 

# Ring Carbon Functionalization of *N*-Heterocyclic Carbene Ligand with Ester Groups. Electronic Effect of Ester Groups on Coordination Properties

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Palladium complexes with an imidazol-2-ylidene ligand functionalized with ester groups at its 4,5-positions were synthesized from a readily available imidazole derivative. $\sigma$-Donation from the carbene ligand to the palladium atom is considerably weakened by functionalization with the two ester moieties.

*N*-Heterocyclic carbenes (NHC) are strong $\sigma$-donating ligands, and their use in synthetic catalytic reactions has expanded.[1,2] Since Herrmann et al. reported the catalytic applications of a palladium complex with a very simple NHC ligand,[1] numbers of studies have been done on the modification of the original imidazol-2-ylidene ring in order to enhance the properties of the ligand. One widespread approach is the modification of the two nitrogen atoms. It has been demonstrated that a highly active catalyst was prepared by the attachment of bulky groups on the nitrogen atoms of the NHC ligands.[2c,3,4] Introduction of functional groups on the nitrogen atoms has also been widely studied.[5,6] These studies have produced a variety of chiral NHC ligands, multidentate NHC ligands, or ligands with special chemical properties or practically useful properties such as recyclability.

In contrast, only a few studies on the modification of an imidazol-2-ylidene ring at its 4,5-positions have been reported.[7–9] Modification at this position would not disturb the steric environment created by the substituents on the nitrogen atoms. Tuning of the electronic properties of a NHC ligand is possible by these modifications. Investigation of the electronic effects of NHC ligands in catalytic reactions would afford mechanistic insights towards further development of the NHC ligands. Fürstner et al. synthesized a ruthenium complex with 4,5-dichloroimidazol-2-ylidene **1** (Fig. 1), but there were only marginal substituent effects in ring-closing alkene metathesis and intramolecular enyne cycloisomerization reactions.[8] Organ et al. prepared the precursor of benzimidazol-2-ylidene **2** having electronically different substituents and showed that electron-donating substitutents on the ligand enhanced the catalytic activity of the complex in the Suzuki–Miyaura reaction.[9] The modification of an imidazol-2-ylidene ligand at its 4,5-positions is, however, still limited despite its potential utility. We report, herein, the preparation and structures of palladium complexes with an imidazol-2-ylidene ligand **3**, which is functionalized with ester groups at its 4,5-positions. The ester groups exerted a considerable electronic influence on the coordination properties of the NHC ligand. The ester groups can potentially be transformed into a wide range of functional groups, which would allow the production of a diverse array of functionalized NHC ligands.

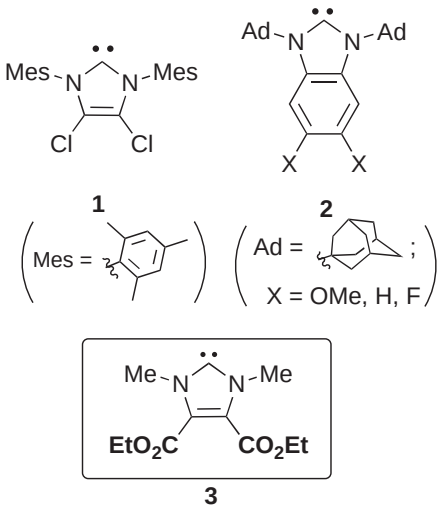


Fig. 1. Ring carbon-functionalized imidazol-2-ylidene ligands.

## Results and Discussion

Synthesis of palladium(II) complexes with the imidazol-2-ylidene ligand bearing ester moieties at the 4,5-positions starts with substituted imidazole **5** as shown in Scheme 1. Imidazole **5** is readily obtained by the reported procedure from commercially available imidazole-4,5-dicarboxylic acid.[10] Treatment of diethyl *N*-methylimidazole-4,5-dicarboxylate (**5**) with MeI in refluxing $CH_3CN$ afforded the imidazolium salt **6** quantitatively. The reaction of palladium(II) acetate with 2.2 equivalent of imidazolium salt **6** in refluxing THF afforded, after purification by flash chromatography, an isomeric mixture of two palladium carbene complexes, *cis*-**7** and *trans*-**7** in 59 and 16% yields, respectively. These complexes are both air- and moisture-stable. Recrystallization of the mixture from $CH_2Cl_2$/hexane afforded two types of crystals: yellow plate crystals and yellow needles. They were separated from each other and characterized separately.

