Synthesis and Reactivity of Ortho-Palladated Arylureas. Synthesis and Catalytic Activity of a C,N,C Pincer Complex. Stoichiometric Syntheses of Some N-Heterocycles

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1-(2-Iodophenyl)-3-*p*-tolylurea (**1**) reacts with $Pd(dba)_2$ ($[Pd_2(dba)_3]\cdot$dba; dba = dibenzylideneacetone) in the presence of the appropriate ligands to give the ortho-palladated arylureas $[Pd\{C_6H_4NHC(O)NHTo\text{-}2\}IL_2]$ (To = C_6H_4Me-4; L_2 = tbubpy (4,4′-di-*tert*-butyl-2,2′-bipyridine) (**2a**), tmeda (*N*,*N*,*N*′,*N*′-tetramethylethylenediamine) (**2b**); L = PPh_3 (**2c**)). Reaction of **2b** with Tl(TfO) (TfO = triflate, CF_3SO_3) results in the formation of cyclopalladated $[Pd\{\kappa^2C,O\text{-}C_6H_4NHC(O)NHTo\text{-}2\}(tmeda)]OTf$ (**3b**). The latter reacts with PPh_3 to yield $[Pd\{C_6H_4NHC(O)NHTo\text{-}2\}(tmeda)(PPh_3)]OTf$ (**4b**). Treatment of **2b** with CO gives the corresponding acyl derivative $[Pd\{C(O)C_6H_4NHC(O)NHTo\text{-}2\}I(tmeda)]$ (**5b**). If Tl(TfO) is added after the bubbling of CO, the C,N coupling product 3-*p*-tolyl-1*H*-quinazoline-2,4-dione (**6**) is formed. Complex **5b** reacts with XyNC (Xy = 2,6-dimethylphenyl) to yield *trans*-$[Pd\{C(O)C_6H_4NHC(O)NHTo\text{-}2\}I(CNXy)_2]$ (**7**). Both **5b** and **7** decompose in solution to give **6**. Complex **2b** reacts with isocyanides to give the iminoacyl derivatives *trans*-$[Pd\{C(=NR)C_6H_4NHC(O)NHTo\text{-}2\}I(CNR)_2]$ (R = Xy (**8x**), ^{t}Bu (**8t**)). The complex **8x** gives the C,N coupling product 4-(xylylimino)-3-*p*-tolyl-3,4-dihydro-1*H*-quinazolin-2-one (**9**) after treatment with TlOTf. **8x** also reacts with bases (K_2CO_3 and Tl_2CO_3) to yield the iminoacyl amido carbene C,N,C pincer palladium complex $[Pd\{\kappa^3C,N,C\text{-}C(=NXy)C_6H_4NC(O)NToC(NHXy)\text{-}2\}(CNXy)]$ (**10**); this complex is an active precatalyst in Heck and Suzuki reactions. The reaction of **2b** with R′C≡CR″ and TlOTf gives $[Pd\{\kappa^2C,N\text{-}CR'{=}CR''C_6H_4NHC(O)NHTo\text{-}2\}(tmeda)]OTf$ (R′ = R″ = Et (**11be**), CO_2Me (**11bm**), Ph (**11bp**); R′ = Ph, R″ = CO_2Me (**11bq**)). These complexes decompose in solution, and in the case of **11bp**, 2,3-diphenylindole-1-carboxylic acid *p*-tolylamide (**12p**) was isolated. **11bq** reacts with PPh_3 to give 3-phenyl-1*H*-indole-2-carboxylic acid methyl ester (**13q**). **11bp** and **11bq** decompose in the presence of CO to yield 3,4-diphenyl-2-quinolone (**14po**) and 2-oxo-4-phenyl-1,2-dihydroquinoline-3-carboxylic acid methyl ester (**14qo**), respectively. Similarly, when **11bq** is reacted with XyNC, the C,N coupling compound 2-xylyl-4-phenyl-1,2-dihydroquinoline-3-carboxylic acid methyl ester (**14qnx**) is formed. The crystal and molecular structures of **3b**, **10**$\cdot 0.5CDCl_3$, **11bp**$\cdot OEt_2$, **11bq**, and **14po** have been determined.

Introduction

Arylpalladium(II) complexes are postulated as intermediates in many catalytic reactions.[1,2] In particular, ortho-substituted arylpalladium derivatives are involved in the catalytic syntheses of some carbo- or heterocycles; in these reactions, the ortho substituents play a key

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role.[3] The importance of such catalytic processes prompted us to prepare and isolate ortho-functionalized arylpalladium derivatives and to study their reactivity toward unsaturated molecules. Thus, we have previously reported the syntheses of palladium complexes with ortho-functionalized aryl ligands such as $C_6H(OMe)_3$-2,3,4-X-6 (X = CHO, C(O)Me, CH_2OEt, C(O)NH^tBu), $C_6H_3(CHO)_2$-2,5, $C_6H_4NH_2$-2, and C_6H_4X-2 (X = NH_2, OH, $CH{=}CH_2$, CHO, C(O)Me, CN, CH=CHR, N=PPh_3, $Ph_2P{=}NR$, N=C=NR, N=NPh, SPh, $CH(SR)_2$) and also ortho-palladated benzyl- and phenethylamines. We have also studied the reactivity of some of these palladium complexes with alkynes, carbon monoxide, and isocyanides to give interesting new organopalladium(II) complexes and organic compounds.[4−10]

This paper describes the synthesis and isolation of arylpalladium derivatives bearing a urea group at the ortho position. Urea derivatives can coordinate through the oxygen or, less frequently, through nitrogen;[11] arylpalladium complexes that contain a urea group in the ortho position are thus candidates to form metallacycles. Another interesting feature of ureas is the occurrence in the same functional group of two nucleophilic nitrogens and one electrophilic carbon. Consequently, C−C and C−N coupling processes may take place from the above-mentioned palladium urea−aryl complexes. Thus, a hydantoin synthesis from cyclohexanecarboxaldehyde, ureas, and CO has been reported,[12] as has the palladium-catalyzed formation of benzoimidazolones via the C−N coupling of (*o*-bromophenyl)-ureas.[13] In at least one case, Alper's palladium-catalyzed quinazolinone synthesis, some of the postulated intermediates are arylpalladium derivatives with urea groups at the ortho position.[14] However, to the best of our knowledge, the complexes here reported are the first isolated examples of such intermediates.

Some of the arylpalladium derivatives prepared in this work react with CO to yield unstable, but isolable, acylpalladium complexes that decompose to give a quinazolinone derivative. These stoichiometric reactions may serve as models for one of the above-mentioned catalytic processes.[14] Reactions with isocyanides have also been studied, allowing us to isolate iminoacyl derivatives that decompose to give quinazolinone imines. The insertion of isocyanides to form iminoacyl palladium complexes is well documented.[6,7,9,10,15,16] There are, however, fewer examples in which the initial iminoacyl complex evolves, giving a new type of palladium complex.[16,17] In some cases, further transformation of the insertion intermediates takes place, giving organic products in stoichiometric[6,10,18,19] or catalytic reactions.[20] One of the isolated iminoacyl complexes was reacted with a base to give an iminoacyl amido carbene C,N,C pincer, which is an active precatalyst in Heck and Suzuki reactions. It is well-known that different types of palladacycles have proved to be very efficient catalysts or precatalysts in cross-coupling proceses.[21]

The insertion of alkynes into Pd−C bonds is also well-known.[5,6,8,9,22] In the present paper, we report the synthesis of some complexes resulting from the monoinsertion of alkynes into the Pd−C bond of one of the ortho-palladated arylureas. The vinylpalladium derivatives thus obtained undergo a C−N coupling process to yield indoles. A number of metal-mediated syntheses

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of indoles, both stoichiometric[19,23] and catalytic,[24] are documented in the literature. In some of these reactions the mechanism may include a C−N coupling process from similar vinylpalladium derivatives.[25] We also report the synthesis of a 2-quinolone as the decomposition product of the complex resulting from a sequential insertion of an alkyne and carbon monoxide into an ortho urea-substituted arylpalladium complex. Recently, the palladium-catalyzed annulation of internal alkynes by N-substituted *o*-iodoanilines under 1 atm of carbon monoxide has been reported to give 3,4-disubstituted 2-quinolones.[26]

Experimental Section

Conductivity was measured in Me_2CO solutions (ca. 10^{-5} M).[27] NMR measurements were performed on Bruker AVANCE spectrometers (200, 300, and 400 MHz). When needed, NMR signals were assigned with the help of standard DEPT, COSY, and $^{13}C-^{1}H$ HMQC and HMBC techniques. The infrared spectra were recorded using a Perkin-Elmer 16F PC FT-IR spectrometer. The mass spectra were recorded on a Fisons VG-Autospec apparatus. C, H, N, and S microanalyses were performed on a Carlo Erba 1108 instrument. $Pd(dba)_2$ ($[Pd_2(dba)_3]\cdot$dba, dba = dibenzylideneacetone) was prepared as described previously.[1,28] 2-Iodoaniline, *p*-tolyl isocyanate, 3-hexyne, and 2-butyne were purchased from Aldrich, XyNC (Xy = 2,6-dimethylphenyl), ^{t}BuNC and PhC≡CPh from Fluka, and $MeO_2CC{\equiv}CCO_2Me$ and $HC{\equiv}CCO_2Me$ from Acros; $PhC{\equiv}CCO_2Me$ was obtained from Lancaster and ^{13}CO from Isotec. Products obtained from commercial sources were used without further purification. The syntheses of the compounds were carried out without precautions against air and moisture, unless otherwise stated. The preparative thin-layer chromatographic separations were performed using silica gel 60 ACC (70−200 μm). In the case of colorless substances fluorescent silica gel (GF_{254}) was added (approximately 5%). Gas chromatographic analyses were performed on a HP-5890 instrument equipped with a WCOT HP-1 fused silica capillary column.

Synthesis of $IC_6H_4NHC(O)NHTo$-2 (1). 2-Iodoaniline (1.94 g, 8.9 mmol) and *p*-tolyl isocyanate (ToNCO, 1.67 g, 8.9 mmol) were mixed in Et_2O (10 mL) and stirred at room temperature overnight. *n*-Hexane (5 mL) was added to the colorless suspension and filtered. The resulting solid was collected by filtration, washed with Et_2O and *n*-hexane, and air-dried to yield **1** as a colorless powder. Yield: 2.80 g, 90%. Mp: 199−201 °C. IR (Nujol, cm^{-1}): 3278 ν(NH), 1644 ν(C=O). ^1H NMR (200 MHz, d_6-acetone): δ 8.75 (br, 1 H, NH), 8.08 (dd, $^3J_{HH}$ = 8.2 Hz, $^4J_{HH}$ = 1.5 Hz, 1 H, C_6H_4), 7.82 (dd, $^3J_{HH}$ = 8.2 Hz, $^4J_{HH}$ = 1.5 Hz, 1 H, C_6H_4), 7.5−7.3 (several m, 4 H, C_6H_4 + NH + *p*-tolyl), 7.09 (d, $^3J_{HH}$ = 8.2, 2 H, *p*-tolyl), 6.82 (td, $^3J_{HH}$ = 8.2 Hz, $^4J_{HH}$ = 1.5 Hz, 1 H, C_6H_4), 2.25 (s, 3 H, Me). $^{13}C\{^1H\}$ NMR: the compound is not soluble enough in common deuterated solvents to record its $^{13}C\{^1H\}$ NMR spectrum. Anal. Calcd for $C_{14}H_{13}IN_2O$: C, 47.75; H, 3.72; N, 7.95. Found: C, 48.13; H, 3.58; N, 7.95.

Synthesis of [Pd{$C_6H_4NHC(O)NHTo$-2}I(tbubpy)] (2a). $Pd(dba)_2$ (254 mg, 0.42 mmol) and 4,4′-di-*tert*-butyl-2,2′-bipyridine (tbubpy; 129 mg, 0.48 mmol) were stirred in freshly distilled toluene (20 mL) under N_2. After 10 min, **1** (200 mg, 0.57 mmol) was added and the mixture stirred for 30 min. The solvent was removed under reduced pressure, Et_2O (15 mL) was added, and the suspension was filtered through anhydrous $MgSO_4$. The solution was concentrated to ca. 1 mL and subjected to silica gel preparative thin-layer chromatography. Elution with Et_2O/*n*-hexane (2:1) gave an orange band, which was collected and extracted with CH_2Cl_2; the solution was dried over anhydrous $MgSO_4$, filtered, and evaporated to dryness. The resulting solid was stirred with Et_2O and filtered and the solid washed with Et_2O (3 × 3 mL) to give **2a** as an orange solid. Yield: 145 mg, 50%. Mp: 138−140 °C. IR (Nujol, cm^{-1}): 1704 ν(C=O). ^1H NMR (200 MHz, $CDCl_3$): δ 9.41 (d, $^3J_{HH}$ = 6.5 Hz, 1 H), 7.93 (d, $^3J_{HH}$ = 5 Hz, 2 H), 7.67 (d, $^3J_{HH}$ = 7.5 Hz, 1 H), 7.59 (s, 1 H, NH), 7.49 (td, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.5 Hz, 2 H), 7.39 (d, $^3J_{HH}$ = 7.5 Hz, 1 H), 7.25 (dd, 1 H), 7.15 (d, $^3J_{HH}$ = 8.5 Hz, 2 H, *p*-tolyl), 7.01 (t, $^3J_{HH}$ = 6.5 Hz, 1 H), 6.89 (d, $^3J_{HH}$ = 8.5 Hz, 3 H, *p*-tolyl + C_6H_4), 6.58 (s, 1 H, NH), 2.16 (s, 3 H, Me), 1.53 (s, 9 H, ^{t}Bu), 1.43 (s, 9 H, ^{t}Bu). $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$): δ 163.43 (C), 163.33 (C), 155.72 (C), 153.93 (C), 153.50 (C), 152.10 (CH), 149.60 (CH), 141.07 (C), 136.88 (CH), 135.96 (C), 132.42 (C), 129.27 (CH, *p*-tolyl), 124.13 (CH), 123.89 (CH), 123.80 (CH), 122.80 (CH), 121.16 (CH), 121.01 (CH, *p*-tolyl), 118.40 (CH), 118.01 (CH), 35.43 (C, ^{t}Bu), 30.32 (Me, ^{t}Bu), 30.13 (Me, ^{t}Bu), 20.68 (Me, To). Anal. Calcd for $C_{32}H_{37}IN_4OP_2Pd$: C, 52.87; H, 5.13; N, 7.71. Found: C, 52.47; H, 5.32; N, 7.42.

