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Insertion reactions of isocyanides into the Metal-C(sp^3) bonds of ylide complexes

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ABSTRACT

The synthesis of the previously reported complexes $[Pd\{(C,C{-}CHCO_2R)_2PPh_2\}(\mu\text{-}Cl)]_2$ (R = Me (**1**), Et (**2**)) has been considerably improved by reacting the phosphonium salts $[Ph_2P(CH_2CO_2R)_2]Cl$ with $Pd(OAc)_2$. Complexes **1** and **2** react with isocyanides R'NC (R' = $C_6H_4Me_2$-2,6 (Xy), C_6H_4I-2 and ^tBu) to give complexes of the type $[Pd\{C,C\text{-}\{C(CO_2R){=}C(NHR')\}(CHCO_2R)\}PPh_2\}Cl(CNR')]$, resulting from the insertion of the unsaturated molecule in one of their Pd−C bonds and the hydrogen transfer from the methine CH to the iminobenzoyl nitrogen. These are the first insertion reactions observed in the Pd−C bond of a P-ylide complex. The crystal structure of the complex $[Pd\{C,C\text{-}\{C(CO_2Me){=}C(NHXy)\}(CHCO_2Me)\}PPh_2\}Cl(CNXy)]$ (**3**) is reported.

1. Introduction

The key step in many organic syntheses catalyzed by organometallic palladium complexes is the insertion of unsaturated molecules into the Pd−C bond they contain [1–4]. Depalladation of the complexes resulting after the insertion reaction often provides a method for obtaining organic species, including fine chemicals [5], that are inaccessible or difficult to prepare by the conventional syntheses (Scheme 1).

When these reactions occur in aryl palladacyclic complexes they lead, after depalladation, to heterocyclic compounds. Our research group has contributed to this chemistry by preparing aryl palladium complexes *ortho*-functionalized with groups such as −CHO, -C(O)Me, −C(R) = NOH, -CH=CHR, −CN, -SR, −N=C=NR, −NHC(Me)CHC(O)Me, amines etc., on which we carried out insertion reactions with various unsaturated species (CO, RNC, alkenes, alkynes, O_2, nitriles, cyanamides, carbodiimides, etc.) that allowed us to isolate amidines, amino acids, amino esters, benzacepines, benzazepinones, benzazocines, benzazocinones, dihydroquinazolinium salts, isocoumarines, isoindolinones, isoquinolines, lactams, or ureas among other heterocycles [6–14].

Although insertion reactions in Pd−C(sp^2) bonds are by far the most studied ones, since the early work by Yamamoto [15,16] a pleiad [17–24] of examples showing the insertion of CO, alkynes or RNC molecules into the Pd−C(sp^3) bond of alkyl complexes have been reported [25]. However, none of them involves the Pd−C(sp^3) bond of an *P*-ylide complex, although two related examples have been reported: (1) the insertion of cyclohexyl isocyanide into the Pd−N bond of a *N*-trimethylsilyliminotriphenylphosphorane complex [26], and (2) the insertion of benzyl isocyanide into the Zr−C(ylide) or Hf−C(ylide) bond of complexes $[M(\eta^5\text{-}C_5H_5)_2(Ph)(CHPPh_3)]$ (M = Zr, Hf) [27].

It is relatively easy to understand why these reactions are so rare by taking into account that *P*-ylide complexes are in fact metalated phosphonium salts. According to the general accepted mechanism for these processes, provided that a coordination site is available in the [M]−R complex for the unsaturated molecule to coordinate to the metal, its migratory insertion into the Pd−C bond is facilitated by the greater electrophilic character of the carbon atom in the unsaturated species and the higher nucleophilicity of the R group [17,28]. Although cationic complexes are found to be better substrates for insertion reactions, it has been shown that it is their

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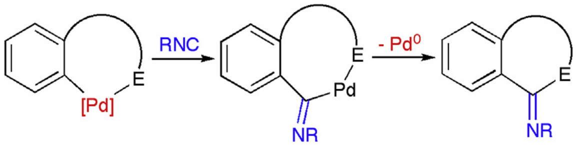


Scheme 1. Synthesis of iminoacyl complexes from insertion of isocyanides into the Pd–C bonds of palladacycles.

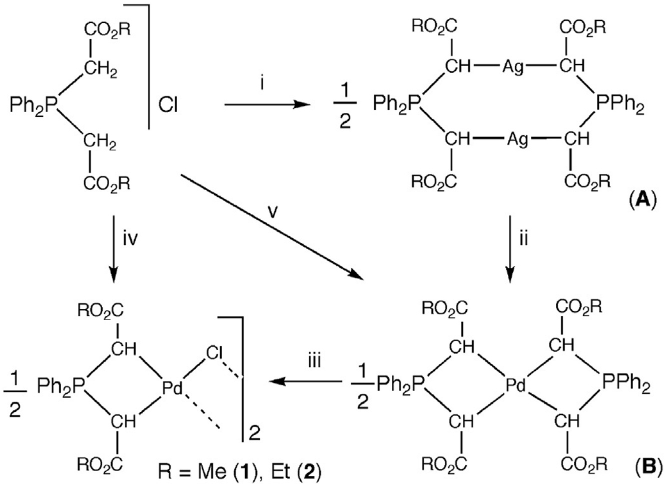
enhanced willingness to coordinate the unsaturated molecule what determines the reaction feasibility [29]; in fact, a positive charge at the metal center would diminish the nucleophilicity of the migrating R group and thus disfavor the insertion reaction. According to the above arguments it seems apparent that ylide complexes are very bad candidates for insertion reactions. We wondered if the high strain in some four-membered palladacycles that we had previously reported [30], derived from the phosphonium salt $[Ph_2P(CH_2CO_2R)_2]Cl$, would facilitate the insertions. We expected that the discovery of a new type of insertion reaction, where the novelty refers not to the *inserted molecule* but to the *complex* in which it inserts, could help to establish the limits for insertion reactions and/or open the way to new syntheses of potential interest.