X-ray crystal structure analysis was possible only for the

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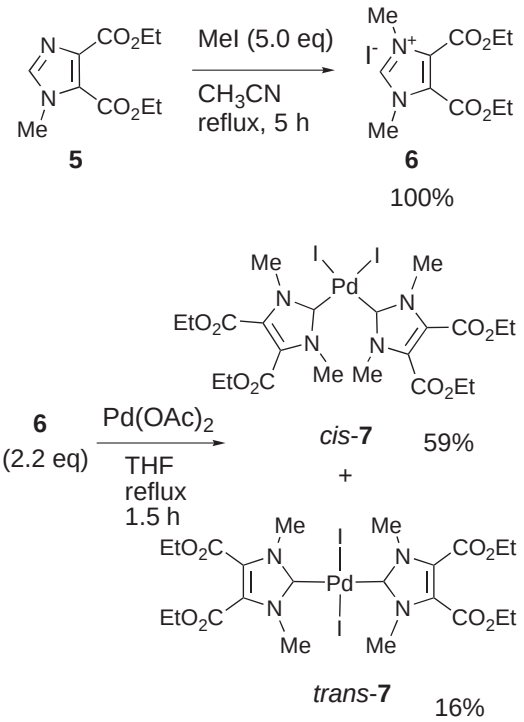



Scheme 1.

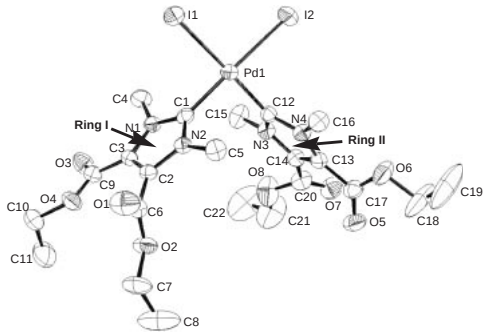


Fig. 2. ORTEP plot (30% probability thermal elipsoids) of the molecular structure of complex *cis*-**7**.

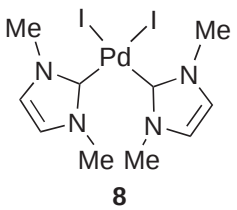


Fig. 3. Reported *N*-heterocyclic carbene–palladium complex.

yellow plate crystals (*cis*-**7**). Complex *cis*-**7** has a square-planar coordination geometry with the two carbene ligands in a *cis* arrangement as shown in Fig. 2. The angles between the coordination plane and each of the carbene rings are 78.4(2)° (ring I) and 77.9(2)° (ring II). Pd–C bond lengths are 2.009(6) Å (ring I) and 2.008(6) Å (ring II). The average of the Pd–C bond lengths is longer than those of the reported values for a native non-substituted palladium complex (**8**)[1] (Fig. 3). Pd–I bond lengths of complex *cis*-**7** are 2.6455(7) Å (*trans* to ring I)

Table 1. Selected Bond Lengths (Å), Angles (deg) Around Palladium Core and NMR Data ($\delta$) for Complexes *cis*-**7** and **8**[1]

| Compound | *cis*-**7** | **8**[1] |
|---|---|---|
| Pd–C (Ring I) | 2.009(6) | 1.990(3), 1.997(3) |
| Pd–C (Ring II) | 2.008(6) | |
| Pd–I (1, *trans* to Ring II) | 2.6419(7) | 2.6479(3), 2.6572(3) |
| Pd–I (2, *trans* to Ring I) | 2.6455(7) | |
| C (Ring I)–Pd–C (Ring II) | 91.4(2) | 90.2 |
| I(1)–Pd–I(2) | 94.29(2) | 93.59 |
| I(1)–Pd–C (Ring I) | 87.0(1) | 87.32, 88.97 |
| I(2)–Pd–C (Ring II) | 87.3(2) | |
| $^{13}$C NMR (carbene-*C*) | 174.6 | 168.2 |
| $^{1}$H NMR (NC$H_3$) | 4.11 | 3.92 |

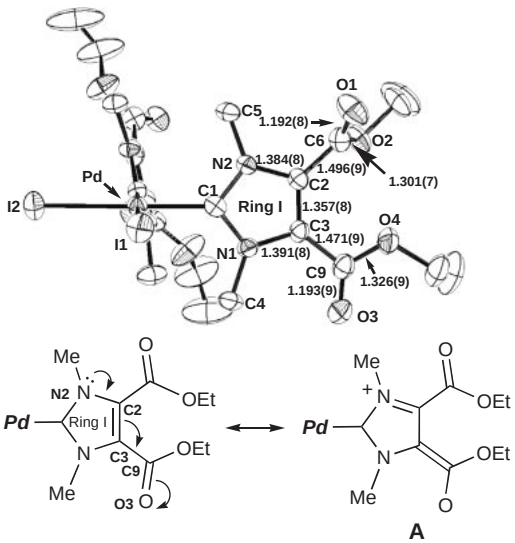



Fig. 4. ORTEP plot (30% probability thermal elipsoids) of the molecular structure of complex *cis*-**7** with selected bond lengths (Å) and possible contributing resonance structures.

