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Air-stable Pd(0) catalyst bearing dual phosphine ligands: a detailed evaluation of air stability and catalytic property in cross-coupling reactions†

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We have synthesised an air-stable Pd(0) catalyst bearing donor and acceptor phosphine ligands (Complex **1**). This study revealed the long-term air stability and catalytic property of Complex **1** as a catalyst for cross-coupling reactions, where it was stable in air for eight months. DFT calculations revealed that the acceptor ligands in Complex **1** decreased the HOMO energy level, which provided the observed air stability. Complex **1** successfully served as a catalyst for direct C–H arylation reactions and Suzuki–Miyaura cross-coupling reactions, and catalysed the reaction of a relatively inactive substrate, 2-chrolopyridine, which could not be achieved by conventional, air-stable Pd(0) catalysts. Isolating the intermediates of the coupling reactions revealed that each intermediate possessed the donor ligand (PCy_3), which was determined to be responsible for imparting the high catalytic activity exhibited by Complex **1**.

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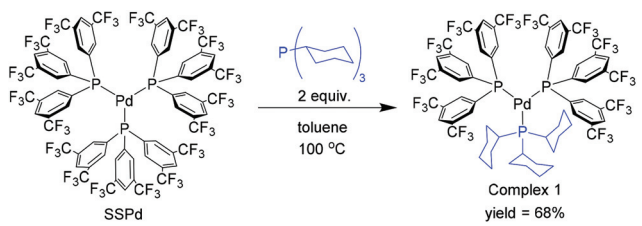
Introduction

The development of transition-metal-catalysed cross-coupling reactions has accelerated syntheses of natural products, agrochemicals, materials in organic electronic devices, *etc.*[1–5] Pd, Ni, and Cu complexes are commonly used as catalysts for cross-coupling reactions. Among them, Pd catalyst precursors and their ligands have been predominantly investigated, as they can achieve high catalytic activity and be employed in a wide range of applications. Bi- or zero-valent Pd catalyst precursors are generally used for various cross-coupling reactions. Pd(II) precatalysts[6–9] are stable in air and easy to handle, while a process of forming a catalytically active Pd(0) species causes decomposition of substrates or additive ligands during the initial stage of cross-coupling reactions.[10–13] The use of Pd(0) catalysts can avoid this because there is no activation process. However, Pd(0) catalysts are generally unstable in air and difficult to handle.[14] Therefore, researchers in the field of catalytic chemistry aspire to develop air-stable Pd(0) catalysts. Precise molecular designs have provided air-stable Pd(0)[15–19] and Ni(0) catalysts in recent years,[20,21] and the basic concept behind them is selecting appropriate electron-deficient (acceptor) ligands. In contrast to air stability, electron-sufficient (donor) ligands are favoured for oxidative addition in the catalytic cycle.[2] Therefore, a new molecular design that provides both air stability and good catalytic activity is necessary. Recently, we have developed an air-stable Pd(0) complex that bears acceptor phosphine ligands for stability and a donor phosphine ligand, PCy_3, to impart catalytic activity (Complex **1**, Scheme 1).[22] Complex **1** showed excellent air stability during an accelerated deterioration test, and high catalytic activity in direct C–H arylation reactions.

In this paper, we report an extensive investigation of Complex **1** regarding its long-term stability and catalytic property in cross-coupling reactions, the results of which compliment those of previous works. DFT calculations revealed that the origin of the air stability of Complex **1** was the acceptor phosphine ligands, while mechanistic studies and catalytic reactions demonstrated that the donor ligand coordinates to the Pd centre during the catalytic reaction and provides high catalytic activity.



Scheme 1 Synthesis of Complex **1**.

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Results and discussion

Evaluation of long-term air stability

Complex **1** was stored in air for a long time to confirm its long-term air stability. The ^{31}P NMR spectrum of Complex **1** was taken before it was stored and then again eight months later (Fig. 1). Both spectra showed doublet and triplet signals with an integral ratio of 2 : 1, which correspond to the complex. This spectroscopic data demonstrated that there was no decomposition of the complex after long-term storage under ambient conditions.