In this paper we report the insertion reactions of isocyanides RNC [R = Xy ($C_6H_3Me_2$-2,6), Ar (C_6H_4I-2), ^{t}Bu] into the Pd–C (sp^3) bond of complexes $[Pd\{(C,C–CHCO_2R)_2PPh_2\}(\mu\text{-}Cl)]_2$ (R = Me, Et) leading to the first iminobenzoyl species derived from a phosphorus ylide complex of palladium (II), along with various failed attempts to insert other unsaturated molecules. The crystal structure of one of the isocyanide insertion products is also reported.

2. Results and discussion

2.1. Synthesis

The synthesis of complexes $[Pd\{(C,C–CHCO_2R)_2PPh_2\}(\mu\text{-}Cl)]_2$ [R = Me (**1**), Et (**2**)] was previously reported by us [30] in three steps (Scheme 2): (i) the reaction of the phosphonium salts $[Ph_2P(CH_2CO_2R)_2]Cl$ (R = Me, Et) with Ag_2CO_3 to give the silver complex **A**, (ii) the ylide transmetalation reaction with $[PdCl_2(NCPh)_2]$ to give **B,** and (iii) the reaction with $PdCl_2$ to afford complexes **1** or **2** with overall yields of 66 or 55%, respectively (Scheme 2). Here we report that the one-pot reaction of the same phosphonium salts with $Pd(OAc)_2$ (1:1, in acetone, at room temperature for 12 h) is the most straightforward synthesis for complexes **1** and **2,** which are isolated in almost quantitative yields (>95%). When the reaction leading to **1** was studied by ^{1}H NMR we found that, after 3–4 h, the phosphonium chloride, and the complexes **B** and **1** were present in the reaction mixture evidencing that the reaction occurs through the intermediacy of **B** (Scheme 2).



i: Ag_2CO_3, - AgCl, - CO_2, - H_2O; ii: $[PdCl_2(NCPh)_2]$, - 2 AgCl, - 2 PhCN; iii: 1/2 $PdCl_2$; iv: $Pd(OAc)_2$, - 2 AcOH; v: $Pd(OAc)_2$, - 2 AcOH, - 1/2 $PdCl_2$

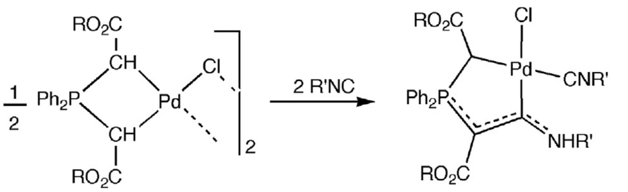
Scheme 2. Improved synthesis of palladium (II) ylide-complexes **1** and **2**.

Complexes **1** and **2** reacted with isocyanides R'NC [R' = Xy ($C_6H_3Me_2$-2,6), C_6H_4I-2, ^{t}Bu] to give complexes **3**–**8,** resulting from the insertion of the unsaturated molecule in one of their C_{ylide}–Pd bonds and the migration of the CH proton to the nitrogen atom in the resulting iminobenzoyl ligand (Scheme 3) as confirmed by spectral data and the X ray crystal structure of complex **3**.

The reactions of **1** and **2** with various isocyanides in CH_2Cl_2 were carried out in 1:4 molar ratio and the resulting complexes were isolated in 67–97% yield by precipitation with Et_2O (**4**–**6**), a 1:1 mixture of Et_2O/*n*-hexane (**3**, **7**) or neat *n*-hexane (**8**), depending on their solubility (See the Experimental Section). Complex **4** needed recrystallization, **7** required repeatedly washing with Et_2O, and **4** and **8** additional drying in an oven. In spite of drying **4** in an oven al 70 °C for 2 h, it was isolated as the solvate **4**$\cdot 0.1Et_2O\cdot 0.2CH_2Cl_2$ as proved by its elemental C, H and N analyses and confirmed by its ^{1}H NMR spectrum. We have previously reported that, upon heating, the oxidative addition to Pd(II) of the C–I bond present in the iminobenzoyl complex $[Pd\{C,N–C(=NC_6H_4I\text{-}2)C_6H_4NCHO\text{-}2\}I(N^\wedge N)]$ ($N^\wedge N$ = 4,4′-di-*tert*-butyl-2,2′-bipyridine) occurs to give a stable Pd(IV) complex [31]. Based on this result, the reaction leading to **4** was attempted also by refluxing the reaction mixture in $CHCl_3$ or toluene for 6 or 3 h, respectively, with the aim to promote a similar oxidative addition process but, unfortunately, decomposition was observed in this case and, after removing the Pd (0), the ^{1}H NMR of the solution proved it to contain the starting material **4**.

In an attempt to prepare the “only-coordination" complex $[Pd\{(C,C–CHCO_2Me)_2PPh_2\}Cl(CN^tBu)]$, which we expected that could give the dinuclear “only insertion” derivative $[Pd\{C,C\text{-}\{C(CO_2R)=C(NHR')\}(CHCO_2R')\}PPh_2\}(\mu\text{-}Cl)]_2$ upon migratory insertion of the isocyanide, an equimolar amount of ^{t}BuNC was slowly added to a solution of **1**, and the reaction mixture was stirred for 10 min at 0 °C. Disappointingly, the reaction mixture was shown by ^{1}H NMR to contain complexes **1** and **4** along with a small amount of the target compound, the “only-coordination" complex.