Synthesis of [Pd{$C_6H_4NHC(O)NHTo$-2}I(tmeda)] (2b). $Pd(dba)_2$ (1.17 g, 2.00 mmol) and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (tmeda; 342 μL, 2.28 mmol) were stirred in freshly distilled toluene (10 mL) under N_2. After 10 min, **1** (0.95 mg, 2.71 mmol) was added and the mixture stirred under N_2 for 4 h. The solvent was removed under reduced pressure, CH_2Cl_2 (20 mL) was added, and the resulting suspension was filtered through anhydrous $MgSO_4$. The solvent was removed and the residue treated with Et_2O (20 mL), precipitating a solid, which was collected by filtration, washed with Et_2O (3 × 4 mL), and dried under a stream of air to give impure **2b** as a pink powder. This solid contains approximately 5% of $[PdI_2(tmeda)]$ (NMR). Analytically pure **2b** was obtained by layering Et_2O over a concentrated solution of the crude product in CH_2Cl_2 until small crystals began to form; after the mixture was left overnight, the crystals were collected by filtration and air-dried. Yield: 880 mg, 64% (crude); 440 mg, 32% (pure). Mp: 177−179 °C. IR (Nujol, cm^{-1}): 3324 ν(NH), 1682 ν(C=O). ^1H NMR (400 MHz, $CDCl_3$): δ 7.75 (s, 1 H, NH), 7.47 (d, $^3J_{HH}$ = 7 Hz, 1 H, C_6H_4), 7.32 (d, $^3J_{HH}$ = 8.4 Hz, 2 H, *p*-tolyl), 7.18 (dd, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 1.5 Hz, 1 H, C_6H_4), 7.13 (d, $^3J_{HH}$ = 8.4 Hz, 2 H, *p*-tolyl), 6.91 (td, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 1.5 Hz, 1 H, C_6H_4), 6.79 (td, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 1.5 Hz, 1 H, C_6H_4), 6.74 (m, 1 H, NH), 2.80−2.29 (several m, 4 H, CH_2), 2.65 (s, 3 H, Me), 2.45 (s, 3 H, Me), 2.39 (s, 3 H, Me), 2.29 (s, 3 H, Me), 2.19 (s, 3 H, Me). $^{13}C\{^1H\}$ APT NMR (75 MHz, $CDCl_3$): δ 154.00 (C=O), 141.03 (C), 135.75 (CH, C_6H_4), 135.26 (C), 134.86 (C), 133.50 (C), 129.45 (CH, *p*-tolyl), 123.83 (CH, C_6H_4), 122.94 (CH, C_6H_4), 122.21 (CH, *p*-tolyl), 121.74 (CH, C_6H_4), 62.08 (CH_2), 58.35 (CH_2), 50.67 (Me, tmeda), 50.22 (Me, tmeda), 48.96 (Me, tmeda), 20.76 (Me, *p*-tolyl). Anal. Calcd for $C_{24}H_{29}IN_4OPd$: C, 41.79; H, 5.09; N, 9.75. Found: C, 41.84; H, 5.35; N, 9.90.

$[PdI_2(tmeda)]$ was independently prepared by addition of tmeda to a stirred acetone solution of $[PdCl_2(NCMe)_2]$ (molar ratio 2:1) and an excess of NaI. The resulting reddish suspension was stirred for 10 min. The suspension was filtered through Celite, and the solution was evaporated to dryness.

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The red residue was treated with Et_2O (10 mL) and filtered. The solid was washed with Et_2O (3 × 2 mL) and air-dried to give $[PdI_2(tmeda)]$ as a red powder. ^1H NMR (200 MHz, $CDCl_3$): δ 2.96 (s, 12 H, Me), 2.68 (s, 4 H, CH_2). Anal. Calcd for $C_6H_{16}N_2I_2Pd$ C, 15.13; H, 3.38; N, 5.88. Found: C, 15.36; H, 3.46; N, 5.83. Addition of a small amount of this solid to a $CDCl_3$ solution of crude **2b** caused an increase in the intensity of the 2.93 ppm signal in the ^1H NMR spectrum.

Synthesis of *trans*-[Pd{$C_6H_4NHC(O)NHTo$-2}I(PPh_3)$_2$] (2c). Method A. $Pd(dba)_2$ (0.92 g, 1.59 mmol) and PPh_3 (1.00 g, 3.81 mmol) were stirred in freshly distilled toluene (10 mL) under N_2. After 10 min, **1** (0.75 g, 2.13 mmol) was added and the mixture stirred under N_2 for 3 h. The solvent was removed under reduced pressure, CH_2Cl_2 (15 mL) was added, and the resulting suspension was filtered through anhydrous $MgSO_4$. The solvent was removed and the residue treated with Et_2O (15 mL) and *n*-hexane (5 mL). A solid precipitated, which was collected by filtration, washed with Et_2O (3 × 4 mL), and air-dried to give an orange solid. Yield: 1.30 g. This crude product contains between 15 and 20% of **1** and 5% of $[PdI_2(PPh_3)_2]$ by NMR (δ 13.31 ppm, ^{31}P NMR) and microanalysis data. Recrystallization of the crude sample from CH_2Cl_2/*n*-hexane results in a greater proportion of **1**.

Method B. PPh_3 (138 mg, 0.53 mmol) was added to a solution of pure **2b** (120 mg, 0.21 mmol) in acetone (10 mL). A colorless precipitate began to form after 15 min. The mixture was stirred for 1 h and then diluted with Et_2O (5 mL) and filtered. The solid was washed with Et_2O (3 × 2 mL) and air-dried to yield **2c** as a colorless powder. This solid was recrystallized by addition of Et_2O to a concentrated solution of the crude sample in CH_2Cl_2 (122 mg in 5 mL) until a turbidity appeared. The suspension was stored in a refrigerator overnight, and the colorless crystals were collected by filtration and air-dried to give analytically pure **2c**·$0.21CH_2Cl_2$. After 18 h under high vacuum the crystals contain 0.17 mol of CH_2Cl_2/mol of **2c**, in agreement with the NMR and microanalysis data. No $[PdI_2(PPh_3)_2]$ was formed during the reaction if pure **2b** was used. If **2b** contaminated with $[PdI_2(PPh_3)_2]$ was used instead, more $[PdI_2(PPh_3)_2]$ was formed but could be removed during the recrystallization. Yield: 142 mg (crude), 89 mg, 51% (pure **2c**·$0.17CH_2Cl_2$). Mp: 181−183 °C. IR (Nujol, cm^{-1}): 1682 ν(C=O). ^1H NMR (300 MHz, $CDCl_3$): δ 7.48−7.41 (m, 12 H, ortho or meta H's, PPh_3), 7.38−7.31 (m, 7 H, para H's PPh_3 + NH), 7.27−7.21 (m, 12 H, ortho or meta H's, PPh_3), 7.16 (d, $^3J_{HH}$ = 8 Hz, 2 H, *p*-tolyl), 7.07 (d, $^3J_{HH}$ = 8 Hz, 2 H, *p*-tolyl), 6.91 (d, $^3J_{HH}$ = 8 Hz, 1 H, H3 or H6, C_6H_4), 6.78 (apparent d, $^3J_{HH}$ = 8 Hz, 1 H, H3 or H6, C_6H_4), 6.57 (t, $^3J_{HH}$ = 8 Hz, 1 H, H4 or H5, C_6H_4), 6.18 (t, $^3J_{HH}$ = 8 Hz, 1 H, H4 or H5, C_6H_4), 5.66 (s, 1 H, NH), 5.30 (s, 0.34 H, CH_2Cl_2), 2.33 (s, 3 H, Me). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 22.68 (s, PPh_3). Anal. Calcd for $C_{50.21}H_{43.42}Cl_{0.42}IN_2OP_2Pd$: C, 59.82; H, 4.33; N, 2.84. Found: C, 59.91; H, 4.34; N, 2.84.

$[PdI_2(PPh_3)_2]$ was independently prepared by treatment of $[PdCl_2(NCMe)_2]$ with PPh_3 (molar ratio 1:2) and an excess of NaI. The mixture was stirred in acetone for 1 h, the solvent was removed, and CH_2Cl_2 was added. The red suspension was filtered through Celite to give a red solution. After 2 h the red needles thus formed were collected by filtration, washed with CH_2Cl_2 and Et_2O, and air-dried to yield $[PdI_2(PPh_3)_2]$ as shining deep red crystals. ^1H NMR (300 MHz, $CDCl_3$): δ 7.73−7.66 (m, 12 H, H ortho or H meta PPh_3), 7.39−7.35 (m, 18 H, ortho or meta H's, PPh_3 + para H's PPh_3). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 13.30 (s, PPh_3).

Synthesis of [Pd{κ^2*C*,*O*-$C_6H_4NHC(O)NHTo$-2}(tmeda)]OTf (3b). TlOTf (60 mg, 0.17 mmol) was added to a stirred solution of **2b** (100 mg, 0.17 mmol) in acetone (10 mL), the green suspension was stirred for a further 2 h and then filtered through Celite, and the solution was concentrated to ca. 1 mL. Et_2O (10 mL) was slowly added, precipitating yellow crystals. The solvent was decanted, and the crystals were washed with Et_2O and air-dried to give yellow **3b**. Yield: 70 mg, 70%. Some of the crystals obtained as described above were suitable for single-crystal X-ray determination studies. Mp: 160 °C dec. Λ_M = 145 Ω^{-1} cm^2 mol^{-1} IR (Nujol, cm^{-1}): 3288, 3192 ν(NH), 1634 ν(C=O), 1296, 1028 ν(OTf). ^1H NMR (300 MHz, $CDCl_3$): δ 9.48 (s, 1 H, NH), 9.16 (s, 1 H, NH), 7.20 (d, $^3J_{HH}$ = 8.2 Hz, 2 H, *p*-tolyl), 7.06 (d, $^3J_{HH}$ = 8.2 Hz, 2 H, *p*-tolyl), 7.01−7.88 (m, 4 H, C_6H_4), 2.81−2.75 (m, 2H, CH_2), 2.75 (s, 6 H, Me), 2.60−2.54 (m, 2 H, CH_2), 2.33 (s, 6 H, Me), 2.92 (s, 3 H, Me *p*-tolyl). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 155.98 (C=O), 136.16 (C), 135.03 (C), 133.92 (C), 132.43 (CH), 129.32 (CH, *p*-tolyl), 126.23 (CH), 124.57 (C), 123.61 (CH), 123.04 (CH, *p*-tolyl), 116.34 (CH), 65.57 (CH_2), 57.30 (CH_2), 51.34 (Me, tmeda), 47.56 (Me, tmeda), 20.91 (Me, *p*-tolyl). Anal. Calcd for $C_{21}H_{29}F_3N_4O_4PdS$: C, 42.25; H, 4.90; N, 9.39; S, 5.37. Found: C, 41.85; H, 5.20; N, 9.17; S, 5.17.

Synthesis of [Pd{$C_6H_4NHC(O)NHTo$-2}(tmeda)(PPh_3)]OTf (4b). PPh_3 (44 mg, 0.17 mmol) was added to a CH_2Cl_2 (5 mL) solution of **3b** (100 mg, 0.17 mmol). After 15 min, the solution was filtered through anhydrous $MgSO_4$, the solvent was removed, and the residue was vigorously stirred in Et_2O (10 mL). The resulting solid was filtered, washed with Et_2O (3 × 3 mL), and air-dried to yield **4b** as a pale yellow powder. Yield: 100 mg, 70%. Mp: 135−137 °C. Λ_M = 112 Ω^{-1} cm^2 mol^{-1}. IR (Nujol, cm^{-1}): 3322, 3294 ν(NH), 1702 ν(C=O), 1188, 1028 ν(OTf). ^1H NMR (400 MHz, $CDCl_3$): δ 8.57 (s, 1 H, NH), 7.76 (s, 1 H, NH), 7.57 (d, $^3J_{HH}$ = 8 Hz, 2 H, H2 + H6, *p*-tolyl) 7.48−7.39 (m, 9 H, ortho and para H's PPh_3), 7.35−7.31 (m, 7 H, meta H's PPh_3 + H3 C_6H_4), 7.27 (d, $^3J_{HH}$ = 4 Hz, 1 H, H6), 7.08 (d, $^3J_{HH}$ = 8 Hz, 2 H, H3 + H5, *p*-tolyl), 6.78 (t, $^3J_{HH}$ = 7.8 Hz, 1 H, H4, C_6H_4), 6.53 (t, $^3J_{HH}$ = 7.8 Hz, 1 H, H5, C_6H_4), 3.42 (m, 1 H, CH_2), 2.94 (m, 1 H, CH_2), 2.52−2.41 (m, 2 H, CH_2), 2.52 (s, 3 H, Me, tmeda), 2.48 (s, 3 H, Me, tmeda), 2.29 (s, 3 H, Me, *p*-tolyl), 2.03 (s, 3 H, Me, tmeda), 1.99 (s, 3 H, Me, tmeda). $^{13}C\{^1H\}$ APT NMR (100 MHz, $CDCl_3$): δ 153.04 (C=O), 142,34 (C, C2, C_6H_4), 140.56 (d, $^2J_{CP}$ = 12.5 Hz, C−Pd), 137.93 (C, C1, *p*-tolyl), 134.74 (d, $^2J_{CP}$ = 11.1 Hz, ortho CH's PPh_3), 134.59 (C6H), 131.66 (para CH's, PPh_3), 131.47 (C, C4, *p*-tolyl), 129.45 (s, C3H + C5H, *p*-tolyl), 129.11 (d, $^3J_{CP}$ = 10.8 Hz, meta CH's, PPh_3), 128.57 (d, $^1J_{CP}$ = 50.7 Hz, ipso C's, PPh_3), 125.41 (C4H, C_6H_4), 123.09 (C3H, C_6H_4), 122.12 (C5H, C_6H_4), 119.85 (C2H + C6H, *p*-tolyl), 62.26 (CH_2), 60.91 (CH_2), 51.95 (Me, tmeda), 50.73 (Me, tmeda), 49.00 (Me, tmeda), 48.60 (Me, tmeda), 21.18 (Me, *p*-tolyl). $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$): δ 4.66 (s, PPh_3). Anal. Calcd for $C_{39}H_{44}F_3N_4O_4PPdS$: C, 54.51; H, 5.16; N, 6.52; S, 3.73. Found: C, 54.24; H, 5.25; N, 6.33; S, 3.42.