and 2.6419(7) Å (*trans* to ring II) (see Table 1), the average of which is slightly shorter than that of complex **8**. These differences are small but suggest that $\sigma$-donation from the NHC to the palladium atom is weakened by functionalization with the ester groups at the 4,5-positions (vide infra for stronger evidence). The torsion angles between the carbene ring and each of the attached carbonyl groups are approximately 10 and 68° for ring I, and 34 and 38° for ring II. These angles are suggestive of the existence of partial $\pi$-orbital overlap between the ester groups and the NHC rings in the solid state. From the X-ray crystal structure analysis (see Fig. 4), the C(2)=C(3) bond is longer than those of complex **8**, and the C(3)–C(9) bond is much shorter than that of the corresponding bond in analogous molecules, which possibly implies the contribution of the resonance structure **A** shown in Fig. 4. Other bond lengths of *cis*-**7** are also consistent with such $\pi$-orbital overlap effect. Extended $\pi$-orbital overlap from the ester group to the carbene core would weaken the $\sigma$-donating ability of the carbene, which is consistent with elongation of the Pd–carbene carbon bonds and the shortening of the Pd–I bonds of ester-functionalized complex *cis*-**7** compared to those of

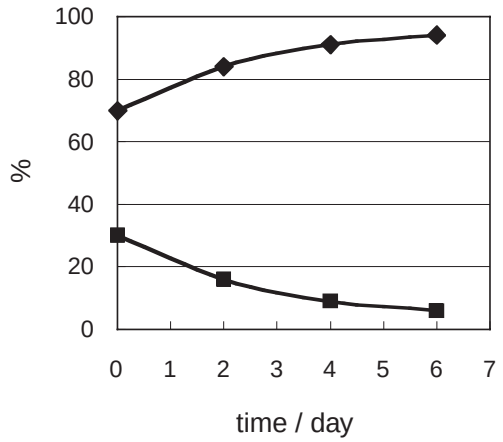
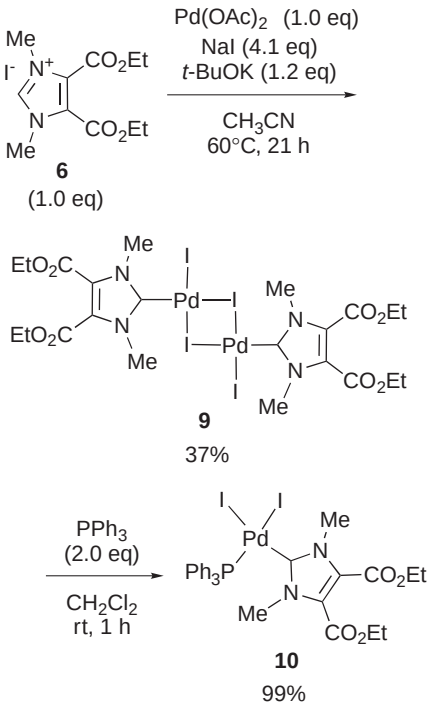



Fig. 5. Thermal isomerization between ester-functionalized NHC-palladium complexes *cis*-**7** (◆) and *trans*-**7** (■) in $CDCl_3$ at 65 °C.




Scheme 2.

native complex **8**.

Small $^{13}C$ NMR chemical shift changes were observed for the carbene carbons of the ester-functionalized complexes when compared with that of non-functionalized complex **8**. The carbene carbon signal of complex *cis*-**7** was observed at 174.6 ppm, which is shifted down-field by 6.4 ppm from that of native complex **8**. The corresponding carbon signal of the other isomer *trans*-**7** was observed at 171.9 ppm.

It was found that these isomeric complexes *cis*-**7** and *trans*-**7** were in slow equilibrium in $CDCl_3$ and that *cis*-**7** was thermodynamically more stable than *trans*-**7**. A $CDCl_3$ solution of *cis*-**7** and *trans*-**7** in a ratio of 70:30 sealed in a NMR tube was converted to a mixture in a 91:9 ratio within 4 days at 65 °C (Fig. 5). This isomerization from *trans* to *cis* is different from that observed for a *N*,*N*-dimethyltriazole-derived NHC

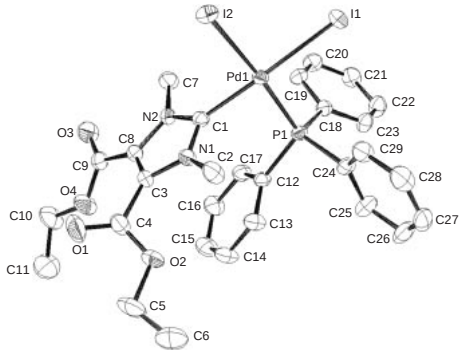



Fig. 6. ORTEP plot (30% probability thermal elipsoids) of the molecular structure of complex **10**.

