Synthesis and Reactivity of Ortho-Palladated Arylcarbodiimides and Aryl Isothiocyanates. Formation of C-Palladated Quinazolines. Synthesis of 2-Aminoquinolines†

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The iminophosphoranes $Ph_3P{=}NC_6H_3X$-2-R-4 (X = I, R = H (**1a**); X = Br, R = NO_2 (**1b**); X = Br, R = Me (**1c**)) react with *p*-tolyl isocyanate and **1a** reacts with CS_2 to give the carbodiimides $ToN{=}C{=}NC_6H_3X$-2-R-4 (To = C_6H_4Me-4; X = I, R = H (**2a**); X = Br, R = NO_2 (**2b**); X = Br, R = Me (**2c**)) and the isothiocyanate $S{=}C{=}NC_6H_4I$-2 (**3**), respectively. The compounds **2** and **3** react with $Pd(dba)_2$ ([$Pd_2(dba)_3$]·dba, dba = dibenzylideneacetone) in the presence of the appropriate ligands to give the ortho-palladated arylcarbodiimides [Pd($C_6H_3N{=}C{=}NTo$-2-R-5)XL_2] (L = PPh_3, X = I, R = H (**4a**); L = PPh_3, X = Br, R = NO_2 (**4b**), Me (**4c**); L_2 = bpy (2,2′-bipyridine), X = I, R = H (**5a**)) and *trans*-[Pd($C_6H_4N{=}C{=}S$-2)I$(PPh_3)_2$] (**6**), respectively. Complex **4a** reacts with pyridine (py) and Tl(TfO) (TfO = triflate, CF_3SO_3) and **5a** reacts with 4-*tert*-butylpyridine (^{t}Bupy) and Tl(TfO) to give the complexes *trans*-[Pd($C_6H_4N{=}C{=}NTo$-2)(py)$(PPh_3)_2$]TfO (**7a**) and [Pd($C_6H_4N{=}C{=}NTo$-2)(^{t}Bupy)(bpy)]TfO (**8a**), respectively. Complex **4a** reacts with XyNC (Xy = 2,6-dimethylphenyl) to give the palladated quinazoline *trans*-[Pd(ToNqXy)I$(CNXy)_2$] (ToNqXy = 3-(2,6-dimethylphenyl)-2-[(4-methylphenyl)imino]-2,3-dihydroquinazolin-4-yl (**9a**)) and with ^{t}BuNC to give [Pd(ToNq^{t}Bu)I(CN^{t}Bu)(PPh_3)] (ToNq^{t}Bu = 3-*tert*-butyl-2-[(4-methylphenyl)imino]-2,3-dihydroquinazolin-4-yl (**10a′**)). Reaction of **10a′** with Tl(TfO) and PPh_3 results in the formation of *trans*-[Pd(ToNHq)(CN^{t}Bu)$(PPh_3)_2$]TfO (**11**; ToNHq = 2-[(4-methylphenyl)amino]quinazolin-4-yl). The reaction of R′C≡CR′ with **4a**, **5a**, or **4c** gives 2-[(4-methylphenyl)amino]-3,4-R′$_2$-6-R-quinoline (R′ = CO_2Me, R = H (**12a**), Me (**12c**); R′ = Ph, R = H (**12a′**)). Some of these reactions require the presence of Tl(TfO). The crystal and molecular structures of **6**, **8a**·$CDCl_3$, **9a**·0.5OEt_2, **11**, **12a**, and **12a′** have been determined.

Introduction

Arylpalladium(II) complexes are of interest as intermediates in important catalytic organic syntheses.[1,2] Some catalytic reactions involve ortho-functionalized aryl palladium(II) complexes, giving carbo- or heterocycles in which the ortho group is included.[3] We have previously reported the synthesis of palladium complexes containing 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^{t}Bu), $C_6H_3(CHO)_2$-2,5, $C_6H_5NH_2$-2, C_6H_4OH-2, and C_6H_4X-2 (X = CH=CH_2, CHO, C(O)Me, CN, PPh_2=NR), as well as ortho-palladated benzyl- and phenethylamines, and studied the reactivity of some of these palladium complexes with alkynes, carbon monoxide, and isocyanides, thereby obtaining interesting new organopalladium(II) complexes and organic compounds.[4−12]

In this paper we report the synthesis of the first arylpalladium complexes whose aryl ligands bear a carbodiimide group at the ortho position. Carbodiimides are very useful intermediates for the synthesis of

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(1) Heck, R. F. *Palladium Reagents in Organic Synthesis*; Academic Press: New York, 1985.

(2) Tsuji, J. *Palladium Reagents and Catalysts*; Wiley: Chichester, U.K., 1995. Hartwig, J. F. *Angew. Chem., Int. Ed.* **1998**, *37*, 2047. Wolfe, J. P.; Wagaw, S.; Marcoux, J.-F.; Buchwald, S. L. *Acc. Chem. Res.* **1998**, *31*, 805. Whitcombe, N. J.; Hii, K. K.; Gibson, S. E. *Tetrahedron* **2001**, *57*, 7449. Li, G. Y.; Zheng, G.; Noonan, A. F. *J. Org. Chem.* **2001**, *66*, 8677. Yin, J. J.; Buchwald, S. L. *J. Am. Chem. Soc.* **2002**, *124*, 6043. Mann, G.; Shelby, Q.; Roy, A. H.; Hartwig, J. F. *Organometallics* **2003**, *22*, 2775. Mann, G.; Baranano, D.; Hartwig, J. F.; Rheingold, A. L.; Guzei, I. A. *J. Am. Chem. Soc.* **1998**, *120*, 9205.

(3) Negishi, E.; Coperet, C.; Ma, S. M.; Mita, T.; Sugihara, T.; Tour, J. M. *J. Am. Chem. Soc.* **1996**, *118*, 5904. Catellani, M.; Motti, E.; Ghelli, S. *Chem. Commun.* **2000**, 2003. Larock, R. C. *Pure Appl. Chem.*. **1999**, *71*, 1435. Ryabov, A. D.; Sakodinskaya, I. K.; Dvoryantsev, S. N.; Eliseev, A. V.; Yatsimirsky, A. K.; Kuz'mina, L. G.; Struchkov, Y. T. *Tetrahedron Lett.* **1986**, *27*, 2169. Dyker, G.; Markwitz, H. *Synthesis* **1998**, 1750. Zhang, H. M.; Larock, R. C. *Org. Lett.* **2001**, *3*, 3083. Roesch, K. R.; Larock, R. C. *J. Org. Chem.* **2001**, *66*, 412. Liao, H. Y.; Cheng, C. H. *J. Org. Chem.* **1995**, *60*, 3711. Ryabov, A. D. *Synthesis* **1985**, 233.