Synthesis of [Pd{$C(O)C_6H_4NHC(O)NHTo$-2}I(tmeda)] (5b). CO was bubbled for 10 min through a stirred solution of **2b** (120 mg, 0.21 mmol) in THF (20 mL). The solution was stirred for a further 20 h under a CO atmosphere, giving some palladium metal. The suspension was filtered through anhydrous $MgSO_4$, and the filtrate was concentrated to ca. 1 mL and treated with *n*-pentane (10 mL). The resulting mixture was stirred vigorously, precipitating a solid, which was collected by filtration, washed with *n*-pentane (3 × 2 mL), and dried under a stream of air to give **5b** containing 4% of $[PdI_2(tmeda)]$ (NMR and microanalysis), which was recrystallized from acetone/Et_2O to give **5b** as yellow-orange crystals. Yield: 76 mg, 60%. Mp: 159−161 °C dec. IR (Nujol, cm^{-1}): 1666 ν(C=O). ^1H NMR (300 MHz, $CDCl_3$): δ 10.51 (s, 1 H, NH), 9.08 (d, $^3J_{HH}$ = 8 Hz, 1 H, H3 or H6), 8.32 (d, $^3J_{HH}$ = 8 Hz, 1 H, H3 or H6), 7.38 (td, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 2 Hz, 1 H, H4 or H5), 7.31 (d, $^3J_{HH}$ = 8 Hz, 2 H, *p*-tolyl), 7.18−7.10 (m, 3 H, *p*-tolyl + H4 or H5), 6.65 (s, 1 H, NH), 2.95 (0.46 H, Me $[PdI_2(tmeda)]$), 2.73−2.66 (m, 2 H, CH_2), 2.60 (s, 6 H, 2Me), 2.54−2.50 (m, 2 H, CH_2), 2.40 (s, 6 H, 2Me), 2.32 (s, 3 H, Me). $^{13}C\{^1H\}$ NMR: the compound decomposes during the experiment. Anal. Calcd for $C_{21}H_{29}IN_4O_2Pd$: C, 41.84; H, 4.85; N, 9.29. Found: C, 41.58; H, 4.74; N, 9.21.

Synthesis of 3-*p*-Tolyl-1*H*-quinazoline-2,4-dione (6). CO was bubbled through an acetone (10 mL) solution of **2b** (200

mg, 0.35 mmol) for 5 min. TlOTf (123 mg, 0.35 mmol) was added. After 20 min the black suspension was filtered through anhydrous $MgSO_4$, the solvent was removed under reduced pressure, and the residue was stirred in Et_2O (10 mL). The precipitate was removed by filtration; the solution was concentrated to ca. 1 mL and subjected to silica gel preparative thin-layer chromatography. Elution with *n*-hexane/AcOEt (3:1) gave a band ($R_f = 0.75$) which was collected and extracted with CH_2Cl_2; the solution was dried over anhydrous $MgSO_4$, filtered, and evaporated to dryness to yield **6** as a colorless solid. Yield: 53 mg, 60%. The same compound was identified among the decomposition products of **5b** and **7**. Mp: 264−266 °C. IR (Nujol, cm^{-1}): 3194 ν(NH), 1732 ν(C=O). ^1H NMR (400 MHz, $CDCl_3$ + DMSO-d_6): δ 9.97 (s, 1 H, NH), 8.03 (dd, $^3J_{HH}$ = 6.6 Hz, $^4J_{HH}$ = 1.3 Hz, 1 H, H5), 7.73−7.68 (m, 3 H, H2 + H6, *p*-tolyl + H7), 7.39 (d, $^3J_{HH}$ = 8 Hz, 1 H, H8), 7.26 (m, 1 H, H6), 7.17 (d, $^3J_{HH}$ = 8 Hz, 2 H, H3 + H8, *p*-tolyl), 2.36 (s, 3 H, Me). $^{13}C\{^1H\}$ APT NMR (100 MHz, $CDCl_3$ + DMSO-d_6): δ 158.3 (C4=O), 149.61 (C2=O), 148.71 (C4a), 135.28 (C7H), 134.21 (C1, *p*-tolyl), 131.20 (C4, *p*-tolyl), 127.91 (C5H + C3H, *p*-tolyl), 127.00 (C5H), 123.48 (C8H), 122.64 (C6H), 118.55 (C2H + C6H, *p*-tolyl), 112.53 (C8a), 19.50 (Me). EI-MS (%): *m/z* 252.00 (M^+, 47), 252.95 (M^+, 8). The NMR data are in accord with those reported in the literature.[14]

Synthesis of *trans*-[Pd{C(O)C_6H_4NHC(O)NHTo-2}I(CNXy)$_2$] (7). XyNC (65 mg, 0.50 mmol) was added to a solution of **5b** (100 mg, 0.17 mmol) in CH_2Cl_2 (5 mL). The solvent was removed, and the residue was triturated with Et_2O (10 mL). The resulting solid was collected by filtration, washed with Et_2O (3 × 2 mL), and dried under high vacuum for 6 h to yield **7**·0.6Et_2O as a pale yellow solid. Yield: 118 mg, 95%. Mp: 129−131 °C dec. IR (Nujol, cm^{-1}): 2182 ν(C≡N), 1708 ν(C=O). ^1H NMR (200 MHz, $CDCl_3$): δ 10.38 (br s, 1 H, NH), 9.00 (d, $^3J_{HH}$ = 8 Hz, 1 H, H3 or H6, C_6H_4), 8.50 (d, $^3J_{HH}$ = 8 Hz, 1 H, H3 or H6, C_6H_4), 7.49 (t, $^3J_{HH}$ = 8 Hz, 1 H, H4 or H5, C_6H_4), 7.32 (d, $^3J_{HH}$ = 10 Hz, 2 H, *p*-tolyl), 7.27−7.14 (several m, 5 H, H4 or H5, C_6H_4 + 2 H, *p*-tolyl + para H's Xy), 7.04 (d, $^3J_{HH}$ = 8 Hz, 4 H, meta H's Xy), 6.54 (br s, 1 H, NH), 3.48 (q, $^3J_{HH}$ = 8 Hz, 2.5 H, CH_2, Et_2O), 2.34 (s, 3 H, Me, *p*-tolyl), 2.27 (s, 12 H, Me, Xy), 1.21 (t, $^3J_{HH}$ = 8 Hz, 3.75 H, Me, Et_2O). $^{13}C\{^1H\}$ NMR: the compound decomposes during the experiment. Anal. Calcd for $C_{40.4}H_{37}IN_4O_{2.6}Pd$: C, 53.59; H, 4.70; N, 7.06. Found: C, 53.23; H, 4.93; N, 6.93.

Synthesis of *trans*-[Pd{C(=NXy)C_6H_4NHC(O)NHTo-2}I(CNXy)$_2$] (8x). XyNC (92 mg, 0.70 mmol) was added to a CH_2Cl_2 (5 mL) solution of **2b** (100 mg, 0.17 mmol). After 20 min the solution was concentrated to ca. 1 mL and Et_2O (10 mL) added. A solid precipitated, which was collected by filtration, washed with Et_2O (3 × 3 mL), and dried under a stream of air to yield pale yellow **8x**. Yield: 130 mg, 90%. Mp: 142−143 °C. IR (Nujol, cm^{-1}): 2184 ν(C≡N), 1674 ν(C=O). ^1H NMR (400 MHz, $CDCl_3$): δ 11.75 (s, 1 H, NH), 8.79 (dd, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1.5 Hz, 1 H, H3 or H6, C_6H_4), 8.54 (dd, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1.5 Hz, 1 H, H3 or H6, C_6H_4), 7.39 (td, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1.5 Hz, 1 H, H4 or H5, C_6H_4), 7.20 (t, $^3J_{HH}$ = 7.5 Hz, 2 H, Pd−CNXy), 7.15 (td, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1.5 Hz, 1 H, H4 or H5) 7.05 (t, J_{HH} = 7.5 Hz, 6 H, *p*-tolyl + Pd−CNXy), 6.94−6.89 (m, 3 H C=NXy), 6.74 (d, $^3J_{HH}$ = 8 Hz, 2 H, *p*-tolyl), 6.13 (s, 1 H, NH), 2.17 (s, 12 H, Me, Pd−CNXy), 2.01 (s, 3 H, Me, *p*-tolyl), 1.94 (s, 6 H, Me, C=NXy). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 183.18 (C), 154.60 (C), 148.41 (C), 137.42 (CH), 137.31 (C), 136.84 (C), 135.97 (C), 135.58 (C), 133.78 (C), 130.50 (CH), 130.05 (CH), 129.67 (CH), 128.16 (CH), 128.01 (CH), 127.19 (C), 124.40 (CH), 123.97 (CH), 121.15 (CH), 119.18 (CH), 20.78 (Me), 19.04 (Me), 18.83 (Me), 18.56 (Me). Anal. Calcd for $C_{41}H_{40}IN_5OPd$: C, 57.79; H, 4.73; N, 8.22. Found: C, 57.91; H, 4.61; N, 8.01.

Synthesis of *trans*-[Pd{C(=N^{t}Bu)C_6H_4NHC(O)NHTo-2}I(CN^{t}Bu)$_2$] (8t). ^{t}BuNC (184 μL, 1.64 mmol) was added to a CH_2Cl_2 (5 mL) solution of **2b** (240 mg, 0.41 mmol). After 20 min, the solution was concentrated to ca. 1 mL and *n*-pentane (5 mL) was added, precipitating a solid, which was collected by filtration, washed with *n*-pentane (3 × 3 mL) and *n*-pentane-Et_2O (1:1) (3 × 2 mL) and dried in a stream of air to yield pale-yellow **8t**. Yield: 242 mg, 85%. Mp: 88−90 °C. IR (Nujol, cm^{-1}): 3340 ν(NH), 2198 ν(C≡N), 1672 ν(C=O), 1590 ν(C=N). ^1H NMR (300 MHz, $CDCl_3$): δ 12.88 (br s, 1 H, NH), 8.87 (d, $^3J_{HH}$ = 8 Hz, 1 H, H6, C_6H_4), 8.71 (d, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1.2 Hz, 1 H, H3, C_6H_4), 7.31−7.23 (m, 3 H, H2 + H6, *p*-tolyl + H4, C_6H_4), 7.12−7.03 (m, 3 H, H3 + H5, *p*-tolyl + H5, C_6H_4), 6.17 (s, 1 H, NH), 2.31 (s, 3 H, Me), 1.66 (s, 9 H, ^{t}Bu), 1.37 (s, 18 H, ^{t}Bu). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 176.5 (*C*=N^{t}Bu), 153.0 (C=O), 137.6 (C6H, C_6H_4), 137.1 (C), 136.1 (C1, *p*-tolyl), 132.6 (C4, *p*-tolyl), 129.5 (C3H + C5H, *p*-tolyl), 129.3 (C4H, C_6H_4), 129.0 (C), 120.8 (C5H), 119.3 (C2H + C6H, *p*-tolyl), 118.4 (C3H, C_6H_4), 57.9 (C=N*C*Me$_3$), 57.8 (Pd−C=N*C*Me$_3$), 31.4 (C=N*Me*$_3$), 29.7 (Pd−C=NC*Me*$_3$), 20.7 (Me, *p*-tolyl). Anal. Calcd for $C_{29}H_{31}IN_5OPd$: C, 49.20; H, 5.69; N, 9.89. Found: C, 48.94; H, 5.81; N, 9.85.

Synthesis of 4-(Xylylimino)-3-*p*-tolyl-3,4-dihydro-1*H*-quinazolin-2-one (9). TlOTf (84 mg, 0.24 mmol) was added to a CH_2Cl_2 (10 mL) solution of **8x** (200 mg, 0.24 mmol) and the volume of the reaction mixture was made up to 20 mL with acetone, precipitating a green solid. The mixture was stirred for 7 h, the resulting suspension was filtered through Celite, the filtrate was concentrated to dryness, and the residue was treated with Et_2O. The solution was decanted, concentrated to ca. 1 mL, and placed on a silica gel chromatographic column. Elution with Et_2O/*n*-hexane (1:2) gave crude **9** ($R_f = 0.80$ by TLC), which was crystallized by cooling (−34 °C) a saturated Et_2O/*n*-hexane solution. The crystals thus formed were collected by filtration, washed with cold Et_2O (1 mL), and dried under high vacuum for 2 h. Yield: 47 mg, 55% for the crude product; 21 mg, 25% for the crystals of **9**·0.2H_2O. Mp: 151 °C. IR (Nujol, cm^{-1}): 3370 ν(NH), 1698 ν(C=O). ^1H NMR (400 MHz, $CDCl_3$): δ 8.26 (d, $^3J_{HH}$ = 7.5 Hz, 1 H), 7.53 (td, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.5 Hz, 1 H, H6 or H7), 7.28−7.16 (m, 4 H), 7.09 (d, $^3J_{HH}$ = 7.5 Hz, 2 H), 7.02−6.96 (m, 3 H), 6.67 (s, 1 H, NH), 2.28 (s, 3 H, Me), 2.15 (s, 6 H, Me), 1.55 (s, 0.4 H, H_2O. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 149.35 (C), 145.37 (C), 145.36 (C), 144.17 (C), 134.62 (C), 133.95 (CH), 133.26 (C), 129.63 (CH), 128.09 (C), 127.81 (CH), 126.92 (CH), 124.60 (CH), 124.45 (CH), 123.25 (CH), 119.37 (CH), 116.21 (C), 18.37 (Me), 18.37 (Me, Xy). Anal. Calcd for $C_{23}H_{21.4}N_3O_{1.2}$: C, 76.94; H, 6.01; N, 11.70. Found: C, 76.88; H, 6.07; N, 11.59.