We have also attempted the insertion of various other unsaturated molecules. In the reaction of **1** with CO (1 atm, 3 days in CH_2Cl_2 at room temperature) abundant decomposition was observed and 41% of **1** was recovered from the solution. When the reaction was carried out in the presence of 1 equiv TlOTf a mixture was obtained containing **1** and $[Ph_2P(CH_2CO_2Me)_2]OTf$ among other unidentified minor components. Attempts to insert dimethyl



R = Me, R' = Xy (**3**), C_6H_4I-2 (**4**), ^{t}Bu (**5**);
R = Et, R' = Xy (**6**), C_6H_4I-2 (**7**), ^{t}Bu (**8**)

Scheme 3. Synthesis of iminoacyl-complexes **4**–**8**.

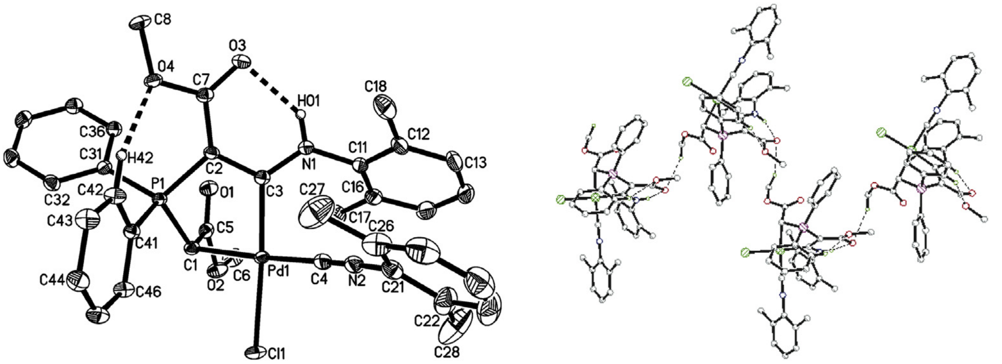


Fig. 1. Left: Thermal ellipsoid plot at the 50% probability level for **3**. Selected bond distances (Å) and angles (°): Pd(1)–C(1) 2.1103 (15), Pd(1)–C(3) 1.9859 (15), Pd(1)–C(4) 1.9809 (17), Pd(1)–Cl(1) 2.3714 (4), C(2)–C(3) 1.409 (2), C(1)–P(1) 1.7817 (15), C(2)–P(1) 1.7538 (15), C(3)–N(1) 1.337 (2); C(4)-Pd(1)-C(3) 92.17 (6), C(3)-Pd(1)-C(1) 84.11 (6), C(4)-Pd(1)-Cl(1) 91.81 (5), C(1)-Pd(1)-Cl(1) 91.82 (4), C(7)-C(2)-P(1) 125.72 (11), C(3)-C(2)-C(7) 123.00 (13), C(3)-C(2)-P(1) 111.18 (11), N(1)-C(3)-C(2) 120.10 (13), N(1)-C(3)-Pd(1) 124.52 (11), C(2)-C(3)-Pd(1) 115.30 (11). Right: Hydrogen bonds in **3**: [N (1)–H(01)···O(3): N–H (01) = 0.86 (2) Å, H(01)···O(3) = 1.98 (2) Å, N(1)-H(01)-O(3) = 140.2 (19)°], [C (42)–H(42) … O(4): C(42)–H(42) = 0.95 Å, H(42)···O(4) = 2.54 Å, C(42)-H(42)-O (4) = 144.8°].

acetylenedicarboxylate (DMAD) in **1**, under different molar ratios, temperatures and reaction times, led, in all cases, to recover **1** in ca. 70%. No reaction was observed between **1** and *p*-tolylisothiocyanate or *p*-tolylcarbodiimide (1:2 or 1:4, refluxing in $CHCl_3$ for 3 h).

2.2. *X-ray crystal structure of 3*

The palladium atom is bonded to three carbon and one chlorine atoms in a distorted square planar environment (sum of angles around Pd, 359.9°) (Fig. 1, left), the C(3)–Pd(1)–C(1) bond angle [84.11 (6)°] deviating from the ideal value because of the small bite of the chelating ligand that adopts an envelop disposition with the phosphorus atom at the vertex of the closing flap. Although the C(3)–N(1) bond distance is typical for single $C(sp^2)$–N (three coordinated) [32] bonds, suggesting some prevalence of the resonance form P(1)–C(2) = C(3)–N (1) (**A** in Fig. 1), the C(2)–C(3) and C(2)–P(1) bond lengths are intermediate between those corresponding to single and double bonds [32,33] suggesting some contribution of the resonance form P(1)=C(2)–C(3)=N(1) (**B**). Two of the bond angles around C(2) and C(3) are ca. 120°, but the five membered heterocycle Pd–C(1)–P(1)–C(2)–C(3) imposes the third angle to be narrower (111-115°).

Intramolecular C–H···O and N–H···O hydrogen bonds form with the participation of one the phenyl groups and the OMe group on C(7) or with N(1) and the C=O oxygen of the same carboxylate group. Additionally, zigzag chains parallel to the *c* axis form by C–H···O hydrogen bonding between the CH of a OMe group and one C=O oxygen in other molecule (Fig. 1, right).