The catalytic activity of air-exposed Complex **1** was compared to that of the pristine complex in a direct C–H arylation reaction. The reaction was carried out under nitrogen atmosphere because Complex **1** was unstable in solution under air. Time course reactions were performed for both versions of Complex **1**, and consisted of 2-cyanothiophene reacting with 4-bromoanisole in the presence of 0.5 mol% of Complex **1** (Fig. 2). The results of the time courses were almost identical, demonstrating that there was no degradation of catalytic activity during storage and Complex **1** displays long-term air stability. Fig. 2 shows the induction period in a reproducible fashion. This observation indicates the three-coordinated Pd (0) complex was stable and slowly converted to the active species.

DFT calculations

Subsequent density functional theory (DFT) calculations were performed on the complexes to estimate their HOMO energy levels, because a low HOMO level is linked to low oxidation potentials and high air stability. The HOMO and LUMO energy levels of Complex **1** were compared to those of related complexes: $Pd(PCy_3)_2$ and superstable Pd ($Pd[P(3,5\text{-}(CF_3)_2C_6H_3)_3]_3$, SSPd, Fig. 3).[19] Complex **1** and SSPd showed much lower HOMO levels than $Pd(PCy_3)_2$. The two acceptor ligands of Complex **1** strongly stabilized it, despite the coordination of the donor ligand.[23] These DFT calculations clarified that $P(3,5\text{-}(CF_3)_2C_6H_3)_3$ ligand lowered the HOMO level of Complex **1**, providing its air-stability.

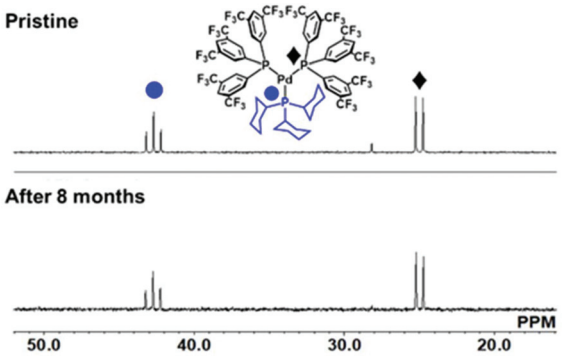


Fig. 1 ^{31}P NMR spectra of Complex **1** before storage (top) and after being stored for eight months in the solid state in air (bottom; 162 MHz, acetone-d_6, r.t., under N_2, external standard: 85% H_3PO_4 0 ppm).

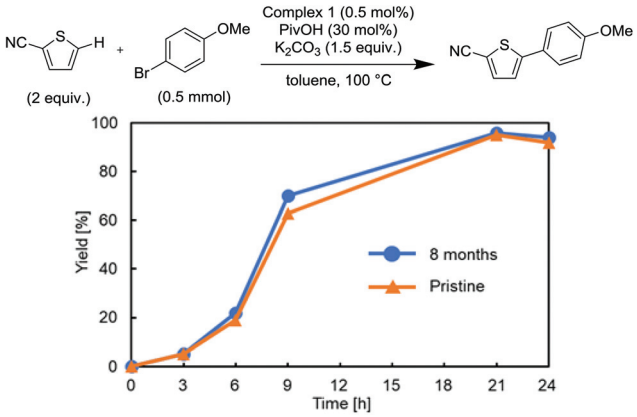


Fig. 2 Time courses of the direct C–H arylation reactions by Complex **1**. Conditions: Pd, 0.0025 mmol; 4-bromoanisole, 0.50 mmol; 2-cyanothiophene, 1.0 mmol; PivOH, 0.15 mmol; K_2CO_3, 0.75 mmol; toluene, 1.7 mL; and temperature, 100 °C. The yields were determined by ^{1}H NMR analysis of the crude product with ferrocene as the internal standard.

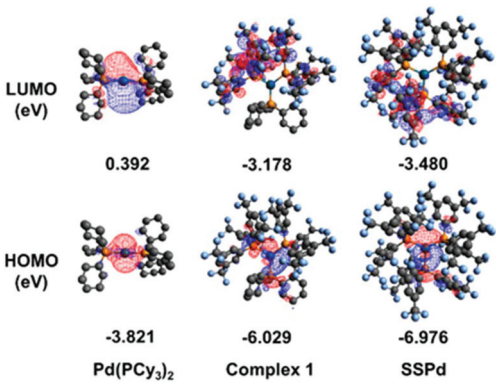
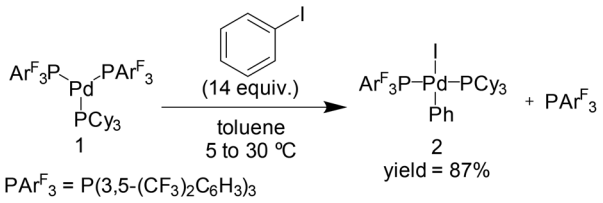


Fig. 3 HOMO and LUMO distributions and energy levels of Complex **1**, $Pd(PCy_3)_2$, and superstable Pd (SSPd) based on DFT calculations.