Synthesis of [Pd{κ^3*C,N,C*-C(=NXy)C_6H_4\{NC(O)NToC(NHXy)\}-2}(CNXy)] (10). 8x (100 mg, 0.12 mmol) was dissolved in acetone/CH_2Cl_2 (2:1). Excess K_2CO_3 was added, and the mixture was stirred overnight (16 h). The suspension was filtered through anhydrous $MgSO_4$, the filtrate was concentrated to ca. 1 mL, and Et_2O (5 mL) was added. After a few minutes yellow crystals began to form. *n*-Pentane (10 mL) was added and the flask cooled (4 °C) overnight. The yellow crystals were collected by filtration, washed with Et_2O (3 × 3 mL) and *n*-pentane (3 × 2 mL), and air-dried to yield crystalline **10**·0.7CH_2Cl_2. A sample of this solid was dried under high vacuum overnight. The NMR of the dried solid showed approximately 0.2 mol of CH_2Cl_2/mol of complex. Yield: 55 mg, 58% for **10**·0.7CH_2Cl_2. Single crystals of **10**·0.5$CDCl_3$, suitable for an X-ray diffraction study, were obtained by liquid diffusion of *n*-pentane into a solution of **10** in $CDCl_3$. Mp: 157−159 °C. IR (Nujol, cm^{-1}): 3240 ν(NH), 2176 ν(C≡N), 1682 ν(C=O). ^1H NMR (400 MHz, $CDCl_3$): δ 8.56 (d, $^3J_{HH}$ = 7.7 Hz, 1 H, C_6H_4), 8.07 (dd, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1.4 Hz, 1 H, C_6H_4), 7.37 (d, $^3J_{HH}$ = 8 Hz, 2 H, *p*-tolyl), 7.27 (td, $^3J_{HH}$ = 7.7 Hz, $^4J_{HH}$ = 1.4 Hz, 1 H, C_6H_4), 7.25 (d, $^3J_{HH}$ = 8 Hz, 2 H, *p*-tolyl), 7.05 (t, $^3J_{HH}$ = 7.7 Hz, 1 H, Xy), 6.92 (t, $^3J_{HH}$ = 7.7 Hz, 1 H, C_6H_4), 6.83 (d, $^3J_{HH}$ = 7.7 Hz, 2 H, Xy), 6.55 (d, $^3J_{HH}$ = 7.6 Hz, 2 H, *p*-tolyl), 6.50 (d, $^3J_{HH}$ = 7.5 Hz, 2 H, *p*-tolyl), 6.09 (t, $^3J_{HH}$ = 7.6 Hz, 1 H, Xy), 5.86 (t, $^3J_{HH}$ = 7.5 Hz, 1 H, Xy), 5.30 (s, 0.28 H, CH_2Cl_2), 2.40 (s, 3 H, Me), 2.22 (s, 6 H, Me, Xy), 2.10 (s, 6 H, Me,

Xy), 1.98 (s, 6 H, Me, Xy). $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$): δ 204.83 (C, carbene), 160.27 (C), 152.88 (C), 152.30 (C), 143.87 (C), 139.92 (C), 136.23 (C), 134.98 (C), 133.43 (C), 132.81 (C), 131.29 (CH, *p*-tolyl), 131.11 (CH, C_6H_4), 128.62 (CH, *p*-tolyl), 128.09 (CH, Xy), 127.98 (CH, Xy), 127.97 (CH, Xy) 127.15 (CH, Xy), 126.87 (CH, Xy), 125.64 (C), 124.83 (CH, C_6H_4), 121.63 (CH, C_6H_4), 121.51 (CH, Xy), 119.05 (CH, C_6H_4), 21.24 (Me, *p*-tolyl), 19.24 (Me, Xy), 18.96 (Me, Xy), 18.24 (Me, Xy). Anal. Calcd for $C_{41}H_{39}N_5OPd\cdot 0.7CH_2Cl_2$: C, 63.91; H, 5.20; N, 8.94. Found: C, 64.10; H, 5.21; N, 9.01. Calcd for $C_{41.14}H_{39.28}Cl_{0.28}N_5OPd$: C, 67.13; H, 5.38; N, 9.51. Found: C, 67.14; H, 5.69; N, 9.66.

Synthesis of [Pd{κ^2*C*,*N*-C(Et)=C(Et)C_6H_4NHC(O)NHTo-2}(tmeda)]OTf (11be). 3-Hexyne (80 μL, 0.70 mmol) and TlOTf (61 mg, 0.17 mmol) were added to a solution of **2b** (100 mg, 0.17 mmol) in THF (5 mL). After 10 min, the solvent was removed and the residue was treated with CH_2Cl_2 (5 mL). The suspension was filtered over Celite, the filtrate was concentrated to 1 mL, and *n*-pentane was added. The mixture was stirred until a solid formed; this was collected by filtration, washed with *n*-pentane, and dried under a stream of air to yield **11be** as a brown powder. Yield: 70 mg. IR (Nujol, cm^{-1}): 3256, 3250 ν(NH), 1650, 1634 ν(CO), 1026 ν(OTf). ^1H NMR (400 MHz, $CDCl_3$): δ 8.74 (s, 1 H, NH), 8.47 (s, 1 H, NH), 7.37 (td, $^3J_{H,H}$ = 7 Hz, $^4J_{H,H}$ = 1.3 Hz, 1 H), 7.28−7.24 (m, 4 H), 7.19−7.15 (m, 1 H), 7.03 (d, $^3J_{H,H}$ = 8.5 Hz, 2 H, *p*-tolyl), 2.70−2.78 (several multiplets, 8 H, CH_2), 2.66 (s, 3 H, Me), 2.44 (s, 3 H, Me), 2.31 (s, 3 H, Me), 2.27 (s, 3 H, Me), 1.79 (s, 3 H, Me), 1.07 (t, $^3J_{H,H}$ = 7.5 Hz, 3 H, *Me*CH_2), 0.83 (t, $^3J_{H,H}$ = 7.5 Hz, 3 H, *Me*CH_2). Because this compound is unstable, minor resonances are also observed that increase with time. $^{13}C\{^1H\}$ NMR: the compound decomposes during the experiment. All attempts to purify the compound to get good elemental analyses failed.

Synthesis of [Pd{κ^2*C*,*N*-C(CO_2Me)=C(CO_2Me)C_6H_4NHC(O)NHTo-2}(tmeda)]OTf (11bm). dmad (85 μL, 0.79 mmol) and TlOTf (61 mg, 0.17 mmol) were added to a solution of **2b** (100 mg, 0.17 mmol) in THF (10 mL). After 10 min, the solvent was removed and the residue was treated with CH_2Cl_2 (10 mL). The suspension was filtered over Celite, and the filtrate was concentrated to dryness. The solid was triturated with Et_2O (5 mL), collected by filtration, washed with Et_2O, and dried under a stream of air to yield **11bm** as a yellow powder. Yield: 80 mg. IR (Nujol, cm^{-1}): 3254, 3246 ν(NH), 1698, 1632 ν(C=O), 1028 (OTf). ^1H NMR (400 MHz, $CDCl_3$): δ 8.78 (s, 1 H, NH), 8.59 (s, 1 H, NH), 7.51−7.38 (m, 3 H), 7.28 (d, $^3J_{HH}$ = 7.5 Hz, 1 H), 7.17 (d, $^3J_{HH}$ = 8 Hz, 2 H, *p*-tolyl), 7.07 (d, $^3J_{HH}$ = 8 Hz, 2 H, *p*-tolyl), 3.76 (s, 3 H, OMe), 3.61 (s, 3 H, OMe), 2.78 (s, 3 H, Me), 2.73−2.15 (several m, 4 H, CH_2), 2.59 (s, 3 H, Me), 2.30 (s, 3 H, Me), 2.20 (s, 3 H, Me), 1.18 (s, 3 H, Me). Other signals appear, and their intensity increases with time. $^{13}C\{^1H\}$ NMR: the compound decomposes during the experiment. Anal. Calcd for $C_{27}H_{35}F_3N_4O_8PdS$: C, 43.88; H, 4.77; N, 7.58; S, 4.34. Found: C, 43.44; H, 4.65; N, 7.32; S, 3.56. All attempts to purify the compound resulted in an increase of the amount of impurities. See Results and Discussion.

Synthesis of [Pd{κ^2*C*,*N*-C(Ph)=C(CO_2Me)C_6H_4NHC(O)NHTo-2}(tmeda)]OTf (11bq). Method A. TlOTf (61 mg, 0.17 mmol) was added to a solution of methyl phenylpropiolate (96 μL, 0.70 mmol) and **2b** in THF (5 mL), and the resulting suspension was stirred for 10 min. The solvent was removed under reduced pressure, and CH_2Cl_2 (10 mL) was added. The suspension was filtered through Celite, the filtrate was concentrated to ca. 1 mL, and Et_2O was added, precipitating a solid, which was collected by filtration, washed with Et_2O (3 × 3 mL), and dried under a stream of air to yield pale yellow **11bq**. Yield: 95 mg, 72%.

Method B. Methyl phenylpropiolate (192 μL, 1.34 mmol) was added to a solution of **3b** (200 mg, 0.34 mmol) in CH_2Cl_2 (5 mL). The solution was stirred for 20 min and concentrated to ca. 1 mL and Et_2O (5 mL) added, precipitating a solid, which was collected by filtration, washed with Et_2O (3 × 2 mL), and air-dried to give **11bq** as a yellow powder. Yield: 222 mg, 86%. Crystals suitable for an X-ray study were obtained by slow diffusion of Et_2O into a $CDCl_3$ solution of **11bq**. Λ_M = 135 Ω^{-1} cm^2 mol^{-1}. Mp: 160−162 °C. IR (Nujol, cm^{-1}): 3298 ν(NH), 1682, 1634 ν(C=O), 1030 (OTf). ^1H NMR (400 MHz, $CDCl_3$): δ 8.83 (s, 1 H, NH), 8.81 (s, 1 H, NH), 7.45−7.35 (m, 3 H), 7.34−7.29 (m, 1 H), 7.25−7.01 m, 9 H), 3.47 (s, 3 H, OMe), 2.87 (s, 3 H, Me, tmeda), 2.66 (s, 3 H, Me, tmeda), 2.69−2.55 (m, 2 H, CH_2), 2.28 (s, 3 H, Me, *p*-tolyl), 2.26 (s, 3 H, Me, tmeda), 2.30−2.14 (m, 2 H, CH_2), 1.87 (s, 3 H, Me, tmeda). $^{13}C\{^1H\}$ APT NMR (75 MHz, $CDCl_3$): δ 171.40 (*C*O_2Me), 160.30 (NH*C*O), 144.10 (C), 140.80 (C), 138.90 (C), 138.8 (C), 135.1 (C), 134.00 (C), 133.3 (C4 *p*-tolyl), 129.50 (CH), 129.40 (CH), 129.10 (C3H + C5H, *p*-tolyl), 128.50 (CH), 128.20 (ortho or meta CH's, Ph), 127.40 (ortho or meta CH's Ph), 127.20 (CH), 120.80 (C2H + C6H, *p*-tolyl), 64.40 (CH_2), 57.60 (CH_2), 54.00 (Me, tmeda), 51.50 (OMe), 49.50 (Me, tmeda), 48.80 (Me, tmeda), 46.10 (Me, tmeda), 20.80 (Me, *p*-tolyl). Anal. Calcd for $C_{31}H_{37}F_3N_4O_6PdS$: C, 49.18; H, 4.93; N, 7.40; S, 4.23. Found: C, 48.81; H, 4.92; N, 7.27; S, 3.92.

Synthesis of [Pd{κ^2*C*,*N*-C(Ph)=C(Ph)C_6H_4NHC(O)NHTo-2}(tmeda)]OTf (11bp) and 2,3-Diphenylindole-1-carboxylic acid *p*-Tolylamide (12p). TlOTf (62 mg, 0.18 mmol) was added to a solution of diphenylacetylene (124 mg, 0.70 mmol) and **2b** (100 mg, 0.17 mmol) in THF (10 mL). The resulting suspension was stirred for 5 min, the solvent was removed under reduced pressure, and CH_2Cl_2 (10 mL) was added. The suspension was filtered through Celite, the filtrate concentrated to dryness, and the solid vigorously stirred overnight in Et_2O. The resulting solid was collected by filtration, washed with Et_2O (3 × 3 mL), and dried under a stream of air to yield yellow **11bp**, which was used without further purification in the synthesis of **12p**. Yield: 110 mg, 82%. Single crystals were obtained by liquid diffusion of Et_2O into a solution of **11bp** in $CDCl_3$. Mp: 118−120 °C. IR (Nujol, cm^{-1}): 3300, 3222 ν(NH), 1634 ν(C=O), 1026 (OTf). ^1H NMR (400 MHz, $CDCl_3$): δ 8.84 (s, 1 H, NH), 8.48 (br s, 1 H, NH), 7.70 (d, $^3J_{HH}$ = 7.5 Hz, 1 H), 7.52 (t, $^3J_{HH}$ = 7.5 Hz, 1 H), 7.41−7.34 (m, 3 H), 7.28−7.23 (m, 4 H), 7.13 (d, $^3J_{HH}$ = 8.5 Hz, 2 H), 7.10−7.05 (m, 3 H), 7.01−6.93 (m, 6 H), 2.54 (s, 3 H, Me), 2.34 (s, 3 H, Me), 2.30 (s, 3 H, Me), 1.97 (s, 3 H, Me), 1.80 (s, 3 H, Me), 2.64−2.04 (several m, 4H, CH_2). $^{13}C\{^1H\}$ NMR: the compound decomposes during the experiment.