Table 2. Selected Bond Lengths (Å), Angles (deg) Around Palladium Core for Complexes **10**, **11**,[5b] and **12**[6]

| Compound | **10** | **11**[5b] | **12**[6] |
|---|---|---|---|
| Pd–C | 1.989(3) | 1.9974(4) | 1.990(3) |
| Pd–P | 2.2827(8) | 2.2812(10) | 2.2788(7) |
| Pd–I (1, *trans* to C) | 2.6515(3) | 2.6519(5) | 2.6482(3) |
| Pd–I (2, *trans* to P) | 2.6516(3) | 2.6370(5) | 2.6467(3) |
| C–Pd–P | 89.65(9) | 92.71(10) | 90.35(8) |
| I(1)–Pd–I(2) | 94.22(1) | 93.27(1) | 92.789(10) |
| I(2)–Pd–C | 86.15(8) | 84.89(9) | 87.42(8) |
| I(1)–Pd–P | 90.18(2) | *N*/*A*[a)] | 89.49(2) |

a) *N*/*A* = not available.

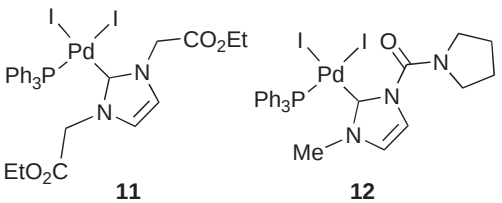
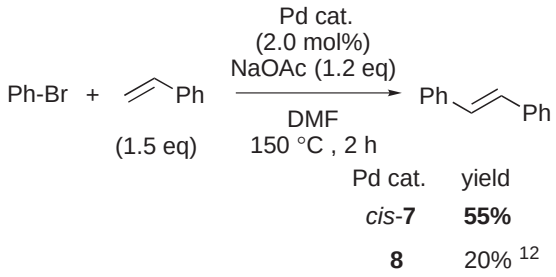



Fig. 7. Reported functionalized *N*-heterocyclic carbene–palladium complexes.

complex of palladium,[11] which isomerizes from *cis* to *trans* on treatment with $H_2O$.

The reaction of palladium(II) acetate with 1.0 equivalent of imidazolium salt **6** in the presence of NaI and KO(*t*-Bu) in refluxing $CH_3CN$ for 21 h afforded an iodo-bridged dimeric monocarbene complex **9** (Scheme 2). Purification by flash chromatography on silica gel afforded complex **9** in 37% yield as red brown powder. Addition of $PPh_3$ to dimeric complex **9** in $CH_2Cl_2$ gave a mixed phosphine–carbene complex **10** as bright yellow crystals in nearly quantitative yield.

From X-ray crystal structure analysis, complex **10** has a square-planar coordination geometry with the carbene ligand and $PPh_3$ in a *cis* arrangement as shown in Fig. 6. Palladium–carbene carbon bond length is 1.989(3) Å, and the angle between the plane of the carbene ring and the coordination plane is 88.79(9)° (see Table 2). The two Pd–I bond lengths are almost identical: 2.6515(3) Å (*trans* to the carbene) and 2.6516(3) Å (*trans* to the phosphine). In the case of *N*,*N*-bis(ethoxycarbonylmethyl)-substituted carbene complex **11**[5b] (Fig. 7), Herrmann et al. reported that the Pd–I bond *trans* to




Scheme 3.

the carbene ring is 0.0149 Å longer than the Pd–I bond *trans* to the phosphine and confirmed that the carbene in complex **11** is still a stronger donor than $PPh_3$. The almost identical two Pd–I bond lengths in complex **10** indicates that $\sigma$-donation from NHC is weakened by the vinylogous modification with the two ester moieties, although partial contribution from crystal packing forces cannot be excluded. *N*-Carbamoyl-substituted carbene complex **12**, reported by Batey et al.,[6] has also almost no difference between the two Pd–I bonds. The present study, therefore, demonstrates that ester-modification of imidazol-2-ylidene at the vinylogous positions exhibits electronic effects comparable to those obtained by the direct modification at the nitrogen atom. Notably, vinylogous modification does not disturb the steric environment around the metal center, although modification of the nitrogen atom does. The ring-functionalization method studied here will help the further development of a new *N*-heterocyclic carbene ligand.