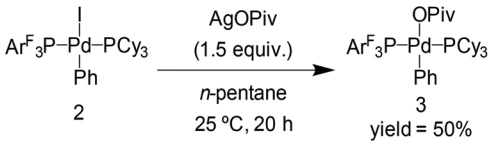
Mechanistic study

A previous study[22] revealed that Complex **1** showed higher catalytic activity in a direct C–H arylation reaction than SSPd, presumably due to the presence of the PCy_3 ligand in Complex **1**. It is desirable that PCy_3 does not dissociate from the Pd centre during the catalytic cycle to ensure accelerated oxidative addition and reductive elimination steps. To confirm PCy_3 coordination, intermediates from each step of a direct C–H arylation reaction were isolated (Fig. S1†). We found that one of the $P(3,5\text{-}(CF_3)_2C_6H_3)_3$ ligands had selectively dissociated from the Pd centre due to the weak basicity of the oxidative addition step (Scheme 2).[22] This formed Complex **2**, whose PCy_3 ligand does not dissociate during the initial step of the direct C–H arylation reaction.

The intermediate of the next step is a Pd pivalato complex (Fig. S1†). The reaction of Complex **2** with silver pivalate gave Complex **3** (Scheme 3) in a 50% yield.[24] The crystal structure of Complex **3** was determined (Fig. 4), which revealed that both



Scheme 2 Synthesis of Complex **2**.[22]



Scheme 3 Synthesis of Complex **3**.

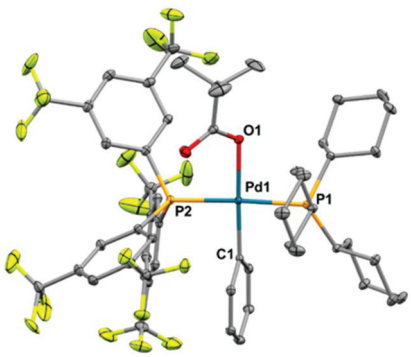
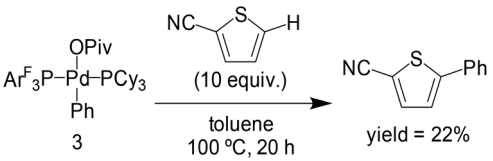


Fig. 4 ORTEP drawing of Complex **3** with thermal ellipsoids at the 30% probability level. All hydrogen atoms and incorporated molecules were omitted for clarity. Selected bond lengths (Å): Pd1–P1 = 2.3322(7), Pd1–P2 = 2.3160(7), Pd1–O1 = 2.120(2), Pd1–C1 = 2.005(3). Selected bond angles (°): P1–Pd1–P2 = 176.98(3), P1–Pd–O1 = 88.26(6), P2–Pd1–O1 = 94.53(6), O1–Pd1–C1 = 178.44(9).

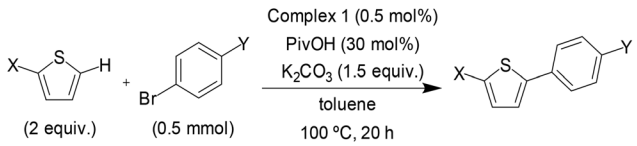
the P(3,5-$(CF_3)_2C_6H_3)_3$ and PCy_3 ligands were coordinated to the Pd centre. The ^{31}P NMR spectrum of Complex **3** exhibited two doublet signals (J = 388 Hz, Fig. S3†). The signal pattern and the J values suggest that the heteroligated complex possesses the trans configuration and is stable in solution.[25,26] These results confirm that the Pd centre maintains coordination with the PCy_3 ligand during the catalytic cycle.

The stoichiometric reaction of Complex **3** with 2-cyanothiophene was conducted to investigate whether Complex **3** was the true intermediate during the direct C–H arylation reaction using Complex **1** (Scheme 4). The reaction gave 5-phenyl-2-cyanothiophene as the coupling product, confirming that Complex **3** is the intermediate of this reaction (Fig. S1†). The low yield of the products is presumably due to the decomposition of a Pd(0) species formed by reductive elimination; released phosphine ligands from the decomposed Pd species may inhibit the reaction of Complex **3** with 2-cyanothiophene.