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heterocycles. For example, recently, they have been used as reagents for the synthesis of 1,3-oxazines,[13] pyrido-[1′,2′:1,2]pyrimido[4,5-*b*]indoles,[14] 4-thiazolidinones,[15] and the antitumoral marine alkaloid Variloin B[16] and also for the palladium-catalyzed syntheses of benzo[*e*]-1,3-oxazin-2-imin-4-ones[17] and quinazolinones.[18] We therefore decided to study the synthesis of ortho-palladated arylcarbodiimides and their reactivity toward isocyanides and alkynes.

The insertion of isocyanides into the Pd−C bond of the new arylcarbodiimide complexes takes place, giving C-palladated quinazolines. The only precedent for this type of compound was unexpectedly isolated by us, but its synthesis could not be repeated.[9] Although the insertion reactions of isocyanides to give iminoacyl palladium complexes are well-known,[6,7,9,11,19−21] there are very few examples in which the initial iminoacyl complex evolves, giving a new type of palladium complex. Thus, tautomerizations of iminoacyl to enamine[20,22] or aminofulvene[23] have been observed. In other cases chemical transformation and depalladation occur, giving organic products such as indazolines,[24] indazoles,[25] ketenimines,[6,26] 2-R-aminoisoindolinium (R = Ph, Xy, ^{t}Bu) salts,[21,27] or indole derivatives.[28] Recently, palladium-catalyzed reactions involving aryl halides and isocyanides, giving 2,3-disubstituted indoles,[29] amidines,[30] mappicines, camptothecins, and homocamptothecins, have been described.[31] Reactions of some of our ortho-palladated arylcarbodiimides with alkynes result in the formation of quinolines. Very few examples of palladium-mediated reactions to give this type of compound are known.[32] Quinolines and their derivatives are very important because of their occurrence in natural products[33] and drugs,[34] for example, the natural substance quinine, as well as synthetic pharmaceuticals such as the antibacterial cloxyquine, an antimalarial agent.[35] Very recent reports describe the potential applications of quinolines as antibacterials,[36] antituberculosis agents,[37] or photoluminescent and electroluminescent materials.[38] Most of the traditional methods of synthesis of quinolines suffer from harsh reaction conditions and/or poor yields,[39] and consequently, more efficient methods are being developed.[35,39,40]

(4) Vicente, J.; Abad, J. A.; Jones, P. G. *Organometallics* **1992**, *11*, 3512. Vicente, J.; Abad, J. A.; Gil-Rubio, J.; Jones, P. G.; Bembenek, E. *Organometallics* **1993**, *12*, 4151. Vicente, J.; Abad, J. A.; Frankland, A. D.; Ramírez de Arellano, M. C. *Chem. Commun.* **1997**, 959. Vicente, J.; Abad, J. A.; Martínez-Viviente, E.; Ramírez de Arellano, M. C.; Jones, P. G. *Organometallics* **2000**, *19*, 752. Vicente, J.; Saura-Llamas, I.; Jones, P. G. *J. Chem. Soc., Dalton Trans.* **1993**, 3619. Vicente, J.; Saura-Llamas, I.; Palin, M. G.; Jones, P. G. *J. Chem. Soc., Dalton Trans.* **1995**, 2535. Vicente, J.; Saura-Llamas, I.; Palin, M. G.; Jones, P. G.; Ramírez de Arellano, M. C. *Organometallics* **1997**, *16*, 826. Vicente, J.; Saura-Llamas, I.; Cuadrado, J.; Ramírez de Arellano, M. C. *Organometallics* **2003**, *22*, 5513. Vicente, J.; Abad, J. A.; Gil-Rubio, J. *Organometallics* **1996**, *15*, 3509. Vicente, J.; Abad, J. A.; Gil-Rubio, J.; Jones, P. G. *Organometallics* **1995**, *14*, 2677. Vicente, J.; Saura-Llamas, I.; Ramírez de Arellano, M. C. *J. Chem. Soc., Dalton Trans.* **1995**, 2529. Vicente, J.; Abad, J. A.; Bergs, R.; Jones, P. G.; Ramírez de Arellano, M. C. *Organometallics* **1996**, *15*, 1422.

(5) Vicente, J.; Abad, J. A.; Fernández-de-Bobadilla, R.; Jones, P. G.; Ramírez de Arellano, M. C. *Organometallics* **1996**, *15*, 24.

(6) Vicente, J.; Abad, J. A.; Shaw, K. F.; Gil-Rubio, J.; Ramírez de Arellano, M. C.; Jones, P. G. *Organometallics* **1997**, *16*, 4557.

(7) Vicente, J.; Abad, J. A.; Rink, B.; Hernández, F.-S.; Ramírez de Arellano, M. C. *Organometallics* **1997**, *16*, 5269. Vicente, J.; Saura-Llamas, I.; Turpín, J.; Ramírez de Arellano, M. C.; Jones, P. G. *Organometallics* **1999**, *18*, 2683.

(8) Vicente, J.; Abad, J. A.; Frankland, A. D.; Ramírez de Arellano, M. C. *Chem. Eur. J.* **1999**, *5*, 3066. Vicente, J.; Abad, J. A.; Martinez-Viviente, E.; Jones, P. G. *Organometallics* **2002**, *21*, 4454.

(9) Vicente, J.; Abad, J. A.; Frankland, A. D.; López-Serrano, J.; Ramírez de Arellano, M. C.; Jones, P. G. *Organometallics* **2002**, *21*, 272.

(10) Vicente, J.; Abad, J. A.; Förtsch, W.; Jones, P. G.; Fischer, A. K. *Organometallics* **2001**, *20*, 2704.