As preliminarily results, the ester-functionalized palladium complex *cis*-**7** exhibited catalytic activity in the Mizoroki–Heck reaction as shown in Scheme 3. In the presence of 2.0 mol % of palladium complex *cis*-**7**, the reaction of bromobenzene with styrene at 150 °C for 2 h afforded stilbene in 55% yield with >98% *trans* selectivity, whereas the reported yield with parent non-substituted complex **8** was 20% in the identical reaction conditions.[12]

## Conclusion

Palladium complexes coordinated by an imidazol-2-ylidene ligand that was functionalized with ester groups at its 4,5-positions were synthesized from a readily available imidazole derivative. These complexes are both air- and moisture-stable. $\sigma$-Donation from the carbene ligand to the palladium atom is weakened considerably by functionalization with the two ester moieties. It is expected that the ester groups can potentially be transformed into a wide range of functional groups. Such transformations would allow the production of a diverse array of functionalized *N*-heterocyclic carbene ligands. Investigation in this line is now underway in our laboratory.

## Experimental

**General.** NMR spectra were obtained with a Varian GEMINI 2000 ($^1$H 300 MHz, $^{13}$C 75 MHz, $^{31}$P 121 MHz) spectrometer and are reported in ppm ($\delta$). Infrared spectra were obtained with a Perkin-Elmer Spectrum One and are reported in $cm^{-1}$. Column chromatographies were performed with silica gel 60 N (40–100 μm, Kanto Chemical Co.).

**Materials.** Anhydrous tetrahydrofuran (THF), hexane, and dichloromethane were purchased from Kanto Chemical Co., Inc. and used without purification. Anhydrous $CH_3CN$ was purchased from Kanto Chemical Co., Inc. and dried over molecular sieves in a bottle. MeOH was purchased from Junsei Chemcal Co., Ltd. and used without purification. MeI was distilled before use. $Pd(OAc)_2$ was purchased from Wako Chemical Industries, Ltd. and used without purification. NaI was purchased from Kanto Chemical Co., Inc. and dried at 70 °C for 10 h in vacuo before use. *t*-BuOK was purchased from Kishida Chemical Co., Ltd. and used without purification. $PPh_3$ was recrystallized from EtOH. 4,5-Bis(ethoxycarbonyl)-1-methylimidazole[10] was prepared by literature procedure.

**4,5-Bis(ethoxycarbonyl)-1,3-dimethylimidazolium Iodide (6).** To a solution of 4,5-bis(ethoxycarbonyl)-1-methylimidazole (734 mg, 3.25 mmol) in $CH_3CN$ (20 mL), MeI (1.42 mL, 16.3 mmol) was added, and the reaction mixture was heated at reflux for 5 h. After cooling to room temperature, the solvent was removed under a reduced pressure to give **6** (1.20 g, 100%). This compound was used for further transformation without purification.

**6**: $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 11.02 (s, 1H, NC*H*N), 4.47 (q, $J = 7.2$ Hz, 4H, $CO_2CH_2$), 4.20 (s, 6H, $NCH_3$), 1.41 (t, $J = 7.2$ Hz, 6H, $CO_2CH_2CH_3$); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 165.53 (2C, *C*=O), 141.31 (N*C*HN), 126.93 (2C, *C*=*C*), 63.46 (2C, O*C*$H_2$-$CH_3$), 36.96 (2C, N*C*$H_3$), 13.60 (2C, $OCH_2CH_3$); IR (neat)/$cm^{-1}$ 2992 (m), 2959 (m), 1720 (s), 1578 (m), 1479 (w), 1408 (w), 1262 (m), 1145 (m), 1109 (m), 1016 (m), 907 (w), 871 (w), 739 (m).

**Bis[4,5-bis(ethoxycarbonyl)-1,3-dimethylimidazolin-2-ylidene]diiodopalladium(II) (7).** A degassed suspension of $Pd(OAc)_2$ (109 mg, 0.49 mmol) and imidazolium iodide **6** (394 mg, 1.07 mmol) in THF (7.5 mL) was heated for 1.5 h at reflux. After cooling to room temperature, the solvent was removed under a reduced pressure. The crude product was recrystallized from $CH_2Cl_2$/hexane to give yellow plate crystals of *cis*-**7** (242 mg, 59%) and yellow needles of *trans*-**7** (67 mg, 16%). The two types of crystals were separately collected. A crystal of *cis*-**7** was used for X-ray diffraction study (vide infra).