Scheme 4 Stoichiometric reaction of Complex **3** with 2-cyanothiophene.

Table 1 Direct C–H arylation reaction by Complex **1**



Entry	X	Y	Yield[a] (%)
1	–CN	–OMe	83
2	–CN	–Me	72
3	–CN	–CF_3	40
4	–Ac	–OMe	29
5	–CHO	–OMe	34

[a] Isolated yield.

Direct C–H arylation reaction

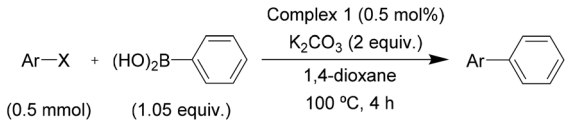
In our previous works,[22] the catalytic properties of Complex **1** had been evaluated by ^{1}H NMR analysis, where the conversion of the substrates was monitored. This study determined the catalytic properties based on the isolated yields of the products (Table 1).

Complex **1** afforded coupling products in moderate to good isolated yields. The yields of reactions with electron-rich bromoarenes were higher than those of reactions with electron-poor bromoarenes (entries 1–3). Therefore, the oxidative addition step may not be the rate-determining step because the PCy_3 ligand promotes faster oxidative addition.[2] 2-Cyanothiophene showed higher reactivity than acetyl- or formyl thiophenes (entry 1 *vs.* 4 and 5). Its strong electron-withdrawing nature, or coordination ability, ascribed to its cyano group, is likely behind this improved direct C–H arylation reaction activity. The strong electron-withdrawing nature provides high reactivity of the C–H bond. In addition, coordination ability of the cyano group may promote the dissociation of one of the phosphine ligands in Complex **1** to generate an active two-coordinate species.

Suzuki–Miyaura cross-coupling

Complex **1** was applied to Suzuki–Miyaura cross-coupling reactions to confirm its catalytic property as a catalyst. Reactions of 4-bromotoluene with phenylboronic acid in the presence of Complex **1** were conducted under several reaction conditions (Table S1†). The reaction under suitable conditions afforded the products in 97% yield (Table 2, entry 1). The other bromoarenes, bearing electron-donating or electron-withdrawing

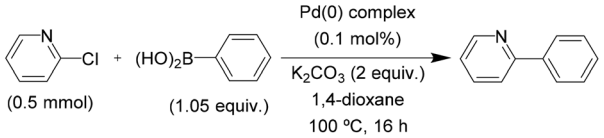
Table 2 Suzuki–Miyaura cross-coupling reaction by Complex **1**



Entry	Ar–X	Yield[a] (%)
1	4-Bromotoluene	97
2	4-Bromoanisole	81
3	4-Bromobenzotrifluoride	83
4	2-Chloropyridine	66

[a] Isolated yield.

Table 3 Suzuki–Miyaura cross-coupling reactions of 2-chloropyridine with phenyl boronic acid by various Pd catalysts



Entry	Pd(0)	Yield[a] (%)
1	Complex **1**	89
2	$Pd(PCy_3)_2$	94
3	SSPd	9

[a] The yield was determined by ^{1}H NMR analysis of the crude product with ferrocene as the internal standard.

substituents, also afforded the corresponding products in high yields (entries 2 and 3). Even for a relatively inactive substrate, 2-chrolopyridine, Complex **1** proved to be a good catalyst (entry 4). The performance of the other Pd(0) catalysts during the reaction of 2-chloropyridine with phenylboronic acid were compared (Table 3), where the catalyst loading was 0.1 mol%.