2.3. *NMR spectra*

The existence of two chiral centers in complexes **1** and **2** is responsible for the presence of different diastereoisomers in their ^1H NMR spectra, but only one such center exists in complexes **3**–**7** and a single set of resonances is observed in their spectra for both indistinguishable enantiomers. APT, HMBC and HMQC experiments have been carried out in some cases in order to assign the signals unequivocally. In the ^1H NMR spectra of complexes **3**–**8** two resonances are assigned to the carboxylate methyl protons in the ranges of 3.2–3.5 (CO_2Me) or 0.6–1.10 (CO_2Et) ppm. The methine PC*H* and N*H* protons give a resonance at 3.6–3.8 and 10.6–11.9 (broad) ppm, respectively. Both appear at lower frequency in complexes with the ^{t}Bu group, more electron-donating than $C_6H_3Me_2$-2,6 (Xy) or C_6H_4I-2. In complexes with XyNC, three resonances are observed for the Me (Xy) protons, one of them assigned to the Xy group in the XyNC ligand (Xy^c) and the two others, of three protons each, corresponding to the Xy group in the iminobenzoyl fragment (Xy^i) which evidences its restricted rotation around the C–N bond, probably because of both steric and electronic reasons (the superscripts c and i refer to coordinated and inserted XyNC, respectively).

In the ^{13}C NMR spectra, the chiral methine carbon gives a doublet towards 30 ppm with a J_{CP} of ca. 60 Hz. The ^{13}C nuclei in the CO_2R groups appear at around 50 (CO_2*Me*) or 51 (CO_2CH_2*Me*), 55 (*C*H_2Me), 165 and 170–175 (*C*O_2, the former being a doublet with $^2J_{CP} = 17$ Hz, and the later a singlet). The resonances of the $Ph_2PC^2 = C^3$(NHR)Pd fragment give doublets at ca. 90 ppm (C^2, J_{CP} from 120 to 170 Hz) and 200 (C^3, J_{CP} 40 Hz approx.) ppm. Many of the resonances of the C_6H_4I-2, Xy^c and Xy^i groups could not be unequivocally assigned in spite of the correlation experiments because of their overlapping. The absence of some quaternary carbon resonances in the spectrum of **3** is justified since no long acquisition times can be allowed because of the scarce stability of the compound in solution, evidenced by the presence of some impurities that are absent in the ^1H spectrum measured on a freshly prepared solution.

The ^{31}P NMR spectra show a single resonance in the 23–30 ppm region. As above-mentioned, this resonance appears at lower frequency in the spectra of complexes **5** and **7** containing ^{t}Bu groups.

2.4. *IR spectra*

The solid state spectra of complexes **3**–**8** show two ν_{asym} (CO_2) bands (in the ranges of 1686–1696 and 1631–1650 cm^{-1}) [34]. The almost invariable position of the former suggests it to be that corresponding to the CO_2R group *trans* to Cl, while the other would modify its position depending on the nature of the isocyanide ligand *trans* to it. Additionally, two ν(CN) bands for the coordinated and the inserted isocyanide (between 2178–2198 and 1515–1555 cm^{-1}, respectively) and one ν(PdCl) band at around 290 cm^{-1} are observed. The low frequency of the later reveals the great *trans* influence of the carbon-donor ligand in *trans*, confirmed by the crystal structure of complex **3**.

3. Conclusion

We report an improved synthesis for complexes $[Pd\{(C,C\text{–}CHCO_2R)_2PPh_2\}(\mu\text{-}Cl)]_2$ (R = Me, Et), previously prepared by us, and their reaction with some isocyanides to give complexes of the type $[Pd\{C,C\text{-}\{C(CO_2R){=}C(NHR')\}(CHCO_2R)\}PPh_2\}Cl(CNR')]$

which result from the first insertion reactions observed in the M – C bond of a ylide complex of any metal. The crystal structure of the complex [Pd{*C,C*-{C(CO_2Me)=C(NHXy)}($CHCO_2Me$)}PPh_2}Cl(CNXy)] is reported.

4. Experimental section

4.1. General procedures

When not stated, the reactions were carried out without precautions to exclude light or atmospheric oxygen or moisture. Melting points are uncorrected. IR spectra were recorded using Nujol mulls between polyethylene sheets. NMR spectra were recorded in 200, 300 or 400 MHz Varian spectrometers. The NMR assignments were performed, in some cases, with the help of APT, HMBC and HMQC experiments. The atom-numbering scheme used in the Experimental Section is shown for complexes **3**–**8** (Scheme 2). [$Pd_3(OAc)_6$] (also denoted as $Pd(OAc)_2$), $ClCH_2CO_2R$ (R = Me, Et), ^{t}BuNC, and XyNC (Xy = 2,6-Me_2-C_6H_3) were obtained from commercial sources and used as received. The phosphonium salts [$Ph_2P(CH_2CO_2R)_2$]Cl (R = Me, Et) were obtained by reacting $ClCH_2CO_2R$ with $PHPh_2$ as previously reported by us [35]. The isocyanide 2-I-C_6H_4NC (ArNC) was prepared according to the procedure reported by Lygin and de Meijere [36].

4.2. Synthesis of palladium(II) complexes

[Pd{(*C,C*–$CHCO_2R$)$_2PPh_2$}(μ-Cl)]$_2$ (R = Me (1), Et (2)]. A suspension containing equimolar amounts of the appropriate phosphonium salt [$Ph_2P(CH_2CO_2Me)_2$]Cl and $Pd(OAc)_2$ was stirred in CH_2Cl_2 for 12 h at room temperature. In the case of R = Me, the resulting suspension was filtered, and the solid was collected, washed with Et_2O (2 × 5 mL) and air-dried to give **1** (95% yield). For R = Et, the resulting suspension was concentrated to half the volume and filtered. The solid was collected and treated as above to give **2** (97%). Both complexes were pale yellow solids and their spectroscopic data coincided with those previously reported [30].