*cis*-**7**: $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 4.38 (q, $J = 7.2$ Hz, 8H, $CO_2CH_2CH_3$), 4.11 (s, 12H, $NCH_3$), 1.37 (t, $J = 7.2$ Hz, 12H, $CO_2CH_2CH_3$); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 174.56 (2C, carbene-*C*), 158.88 (4C, *C*=O), 128.39 (4C, *C*=*C*), 62.30 (4C, $OCH_2CH_3$), 37.94 (4C, N*C*$H_3$), 13.88 (4C, $OCH_2CH_3$); IR (neat)/$cm^{-1}$ 2982 (w), 2954 (w), 1717 (s), 1595 (m), 1454 (m), 1380 (s), 1240 (s), 1124 (m), 1084 (s), 1013 (m), 916 (m), 854 (m), 774 (w), 745 (w), 701 (m).

*trans*-**7**: $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 4.38 (q, $J = 7.2$ Hz, 8H, $CO_2CH_2CH_3$), 4.16 (s, 12H, $NCH_3$), 1.37 (t, $J = 7.2$ Hz, 12H, $CO_2CH_2CH_3$); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 171.88 (2C, carbene-*C*), 158.45 (4C, *C*=O), 128.72 (4C, *C*=*C*), 62.72 (4C, $OCH_2CH_3$), 38.76 (4C, N*C*$H_3$), 13.97 (4C, $OCH_2CH_3$); IR (neat)/$cm^{-1}$ 2982 (w), 2936 (w), 1738 (s), 1717 (s), 1614 (m), 1445 (s), 1377 (s), 1280 (s), 1248 (s), 1138 (s), 1075 (s), 1012 (m), 919 (w), 854 (m), 776 (w), 742 (w), 695 (m); Found: C, 31.50; H, 3.60; N, 6.61%. Calcd for $C_{22}H_{32}I_2N_4O_8Pd$: C, 31.43; H, 3.84; N, 6.66%.

**Di-$\mu$-iodobis[4,5-bis(ethoxycarbonyl)-1,3-dimethylimidazolin-2-ylidene]diiododipalladium(II) (9).** A mixture of $Pd(OAc)_2$ (361 mg, 1.61 mmol), imidazolium iodide **6** (592 mg, 1.61 mmol), NaI (978 mg, 6.52 mmol), and *t*-BuOK (220 mg, 1.96 mmol) in $CH_3CN$ (55 mL) was stirred for 21 h at 60 °C. After cooling to room temperature, the solvent was removed under a reduced pressure. The residue was purified by silica gel column chromatography (MeOH/$CH_2Cl_2$) to give **9** (357 mg, 37%) as red brown powder.

**9**: $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 4.39 (q, $J = 7.2$ Hz, 8H, $CO_2$-$CH_2CH_3$), 4.20 (s, 12H, $NCH_3$), 1.38 (t, $J = 7.2$ Hz, 12H, $CO_2$-

Table 3. Summary of Crystal Data and Details of Data Collection and Refinement Parameters for *cis*-**7** and **10**

| | *cis*-**7** | **10** |
|---|---|---|
| Formula | $C_{22}H_{32}I_2N_4O_8Pd$ | $C_{29}H_{31}I_2N_2O_4PPd$ |
| MW | 840.73 | 862.76 |
| Crystal system | triclinic | monoclinic |
| Space group | $P\bar{1}$ (#2) | $P2_1/c$ (#14) |
| $a$/Å | 11.670(3) | 11.1658(9) |
| $b$/Å | 11.840(2) | 17.3109(8) |
| $c$/Å | 13.690(3) | 16.882(1) |
| $\alpha$/deg | 64.33(1) | 90.00 |
| $\beta$/deg | 85.80(1) | 100.299(1) |
| $\gamma$/deg | 63.49(1) | 90.00 |
| $V$/Å$^3$ | 1508.6(6) | 3210.5(4) |
| $Z$ | 2 | 4 |
| $D_{calcd}$/g cm$^{-3}$ | 1.851 | 1.785 |
| Crystal size/mm$^3$ | 0.20 × 0.10 × 0.05 | 0.20 × 0.20 × 0.20 |
| $\mu$(Mo K$\alpha$)/cm$^{-1}$ | 27.10 | 25.87 |
| $2\theta_{max}$/deg | 55.0 | 55.0 |
| No. of measd reflns | 12258 | 26302 |
| Unique reflns | 6796 ($R_{int} = 0.020$) | 7340 ($R_{int} = 0.015$) |
| Obsd reflns | 3995 ($I > 3.00\sigma(I)$) | 5975 ($I > 2.90\sigma(I)$) |
| No. of variables | 334 | 352 |
| $R$ | 0.048 | 0.029 |
| $Rw$ | 0.060 | 0.040 |
| GOF | 1.20 | 1.04 |
| Max Shift/erorr in final cycle | 0.043 | 0.001 |
| Max peak in diff Fourier map/eÅ$^{-3}$ | 1.20 | 0.94 |
| Min peak in diff Fourier map/eÅ$^{-3}$ | −1.22 | −1.10 |