The reaction with 0.1 mol% of Complex **1** gave 2-phenylpyridine in 89% yield (entry 1), which was similar to that obtained when $Pd(PCy_3)_2$ was used (entry 2). In contrast, the reaction employing SSPd under the same conditions resulted in a low yield (9%, entry 3). Soós and co-workers[19] have also reported a low yield (25%) for a similar coupling reaction, where 2-chloropyridine and 4-ethoxy-3-methylphenyldioxaborolane reacted with 0.33 mol% of SSPd at 110 °C for 24 h. Complex **1** showed almost the same activity as the unstable $Pd(PCy_3)_2$ complex, but distinctly higher catalytic activity than that of the conventional, air-stable Pd(0) complex used in Suzuki–Miyaura cross-coupling reactions. These results show that the PCy_3 ligand of Complex **1** can be ascribed to the accelerated oxidative addition that was observed for the inactive C–Cl bond in 2-chloropyridine. To confirm this, a plausible active species of Complex **1** and SSPd were analysed by DFT calculations. One of the $P(3,5\text{-}(CF_3)_2C_6H_3)_3$ ligands may dissociate from the Pd centre before the oxidative addition step, which would form two coordinated Pd(0) complexes, $Pd(PCy_3)P(3,5\text{-}(CF_3)_2C_6H_3)_3$ and $Pd[P(3,5\text{-}(CF_3)_2C_6H_3)_3]_2$, from Complex **1** and SSPd, respectively (Fig. S4†).[27] Based on the results, the HOMO was located on the Pd centre in both species, and the HOMO energy level of $Pd(PCy_3)P(3,5\text{-}(CF_3)_2C_6H_3)_3$ was higher than that of $Pd[P(3,5\text{-}(CF_3)_2C_6H_3)_3]_2$. The high energy Pd-centred HOMO would be an origin of high reactivity in the oxidative addition step because a transition state of oxidative addition involves interaction between a 4d orbital of a Pd centre and a σ*(and π*) orbital of a substrate (see ESI†).[28–32] The PCy_3 ligand is likely to provide high reactivity to plausible active species from Complex **1**, $Pd(PCy_3)P(3,5\text{-}(CF_3)_2C_6H_3)_3$ due to its strong donor nature.

Conclusion

Complex **1** showed high stability in air for eight months, and DFT calculations revealed that the low HOMO energy level contributed to this stability. These results also showed the stabilising effect from the acceptor ligand, $P(3,5\text{-}(CF_3)_2C_6H_3)_3$. Isolating the intermediate of the direct C–H arylation reaction confirmed that PCy_3 coordinates to the Pd centre during each step of the reaction and imparts catalytic activity. Complex **1** showed high catalytic activity for direct C–H arylation reactions and Suzuki–Miyaura cross-coupling reactions. Moreover, Complex **1** was able to catalyse the reaction of a relatively inactive substrate, 2-chrolopyridine, which could not be achieved by conventional, air-stable Pd(0) catalysts, due to the activating effect of its donor ligand, PCy_3. This study clarified the working principle of Complex **1**, which satisfied the demands for air stability and catalytic activity.

Experimental section

General, measurement, and materials

^{1}H and ^{31}P{^{1}H} NMR spectra were recorded using a Bruker AVANCE-400 NMR spectrometer. Elemental analyses were carried out using a PerkinElmer 2400 CHN elemental analyzer. SSPd was purchased from FUJIFILM Wako Pure Chemical Corporation. Anhydrous methanol, *n*-pentane, *n*-hexane and toluene were purchased from Kanto Chemical and used as dry solvents. The density functional theory (DFT) calculations were performed at the B3LYP/6-31G(d) level with the Gaussian09 Rev. D.01 program (Gaussian, Inc., Wallingford, CT, USA).

Synthetic methods

Complex **1** and **2** were synthesized as previously reported.[22]

Complex 3

A solution of Complex **2** (126 mg, 0.10 mmol) and silver pivalate (31 mg, 0.15 mmol) was stirred in *n*-pentane (4 mL) at 25 °C for 20 h. The resulting mixture was filtered through glass filter and concentrated under vacuum. Recrystallization from *n*-pentane gave Complex **3** (62 mg, 50%). ^{1}H NMR (400 MHz, acetone-d_6, room temperature): δ 8.18 (s, 3 H), 8.16 (s, 6 H), 7.06 (br, 2 H), 6.57 (br, 3 H), 1.78–1.66 (m, 16 H),

1.31–1.07 (m, 14 H), 0.87 (t, 3 H, J = 8.0 Hz), 0.61 (s, 9 H). ^{31}P {^{1}H} NMR (162 MHz, acetone-d_6, room temperature): δ 29.8 (d, 1 P, J = 388 Hz), 24.0 (d, 1 P, J = 389 Hz). Elemental analysis: Found: C 51.28%, H 4.67%; Calcd for $C_{52}H_{47}F_{18}O_2P_2Pd$: C 51.53%, H 4.57%.