[Pd{*C,C*-{C(CO_2R)=C(NHR′)}($CHCO_2R$)}PPh_2}Cl(CNR′)] [R = Me, R’ = $C_6H_3Me_2$-2,6, Xy (3), C_6H_4I-2 (4), ^{t}Bu (5); R = Et, R’ = Xy (6), C_6H_4I-2 (7), ^{t}Bu (8)]. To a solution of **1** (for **3**, 105 mg, 0.22 mmol; for **4**, 155 mg, 0.32 mmol; for **5**, 104 mg, 0.22 mmol) or **2** (for **6**, 95 mg, 0.19 mmol; for **7**, 90 mg, 0.18 mmol; for **8**, 121.5 mg, 0.24 mmol) in CH_2Cl_2 (10 mL, for **6** at 0 °C) was added the appropriate R'NC (for **3**, R’ = Xy, 59 mg, 0.45 mmol; for **4**, R’ = C_6H_4I-2, 155 mg, 0.68 mmol; for **5**, R’ = ^{t}Bu, 50 μL, 0.44 mmol; for **6**, R’ = Xy, 57 mg, 0.43 mmol; for **7**, R’ = C_6H_4I-2, 83 mg, 0.36 mmol; for **8**, R’ = ^{t}Bu, 55 μL, 0.49 mmol). After stirring for 12 h (1 h for **5** and **8** or 4 h for **7**) the solution was concentrated under vacuum (1 mL) and Et_2O (20 mL), a 1:1 mixture of Et_2O/*n*-hexane (20 mL, **3** or **7**), or *n*-hexane (20 mL, **8**) was added. The suspension was filtered, and the solid was collected and washed with Et_2O (2 × 5 mL), or a 1:1 mixture of Et_2O/*n*-hexane (2 × 5 mL, **3**), or *n*-hexane (2 × 5 mL, **8**) and air-dried. Additionally **4**, was recrystallized from CH_2Cl_2 and Et_2O and dried in an oven at 70 °C for 2 h, yielding **4**·0.1Et_2O·0.2CH_2Cl_2 as confirmed by the ^{1}H NMR spectrum and elemental analysis; **8** was dried at 70 °C for 1 h. Complexes **3**–**8** were off-white or very pale-yellow solids.

3. Yield: 129 mg, 0.18 mmol, 80%. Mp: 134 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 2.12 (s, 6 H, Me, Xy^c), 2.26 (s, 3 H, Me, Xy^i), 2.65 (s, 3 H, Me, Xy^i), 3.49 (s, 3 H, CO_2Me), 3.51 (s, 3 H, CO_2Me), 3.80 (s, 1 H, CH), 6.63 (d, 1 H, *m*-H, Xy^i, $^3J_{HH}$ = 7 Hz), 6.67 (t, 1 H, *p*-H, Xy^i, $^3J_{HH}$ = 7 Hz), 6.94 (d, 2 H, *m*-H, Xy^c, $^3J_{HH}$ = 8 Hz), 7.03 (d, 1 H, *m*-H, Xy^i, $^3J_{HH}$ = 7 Hz), 7.10 (t, 1 H, *p*-H, Xy^c, $^3J_{HH}$ = 7 Hz), 7.41–7.45 (m, 2 H, *o*-H, Ph), 7.51–7.63 (m, 4 H, *o* + *p*-H, Ph), 7.67–7.73 (m, 2 H, *m*-H, Ph), 8.21–8.27 (m, 2 H, *m*-H, Ph), 11.65 (br s, 1 H, NH). ^{13}C{^{1}H}-APT ($CDCl_3$, 100 MHz, 25 °C): δ 18.6 (s, Me, Xy^c), 19.3 (s, Me, Xy^i), 19.8 (s, Me, Xy^i), 30.0 (d, CH, J_{CP} = 61 Hz), 50.1 (s, CO_2*Me*), 51.3 (s, CO_2*Me*), 87.5 (d, *C*CO_2Me, J_{CP} = 120 Hz), 126.9 (s, *p*-CH, Xy^i), 127.36 (s, *m*-CH, Xy^i), 127.42 (s, *m*-CH, Xy^c), 127.85 (d, *o*-CH, Ph, $^2J_{CP}$ = 12 Hz), 127.90 (d, *p*-C, Ph, J_{CP} = 82 Hz), 128.1 (d, *i*-C, Ph, J_{CP} = 70 Hz), 128.9 (d, *o*-CH, Ph, $^2J_{CP}$ = 12 Hz), 129.0 (s, *p*-CH of Xy^c + *m*-CH of Xy^i), 131.8 (d, *p*-CH, Ph, $^4J_{CP}$ = 2 Hz), 132.2 (d, *p*-CH, Ph, $^4J_{CP}$ = 2 Hz), 132.9 (d, *m*-CH, Ph, $^3J_{CP}$ = 9 Hz), 133.0 (d, *m*-CH, Ph, $^3J_{CP}$ = 10 Hz), 133.3 (s, *o*-C, Xy^i), 134.6 (s, *o*-C, Xy^c), 135.0 (s, *o*-C, Xy^i), 141.7 (s, *i*-C, Xy^i), 145.4 (s, *C*≡NXy), 166.5 (d, *C*O_2Me, $^2J_{CP}$ = 17 Hz), 172.4 (s, *C*O_2Me), 198.8 (d, *C*═N, $^2J_{CP}$ = 36 Hz). ^{31}P{^{1}H} NMR ($CDCl_3$, 121 MHz, 25 °C): δ 28.3. IR (cm^{-1}): *ν*(C≡N), 2178, ν$_{asym}$ (CO_2), 1690, 1678; *ν*(C···C + C···N), 1521; *ν*(PdCl), 292. Analysis Calcd for $C_{36}H_{36}ClN_2O_4PPd$: C, 58.95; H, 4.95; N, 3.82. Found: C, 58.84; H, 4.96; N, 3.76.