$CH_2CH_3$); $^{13}$C NMR (75 MHz, DMSO-$d_6$) $\delta$ 157.92 (4C, *C*=O), 128.20 (4C, *C*=*C*), 62.68 (4C, O*C*H$_2$CH$_3$), 38.26 (4C, N*C*H$_3$), 13.16 (4C, OCH$_2$*C*H$_3$), carbene carbon signal was not detected; Found: C, 22.04; H, 2.61; N, 4.55; I, 42.19%. Calcd for $C_{22}H_{32}N_4I_4O_8Pd_2$: C, 22.00; H, 2.69; N, 4.67; I, 42.27%.

***cis*-[4,5-Bis(ethoxycarbonyl)-1,3-dimethylimidazolin-2-ylidene]diiodo(triphenylphosphino)palladium(II) (10).** To a solution of diiodopalladium complex **9** (305 mg, 0.25 mmol) in $CH_2Cl_2$ (23 mL), $PPh_3$ (133 mg, 0.51 mmol) was added at room temperature. The reaction mixture turned orange gradually. The mixture was stirred for 1 h at room temperature. After evaporation of the solvent, the crude product was washed with hexane (5 mL × 3) to give **10** (432 mg, 99%). Bright yellow crystals of **10** suitable for the X-ray diffraction study (vide infra) were obtained by recrystallization from $CH_2Cl_2$/hexane.

**10**: $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.67–7.61 (m, 6H, phenyl), 7.45–7.36 (m, 9H, phenyl), 4.30 (q, $J$ = 7.2 Hz, 4H, CO$_2$C*H*$_2$CH$_3$), 3.74 (s, 6H, NC*H*$_3$), 1.33 (t, $J$ = 7.2 Hz, 6H, CO$_2$CH$_2$C*H*$_3$); $^{13}$C NMR (75 MHz, DMSO-$d_6$) $\delta$ 170.89 (carbene-*C*), 157.79 (2C, *C*=O), 134.26 (br d, $J$ = 10 Hz, 6C, phenyl), 131.62 (br s, 3C, phenyl), 130.83 (d, $J$ = 51 Hz, 3C, phenyl), 128.94 (d, $J$ = 11 Hz, 6C, phenyl), 128.28 (2C, N*C*=*C*N), 62.57 (2C, O*C*H$_2$CH$_3$), 37.51 (2C, N*C*H$_3$), 13.79 (2C, OCH$_2$*C*H$_3$); $^{31}$P NMR (121 MHz, DMSO-$d_6$) $\delta$ 24.42; Found: C, 40.39; H, 3.58; N, 3.11; I, 29.45%. Calcd for $C_{29}H_{31}I_2N_2O_4PPd$: C, 40.37; H, 3.62; N, 3.25; I, 29.42%.

**X-ray Crystal Structure Analysis of *cis*-7 and 10.** The data were collected at 20 °C on a Rigaku/MSC Mercury CCD diffractometer with graphite monochromated Mo K$\alpha$ radiation ($\lambda$ = 0.71070 Å). Cell constants and an orientation matrix for data collection were obtained. All of the data were corrected for Lorentz and polarization effects. A summary of the cell parameters, data collection conditions, and refinement results are given in Table 3.

The structures were solved by heavy-atom Patterson methods[13] for *cis*-**7**, or direct methods for complex **10**, and expanded using Fourier techniques.[14] The positional parameters and thermal parameters of non-hydrogen atoms of the complexes *cis*-**7** and **10** were refined using a full-matrix least-square method. Hydrogen atoms were included but not refined. All calculations were performed using the teXsan crystallographic software package.[15]

Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposition number CCDC-610576 for *cis*-**7**; CCDC-610575 for **10**. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

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## References

1 W. A. Herrmann, M. Elison, J. Fischer, C. Köcher, G. R. J. Artus, *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2371.

2 For reviews, see: a) W. A. Herrmann, C. Köcher, *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2162. b) D. Bourissou, O. Guerret, F. P. Gabbai, G. Bertrand, *Chem. Rev.* **2000**, *100*, 39. c) W. A. Herrmann, *Angew. Chem., Int. Ed.* **2002**, *41*, 1290. d) M. C. Perry, K. Burgess, *Tetrahedron: Asymmetry* **2003**, *14*, 951. e) V. Nair, S. Bindu, V. Sreekumar, *Angew. Chem., Int. Ed.* **2004**, *43*, 5130. f) C. M. Crudden, D. P. Allen, *Coord. Chem. Rev.* **2004**, *248*, 2247. g) V. César, S. Bellemin-Laponnaz, L. H. Gade, *Chem. Soc. Rev.* **2004**, *33*, 619.

