar−C), 127.8 (t, ^2J(P,C) = 7.3 Hz, $C_{carbene}$), 121.0 (m, ^1J(F,C) = 320.8 Hz, CF_3), 42.2 (s, CH_2), 34.2 (s, NCH_3), 14.9, 14.4, 14.0 (s, C CH_3/CH_2CH_3). Anal. Calcd for $C_{45}H_{44}IN_2P_2PdO_3SF_3$: C, 50.25; H, 4.17; N, 2.58. Found: C, 50.28; H, 4.07; N, 2.56. MS (ESI): *m*/*z* 895 $[M - CF_3SO_3]^+$.

General Procedure for the Suzuki−Miyaura Cross-coupling Reaction. In a typical run, a test tube was charged with a mixture of aryl halide (1.0 mmol), phenylboronic acid (1.2 mmol), potassium carbonate (1.5 mmol), precatalyst (0.01 mmol) and $[N(n\text{-}C_4H_9)_4]Br$ (1.5 mmol) (for entries 9–16 in Table 3). To the mixture was added H_2O (3 mL). The reaction mixture was vigorously stirred at the appropriate temperature. After the desired reaction time, the solution was allowed to cool. A total of 10 mL of dichloromethane was added to the reaction mixture, and the organic phase was extracted with water (6 × 5 mL) and dried over $MgSO_4$. The solvent was removed by evaporation to give a crude product, which was analyzed by ^{1}H NMR spectroscopy.

X-ray Diffraction Studies. Diffraction data for complexes **6a/b** were collected with a Bruker AXS APEX CCD diffractometer equipped with a rotation anode at 293(2) K (**6a**) or 223(2) K (**6b**) using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). Data were collected over the full sphere and were corrected for absorption. Structure solutions were found by the Patterson method. Structure refinement was carried out by full-matrix least squares on F^2 using *SHELXL-97*[8] with first isotropic and later anisotropic displacement parameters for all non-H atoms. A summary of the most important crystallographic data is given in Table 2.

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Supporting Information Available: Crystallographic data for **6a** and **6b** as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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(8) Sheldrick, G. M. *SHELXL-97*; Universität Göttingen: Göttingen, Germany, 1997.