4·0.1Et_2O·0.2CH_2Cl_2: Yield: 280 mg, 0.29 mmol, 92%. Mp: 170 °C (dec). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 1.20 (t, 0.6H, Et_2O, $^3J_{HH}$ = 7 Hz), 3.47 (q, 0.4H, Et_2O, $^3J_{HH}$ = 7 Hz), 3.50 (s, 3 H, CO_2Me), 3.55 (s, 3 H, CO_2Me), 3.73 (d, 1 H, CH, $^2J_{HP}$ = 1 Hz), 5.30 (s, 0.4H, CH_2Cl_2), 6.78 (td, 1 H, Ar, $^3J_{HH}$ = 8, $^4J_{HH}$ = 1 Hz), 7.02–7.07 (m, 2 H, Ar), 7.26 (td, 1 H, Ar, $^3J_{HH}$ = 8, $^4J_{HH}$ = 1 Hz), 7.40–7.85 (m, 8 H, Ph + 2 H, Ar), 7.73 (dd, 1 H, Ar, $^3J_{HH}$ = 8, $^4J_{HH}$ = 1 Hz), 8.14 (dd, 1 H, Ar, $^3J_{HH}$ = 8, $^4J_{HH}$ = 1 Hz), 8.14–8.20 (m, 2 H, Ar), 11.88 (s, br, 1 H, NH). ^{13}C{^{1}H}-APT NMR ($CDCl_3$, 75 MHz, 25 °C): δ 15.2 (s, Me, Et_2O), 29.9 (d, CH, J_{CP} = 58 Hz), 50.5 (s, CO_2*Me*), 51.5 (s, CO_2*Me*), 53.5 (s, CH_2Cl_2), 65.8 (s, CH_2, Et_2O), 90.5 (d, *C*CO_2Et, J_{CP} = 140 Hz), 92.0 (s, *C*—I), 94.1(s, *C*—I), 126.6 (s, CH, Ar), 127.1 (s, CH, Ar), 127.9 (s, CH, Ar), 128.0 (s, CH, Ar), 128.2 (s, CH, Ph), 128.4 (s, CH, Ph), 128.9 (s, CH, Ph), 129.0 (s, CH, Ph), 129.4 (s, CH, Ph), 130.9 (s, CH, Ar), 132.1 (s, CH, Ph), 132.5 (s, CH, Ph), 132.7 (s, CH, Ph), 132.8 (s, CH, Ar + CH, Ph), 132.9 (s, CH, Ph), 138.6 (s, CH, Ar), 139.4 (s, CH, Ar), 145.7 (s, *C*≡NAr), 166.0 (d, *C*O_2Me, $^2J_{CP}$ = 16 Hz), 172.7 (s, *C*O_2Me), 195.8 (d, =*C*NHAr, $^2J_{CP}$ = 36 Hz). Most quaternary carbon resonances are not observed. ^{31}P{^{1}H} NMR ($CDCl_3$, 121 MHz, 25 °C): δ 29.5. IR (cm^{-1}): *ν*(C≡N), 2183, ν$_{asym}$ (CO_2), 1696, 1650; *ν*(C···C + C···N), 1515; *ν*(PdCl), 287. Analysis Calcd for $C_{32.6}H_{27.4}Cl_{1.4}I_2N_2O_{4.1}PPd$: C, 41.06; H, 2.90; N, 2.94. Found: C, 40.85; H, 2.82; N, 3.01.

5: Yield: 102 mg, 0.16 mmol, 72%. Mp: 194 °C (dec). ^{1}H NMR ($CDCl_3$, 200 MHz, 25 °C): δ 1.41 (s, 9 H, Me, ^{t}Bu), 1.57 (s, 9 H, Me, ^{t}Bu), 3.27 (s, 3 H, CO_2Me), 3.47 (s, 3 H, CO_2Me), 3.67 (s, 1 H, CH), 7.34–7.44 (m, 2 H, *m*-H, Ph), 7.54–7.58 (m, 6 H: 2 H, m-H, Ph + 2 H, *p*-H, Ph + 2 H, *o*-H, Ph), 8.09–8.19 (m, 2 H, *o*-H, Ph), 10.59 (br s, 1 H, NH). ^{13}C{^{1}H}-APT NMR ($CDCl_3$, 50 MHz, 25 °C): δ 28.2 (d, CHPd, J_{CP} = 63 Hz), 29.7 (s, Me, ^{t}Bu), 30.9 (s, Me, ^{t}Bu), 49.5 (s, CO_2*Me*), 51.1 (s, CO_2*Me*), 55.1 (s, *C*Me_3), 57.3 (s, *C*Me_3), 127.8 (d, *m*-CH, Ph, $^3J_{CP}$ = 12 Hz), 128.2 (d, *i*-C, Ph, J_{CP} = 90 Hz), 128.7 (d, *m*-CH, Ph, $^3J_{CP}$ = 12 Hz), 131.5 (d, *p*-CH, Ph, $^3J_{CP}$ = 3 Hz), 132.0 (d, *p*-CH, Ph, $^3J_{CP}$ = 3 Hz), 132.7 (d, *o*-CH, Ph, $^3J_{CP}$ = 10 Hz), 132.9 (d, *o*-CH, Ph, $^3J_{CP}$ = 10 Hz), 166.2 (d, *C*O_2Me, $^2J_{CP}$ = 18 Hz), 172.5 (*C*O_2Me), 197.8 (d, *C*NH^{t}Bu, $^2J_{CP}$ = 34 Hz). ^{31}P{^{1}H} NMR ($CDCl_3$, 121 MHz, 25 °C): δ 23.0. IR (cm^{-1}): *ν*(C≡N), 2194; ν$_{asym}$ (CO_2), 1689, 1635; *ν*(C···C + C···N), 1532; *ν*(PdCl), 291. Analysis Calcd for $C_{28}H_{36}ClN_2O_4PPd$: C, 52.76; H, 5.69; N, 4.39. Found: C, 52.73; H, 5.62; N, 4.43.