(11) Vicente, J.; Abad, J. A.; López-Serrano, J.; Clemente, R.; Ramírez de Arellano, M. C.; Jones, P. G.; Bautista, D. *Organometallics* **2003**, *22*, 4248.

(12) Vicente, J.; Abad, J. A.; Lopez-Pelaez, B.; Martinez-Viviente, E. *Organometallics* **2002**, *21*, 58.

(13) Larksarp, C.; Alper, H. *J. Org. Chem.* **1999**, *64*, 4152.

(14) Lu, X.; Petersen, J. L.; Wang, K. K. *J. Org. Chem.* **2002**, *67*, 7797.

(15) Srivastava, T.; Haq, W.; Katti, S. B. *Tetrahedron* **2002**, *58*, 7619.

(16) Molina, P.; Fresneda, P. M.; Delgado, S. *J. Org. Chem.* **2003**, *68*, 489.

(17) Larksarp, C.; Alper, H. *J. Org. Chem.* **1999**, *64*, 9194.

(18) Larksarp, C.; Alper, H. *J. Org. Chem.* **2000**, *65*, 2773.

(19) Takei, F.; Yanai, K.; Onitsuka, K.; Takahashi, S. *Chem. Eur. J.* **2000**, *6*, 983. Onitsuka, K.; Joh, T.; Takahashi, S. *J. Organomet. Chem.* **1994**, *464*, 247. Owen, G. R.; Vilar, R.; White, A. J. P.; Williams, D. J. *Organometallics* **2002**, *21*, 4799. Delis, J. G. P.; Aubel, P. G.; Vanleeuwen, P.; Vrieze, K.; Veldman, N.; Spek, A. L. *J. Chem. Soc., Chem. Commun.* **1995**, 2233.

(20) Campora, J.; Hudson, S. A.; Massiot, P.; Maya, C. M.; Palma, P.; Carmona, E.; Martinez Cruz, L. A.; Vegas, A. *Organometallics* **1999**, *18*, 5225.

(21) Vicente, J.; Saura-Llamas, I.; Grünwald, C.; Alcaraz, C.; Jones, P. G.; Bautista, D. *Organometallics* **2002**, *21*, 3587.

(22) Bertani, R.; Castellani, C. B.; Crociani, B. *J. Organomet. Chem.* **1984**, *269*, C15. Veya, P.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Organometallics* **1993**, *12*, 4899.

(23) Alias, F. M.; Belderrain, T. R.; Paneque, M.; Poveda, M. L.; Carmona, E.; Valerga, P. *Organometallics* **1997**, *16*, 301. Alias, F. M.; Belderrain, T. R.; Paneque, M.; Poveda, M. L.; Carmona, E.; Valerga, P. *Organometallics* **1998**, *17*, 5620.

(24) Yamamoto, Y.; Yamazaki, H. *Synthesis* **1976**, 750.

(25) Gehrig, K.; Klaus, A. J.; Rys, P. *Helv. Chim. Acta* **1983**, *66*, 2603.

(26) Albinati, A.; Pregosin, P. S.; Rüedi, R. *Helv. Chim. Acta* **1985**, *68*, 2046. Tanase, T.; Fukushima, T.; Nomura, T.; Yamamoto, Y.; Kobayashi, K. *Inorg. Chem.* **1994**, *33*, 32.

(27) O'Sullivan, R. D.; Parkins, A. W. *J. Chem. Soc., Chem. Commun.* **1984**, 1165.

(28) Onitsuka, K.; Yamamoto, M.; Suzuki, S.; Takahashi, S. *Organometallics* **2002**, *21*, 581.

(29) Onitsuka, K.; Suzuki, S.; Takahashi, S. *Tetrahedron Lett.* **2002**, *43*, 6197.

(30) Saluste, C. G.; Whitby, R. J.; Furber, M. *Angew. Chem., Int. Ed. Engl.* **2000**, *39*, 4156.

(31) Curran, D. P.; Du, W. *Org. Lett.* **2002**, *4*, 3215.

(32) Pfeffer, M.; Sutter, J. P.; Decian, A.; Fischer, J. *Organometallics* **1993**, *12*, 1167. Beydoun, N.; Pfeffer, M. *Synthesis* **1990**, 729. Kang, S. K.; Park, S. S.; Kim, S. S.; Choi, J. K.; Yum, E. K. *Tetrahedron Lett.* **1999**, *40*, 4379.

(33) Morimoto, Y.; Matsuda, F.; Shirahama, H. *Synlett* **1991**, 202. Isobe, M.; Nishikawa, T.; Yamamoto, N.; Tsukiyama, T.; Ino, A.; Okita, T. *J. Heterocycl. Chem.* **1992**, *29*, 619. Michael, J. P. *Nat. Prod. Rep.* **1997**, *14*, 605.

(34) Markees, D. G.; Dewey, V. C.; Kidder, G. W. *J. Med. Chem.* **1970**, *13*, 324. Alhaider, A. A.; Abdelkader, M. A.; Lien, E. J. *J. Med. Chem.* **1985**, *28*, 1398. Campbell, S. F.; Hardstone, J. D.; Palmer, M. J. *J. Med. Chem.* **1988**, *31*, 1031.

(35) Beller, M.; Thiel, O. R.; Trauthwein, H.; Hartung, H. *Chem. Eur. J.* **2000**, *6*, 2513 and references therein.

(36) Sadana, A. K.; Mirza, Y.; Aneja, K. R.; Prakash, O. *Eur. J. Med. Chem.* **2003**, *38*, 533.

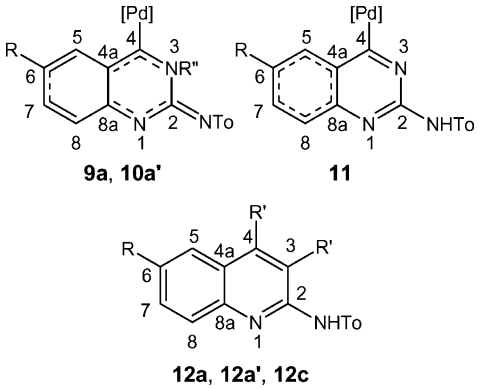
(37) Jain, R.; Vaitilingam, B.; Nayyar, A.; Palde, P. B. *Bioorg. Med. Chem. Lett.* **2003**, *13*.