3 For recent selected papers, see: a) C. W. K. Gstöttmayr, V. P. W. Böhm, E. Herdtweck, M. Grosche, W. A. Herrmann, *Angew. Chem., Int. Ed.* **2002**, *41*, 1363. b) Y. Ma, C. Song, W. Jiang, Q. Wu, Y. Wang, X. Liu, M. B. Andrus, *Org. Lett.* **2003**, *5*, 3317. c) K. Arentsen, S. Caddick, F. G. N. Cloke, A. P. Herring, P. B. Hitchcock, *Tetrahedron Lett.* **2004**, *45*, 3511. d) O. Navarro, H. Kaur, P. Mahjoor, S. P. Nolan, *J. Org. Chem.* **2004**, *69*, 3173. e) G. Altenhoff, R. Goddard, C. W. Lehmann, F. Glorius, *J. Am. Chem. Soc.* **2004**, *126*, 15195. f) N. Hadei, E. A. B. Kantchev, C. J. O'Brien, M. G. Organ, *J. Org. Chem.* **2005**, *70*, 8503. g) C. Song, Y. Ma, Q. Chai, C. Ma, W. Jiang, M. B. Andrus, *Tetrahedron* **2005**, *61*, 7438.

4 For recent development of a novel NHC ligand bearing bulky substituents on the nitrogen atoms, see: M. Yamashita, K. Goto, T. Kawashima, *J. Am. Chem. Soc.* **2005**, *127*, 7294.

5 See for example: a) W. A. Herrmann, C. Köcher, L. J. Goossen, G. R. J. Artus, *Chem. Eur. J.* **1996**, *2*, 1627. b) W. A. Herrmann, L. J. Gooßen, M. Spiegler, *J. Organomet. Chem.* **1997**, *547*, 357. c) A. Fürstner, H. Krause, L. Ackermann, C. W. Lehmann, *Chem. Commun.* **2001**, 2240. d) A. A. Danopoulos, S. Winston, T. Gelbrich, M. B. Hursthouse, R. P. Tooze, *Chem. Commun.* **2002**, 482. e) D. Broggini, A. Togni, *Helv. Chim. Acta* **2002**, *85*, 2518. f) C. Bolm, M. Kesselgruber, G. Raabe, *Organometallics* **2002**, *21*, 707. g) T. Fujihara, Y. Obora, M. Tokunaga, H. Sato, Y. Tsuji, *Chem. Commun.* **2005**, 4526.

6 R. A. Batey, M. Shen, A. J. Lough, *Org. Lett.* **2002**, *4*, 1411.

7 a) A. J. Arduengo, III, F. Davidson, H. V. R. Dias, J. R. Goerlich, D. Khasnis, W. J. Marshall, T. K. Prakasha, *J. Am. Chem. Soc.* **1997**, *119*, 12742. b) J. Schütz, W. A. Herrmann, *J. Organomet. Chem.* **2004**, *689*, 2995. c) M. Bortenschlager, J. Schütz, D. von Preysing, O. Nuyken, W. A. Herrmann, R. Weberskirch, *J. Organomet. Chem.* **2005**, *690*, 6233.

8 A. Fürstner, L. Ackermann, B. Gabor, R. Goddard, C. R. Lehmann, R. Mynott, F. Stelzer, O. R. Thiel, *Chem. Eur. J.* **2001**, *7*, 3236.

9 N. Hadei, E. A. B. Kantchev, C. J. O'Brien, M. G. Organ, *Org. Lett.* **2005**, *7*, 1991.

10 P. M. Hay, W. R. Wilson, W. A. Denny, *Tetrahedron* **2000**, *56*, 645.

11 W. A. Herrmann, J. Fischer, K. Öfele, G. R. J. Artus, *J. Organomet. Chem.* **1997**, *530*, 259.

12 V. P. W. Böhm, W. A. Herrmann, *Chem. Eur. J.* **2000**, *6*, 1017.

13 PATTY: P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, R. de Gelder, R. Israel, J. M. M. Smits, *The DIRDIF-94 Program System, Technical Report of the Crystallography Laboratory*, University of Nijmegen, The Netherlands, **1994**.

14 DIRDIF94: P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, R. de Gelder, R. Israel, J. M. M. Smits, *The DIRDIF-94 Program System, Technical Report of the Crystallography Laboratory*, University of Nijmegen, The Netherlands, **1994**.

15 teXsan: *Crystal Structure Analysis Package*, Molecular Structure Corporation, **1985** & **1999**.