Stoichiometric reaction of Complex 3 with 2-cyanothiophene

A mixture of Complex **3** (67.5 mg, 0.055 mmol), 2-cyanothiophene (51.3 μL, 0.55 mmol) and K_2CO_3 (15.2 mg, 0.11 mmol) was stirred in toluene (1.3 mL) for 20 h at 100 °C under nitrogen atmosphere. The reaction mixture was cooled to room temperature and diluted with ethyl acetate. The organic phase was washed with water and brine, and dried over Na_2SO_4. The product was isolated by column chromatography on silica gel using a mixture of hexane and ethyl acetate (32 : 1) as an eluent and HPLC. The solvents were removed *in vacuo* to give 5-phenyl-2-cyanothiophene (2.2 mg, 22%). ^{1}H NMR (400 MHz, $CDCl_3$, room temperature): δ 7.62–7.58 (m, 3H), 7.46–7.38 (m, 3H), 7.28 (d, J = 4.0 Hz, 1H). The NMR data is consistent with reported data.[33]

General procedure of catalytic reaction

Direct C–H arylation reaction

Synthesis of 5-(4-methoxyphenyl)-2-cyanothiophene (Table 1, entry 1). A mixture of Complex **1** (4.3 mg, 0.0025 mmol), pivalic acid (17.5 μL, 0.15 mmol), 2-cyanothiophene (93 μL, 1.0 mmol), 1-bromo-4-methoxybenzene (62 μL, 0.50 mmol), and K_2CO_3 (104 mg, 0.75 mmol) was stirred in toluene (1.7 mL) for 20 h at 100 °C under a nitrogen atmosphere. The reaction mixture was cooled to room temperature and diluted with $CHCl_3$. The organic phase was washed with water and brine, and dried over $MgSO_4$. The product was isolated by column chromatography on silica gel using a mixture of hexane and ethyl acetate (32 : 1) as an eluent. The solvents were removed *in vacuo* to give 5-(4-methoxyphenyl)-2-cyanothiophene (89 mg, 83%). ^{1}H NMR (400 MHz, $CDCl_3$, room temperature): δ 7.56 (d, J = 4.0 Hz, 1H), 7.53 (d, J = 9.2 Hz, 2H), 7.16 (d, J = 4.0 Hz, 1H), 6.95 (d, J = 9.2 Hz, 2H), 3.85 (s, 3H).[22]

Synthesis of 5-(4-methylphenyl)-2-cyanothiophene (Table 1, entry 2). Purification by column chromatography on silica gel using a mixture of hexane and ethyl acetate (30 : 1) as an eluent gave 5-(4-methylphenyl)-2-cyanothiophene (72 mg, 72%). ^{1}H NMR (400 MHz, $CDCl_3$, room temperature): δ 7.57 (d, J = 3.6 Hz, 3H), 7.49 (d, J = 8.4 Hz, 2H), 7.24–7.22 (m, 3H), 2.39 (s, 3H).[34]

Synthesis of 5-(4-trifluoromehylphenyl)-2-cyanothiophene (Table 1, entry 3). Purification by column chromatography on silica gel using a mixture of hexane and ethyl acetate (30 : 1) as an eluent gave 5-(4-trifluoromehylphenyl)-2-cyanothiophene (51 mg, 40%). ^{1}H NMR (400 MHz, $CDCl_3$, room temperature): δ 7.71 (m, 4H), 7.63 (d, J = 3.6 Hz, 1H), 7.36 (d, J = 4 Hz, 1H).[35]

Synthesis of 5-(4-methoxyphenyl)-2-acetylthiophene (Table 1, entry 4). Purification by column chromatography on silica gel using a mixture of hexane and ethyl acetate (30 : 1) as an eluent gave 5-(4-methoxyphenyl)-2-acetylthiophene (34 mg, 29%). ^{1}H NMR (400 MHz, $CDCl_3$, room temperature): δ 7.64 (d, J = 4 Hz, 1H), 7.59 (d, J = 8.8 Hz, 2H), 7.22 (d, J = 4 Hz, 1H), 6.94 (d, J = 8.8 Hz, 2H), 3.86 (s, 3H), 2.56 (s, 3H).[36]

Synthesis of 5-(4-methoxyphenyl)-2-formylthiophene (Table 1, entry 5). Purification by column chromatography on silica gel using a mixture of hexane and ethyl acetate (30 : 1) as an eluent gave 5-(4-methoxyphenyl)-2-formylthiophene (37 mg, 34%). ^{1}H NMR (400 MHz, $CDCl_3$, room temperature): δ 9.86 (s, 1H), 7.71 (d, J = 3.6 Hz, 1H), 7.62 (d, J = 8.8 Hz, 1H), 7.30 (d, J = 4 Hz, 2H), 6.96 (d, J = 8.8 Hz, 2H), 3.86 (s, 3H).[37]