(38) Liang, F. S.; Chen, J. S.; Cheng, Y. X.; Wang, L. X.; Ma, D. G.; Jing, X. B.; Wang, F. S. *J. Mater. Chem.* **2003**, *13*, 1392.

(39) Huma, H. Z. S.; Halder, R.; Kalra, S. S.; Das, J.; Iqbal, J. *Tetrahedron Lett.* **2002**, *43*, 6485. O'Dell, D. K.; Nicholas, K. M. *J. Org. Chem.* **2003**, *68*, 6427.

(40) Jacob, J.; Jones, W. D. *J. Org. Chem.* **2003**, *68*, 3563. Suginome, M.; Fukuda, T.; Ito, Y. *Org. Lett.* **1999**, *1*, 1977. Takahashi, T.; Li, Y.; Stepnicka, P.; Kitamura, M.; Liu, Y.; Nakajima, K.; Kotora, M. *J. Am. Chem. Soc.* **2002**, *124*, 576. Dormer, P. G.; Eng, K. K.; Farr, R. N.; Humphrey, G. R.; McWilliams, J. C.; Reider, P. J.; Sager, J. W.; Volante, R. P. *J. Org. Chem.* **2003**, *68*, 467. Swenson, R. E.; Sowin, T. J.; Zhang, H. Q. *J. Org. Chem.* **2002**, *67*, 9182. Du, W.; Curran, D. P. *Org. Lett.* **2002**, *5*, 1765. Arcadi, A.; Chiarini, M.; Digiuseppe, S.; Marinelli, F. *Synlett* **2003**, 203. Kobayashi, K.; Yoneda, K.; Mano, M.; Morikawa, O.; Konishi, H. *Chem. Lett.* **2003**, *32*, 76. Mahata, P. K.; Venkatesh, C.; Kumar, U. K. S.; H., I.; Junjappa, H. *J. Org. Chem.* **2003**, *68*.

Chart 1



Experimental Section

Conductivity measurements were made in Me_2CO. When needed, NMR assignments were performed with the help of DEPT, COSY, and HETCOR techniques. The mass spectra were recorded in a Fisons VG-autospec apparatus. $Pd(dba)_2$ ($[Pd_2(dba)_3]$.dba; dba = dibenzylideneacetone) was prepared as described previously.[1,41] The iminophosphoranes $Ph_3P{=}NC_6H_3X$-2-R-4 (X = I, R = H (**1a**); X = Br, R = NO_2 (**1b**); X = Br, R = Me (**1c**)) were prepared by following the Kirsanov method[42] from the corresponding amines and Ph_3PBr_2.[11] 2-Iodoaniline, 2-bromo-4-methylaniline, and *p*-tolyl isocyanate were purchased from Aldrich, 2-bromo-4-nitroaniline was obtained from Merck, XyNC (Xy = 2,6-dimethylphenyl), ^{t}BuNC,and PhC≡CPh were purchased from Fluka, and $MeO_2CC{\equiv}CCO_2Me$ was obtained from Acros. The syntheses were carried out without precautions against light and moisture, unless otherwise stated. The products were filtered in air and dried under a current of air. 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%). See Chart 1 for the atom numbering of complexes **9**−**11**.

Synthesis of ToN=C=NC_6H_4I-2 (2a; To = C_6H_4Me-4). *p*-Tolyl isocyanate (0.44 g, 3.29 mmol) was added to a solution of **1a** (1.55 g, 3.29 mmol) in toluene (10 mL) under nitrogen. The mixture was stirred for 16 h and concentrated to dryness. The residue was treated with *n*-hexane, without the nitrogen atmosphere, giving a colorless suspension which was filtered through anhydrous $MgSO_4$. The solvent of the filtrate was evaporated, giving **2a** as an oily colorless liquid. Yield: 102 g, 95%. IR (Nujol, cm^{-1}): ν 2137 (N=C=N). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.78 (dd, 1 H, H3 or H6, C_6H_4I, $^3J_{H,H}$ = 8 Hz, $^4J_{H,H}$ = 1.5 Hz), 7.27 (td, 1 H, H4 or H5, C_6H_4I, $^3J_{H,H}$ = 8 Hz, $^4J_{H,H}$ = 1.5 Hz), 7.21 (dd, 1 H, H6 or H3, C_6H_4I, $^3J_{H,H}$ = 8 Hz, $^4J_{H,H}$ = 1.5 Hz), 7.11 (s, 4 H, To), 6.83 (td, 1 H, H5 or H4, C_6H_4I, $^3J_{H,H}$ = 8 Hz, $^4J_{H,H}$ = 1.5 Hz), 2.32 (s, 3 H, Me). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 141.32 (C, *C*N, C_6H_4I), 139.45 (C3H, C_6H_4I), 135.54 (C4, To), 134.69 (*C*N, To), 130.02 (C3H, C5H, To), 129.17 (C5H, C_6H_4I), 126.52 (C4H, C_6H_4I), 124.57 (C6H, C_6H_4I), 124.24 (C2H, C6H, To), 93.50 (CI), 20.96 (Me). Anal. Calcd for $C_{14}H_{11}IN_2$: C, 50.32; H, 3.32; N, 8.32. Found: C, 50.69; H, 3.58; N, 8.54.