6: Yield: 141 mg, 0.19 mmol, 97%. Mp: 134 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C): δ 0.86 (t, 3 H, Me, Et, $^3J_{HH}$ = 7 Hz), 1.07 (t, 3 H, Me, Et, $^3J_{HH}$ = 7 Hz), 2.11 (s, 6 H, Me, Xy^c), 2.24 (s, 3 H, Me, Xy^i), 2.68 (s, 3 H, Me, Xy^i), 3.74 (s, 1 H, $CHCO_2Et$), 3.94–4.01 (m, 4 H, CH_2, Et), 6.62–6.66 (m, 2 H, Xy), 6.93 (d, 2 H, *m*-Xy^c, $^3J_{HH}$ = 8 Hz), 7.02–7.11 (m, 2 H, Xy), 7.38–7.44 (m, 2 H, *m*-H, Ph), 7.49–7.62 (m, 4 H: 2 H, *m*-H, Ph + 2 H, *p*-H, Ph), 7.68–7.74 (m, 2 H, *o*-H, Ph), 8.21–8.28 (m, 2 H, *o*-H, Ph), 11.68 (br s, NH). ^{13}C{^{1}H}-APT NMR ($CDCl_3$, 75 MHz, 25 °C): δ 13.8 (s, Me), 14.3 (s, Me), 18.6 (s, Me, Xy^c), 19.3 (s, Me, Xy^i), 19.9 (s, Me, Xy^i), 30.5 (d, $CHCO_2Et$, J_{CP} = 60 Hz), 59.2 (s, CH_2), 53.0 (s, CH_2), 88.3 (d, *C*CO_2Et, J_{CP} = 143 Hz), 126.8 (s, *m*-CH, Xy^i), 127.3 (s, *m*-CH, Xy^i), 127.4 (s, *m*-CH, Xy^c), 127.8 (d, *m*-CH, Ph, $^3J_{CP}$ = 12 Hz), 128.0 (d, *i*-C, Ph, J_{CP} = 78 Hz), 128.8 (d, *m*-CH, Ph, $^{3}J_{CP}$ = 12 Hz), 131.7 (d, *p*-CH, Ph, $^{4}J_{CP}$ = 3 Hz), 132.1 (d, *p*-CH, Ph, $^{4}J_{CP}$ = 3 Hz), 132.9 (d, *o*-CH, Ph, $^{2}J_{CP}$ = 15 Hz), 133.0 (d, *o*-CH, Ph, $^{2}J_{CP}$ = 16 Hz), 133.2 (s, *o*-C, Xy^{i}), 134.6 (s, *o*-C, Xy^{c}), 135.0 (s, *o*-C, Xy^{i}), 141.7 (s, *i*-C, Xy^{i}), 166.0 (s, *C*≡NXy^{i}), 166.2 (d, *C*O_2Me, $^{2}J_{CP}$ = 17 Hz), 171.9 (s, *C*O_2Me), 198.6 (d, *C*=NXy, $^{2}J_{CP}$ = 36 Hz). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 121 MHz, 25 °C): δ 28.7. IR (cm^{-1}): ν(C≡N), 2175; ν_{asym} (CO_2), 1691, 1634; ν(C···C + C···N), 1525; ν(PdCl), 288. Analysis Calc for $C_{38}H_{40}ClN_2O_4PPd$: C, 59.93; H, 5.29; N, 3.68. Found: C, 59.95; H, 5.31; N, 3.88.