Tracking of the direct C–H arylation reaction. A mixture of Complex **1** (4.3 mg, 0.0025 mmol), pivalic acid (17.5 μL, 0.15 mmol), 2-cyanothiophene (93 μL, 1.0 mmol), 1-bromo-4-methoxybenzene (62 μL, 0.50 mmol), K_2CO_3 (104 mg, 0.75 mmol) and ferrocene (18.6 mg, 0.1 mmol) was stirred in toluene (1.7 mL) at 100 °C under a nitrogen atmosphere. A portion of a reaction mixture (*ca.* 10 μL) was taken out at 0, 3, 6, 9, 21, 24 h. The NMR yield at each reaction time was obtained from the integral value of the signal for the product at 3.85 ppm on the basis of the internal standard (ferrocene).[22]

Suzuki–Miyaura cross-coupling reaction

Synthesis of 4-methylbiphenyl (Table 2, entry 1). A mixture of Complex **1** (4.3 mg, 0.0025 mmol), phenylboronic acid (64 mg, 0.53 mmol), 1-bromo-4-methylbenzene (62 μL, 0.50 mmol), and K_2CO_3 (138 mg, 1.0 mmol) was stirred in 1,4-dioxane (1.0 mL) for 4 h at 100 °C under a nitrogen atmosphere. The reaction mixture was cooled to room temperature and diluted with ethyl acetate. The organic phase was washed with NH_4Cl aq. and brine, and dried over Na_2SO_4. The product was isolated by column chromatography on silica gel using hexane as an eluent. The solvents were removed *in vacuo* to give 4-methylbiphenyl (82 mg, 97%). ^{1}H NMR (400 MHz, $CDCl_3$, room temperature): 7.58 (d, J = 7.2 Hz, 2H), 7.49 (d, J = 8.0 Hz, 2H), 7.42 (t, J = 7.6 Hz, 2H), 7.32 (t, J = 7.2 Hz, 1H), 7.25 (d, J = 8.0 Hz, 2H), 2.40 (s, 3H).[38]

Synthesis of 4-methoxybiphenyl (Table 2, entry 2). Purification by column chromatography on silica gel using hexane as an eluent gave 4-methoxybiphenyl (75 mg, 81%). ^{1}H NMR (400 MHz, $CDCl_3$, room temperature): 7.54 (t, J = 5.5 Hz, 4H), 7.41 (t, J = 7.6 Hz, 2H), 7.30 (t, J = 7.4 Hz, 1H), 6.98 (d, J = 8.8 Hz, 2H), 3.85 (s, 3H).[38]

Synthesis of 4-trifluoromethylbiphenyl (Table 2, entry 3). Purification by column chromatography on silica gel using hexane as an eluent gave 4-trifluoromethylbiphenyl (92 mg, 83%). ^{1}H NMR (400 MHz, $CDCl_3$, room temperature): 7.70 (m, 4H), 7.60 (d, J = 6.8 Hz, 2H), 7.48 (t, J = 7.4 Hz, 2H), 7.41 (t, J = 7.2 Hz, 1H).[38]

Synthesis of 2-phenylpyridine (Table 2, entry 4). Purification by column chromatography on silica gel using ethyl acetate and hexane (1 : 6) as an eluent gave 2-phenylpyridine (51 mg, 66%). ^{1}H NMR (400 MHz, $CDCl_3$, room temperature): 8.70 (d, J = 4.8 Hz, 1H), 8.00 (d, J = 7.2 Hz, 2H), 7.76–7.72 (m, 2H), 7.48 (t, J = 7.4 Hz, 2H), 7.42 (t, J = 7.2 Hz, 1H), 7.26–7.21 (m, 1H).[39]

Crystal structure determination. Recrystallization from toluene/methanol gave a single crystal of Complex **3** for crystal structure determination. Intensity data were collected on a

Bruker SMART APEX II ULTRA with Mo Kα radiation. A full matrix least-squares refinement was used for non-hydrogen atoms with anisotropic thermal parameters using the SHELXL-97 program. CCDC 1950052† contains the supplementary crystallo-graphic data for this paper.

Conflicts of interest

There are no conflicts to declare.

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