Synthesis of ToN=C=NC_6H_3Br-2-NO_2-4 (2b). *p*-Tolyl isocyanate (0.42 g, 3.15 mmol) was added to a solution of **1b** (1.50 g, 3.15 mmol) in toluene (10 mL) under nitrogen. The mixture was refluxed for 2.5 h and concentrated to dryness. The residue was applied to a silica gel chromatographic column. Elution with *n*-hexane/ethyl acetate gave an orange band, which was collected, dried over anhydrous $MgSO_4$, filtered, and concentrated to dryness. The resulting oil was dissolved in the minimum amount of warm Et_2O, giving yellow crystals of **2b** on cooling. Yield: 0.81 g, 77%. Mp: 65−67 °C. IR (Nujol, cm^{-1}): ν 2166 (N=C=N). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.46 (d, 1 H, H3, C_6H_3, $^4J_{H,H}$ = 2.5 Hz), 8.13 (dd, 1 H, H5, C_6H_3, $^3J_{H,H}$ = 9 Hz, $^4J_{H,H}$ = 2.5 Hz), 7.30 (d, 1 H, H6, C_6H_3, $^3J_{H,H}$ = 9 Hz), 7.2−7.1 (m, 4 H, To), 2.35 (s, 3 H, Me). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 145.2 (C, C_6H_3), 144.3 (C, C_6H_3), 136.6 (C, *C*Me), 132.7 (*C*N, To), 130.2 (C3H, C5H, To), 129.3 (NCN), 128.7 (C3H, C_6H_3), 125.3 (C6H, C_6H_3), 124.6 (C2H, C6H, To), 123.6 (C5H, C_6H_3), 118.7 (C), 21.0 (Me). Anal. Calcd for $C_{14}H_{10}BrN_3O_2$: C, 50.62; H, 3.03; N, 12.65. Found: C, 50.59; H, 3.01; N, 12.52.

Synthesis of ToN=C=NC_6H_3Br-2-Me-4 (2c). The colorless oil **2c** was obtained as for **2a** from *p*-tolyl isocyanate (500 mg, 3.73 mmol) and **1c**. Reaction time: 5 h. Yield: 970 mg, 88%. IR (Nujol, cm^{-1}): ν 2133 (N=C=N). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.38 (d, 1 H, H3, C_6H_3, $^4J_{H,H}$ = 1 Hz), 7.13−7.0 (m, 6 H), 2.33 (s, 3 H, Me, To), 2.30 (s, 3 H, Me). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 136.6 (C4, C_6H_3), 135.3 (C), 135.2 (C), 134.9 (C), 133.5 (C3H, C_6H_3), 133.2 (NCN), 130.0 (C3H, C5H, To), 129.0 (C5H, C_6H_3), 125.3 (C6H, C_6H_3), 124.1 (C2H, C6H, To), 118.5 (CBr), 20.9 (Me, To), 20.6 (Me). Anal. Calcd for $C_{15}H_{13}BrN_2$: C, 59.82; H, 4.35; N, 9.30. Found: C, 60.29; H, 4.50; N, 9.36.

Synthesis of S=C=NC_6H_4I-2 (3). 1a was dissolved in carbon disulfide (5 mL) in a closed tube. The resulting solution was heated at 100 °C for 2 h. After this time the mixture was cooled to room temperature and concentrated to dryness. The residue was applied to a silica chromatographic column and eluted with Et_2O/*n*-hexane (1:5). The resulting solution was concentrated to dryness, leaving **3** as a colorless liquid contaminated with ca. 10% of the carbodiimide 2-$IC_6H_4N{=}C{=}NC_6H_4$I-2. Yield: 771 mg. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (dd, 1 H, H6, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1.3 Hz), 7.34−7.30 (m, 1 H, H4), 7.25 (dd, 1 H, H3, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1.3 Hz), 6.99−6.24 (m, 1 H, H5). The signals corresponding to the carbodiimide appear at δ 7.83−7.76 (m), 7.33−7.30 (m), and 6.91−6.86 (m).

Synthesis of *trans*-[Pd(C_6H_4N=C=NTo-2)I(PPh_3)$_2$] (4a). $Pd(dba)_2$ ($[Pd_2(dba)_3]$·dba, dba = dibenzylideneacetone; 1.06 g, 1.84 mmol) and PPh_3 (0.96 g, 3.68 mmol) were mixed in dry degassed toluene (10 mL) under nitrogen and stirred for 10 min in an ice bath. The compound **2a** (0.82 g, 2.44 mmol) and toluene (20 mL) were added to the mixture and stirred for 5 h, allowing the temperature to rise to room temperature. The greenish suspension was concentrated to dryness, and the residue was treated with CH_2Cl_2 (40 mL) without the protective nitrogen atmosphere. The resulting suspension was filtered over anhydrous $MgSO_4$ and the corresponding solution concentrated to dryness. The residue was triturated with Et_2O (20 mL), filtered, and dried to give colorless **4a**. Yield: 1.31 g, 70%. Mp: 150 °C dec. IR (Nujol, cm^{-1}): ν 2120 (N=C=N). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.56−7.48 (m, 12 H, ortho H's PPh_3), 7.34−7.29 (m, 6 H, para H's PPh_3), 7.25−7.18 (m, 12 H, meta H's PPh_3), 7.13 (d, 2 H, To, $^3J_{H,H}$ = 8 H), 6.97−6.89 (m, 3 H), 6.45 (br t, 1 H, H4 or H5, C_6H_4, $^3J_{H,H}$ = 7.5 Hz), 6.32 (br t, 1 H, H4 or H5, C_6H_4, $^3J_{H,H}$ = 7.5 Hz), 6.05 (m, 1 H, C_6H_4), 2.37 (s, 3 H, Me). $^{13}C\{^1H\}$ NMR: not sufficiently soluble. $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 22.00 (s, PPh_3). Anal. Calcd for $C_{50}H_{41}IN_2P_2Pd$: C, 62.22; H, 4.28; N, 2.90. Found: C, 61.66; H, 4.01; N, 3.30.

Synthesis of *trans*-[Pd(C_6H_3N=C=NTo-2-NO_2-5)Br(PPh_3)$_2$] (4b). $Pd(dba)_2$ (0.91 g, 1.58 mmol) and PPh_3 (1.06 g, 4.05 mmol) were mixed in dry degassed toluene (10 mL) under nitrogen and stirred for 10 min. The compound **2b** (0.70 g, 2.08 mmol) was added to the mixture, which was slowly heated to boiling temperature and, then, boiled for 15 min (whereby black palladium started to form). The mixture was cooled to room temperature and, operating as for **4a**, yellow **4b** could be isolated. Yield: 1.18 g, 78%. Mp: 170−172 °C. IR (Nujol,

(41) Takahashi, Y.; Ito, S.; Sakai, S.; Ishii, Y. *J. Chem. Soc., Chem. Commun.* **1970**, 1065.