Complex **11bp** (200 mg, 0.26 mmol) was dissolved in CH_2Cl_2 (10 mL). After 15 min a black precipitate began to appear. After 48 h the mixture was filtered through Celite and the solution concentrated to ca. 1 mL and placed on a silica gel chromatographic column. Elution with Et_2O/*n*-hexane (1:2) rendered a colorless solid, which was dissolved in acetone, and *n*-hexane was added. Slow evaporation of the solvents gave crystals, which were filtered off, washed with *n*-hexane, and air-dried to give **12p** as a colorless crystalline solid. Yield: 75 mg, 72% (crude); 30 mg, 29% (pure). Mp: 203−205 °C. IR (Nujol, cm^{-1}): 3296 ν(NH), 1676 ν(C=O). ^1H NMR (400 MHz, $CDCl_3$): δ 8.33 (d, $^3J_{HH}$ = 8 Hz, 1 H), 7.64 (d, $^3J_{HH}$ = 8 Hz, 1 H), 7.44−7.39 (several m, 6 H), 7.32−7.26 (several m, 6 H), 7.03 (d, $^3J_{HH}$ = 8 Hz, 2 H, *p*-tolyl), 6.88 (d, $^3J_{HH}$ = 8 Hz, 2 H, *p*-tolyl), 6.59 (s, 1 H, NH), 2.27 (s, 3 H, Me). $^{13}C\{^1H\}$ APT NMR (100 MHz, $CDCl_3$): δ 149.40 (C=O), 137.06 (C7a), 134.25 (C), 134.21 (C), 133.27 (C), 133.00 (C), 131.37 (C), 130.73 (CH), 130.09 (CH), 129.45 (CH), 129.21 (C3′H + C5′H, *p*-tolyl), 129.05 (CH), 128.61 (C3a), 128.34 (CH), 126.84 (CH), 124.89 (C6H), 122.82 (C5H), 121.50 (C3), 119.71 (CH), 129.68 (CH), 114.72 (CH), 20.79 (Me). Anal. Calcd for $C_{28}H_{22}N_2O$: C, 83.56; H, 5.51; N, 6.69. Found: C, 83.21; H, 5.70; N, 6.94.

Synthesis of 3-Phenyl-1*H*-indole-2-carboxylic acid Methyl Ester (13q). PPh_3 (278 mg, 1.06 mmol) was added to a solution of **11bq** (200 mg, 0.26 mmol) in CH_2Cl_2 (10 mL). The yellow solution was stirred overnight (16 h), and the solvent was removed under reduced pressure. The residue was

placed on a silica gel chromatographic column. Elution with *n*-hexane/Et_2O (3:1) rendered a fraction (R_f = 0.6 by TLC), which was collected, dried over anhydrous $MgSO_4$, filtered, and evaporated to dryness to give crude **13q**. This solid was crystallized by addition of *n*-hexane (1 mL) to a solution in the minimum amount of Et_2O. The resulting suspension was concentrated to ca. 0.5 mL and placed in a refrigerator at −34 °C overnight. The resulting crystals were collected by filtration and dried under high vacuum for 12 h to yield **13q**·$0.2H_2O$ as a yellow crystalline solid. Yield: 34 mg, 51% (crude); 5 mg, 8% (pure). Mp: 129−131 °C. IR (Nujol, cm^{-1}): 3332 ν(NH), 1674 ν(C=O). ^1H NMR (400 MHz, $CDCl_3$): δ 8.95 (s, 1 H, NH), 7.64 (d, $^3J_{HH}$ = 8 Hz, 1 H, H4 or H7), 7.57−7.55 (m, 2 H), 7.49−7.45 (several m, 3 H), 7.41−7.35 (several m, 2 H), 7.15 (td, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1 Hz, H5 or H6), 3.82 (s, 3 H, OMe), 1.55 (s, 0.4 H, H_2O). $^{13}C\{^1H\}$ APT NMR (100 MHz, $CDCl_3$): δ 162.40 (C=O), 135.73 (C), 133.37 (C), 130.52 (CH, Ph), 127.85 (CH, Ph), 127.24 (CH), 125.88 (CH), 124.40 (C), 122.36 (C), 121.77 (CH), 120.89 (CH), 111.68 (CH), 51.77 (OMe). EI-MS (*m/z* (%)): 251.1 (M^+, 92.4), 220.1 (M^+ − OMe, 100), 192.1 (M^+ − CO_2Me, 98.7). Anal. Calcd for $C_{16}H_{13.4}NO_{2.2}$: C, 75.40; H, 5.30; N, 5.50. Found: C, 75.61; H, 5.51; N, 5.69.

Synthesis of 3,4-Diphenyl-2-quinolone (14po). CO was bubbled through a solution of **12p** (120 mg, 0.163 mmol) in CH_2Cl_2 (10 mL). After a few minutes a black precipitate was formed. The suspension was stirred for 2 h under a CO atmosphere and filtered through Celite and the filtrate concentrated to dryness. The residue was placed on a silica gel chromatographic column. Elution with *n*-hexane/Et_2O (1:1) gave a fraction (R_f = 0.7 by TLC) which was collected and dried over anhydrous $MgSO_4$, and the solvents were removed to give crude **14po**. This solid was recrystallized by addition of *n*-hexane to a solution in the minimum amount of AcOEt until small crystals began to form. After the mixture was cooled (−34 °C) overnight, the resulting crystals were collected by filtration and dried under high vacuum for 2 h to yield **14po**·$0.4H_2O$ as a colorless crystalline solid. Single crystals suitable for X-ray diffraction studies were obtained by slow diffusion of Et_2O into concentrated solutions of amorphous **14po** in $CDCl_3$. Yield: 40 mg, 88% (crude); 5 mg, 11% (pure). Mp: 272−274 °C. IR (Nujol, cm^{-1}): 1652 ν(C=O). ^1H NMR (400 MHz, $CDCl_3$): δ 11.89 (br s, 1H, NH), 7.45 (td, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 1 Hz, 1 H), 7.33 (d, $^3J_{HH}$ = 7 Hz, 1 H), 7.29−7.04 (m, 12 H), 1.55 (s, 0.8 H, H_2O). $^{13}C\{^1H\}$ APT NMR (50 MHz, $CDCl_3$): δ 163.00 (C=O), 149.70 (C), 137.80 (C), 136.3 (C), 135.20 (C), 131.90 (C), 130.80 (CH), 130.20 (CH), 129.8 (CH), 128.00 (CH), 127.60 (CH), 127.50 (CH), 127.00 (CH), 122.3 (CH), 120.90 (CH), 115.80 (CH). HRMS: calcd for $C_{21}H_{15}NO$, 297.114; found, 297.115. Anal. Calcd for $C_{21}H_{15.8}NO_{1.4}$: C, 82.82; H, 5.23; N, 4.60. Found: C, 82.89; H, 5.28; N, 4.75.

Synthesis of 2-Oxo-4-phenyl-1,2-dihydroquinoline-3-carboxylic Acid Methyl Ester (14qo). CO was bubbled through a CH_2Cl_2 (5 mL) solution of **11bq** (144 mg, 0.19 mmol), giving palladium metal. The suspension was stirred overnight under a CO atmosphere, and the resulting suspension was filtered through anhydrous $MgSO_4$. The solution was concentrated and placed on a silica gel chromatographic column. Elution with *n*-hexane/AcOEt (1:2) gave a fraction which was collected, dried over anhydrous $MgSO_4$, filtered, and concentrated to dryness to yield a colorless solid. This crude sample was recrystallized from CH_2Cl_2/Et_2O/*n*-hexane to give **14qo** as colorless crystals. Yield: 59 mg, 57%. Mp: 226−228 °C. IR (Nujol, cm^{-1}): 1736 ν(C=O). ^1H NMR (300 MHz, $CDCl_3$): δ 12.88 (br s, 1 H, NH), 7.56−7.47 (several m, 5 H), 7.41−7.37 (m, 2 H), 7.31 (d, J_{HH} = 8 Hz, 1 H), 7.14 (ddd, J_{HH} = 8 Hz, J_{HH} = 5 Hz, J_{HH} = 3 Hz, 1 H, C_6H_4), 3.65 (s, 3 H, OMe). $^{13}C\{^1H\}$ APT NMR (50 MHz, $CDCl_3$): δ 166.21 (CO_2), 161.14 (C=O), 150.83 (C), 138.46 (C), 134.57 (C), 131.62 (CH), 128.91 (CH), 128.63 (CH), 128.39 (CH), 127.62 (CH), 125.96 (C), 122.96 (CH), 119.41 (C), 116.91 (CH), 52.30 (s, OMe). Anal. Calcd for $C_{17}H_{13}NO_3$: C, 73.11; H, 5.02; N, 4.69. Found: C, 72.72; H, 4.99; N, 5.04.

Synthesis of 2-Xylyl-4-phenyl-1,2-dihydroquinoline-3-carboxylic Acid Methyl Ester (14qnx). XyNC (50 mg, 0.38 mmol) was added to a solution of **11bq** (280 mg, 0.37 mmol) in CH_2Cl_2 (10 mL) under N_2. The mixture was stirred for 24 h, as the yellow solution turned into a green suspension. The suspension was filtered through Celite, and the filtrate was concentrated to dryness. The solid was placed on a silica gel chromatographic column. Elution with *n*-hexane/acetone (5:1) rendered a yellow solid (R_f = 0.45 by TLC). The resulting solid was crystallized by cooling concentrated pentane solutions (−34 °C) overnight. The crystals were collected by filtration, washed with cold pentane (2 × 1 mL), and dried under high vacuum to give colorless crystals of **14qnx**. Yield: 46 mg, 32% (crude); 5 mg, 3% (pure). Mp: 146−148 °C. IR (Nujol, cm^{-1}): 3394 ν(NH), 1712 ν(C=O), 1598 ν(C=N). ^1H NMR (200 MHz, $CDCl_3$): δ 7.96 (br s, 1 H, NH), 7.6 (dd, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1 Hz, 1 H), 7.55−7.43 (m, 4 H), 7.39−7.32 (m, 3 H), 7.14−7.07 (m, 4 H), 3.43 (s, 3 H, OMe), 2.31 (s, 6 H, 3Me, Xy). $^{13}C\{^1H\}$ APT NMR (100 MHz, $CDCl_3$): δ 169.36 (C=O), 151.90 (C=N), 151.24 (C), 148.59 (C), 137.69 (C), 136.77 (C−N, Xy), 135.34 (*C*−Me, Xy), 130.96 (CH), 128.80 (CH), 128.035 (CH), 128.01 (CH), 127.91 (CH), 127.23 (CH), 125.83 (CH), 122.79 (CH), 122.52 (C), 113.30 (C, C3), 51.95 (OMe), 19.00 (Me). Anal. Calcd for $C_{25}H_{22}N_2O_2$: C, 78.51; H, 5.80; N, 7.32. Found: C, 78.71; H, 6.14; N, 7.33.

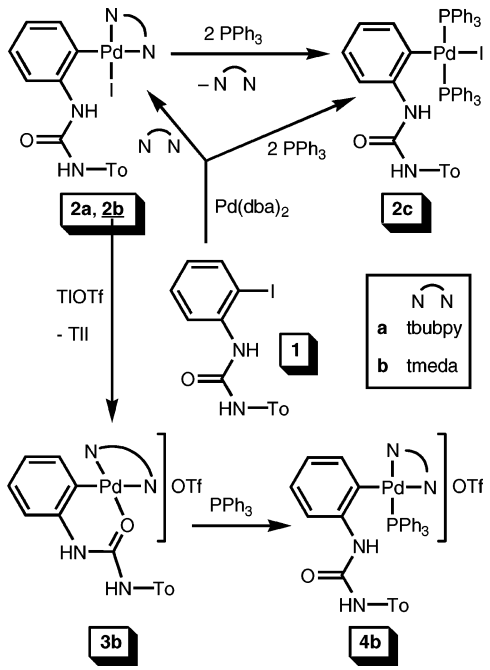
Heck Coupling of 4-Chloroiodobenzene with Methyl Acrylate. Method A. A 25 mL round-bottom flask was charged with 4-chloroiodobenzene (476 mg, 2 mmol), methyl acrylate (216 μL, 2.4 mmol), Et_3N (393 μL, 2.8 mmol), complex **10** (145 μg, 2×10^{-4} mmol, 0.01 mol % Pd), and DMF (4 mL). The solution was stirred at 110 °C in air, and the reaction progress was analyzed by GLC. After completion the reaction mixture was cooled and poured into water (30 mL) and this mixture was extracted with AcOEt (2 × 20 mL). The resulting organic phase was washed with water (3 × 30 mL) and dried over Na_2SO_4, and the solvents were evaporated to obtain the corresponding methyl cinnamate in 95% yield.

Method B. A 25 mL round-bottom flask was charged with 4-bromonitrobenzene (404 mg, 2 mmol), methyl acrylate (216 μL, 2.4 mmol), potassium carbonate (386 mg, 2.8 mmol), (*n*-Bu_4N)Br (129 mg, 0.4 mmol), complex **10** (8.3 mg, 1.15×10^{-2} mmol, 0.6 mol % Pd), and DMF (4 mL). The solution was stirred at 110 °C in air, and the reaction progress was analyzed by GLC. After completion the reaction mixture was cooled and poured into water (30 mL) and the mixture was extracted with AcOEt (2 × 20 mL). The resulting organic phase was washed with water (3 × 30 mL) and dried over Na_2SO_4, and the solvents were evaporated to obtain the corresponding methyl cinnamate in 97% yield.