7: Yield: 115 mg, 0.12 mmol, 67%. Mp: 168 °C (dec). ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C): δ 0.85 (t, 3 H, Me, $^{3}J_{HH}$ = 7 Hz), 1.08 (t, 3 H, Me, $^{3}J_{HH}$ = 7 Hz), 3.68 (d, 1 H, CH, $^{2}J_{CP}$ = 1.2 Hz), 3.95–4.06 (m, 4 H, CH_2, Et), 6.78 (td, 1H, Ar, $^{3}J_{HH}$ = 8, $^{4}J_{HH}$ = 1 Hz), 7.02–7.07 (m, 2 H, Ar), 7.26 (td, 1H, Ar, $^{3}J_{HH}$ = 8, $^{4}J_{HH}$ = 1 Hz), 7.39–7.77 (various m, 9 H: 8 H, Ph + 1 H, Ar), 7.49 (dd, 1 H, Ar, $^{3}J_{HH}$ = 8, $^{4}J_{HH}$ = 1 Hz), 7.73 (dd, 1 H, Ar, $^{3}J_{HH}$ = 8, $^{4}J_{HH}$ = 1 Hz), 8.18 (dd, 1 H, Ar, $^{3}J_{HH}$ = 8, $^{4}J_{HH}$ = 1 Hz), 8.19–8.26 (m, 2 H, Ph), 11.94 (br s, 1 H, NH). $^{13}C\{^{1}H\}$-APT NMR ($CDCl_3$, 50 MHz, 25 °C): δ 13.9 (s, CO_2Me), 14.4 (s, CO_2Me), 30.6 (d, *C*HCO_2Et, $^{2}J_{PH}$ = 57 Hz), 59.6 (s, CH_2, Et), 60.3 (s, CH_2, Et), 91.0 (d, *C*CO_2Et, J_{CP} = 141 Hz), 92.0 (s, *C*–I), 94.1(s, *C*–I), 126.4 (s, CH, Ar), 127.0 (s, CH, Ar), 127.99 (s, CH, Ar), 128.05 (s, CH, Ar), 128.1 (s, CH, Ph), 128.4 (s, CH, Ph), 128.9 (s, CH, Ph), 129.0 (s, CH, Ph), 129.3 (s, CH, Ph), 130.9 (s, CH, Ar), 132.0 (s, CH, Ph), 132.5 (s, CH, Ph), 132.8 (2 CH, Ph), 132.9 (CH, Ar + CH, Ph), 138.6 (s, CH, Ar), 139.6 (s, CH, Ar), 145.8 (s, *C*≡NAr, Ph), 166.0 (d, *C*O_2Et, $^{2}J_{CP}$ = 17 Hz), 172.2 (s, *C*O_2Et), 196.2 (d, =*C*NHAr, $^{2}J_{CP}$ = 37 Hz). The quaternary carbon resonances observed at δ 126.9, 127.5, 127.86, 130.5 and 145.2 could not be assigned. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 121 MHz, 25 °C): δ 22.5. IR (cm^{-1}): ν(C≡N), 2195; ν_{asym} (CO_2), 1692, 1652; ν(C···C + C···N), 1570, 1513; ν(PdCl), 305. Analysis Calc for $C_{34}H_{30}ClI_2N_2O_4$ PPd: C, 42.66; H, 3.16; N, 2.93. Found: 42.68; H, 3.19; N, 2.99.

8: Yield: 120 mg, 0.18 mmol, 75%. Mp: 145 °C. ^{1}H NMR ($CDCl_3$, 200 MHz, 25 °C): δ 0.69 (t, 3 H, Me, $^{3}J_{HH}$ = 7 Hz), 1.10 (t, 3 H, Me, $^{3}J_{HH}$ = 7 Hz), 1.42 (s, 9 H, Me, ^{t}Bu), 1.58 (s, 9 H, Me, ^{t}Bu), 3.65 (d, 1 H, CH, $^{2}J_{CP}$ = 2 Hz), 3.74–3.85 (m, 2 H, CH_2, Et), 3.90–3.98 (m, 2 H, CH_2, Et), 7.26–7.36 (m, 2 H, Ph), 7.41–7.45 (m, 1 H, Ph), 7.50–7.63 (m, 5 H, Ph), 8.15–8.21 (m, 2 H, Ph), 10.62 (br s, 1 H, NH). $^{13}C\{^{1}H\}$-APT NMR ($CDCl_3$, 50 MHz, 25 °C): δ 13.7 (s, Me), 14.4 (s, Me), 28.9 (d, *C*HCO_2Et, $^{2}J_{PH}$ = 61 Hz), 29.8 (s, CH_2, Et), 30.9 (s, CH_2, Et), 55.0 (s, C, ^{t}Bu), 58.4 (d, CH_2, Et, J_{CH} = 29 Hz), 59.9 (d, CH_2, Et, J_{CP} = 29 Hz), 82.5 (s, *C*CO_2Et), 127.8 (d, *o*-CH, Ph, $^{3}J_{CP}$ = 12 Hz), 128.6 (d, *o*-CH, Ph, $^{3}J_{CP}$ = 12 Hz), 129.9 (d, *i*-C, Ph, J_{CP} = 83 Hz), 131.4 (d, *p*-CH, Ph, $^{4}J_{CP}$ = 3 Hz), 132.0 (d, *p*-CH, Ph, $^{4}J_{CP}$ = 3 Hz), 132.8 (d, *m*-CH, Ph, $^{3}J_{CP}$ = 9 Hz), 132.9 (d, *m*-CH, Ph, $^{3}J_{CP}$ = 9 Hz), 165.9 (*C*O_2Et), 166.1 (d, *C*O_2Et, $^{2}J_{CP}$ = 17 Hz), 172.1 (s, *C*O_2Et), 197.7 (d, CNH^{t}Bu, $^{2}J_{PH}$ = 34 Hz). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 121 MHz, 25 °C): δ 22.9. IR (cm^{-1}): ν(C≡N), 2198; ν_{asym} (CO_2), 1686, 1632; ν(C···C + C···N), 1554; ν(PdCl), 292. Analysis Calcd for $C_{30}H_{40}ClN_2O_4PPd$: C, 54.14; H, 6.02; N, 4.21. Found: C, 53.82; H, 5.91; N, 4.17.

4.3. *X-ray structure determinations of complex 3*

The complex was measured on a Bruker Smart APEX machine at 100 K. Data were collected using monochromated Mo-Kα radiation in ω scan mode. The structure was solved by direct methods and refined anisotropically on F^2. The methyl groups were refined using rigid groups (AFIX 137), and the others were refined using a riding model.

Crystallography data (excluding structure factors) for the structure reported in this paper has been deposited with the Cambridge Crystallographic Data Center, CCDC number: 1856773. Copies of these data can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB2 IEZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.ac.uk or http://www.ccdc.cam.ac.hk).

Note

The authors declare no competing financial interest.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jorganchem.2019.05.006.

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