(42) Johnson, A. V. *Ylides and Imines of Phosphorus*; Wiley: New York, 1993.

cm^{-1}): ν 2124, 2101 (N═C═N). ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.7−7.5 (m, 13 H, ortho H's PPh_3 + H6, C_6H_3), 7.4−7.2 (m, 19 H, meta H's PPh_3 + para H's PPh_3 + H4, C_6H_3), 7.11 (d, 2 H, To, $^3J_{HH}$ = 8 Hz), 6.90 (d, 2 H, To, $^3J_{HH}$ = 8 Hz), 6.12 (d, 1 H, H4, C_6H_3, $^3J_{H,H}$ = 8 Hz), 2.37 (s, 3 H, Me). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 158.42 (t, CPd, $^2J_{PC}$ = 4.5 Hz), 148.49 (C2, C_6H_3), 143.19 (C5, C_6H_3), 135.51 (C, To), 134.91 (C, To), 134.64 ("t", CH, ortho C's PPh_3, $|^2J_{PC} + {}^4J_{PC}|$ = 13 Hz), 131.90 (t, C6H, C_6H_3, $^3J_{PC}$ = 4 Hz), 131.70 (s, C), 130.60 ("t", ipso C's PPh_3, $|^1J_{PC} + {}^3J_{PC}|$ = 46 Hz), 130.16 (para CH's PPh_3), 130.13 (C2H and C6H, To), 127.98 ("t", meta CH's PPh_3, $|^3J_{PC} + {}^5J_{PC}|$ = 10 Hz), 124.08 (C3H and C5H, To), 122.97 (C3H, C_6H_3), 119.23 (C4H, C_6H_3), 21.03 (Me). ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$): δ 24.03 (s, PPh_3). Anal. Calcd for $C_{50}H_{40}BrN_3O_2P_2Pd$: C, 62.35; H, 4.19; N, 4.36. Found: C, 62.36; H, 4.24; N, 4.16.

Synthesis of *trans*-[Pd(C$_6$H$_3$N═C═NTo-2-Me-5)Br(PPh$_3$)$_2$] (4c). $Pd(dba)_2$ (1.48 g, 2.55 mmol) and PPh_3 (1.67 g, 6.38 mmol) were mixed in dry degassed toluene (10 mL) under nitrogen and stirred for 10 min. The compound **2c** (1.00 g, 3.32 mmol) was added to the mixture, which was slowly heated to reflux temperature and then refluxed for 40 min (whereby black palladium started to form). Working up as described for **4a**,**b** gave colorless **4c**. Yield: 1.36 g, 57%. Mp: 140−142 °C dec. IR (Nujol, cm^{-1}): ν 2122 (N═C═N). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.6−7.45 (m, 12 H, ortho H's, PPh_3), 7.4−7.29 (m, 6 H, para H's, PPh_3), 7.25−7.18 (m, 12 H, meta H's, PPh_3), 7.06 (d, 2 H, H3 and H5, To, $^3J_{HH}$ = 8 Hz), 6.86 (d, 2 H, H2 and H6, To, $^3J_{HH}$ = 8 Hz), 6.52 (d, 1 H, H6, C_6H_3, $^4J_{H,H}$ = 2 Hz), 6.22 (d, 1 H, H4, C_6H_3, $^3J_{H,H}$ = 8 Hz), 5.99 (d, 1 H, H3, C_6H_3, $^3J_{H,H}$ = 8 Hz), 2.34 (s, 3 H, Me, To), 1.74 (s, 3 H, Me). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 153.8 (NCN), 138.7 (C2, C_6H_3), 137.3 (NC, To), 137.1 (C6H, C_6H_3), 134.8 ("t", ortho CH's, PPh_3, $|^2J_{PC} + {}^4J_{PC}|$ = 12.5 Hz), 134.2 (C, *C*Me), 133.5 (C, C1 or C5, C_6H_3), 133.3 (C, C1 or C5, C_6H_3), 131.1 ("t", C, ipso C's, PPh_3, $|^1J_{PC} + {}^3J_{PC}|$ = 46 Hz), 129.9 (C3H and C5H, To), 129.7 (para C's, PPh_3), 127.7 ("t", meta CH's, PPh_3, $|^3J_{PC} + {}^5J_{PC}|$ = 10.5 Hz), 124.8 (C3H, C_6H_3), 124.3 (C4H, C_6H_3), 123.8 (C2H and C6H, To), 21.0 (Me, To), 20.8 (Me). ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ 24.10 (s, PPh_3). Anal. Calcd for $C_{51}H_{43}BrN_2P_2Pd$: C, 65.71; H, 4.65; N, 3.01. Found: C, 65.32; H, 4.80; N, 2.95.

Synthesis of [Pd(C$_6$H$_4$N═C═NTo-2)I(bpy)] (5a; bpy = 2,2′-Bipyridine). $Pd(dba)_2$ (1.48 g, 2.55 mmol) and bpy (0.61 g, 3.9 mmol) were mixed in dry degassed toluene (10 mL) under nitrogen and stirred for 10 min at 0 °C. Then, **2a** (1.14 g, 3.4 mmol) and toluene (20 mL) were added and the resulting mixture was stirred, allowing the temperature to rise to room temperature for 16 h. The residue was treated with CH_2Cl_2 (40 mL), without the protective nitrogen atmosphere, and the new suspension filtered through $MgSO_4$. The resulting solution was concentrated to dryness, leaving a residue that was triturated with Et_2O (20 mL) and then filtered, washed with Et_2O (2 × 5 mL), and dried to give orange **5a**. Yield: 1.07 g, 70%. Mp: 102−104 °C dec. IR (Nujol, cm^{-1}): ν 2088 (N═C═N). ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.29 (d, 1 H, bpy, $^3J_{HH}$ = 5 Hz), 7.97 (td, 1 H, H4 or H5, C_6H_4, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1.5 Hz), 7.9−7.75 (m, 3 H), 7.65−7.60 (m, 1 H), 7.57−7.50 (m, 1 H), 7.37−7.27 (m, 2 H), 6.97−6.85 (m, 3 H), 6.61−6.54 (m, 4 H, To), 2.14 (s, 3 H, Me).^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 155.76 (C), 155.39 (C), 152.60 (CH), 149.61 (CH), 144.14 (C), 143.66 (C), 138.76 (CH), 138.62 (CH), 138.02 (CH), 136.55 (C), 136.23 (C), 133.46 (C), 129.11 (CH, To), 126.59 (CH), 126.25 (CH), 124.25 (CH), 124.15 (CH), 123.84 (CH), 123.70 (CH, To), 122.12 (CH), 121.30 (CH), 20.86 (Me). Anal. Calcd for $C_{24}H_{19}IN_4Pd$: C, 48.31; H, 3.21; N, 9.39. Found: C, 48.61; H, 3.46; N, 9.08.