General Procedure for Suzuki Couplings. A 25 mL round-bottom flask was charged with the corresponding aryl halide (2 mmol), arylboronic acid (366 mg, 3 mmol), K_2CO_3 (553 mg, 4 mmol), (*n*-Bu_4N)Br (322 mg, 1 mmol, only for aryl chlorides), complex **10** (see Table 2), and solvent (7 mL, see Table 2). The mixture was heated (see Table 2) and stirred in air, and the reaction progress was analyzed by GLC. After completion the reaction mixture was cooled and poured into AcOEt (40 mL) and the mixture was washed with aqueous 2 M NaOH (2 × 20 mL) and water (3 × 20 mL). The organic layer was dried over Na_2SO_4, and the solvents were evaporated to obtain the corresponding biphenyl.

X-ray Structure Determinations. Data were obtained using Mo Kα radiation on a Bruker SMART 1000 CCD diffractometer. Absorption corrections were based on indexed faces (**3b** and **10**) or multiple scans (program SADABS; **11bp** and **11bq**). Structures were refined anisotropically on F^2 (program SHELXL-97, G. M. Sheldrick, University of Göttingen, Göttingen, Germany). Hydrogens of NH groups were refined freely but with N−H distance restraints (*SADI*).

Scheme 1



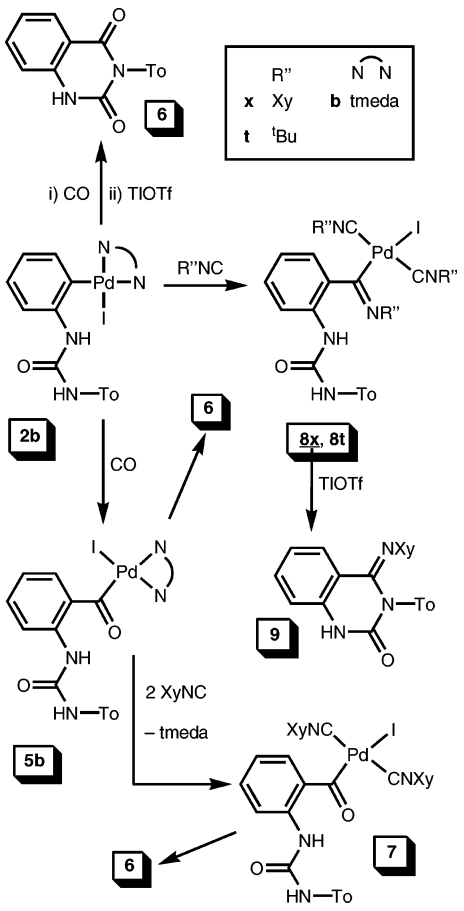
Methyl hydrogens were identified in difference syntheses and refined as rigid groups allowed to rotate but not tip; other hydrogens were included using a riding model. Crystal data are presented in Table 3. *Special features*/*exceptions*: The solvent methyl groups in **11bp** were set ideally staggered and refined using a riding model. To improve the stability of the refinement, restraints to light atom displacement parameters were employed (*DELU*, *SIMU*). For **11bq** and **14po**, NH hydrogens were refined freely without restraints.

Results and Discussion

Synthesis of Ortho-Palladated Arylureas. 2-Iodoaniline and *p*-tolyl isocyanate were reacted to give the (iodoaryl)urea $IC_6H_4NHC(O)NHTo$-2 (**1**; To = C_6H_4Me-4). This compound adds oxidatively to $Pd(dba)_2$ ($[Pd_2(dba)_3]\cdot$dba, dba = dibenzylideneacetone), in the presence of 1 equiv of 4,4′-di-*tert*-butyl-2,2′-bipyridine (tbubpy) or *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (tmeda) or 2 equiv of PPh_3, to yield the corresponding complexes [Pd{$C_6H_4NHC(O)NHTo$-2}IL_2] (L_2 = tbubpy (**2a**), tmeda (**2b**), L = PPh_3 (**2c**)) (Scheme 1). Complexes **2b**,**c** were obtained contaminated with [PdI_2(tmeda)] (ca. 5%) and with **1** plus [$PdI_2(PPh_3)_2$] (ca. 5%), respectively. These impurities seem to form as decomposition products of some intermediate in the synthesis of **2b** and **2c**, as the isolated complexes are stable in solution at room temperature. Analytically pure samples of **2b** and **2c** were obtained by recrystallization and by reaction of pure **2b** with PPh_3, respectively. An X-ray diffraction study of **2b** confirmed the proposed structure, but it could not be refined adequately because of disorder in the tmeda ligand.

Complex **2b** reacts with TlOTf to give the cationic cyclometalated complex [Pd{κ^2C,O-$C_6H_4NHC(O)NHTo$-2}(tmeda)]OTf (**3b**). The urea group at the ortho position coordinates to the palladium atom through the oxygen to form a six-membered metallacycle (see below). Other attempts to obtain metallacycles were fruitless. Thus, oxidative addition of **1** to $Pd(dba)_2$ in the absence of other ligands or in the presence of 1 equiv of PPh_3 gave

Scheme 2



complex mixtures. On the other hand, addition of PPh_3 to **3b** resulted in the opening of the metallacycle to yield [Pd{$C_6H_4NHC(O)NHTo$-2}(tmeda)(PPh_3)]OTf (**4b**).

Reactions with CO and Isocyanides. Synthesis of Quinazolinones. Complex **2b** reacts with CO to give the acylpalladium derivative [Pd{$C(O)C_6H_4NHC(O)NHTo$-2}I(tmeda)] (**5b**) (Scheme 2). If Tl(TfO) is added after the bubbling of CO, the C,N coupling product 3-*p*-tolyl-1*H*-quinazoline-2,4-dione (**6**) is formed. The analogous reaction using **2c** gave complex mixtures. Treatment of **5b** with XyNC (1:3 molar ratio) gave *trans*-[Pd{$C(O)C_6H_4NHC(O)NHTo$-2}I($CNXy)_2$] (**7**). The reaction of **5b** with PPh_3 (1:2 molar ratio) resulted in the substitution of the tmeda by PPh_3; the resulting complex was identified in solution as *trans*-[Pd{$C(O)C_6H_4NHC(O)NHTo$-2}I($PPh_3)_2$] but could not be isolated because of its low stability. An analytically pure sample of **5b** gives, after 24 h in $CDCl_3$ at room temperature, a palladium mirror and a solution containing **5b** and **6** in an approximately 1:1 molar ratio, ca. 20 mol % [PdI_2(tmeda)], free tmeda, and minor quantities of other unidentified products. Similarly, a $CDCl_3$ solution of **7** forms, after 24 h, a palladium mirror, compound **6**, free XyNC, and another compound (^{1}H NMR δ 2.57 ppm), probably the isocyanide−palladium(I) complex [$Pd_2I_2(CNXy)_2$].[29] Elution of the mixture in a GC/MS apparatus confirmed the presence of XyNC (*m*/*e* 131, M^+) and **6** (*m*/*e* 253, M^+). Compound **6** was also formed in the decomposition of *trans*-[Pd{$C(O)C_6H_4NHC(O)NHTo$-

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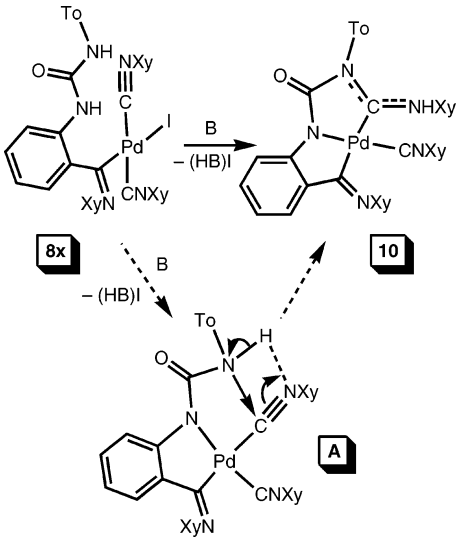
Scheme 3

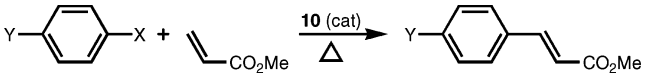


2}I(PPh_3)$_2$] in solution. As mentioned in the Introduction, a work by Alper et al. on the synthesis of quinolones describes the preparation of **6** from 2-iodoaniline, isocyanates, CO, and a palladium catalyst.[14] This work postulates the formation of ortho-palladated arylureas and their acyl derivatives as intermediates in the reaction. Here we confirm this proposal, isolating and characterizing some of these intermediates and proving that the acyl derivatives (**5b** and **7**) undergo a C,N coupling to give the quinolone **6**.

The complex **2b** reacts with isocyanides RNC (R = Xy (=2,6-dimethylphenyl), ^{t}Bu; 1:4 molar ratio), to give the corresponding iminoacyl derivatives *trans*-[Pd{C(=NR)C_6H_4NHC(O)NHTo-2}I(CNR)$_2$] (R = Xy (**8x**), ^{t}Bu (**8t**)). An X-ray diffraction study of **8t** confirmed the proposed structure, but the X-ray data could not be refined. The complex **8x** can also be obtained in low yield (12%) from **2c** (120 mg, 0.12 mmol) and XyNC in CH_2Cl_2. The orange solid obtained from this reaction contained impure **8x**, which was isolated after recrystallization from CH_2Cl_2/*n*-pentane. These iminoacyl complexes are more stable in solution than their acyl counterparts; nevertheless, treatment of **8x** with TlOTf resulted in the formation of the quinazolinone imine 4-(xylylimino)-3-*p*-tolyl-3,4-dihydro-1*H*-quinazolin-2-one (**9**). The yield of this reaction is low (40% for the crude, 25% for the pure sample), but no other compounds appeared in the GC/MS spectra of crude samples of the reaction mixture, and the low yield may be partly due to losses during the workup. **9** was also identified among the products of the reaction between **2b** and XyNC in a 1:1 molar ratio, which takes place with formation of palladium metal.

Synthesis of an Amido Carbene C,N,C Pincer Compound. Catalytic Activity. All acyl and iminoacylpalladium derivatives described here (**5b**, **7**, **8x**, and **8t**) exhibit one low-field resonance (δ > 10.30 ppm) in their proton NMR spectra. These resonances were assigned to one of the NH protons of their urea fragment. This prompted us to investigate the behavior of these complexes toward bases. Thus, reaction of **8x** with K_2CO_3 resulted in the formation of the amido carbene C,N,C pincer complex [Pd{κ^3*C,N,C*-C(=NXy)C_6H_4}{NC(O)NToC(NHXy)}-2}(CNXy)] (**10**) (Scheme 3). The same

Table 1. Heck Reaction



Y	X	reacn conditions	TON/TOF (h^{-1})	conversn (%)[a]
Cl	I	10^{-2} mol % Pd, Et_3N, DMF, 110 °C, 2 h	9500/4250	95
NO_2	Br	0.6 mol % Pd, K_2CO_3, (*n*-Bu_4N)Br, DMF, 130 °C, 2 h	162/81	97

[a] Isolated yields.

result was obtained using Tl_2CO_3. The pathway for this reaction may include abstraction of the acidic proton of one of the NH groups by the base and formation of the amide complex **A** with replacement of iodide. Complex **A** may undergo cyclization after nucleophilic attack of the remaining NH to the isocyanide ligand.[30] Unfortunately, attempts to obtain similar complexes from **5b**, **7**, or **8t** resulted in complex mixtures.

One of the interesting features of pincer compounds, including NHC (N-heterocyclic carbene) pincers, is their ability to catalyze carbon−carbon or carbon−heteroatom coupling reactions,[31] such as the Heck,[32] Suzuki,[33] and amination reactions,[34] along with other catalytic reactions.[35] Apart from this, amido complexes of palladium seem to be intermediates in palladium-catalyzed amination reactions.[36] Also described are amido diphosphino complexes that catalyze the Heck reaction.[37] We therefore decided to study the activity of **10** as a precatalyst in cross-coupling processes under the reaction conditions previously described for the Heck[38] and Suzuki[39] reactions using oxime-derived palladacycles as precatalysts. Thus, methyl acrylate reacted with 4-chloroiodobenzene, using triethylamine as base and complex **10** (0.01 mol %) as catalyst in DMF at 110 °C (method A), to give methyl 4-chlorocinnamate in 95% yield (Table 1). In the case of the arylation of methyl acrylate with 4-bromonitrobenzene, K_2CO_3 as base, (*n*-Bu_4N)Br as additive, and higher loading of complex **10** (0.6 mol %) at 130 °C were used (method B), affording after 2 h methyl 4-nitrocinnamate in 97% yield (Table 1). These TON and TOF values were similar to those obtained with oxime-derived palladacycles.[38]

Complex **10** also catalyzed the cross-coupling of phenylboronic acid and bromo- or chloroarenes in water and organic solvents, giving the corresponding biaryls (Table 2). This reaction takes place at 100−110 °C but not at room temperature, which indicates the necessity of

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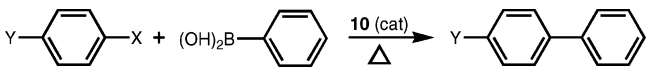
Table 2. Suzuki Reaction



Y	X	reacn conditions	TON/TOF (h^{-1})	conversn (%)[a]
C(O)Me	Br	10^{-2} mol % Pd, KOH, MeOH/H_2O (3:1), room temp, 1 day		0
CH_2CO_2H	Br	0.1 mol % Pd, K_2CO_3, H_2O, room temp, 1 day		0
OMe	Br	1.1×10^{-2} mol % Pd, K_2CO_3, toluene, 100 °C, 1.3 h	7818/6014	86
OMe	Br	1.1×10^{-2} mol % Pd, K_2CO_3, toluene/H_2O (95:5), 110 °C, 1.3 h	8727/6713	96
C(O)Me	Cl	1.3×10^{-2} mol % Pd, K_2CO_3, Bu_4NBr, H_2O, reflux, 2.5 h	7308/2943	95

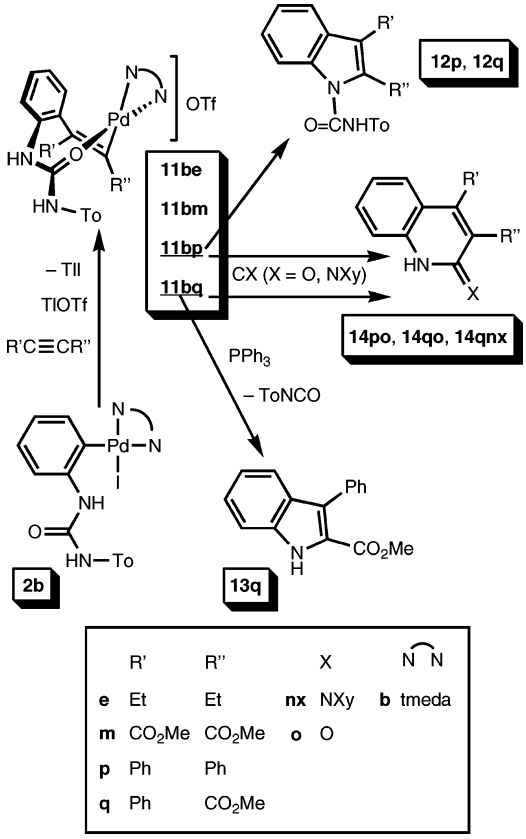
[a] Isolated yields.

generating the catalytically active species. Deactivated 4-methoxybromobenzene could be coupled with phenylboronic acid either in toluene or in a 95:5 mixture of toluene and water with K_2CO_3 as base, with high TON and TOF values. In the case of the coupling of phenylboronic acid and 4-chloroacetophenone, the reaction was performed in neat water with (*n*-Bu_4N)Br as additive to give 4-acetylbiphenyl in 95% yield with efficiency similar to that for oxime-derived palladacycles.[39] In conclusion, complex **10** is an efficient precatalyst for the Suzuki and Heck reactions, in water or organic solvents, and under an air atmosphere.