Synthesis of *trans*-[Pd(C$_6$H$_4$N═C═S-2)I(PPh$_3$)$_2$] (6). $Pd(dba)_2$ (179 mg, 0.31 mmol) and PPh_3 (204 mg, 0.78 mmol) were mixed in dry degassed toluene (10 mL) under nitrogen and stirred for 15 min. 2-Iodophenyl isothiocyanate (135 mg, approximately 0.47 mmol) was added, and the resulting mixture was stirred for a further 5 h. The suspension was concentrated to dryness, the residue was extracted with CH_2Cl_2 (10 mL), without the protective nitrogen atmosphere, and the extract was filtered over anhydrous $MgSO_4$. The filtrate was concentrated (ca. 1 mL) and Et_2O (5 mL) added, causing the precipitation of a solid, which was collected by filtration, washed with Et_2O (5 × 3 mL), and air-dried to give orange **6**. Yield: 210 mg, 76%. Mp: 184−186 °C. IR (KBr, cm^{-1}): ν 2146, 2100 (SCN). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62−7.55 (m, 12 H, ortho H's, PPh_3), 7.35−7.31 (m, 6 H, para H's, PPh_3), 7.29−7.24 (m, 12 H, meta H's, PPh_3), 6.97−6.94 (m, 1 H, C_6H_4), 6.40−6.35 (m, 2 H, C_6H_4), 6.00−6.35 (m, 1 H, C_6H_4). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 160.51 (t, C1, C_6H_4, $^2J_{PC}$ = 4.5 Hz), 135.53 (t, C6H, C_6H_4, $^3J_{PC}$ = 4.2 Hz), 134.96 (C2, C_6H_4), 134.83 ("t", ortho CH's, PPh_3, $|^1J_{PC} + {}^3J_{PC}|$ = 12.2 Hz), 131.48 ("t", ipso C's, PPh_3, $|^1J_{PC} + {}^3J_{PC}|$ = 47.2 Hz), 129.96 (para CH's, PPh_3), 127.82 ("t", meta CH's, PPh_3, $|^1J_{PC} + {}^3J_{PC}|$ = 10.8 Hz), 126.45 (CH, C_6H_4), 125.50 (CH, C_6H_4), 123.41 (CH, C_6H_4). ^{31}P-{^{1}H} NMR (161 MHz, $CDCl_3$): δ 22.04 (s, PPh_3). Anal. Calcd for $C_{43}H_{34}INP_2PdS$: C, 57.90; H, 3.84; N, 1.57; S, 3.59. Found: C, 57.54; H, 3.92; N, 1.60; S, 3.24. Single crystals were obtained by slow diffusion of Et_2O into solutions of **6** in $CDCl_3$.

Synthesis of *trans*-[Pd(C$_6$H$_4$N═C═NTo-2)(py)(PPh$_3$)$_2$]-TfO (7a). Pyridine (py; 43 μL, 0.52 mmol) and Tl(TfO) (TfO = triflate, CF_3SO_3; 91 mg, 0.26 mmol) were added to a suspension of **4a** (250 mg, 0.26 mmol) in a CH_2Cl_2 (5 mL)/Me_2CO (5 mL) mixture. The mixture was stirred for 10 min, and the suspension was filtered through Celite; the filtrate was concentrated to dryness and the residue triturated with Et_2O (10 mL). The suspension was filtered, and the solid was washed with Et_2O (3 × 3 mL) and dried in vacuo overnight to give colorless **7a**. Yield: 223 mg, 81%. Mp: 131 °C dec. Λ_M = 134 Ω^{-1} cm^2 mol^{-1}. IR (Nujol, cm^{-1}): ν 2132, 2114 (N═C═N), 1030 (OTf). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (dd, 2 H, py, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 1 Hz), 7.41−7.36 (m, 6 H, PPh_3), 7.30 (t, 1 H, $^3J_{HH}$ = 8 Hz), 7.27−7.18 (m, 24 H, PPh_3), 7.14 (d, 2 H, To, $^3J_{HH}$ = 13.5 Hz), 6.96 (dd, 1 H, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1 Hz), 6.82 (d, 2 H, To, $^3J_{HH}$ = 13.5 Hz), 6.78−6.72 (m, 3 H), 6.45 (t, 1 H, $^3J_{HH}$ = 7.5 Hz), 6.43 (dd, 1 H, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1 Hz), 2.37 (s, 3 H, Me). ^{13}C-{^{1}H} NMR (100 MHz, $CDCl_3$): δ 150.75 (CH py), 142.20 (C), 141.69 (C), 137.86 (CH), 137.28 (CH), 136.03 (C), 135.48 (C), 133.58 ("t", ortho CH's, PPh_3, $|^2J_{PC} + {}^4J_{PC}|$ = 12 Hz), 130.97 (para CH's, PPh_3), 130.26 (CH, To), 128.81 ("t", meta CH's, PPh_3, $|^3J_{PC} + {}^5J_{PC}|$ = 10 Hz), 127.94 ("t", C, ipso C's, PPh_3, $|^1J_{PC} + {}^3J_{PC}|$ = 46 Hz), 125.75 (CH), 125.28 (CH), 125.15 (CH), 124.90 (CH), 123.82 (CH, To), 20.99 (Me). ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ 19.77 (s, PPh_3). Anal. Calcd for $C_{56}H_{46}F_3IN_3O_3P_2PdS$: C, 63.07; H, 4.35; N, 3.94; S, 3.01. Found: C, 62.99; H, 4.27; N, 4.07; S, 2.73.