Reactions with Alkynes. The complex **2b** reacts with internal alkynes and TlOTf at room temperature, to give the cationic complexes [Pd{κ^2*C*,*N*-CR′=CR″C_6H_4-NHC(O)NHTo-2}(tmeda)]OTf (R′ = R″ = Et (**11be**), CO_2Me (**11bm**), Ph (**11bp**); R′ = Ph, R″ = CO_2Me (**11bq**)) (Scheme 4). In these reactions, only one molecule of alkyne inserts into the palladium−carbon bond, despite the use of a 4-fold excess of alkyne. All complexes **11**, except **11bq**, are unstable in solution, which precludes recording their ^{13}C NMR spectra and recrystallization to obtain analytically pure species. However, all could be identified unequivocally by ^{1}H NMR spectroscopy, and **11bp** and **11bq** were also identified by X-ray diffraction studies. Interestingly, the insertion of $MeO_2CC{\equiv}CPh$ into the Pd−C bond of **2b** to give **11bq** is regioselective. The isomer is that in which the CCO_2Me moiety is attached to the palladium atom. This behavior is an exception to that generally observed for unsymmetrical alkynes.[8] **11bq** was also synthesized by reaction of **3b** with a 3-fold excess of $MeO_2CC{\equiv}CPh$. The same reaction using the stoichiometric amount of alkyne also gave **11bq**, but longer reaction times (24 h instead of 5 min) were necessary. Reactions with other internal (2-butyne) or terminal alkynes (phenylacetylene, methyl propiolate) gave compounds that decomposed rapidly and could not be identified. The reaction of **2b** with $MeO_2CC{\equiv}CCO_2Me$ (DMAD), CO, and TlOTf gave **6** (Scheme 2), indicating that the insertion of carbon monoxide is faster than that of the alkyne.

When a sample of **11bp** was stirred in CH_2Cl_2 overnight and the mixture separated by chromatography, the decomposition product 2,3-diphenylindole-1-carboxylic acid *p*-tolylamide (**12p**) (Scheme 4) was isolated (72% yield). As mentioned above, complex **11bq** is stable in solution, but addition of PPh_3 to a solution of the compound in CH_2Cl_2 led to a mixture containing

Scheme 4



(using GC/MS) PPh_3, **12q** (the homologue of **12p** with R′ = Ph, R″ = CO_2Me), *p*-tolyl isocyanate, and 3-phenyl-1*H*-indole-2-carboxylic acid methyl ester (**13q**). This indole could be isolated in 52% yield. The reaction pathway for the formation of the indole derivatives **12p** and **13q** (Scheme 5) may include a C,N coupling involving the vinylic carbon attached to palladium and the appropriate NH of the urea group. The indole **13q** is the product of the decomposition of the corresponding **12q**, in agreement with the GC/MS data of the corresponding reaction mixture.

The vinylpalladium complexes **11bp** and **11bq** react with carbon monoxide to give palladium and the quinolone derivatives **14po** and **14qo** (Scheme 4). The ^{13}C NMR spectrum of the resulting quinolone using ^{13}CO showed that the CO group of **14qo** originates from carbon monoxide. In addition, as *p*-tolyl isocyanate was detected by GC/MS in the reaction mixtures of **11bp** and **11bq** with CO, the reaction pathway depicted in Scheme 5 can explain the formation of **14po** and **14qo**: CO inserts into the Pd−C_{vinyl} bond of **11** to give an acyl palladium derivative, which undergoes a C,N coupling with loss of Pd and *p*-tolyl isocyanate. Similarly, the reaction of **11bq** and XyNC gave the quinolone imine **14qnx**. In this case, no palladium precipitate was observed, presumably because of the formation of some palladium(0)−isocyanide complex. The mechanism of the reaction may be similar to that proposed for the insertion of CO (Scheme 5).

Spectroscopic Data. The infrared spectra of the arylurea **1**, complexes **2a**−**c**, **3b**, **4b**, **5b**, **7**, **8x**,**t**, **10**, and **11**, and the organic products **6**, **9**, **12p**, **13q**, and **14** show one or two bands in the region 1632−1736 cm^{-1} assignable to the ν(C=O) mode. Complexes **7**, **8x**,**t**, and **10**

Scheme 5

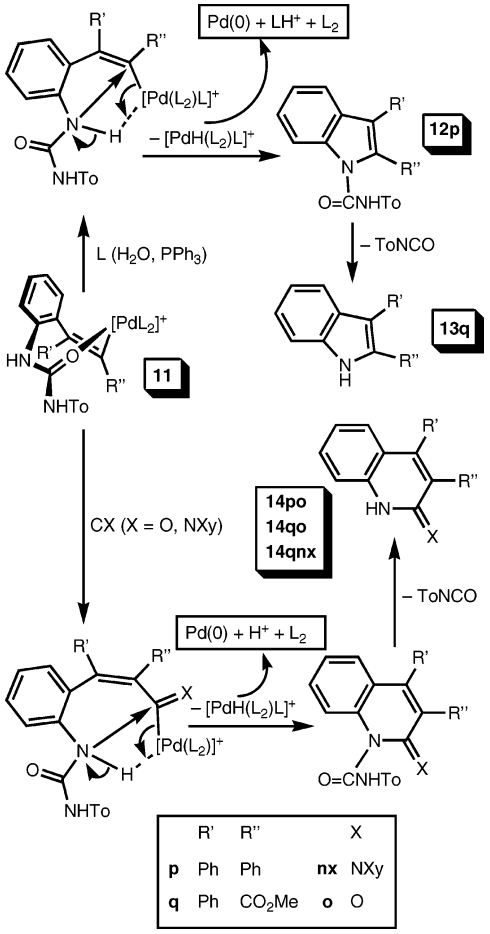


exhibit bands assignable to the ν(C≡N) mode of the isocyanide ligands in the range 2176−2198 cm^{-1}.

The NMR spectra of the new compounds are in agreement with the proposed structures. Thus, the ^{1}H NMR spectra of **2b**, **4b**, and **11** show four signals in the methyl region corresponding to the tmeda ligand, while in the spectra of **3b** and **5b** there are only two. In the case of **2b** and **4b**, the four signals are due to the restricted rotation of the aryl group around the Pd−C bond, whereas in the case of **5b** the insertion of the CO allows the free rotation of the acyl ligand. The metallacycle in **11** must be rigid enough to prevent the equivalence of two methyl groups of each nitrogen atom.

Complexes **5b**, **7**, and **8** show one very low-field resonance (δ >10.3 ppm) assignable to one of their NH protons, probably that involved in a six-membered intramolecular hydrogen bond[40] with the C=O oxygen (**5b** and **7**) or the C=N nitrogen (**8**), respectively. In complexes **3b**, **4b**, and **11** both NH protons appear at low field (δ >7.8 ppm) because of the formation of hydrogen bonds in solution with the triflate anion. These hydrogen bonds have been observed in the solid state in the case of **3b**, **11bp**, and **11bq** (see below). In the ^{13}C NMR of **10** the resonance at 204.83 ppm, corresponding to a quaternary carbon, is tentatively assigned to the carbene carbon.

X-ray Structures of Complexes 3b, 10·0.5CDCl$_3$, 11bp·OEt$_2$, 11bq, and 14po. The crystal and molecular structures of the compounds **3b** (Figure 1), **10**·0.5CDCl$_3$ (Figure 2), **11bp**·0.5OEt$_2$ (Figure 3), **11bq** (Figure 4), and **14po** (Figure 5) have been determined by X-ray diffraction studies. Crystallographic data for all of these complexes are given in Table 3. In complexes **3b** and **10** there are two independent formula units in the asymmetric unit; the cations are closely similar except for ring rotations, with rms deviations of 0.09 Å, excluding peripheral ring atoms, in both cases. The palladium complexes **3b**, **10**, **11bp**, and **11bq** show slightly distorted square planar structures. In complexes **3b**, **11bp**, and **11bq** the triflate is connected to the

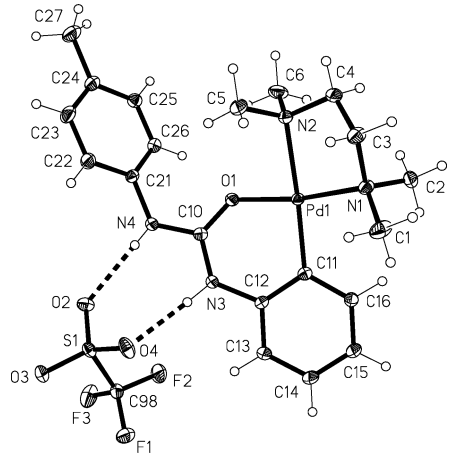


Figure 1. Thermal ellipsoid plot (30% probability) of one of the two independent formula units of **3b**. Selected bond lengths (Å) and angles (deg) for this formula unit: Pd(1)−C(11) = 2.0030(17), Pd(1)−O(1) = 2.0227(12), Pd(1)−N(1) = 2.0752(15), Pd(1)−N(2) = 2.1703(15), N(3)−C(10) = 1.338(2), N(3)−C(12) = 1.423(2), N(4)−C(10) = 1.353(2), N(4)−C(21) = 1.422(2), O(1)−C(10) = 1.257(2); C(11)−Pd(1)−O(1) = 89.56(6), C(11)−Pd(1)−N(1) = 98.88(7), O(1)−Pd(1)−N(2) = 87.07(5), N(1)−Pd(1)−N(2) = 84.48(6).

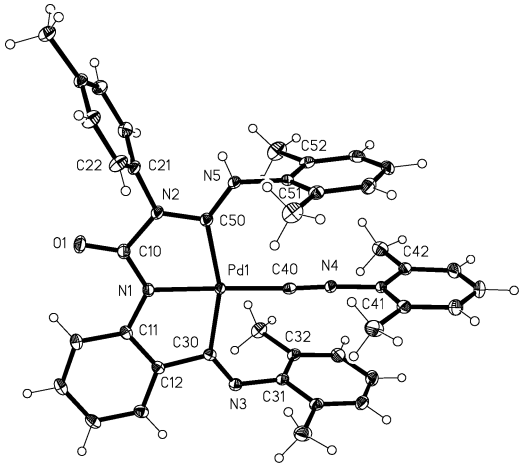


Figure 2. Thermal ellipsoid plot (30% probability) of one of the two independent molecules of **10**·0.5CDCl$_3$. The molecule of CDCl$_3$ is omitted for clarity. Selected bond lengths (Å) and angles (deg) for this molecule: Pd(1)−C(40) = 1.9435(16), Pd(1)−N(1) = 1.9968(13), Pd(1)−C(30) = 2.0579(15), Pd(1)−C(50) = 2.1045(15), N(1)−C(10) = 1.346(2), N(1)−C(11) = 1.4027(19), N(2)−C(50) = 1.3585(19), N(2)−C(10) = 1.455(2), N(3)−C(30) = 1.269(2), N(4)−C(40) = 1.157(2), N(5)−C(50) = 1.323(2), O(1)−C(10) = 1.2122(19); C(40)−Pd(1)−C(30) = 97.23(6), N(1)−Pd(1)−C(30) = 82.08(6), C(40)−Pd(1)−C(50) = 101.18(6), N(1)−Pd(1)−C(50) = 79.46(6).

(40) Günther, H. *NMR Spectroscopy*; Wiley: New York, 1996.

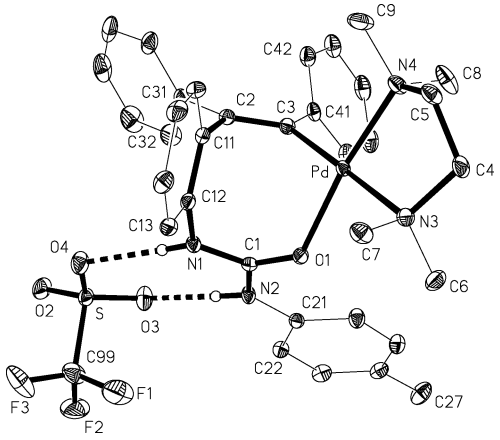


Figure 3. Thermal ellipsoid plot (30% probability) of **11bp**·OEt_2. The hydrogen atoms not involved in hydrogen bonds and the molecule of Et_2O are omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd−C(3) = 2.0009(19), Pd−N(4) = 2.0635(17), Pd−O(1) = 2.0720(13), Pd−N(3) = 2.1632(16), O(1)−C(1) = 1.264(2), N(1)−C(1) = 1.342(2), N(1)−C(12) = 1.437(2), N(2)−C(1) = 1.349(2); C(3)−Pd−N(4) = 94.93(7), C(3)−Pd−O(1) = 91.60(7), N(4)−Pd−N(3) = 85.24(6), O(1)−Pd−N(3) = 88.39(6), C(1)−O(1)−Pd = 127.30(12).

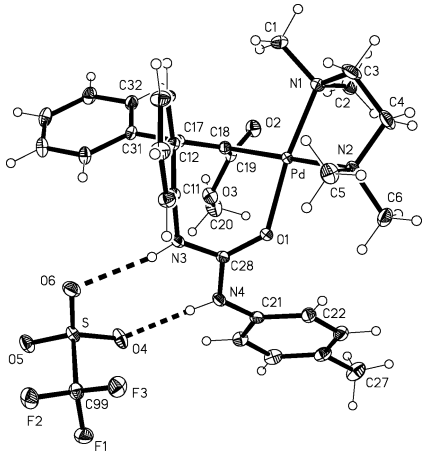


Figure 4. Thermal ellipsoid plot (30% probability) of **11bq**. Selected bond lengths (Å) and angles (deg): Pd−C(18) = 1.9997(11), Pd−O(1) = 2.0388(9), Pd−N(1) = 2.0567(11), Pd−N(2) = 2.1416(10), N(3)−C(28) = 1.3466(15), N(4)−C(28) = 1.3490(15), O(1)−C(28) = 1.2595(14), O(2)−C(19) = 1.2140(15); C(18)−Pd−O(1) = 90.34(4), C(18)−Pd−N(1) = 96.18(5), O(1)−Pd−N(2) = 88.57(4), N(1)−Pd−N(2) = 85.34(4).

cation through two N−H···O hydrogen bonds involving the two NH groups of the urea moiety of the cation and two oxygen atoms of the triflate anion (details of the hydrogen bonds may be found in the Supporting Information). These interactions seem also to be present in solution, as mentioned above. The crystal packing of **3b** also involves six C−H···O interactions with $H\cdots O_{triflate} \leq 2.6$ Å that may be regarded as hydrogen bonds. Cations 1 (unprimed) and cations 2 (primed atom names) occupy the regions at $y \approx 0$, $^1/_2$, 1 and $^1/_4$, $^3/_4$, respectively, and are linked by the anions to form tubes or layers. In **10**·0.5$CDCl_3$ there is a $Cl_3CD\cdots O{=}C$ interaction to the second independent molecule, with a short D···O distance of 2.41 Å but a narrow angle of 124°; surprisingly, there are no short contacts from the N−H groups and no C−H···O < 2.6 Å. Compound **11bp** has a contact within the asymmetric unit from H(25) to the ether oxygen, but this is rather long at 2.75 Å; again, there are no C−H···O < 2.6 Å. Compound **11bq** has one extremely short C(3)−H(3B)···O5 interaction of 2.29 Å, which links the residues to form chains parallel to [110], but no other C−H···O < 2.57 Å. In **14po**, N−H···O interactions lead to dimers, which are arranged in layers parallel to the *xz* plane at $y \approx 0$, $^1/_2$, 1; the quinolone moieties are parallel to the layers, and the phenyl substituents project between them.

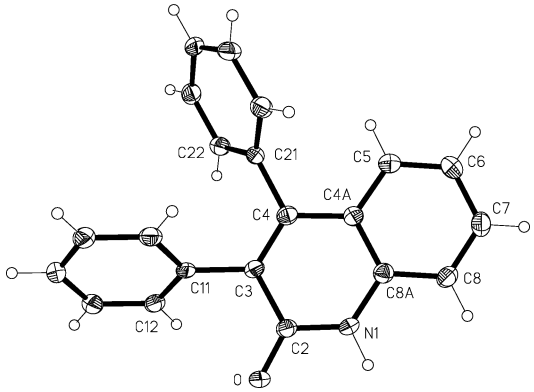


Figure 5. Thermal ellipsoid plot (50% probability) of **14po**. Selected bond lengths (Å) and angles (deg): O−C(2) = 1.2506(16), N(1)−C(2) = 1.3623(18), N(1)−C(8A) = 1.3850(18), C(2)−C(3) = 1.471(2), C(3)−C(4) = 1.3735(18), C(4)−C(4A) = 1.454(2), C(4A)−C(8A) = 1.406(2); C(2)−N(1)−C(8A) = 125.05(12), O−C(2)−N(1) = 119.87(13), O−C(2)−C(3) = 123.44(13), N(1)−C(2)−C(3) = 116.69(13), C(4)−C(3)−C(2) = 119.95(13), C(4)−C(3)−C(11) = 122.59(13), C(2)−C(3)−C(11) = 117.44(12), C(3)−C(4)−C(4A) = 120.84(13), C(3)−C(4)−C(21) = 120.70(13), C(4A)−C(4)−C(21) = 118.43(12), C(8A)−C(4A)−C(5) = 117.61(13), C(8A)−C(4A)−C(4) = 118.27(13), C(5)−C(4A)−C(4) = 124.11(13).

The NHC(O)NH group in the palladium complexes **3b**, **11bp**, and **11bq** shows a high degree of delocalization. Thus, the C−NHC(O)NH−C systems are essentially planar (mean deviation of non-H atoms ≤0.06 Å) and the C−N distances (range 1.338−1.352 Å) are intermediate between single C−N (for example, 1.48 Å in the tmeda ligands of the same complexes) and double C=N (1.28 Å)[41] bond lengths. In PhNHC(O)NHPh the (O)C−NH distances are similar (1.340, 1.358 Å) but the C−O distance (1.233 Å)[42] is shorter than in our complexes (range 1.257(2)−1.264(2) Å) because of the O coordination to Pd. There is no reported crystal structure of a metal complex containing an O-bonded ArNHC(O)NHAr (Ar = aryl) ligand to compare with our C−O(Pd) distancer, nor is there a crystal structure of any palladium complex with an O-bonded urea ligand. In complex **10**, there is delocalization over the O−C−N(1) (N(1)−C(10) = 1.346(2), 1.3443(19) Å; cf. N(2)−C(10) = 1.455(2), 1.4410(19) Å) and carbene groups (N(2)−C(50) = 1.3585(19), 1.3541(18) Å; N(5)−C(50) = 1.323(2), 1.3197(19) Å).

The Pd−O bond distance in the palladium complex **3b** or **11bq** (range 2.0221(12)−2.0388(9) Å) is, surprisingly, significantly shorter than in **11bp** (2.0720(13) Å)

(41) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1.
(42) Dannecker, W.; Kopf, J.; Rust, H. *Cryst. Struct. Commun.* **1979**, *8*, 429.

Table 3. Crystallographic Data for Complexes 3b, 10·0.5CDCl$_3$, 11bp·OEt$_2$, 11bq, and 14po

	3b	**10**·0.5CDCl$_3$	**11bp**·OEt$_2$	**11bq**	**14po**
formula	$C_{21}H_{29}F_3N_4O_4$-PdS	$C_{39.5}H_{40}D_{0.5}Cl_{1.5}$-$N_5OPd$	$C_{39}H_{49}F_3N_4O_5$-PdS	$C_{31}H_{37}F_3N_4O_6$-PdS	$C_{21}H_{15}NO$
M_r	596.94	761.34	849.28	757.11	297.34
cryst size (mm)	0.36 × 0.28 × 0.08	0.36 × 0.35 × 0.20	0.20 × 0.16 × 0.11	0.35 × 0.20 × 0.19	0.17 × 0.13 × 0.03
cryst syst	monoclinic	triclinic	monoclinic	triclinic	monoclinic
space group	$P2_1/c$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$P2_1/c$
cell constants					
a, Å	11.4308(6)	13.2337(9)	14.6886(12)	11.2565(6)	12.494(2)
b, Å	36.692(2)	16.0883(9)	13.9976(12)	12.1297(6)	8.2559(14)
c, Å	12.6396(8)	18.6439(11)	19.3570(16)	12.7493(6)	14.828(3)
α, deg	90	77.246(4)	90	96.519(4)	90
β, deg	103.788(4)	74.208(4)	92.820(3)	94.892(4)	93.018(8)
γ, deg	90	78.201(4)	90	105.625(4)	90
V, Å^3	5148.5	3681.0	3975.1	1653.34	1527.4
Z	8	4	4	2	4
λ, Å	0.71073	0.71073	0.71073	0.71073	0.71073
ρ(calcd), Mg m^{-3}	1.540	1.374	1.419	1.521	1.293
μ, mm^{-1}	0.86	0.65	0.58	0.69	0.08
F(000)	2432	1568	1760	776	624
T, K	133	133	133	133	133
$2\theta_{max}$, deg	60	60	60	60	52.7
no. of rflns measd	108 507	77 572	81 564	32 571	13 845
no. of indep reflns	15 062	21 464	11 642	9591	3127
transmissn	0.74−0.93	0.79−0.89	0.87−0.96	0.81−0.93	no cor
R_{int}	0.050	0.033	0.045	0.019	0.051
no. of restraints/params	6/639	1/923	121/491	0/429	0/212
$R_w(F^2)$ (all rflns)	0.0656	0.0742	0.0851	0.0571	0.0100
$R(F)$ ($>4\sigma(F)$)	0.0275	0.0274	0.0314	0.0208	0.0391
S	0.98	1.05	1.01	1.04	0.98
max $\Delta\rho$, e Å^{-3}	0.60	0.86	0.81	0.57	0.24

despite the similarities between these complexes and, in particular, of the same ligand in a trans position. In these three complexes, the tmeda N−Pd bond distance trans to oxygen (range 2.0752(15)−2.0567(11) Å) is shorter than that trans to carbon (range 2.1703(15)−2.1416(10) Å) because of the greater trans influence of the aryl or vinyl ligands.

The reported Pd−N distances in amido palladium complexes are in the broad range 2.348−1.923 Å (mean value 2.025 Å) because of the very different natures of the ligands in trans positions.[43] The Pd−N distances in complex **10** (1.9968(13), 2.0037(12) Å) are in the range of amido palladium complexes containing ligands with little trans influence (Cl, imino (bpy or phen), or amido).[44]

Most of the data for *trans*-C−Pd^{II}−C$_{CN_2-carbene}$ complexes correspond to *trans*-"Pd(CN$_2$-carbene)$_2$" species.[43] The broad range of Pd−C$_{CN_2carbene}$ distances in these complexes (range 2.004[45]− 2.137[46] Å, mean value 2.045 Å) implies that they depend mainly on steric factors. There are only a few such carbene complexes having other carbon donor ligands, such as Me or π-allyl, in trans positions; the corresponding range of Pd−C$_{CN_2carbene}$ distances (2.028[47]−2.090[48] Å, mean value 2.053 Å) lies below that of our complex **10** (2.1045(15), 2.1029(15) Å).

Complexes **11bp**·Et$_2$O and **11bq** (Figures 3 and 4) show eight-membered palladacycles adopting a "boat" conformation. In the case of **11bq**, the crystal structure confirms that the isolated isomer is that in which the CCO$_2$Me moiety is attached to the palladium atom. The crystal structure of **14po** (Figure 5) exhibits a planar disposition of the quinoline ring system. The bond lengths and angles are similar to those of 2-quinolone and some of its derivatives.[49] Single crystals of **8t**·0.7Et$_2$O and **2b** were obtained and studied by X-ray diffraction, supporting the suggested structures; however, the data could not be refined adequately because of disorder phenomena.

Conclusions

We report the first ortho-palladated arylurea complexes, obtained by oxidative addition reactions, and have studied their reactivity toward different reagents. Thus, with Tl(TfO) a cyclopalladated complex is formed after coordination of the urea oxygen atom. The reaction with CO gives the corresponding acyl derivative and, if Tl(TfO) is added after the bubbling of CO, the C,N coupling product 3-*p*-tolyl-1*H*-quinazoline-2,4-dione is formed. Alkynes monoinsert, giving complexes that decompose to result in indole derivatives, or react with CO or XyNC, giving quinolone derivatives. Iminoacyl complexes are obtained by reacting isocyanides with

(43) CSD version 5.25; CCDC, Dec 2004.

(44) See for example: Mazet, C.; Gade, L. H. *Chem. Eur. J.* **2003**, *9*, 1759. Paul, F.; Fischer, J.; Ochsenbein, P.; Osborn, J. A. *Angew. Chem., Int. Ed.* **1993**, *32*, 1638. Khoury, R. G.; Senge, M. O.; Colchester, J. E.; Smith, K. M. *J. Chem. Soc., Dalton Trans.* **1996**, 3937. Vogel, E.; Michels, M.; Zander, L.; Lex, J.; Tuzun, N. S.; Houk, K. N. *Angew. Chem., Int. Ed.* **2003**, *42*, 2857. Liu, Q.; Thorne, L.; Kozin, I.; Song, D.; Seward, C.; D'Iorio, M.; Tao, Y.; Wang, S. *Dalton Trans.* **2002**, 3234. Tian, G.; Boyle, P. D.; Novak, B. M. *Organometallics* **2002**, *21*, 1462.

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[Pd{C_6H_4NHC(O)NHTo-2}I(tmeda)]. The product of the reaction with XyNC reacts with TlOTf to give the C,N coupling product 4-(xylylimino)-3-*p*-tolyl-3,4-dihydro-1*H*-quinazolin-2-one. An amido carbene C,N,C pincer complex is obtained, which is a precatalyst in Heck and Suzuki cross-coupling processes.

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Supporting Information Available: Text giving experimental details of the preparation of **11be** and **11bm**, listings of all refined and calculated atomic coordinates, anisotropic thermal parameters, and bond lengths and angles, and CIF files for **3b**, **10**·0.5$CDCl_3$, **11bp**·Et_2O, **11bq**, and **14po**. This material is available free of charge via the Internet at http://pubs.acs.org.

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