Synthesis of [Pd(C$_6$H$_4$N═C═NTo-2)(^{t}Bupy)(bpy)]TfO (8a; ^{t}Bupy = 4-*tert*-Butylpyridine). The colorless complex **8a** was similarly prepared as for **7a** from **5a** (100 mg, 0.17 mmol), ^{t}Bupy (50 μL, 0.34 mmol), and Tl(TfO) (60 mg, 0.17 mmol) in Me_2CO (10 mL). Yield: 115 mg, 90%. Mp: 172 °C. Λ_M = 132 Ω^{-1} cm^2 mol^{-1}. IR (Nujol, cm^{-1}): ν 2108, 2090 (N═C═N), 1030 (OTf). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.85 (dd, 2 H, H2 and H6**,** ^{t}Bupy, $^3J_{HH}$ = 5.5 Hz, $^4J_{HH}$ = 1.5 Hz), 8.28 (d, 1 H, $^3J_{HH}$ = 7.5 Hz), 8.22 (d, 1 H, $^3J_{HH}$ = 8 Hz), 8.13 (td, 1 H, $^3J_{HH}$ = 7.5 Hz, ^4J = 1.5 Hz), 8.09 (td, 1 H, $^3J_{HH}$ = 7.5 Hz, ^4J = 1.5 Hz), 7.61−7.55 (m, 4 H, H3 and H5**,** ^{t}Bupy and other aromatic protons), 7.52 (m, 1 H), 7.39 (dd, 1 H, ^3J = 5.5 Hz, $^4J_{HH}$ = 1 Hz), 7.33 (m, 1 H), 7.08 (td, 1 H, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.5 Hz), 7.01−6.95 (m, 2 H), 6.56 (d, 2 H, H3 and H5, To, $^3J_{HH}$ = 8 Hz), 6.30 (d, 2 H, H2 and H6, To, $^3J_{HH}$ = 8 Hz), 2.18 (s, 3 H, Me), 1.37 (s, 9 H, ^{t}Bu). ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$): δ 164.5 (C4, ^{t}Bupy), 156.4 (C), 153.2(C), 151.4 (C2H and C6H, ^{t}Bupy), 150.8 (C), 150.7 (CH), 147.0 (CH), 142.9 (C), 140.8 (CH), 140.5 (CH), 137.2 (C), 135.1 (C4 or C1, To), 135.0 (C4 or C1, To), 133.6 (CH), 129.8 (C3H and C5H, To), 127.5 (CH), 127.0 (CH), 125.8 (CH), 125.4 (C3H and C5H**,** ^{t}Bupy), 124.7 (CH), 124.2 (C2H and C6H, To), 123.6 (CH), 122.4 (CH),

35.4 (C, *C*Me$_3$), 30.1 (C*Me*$_3$), 20.7 (Me). Anal. Calcd for $C_{34}H_{32}F_3N_5O_3PdS$: C, 54.15; H, 4.28; N, 9.29; S, 4.25. Found: C, 54.10; H, 4.21; N, 9.23; S, 3.88. Single crystals of **8a**·$CDCl_3$ were obtained by slow diffusion of *n*-hexane into solutions of **8a** in $CDCl_3$.

Synthesis of *trans*-[Pd(ToNqXy)I(CNXy)$_2$] (9a; ToNqXy = 3-(2,6-Dimethylphenyl)-2-[(4-methylphenyl)imino]-2,3-dihydroquinazolin-4-yl). Method A. Complex **4a** (240 mg, 0.24 mmol) was reacted with XyNC (Xy = 2,6-dimethylphenyl; 130 mg, 1.00 mmol) in CH_2Cl_2 (10 mL) for 30 min. The resulting purple solution was filtered through Celite and the filtrate concentrated to dryness. The residue was treated with Et_2O (10 mL), giving a solid which was filtered, washed with Et_2O (3 × 3 mL), and dried to give purple **9a**. Yield: 165 mg, 83%.

Method B. **9a** was obtained similarly from **5a** (120 mg, 0.20 mmol) and XyNC (105 mg, 0.80 mmol). Yield: 120 g, 75%.

Method C. Pd(dba)$_2$ (664 mg, 1.16 mmol) and XyNC (664 mg, 5.03 mmol) were mixed and stirred in dry degassed toluene (10 mL), under nitrogen, at 0 °C for 10 min. Then **2a** (515 mg, 1.54 mmol) and more toluene (10 mL) were added, and the resulting mixture was stirred for 6 h, allowing it to reach room temperature. The residue was treated with CH_2Cl_2 (20 mL), without the protective nitrogen atmosphere, giving a suspension which was filtered through anhydrous $MgSO_4$. The filtrate was concentrated to dryness and the residue triturated with Et_2O (10 mL), giving a solid which was collected by filtration, washed with Et_2O (3 × 3 mL), and dried to give purple **9a**. Yield: 610 mg, 62%. Mp: 168−170 °C. IR (Nujol, cm^{-1}): ν 2296 (C≡N), 1640 (C═N). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, 1 H, H5 or H8, C_6H_4, $^3J_{HH}$ = 7.5 Hz), 7.33 (td, 1 H, H6 or H7, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.5 Hz), 7.31−7.23 (m, 3 H), 7.12−7.09 (m, 7 H), 7.05 (d, 2 H, To, $^3J_{HH}$ = 8 Hz), 6.97 (d, 2 H, To, $^3J_{HH}$ = 8 Hz), 6.73 (t, 1 H, H6 or H7, $^3J_{HH}$ = 7.5 Hz), 2.27 (s, 12 H, 4 Me, *trans*-CNXy), 2.23 (s, 3 H, Me, To), 2.20 (s, 6 H, 2 Me inserted XyNC). ^{13}C{^{1}H} NMR (75 and 100 MHz, $CDCl_3$): δ 191.72 (C−Pd), 154.03 (C), 152.05 (C), 147.87 (C), 143.91 (C), 136.30 (C), 136.08 (CH), 134.12 (CH), 133.79 (C), 130.73 (CH), 129.48 (C), 128.74 (CH), 128.69 (CH), 128.32 (CH), 128.22 (CH), 125.76 (C), 125.56 (CH), 122.99 (CH), 118.32 (CH), 20.86 (Me), 18.64 (Me), 18.36 (Me). Anal. Calcd for $C_{41}H_{38}IN_5Pd$: C, 59.04; H, 4.59; N, 8.39. Found: C, 58.67; H, 4.59; N, 8.29. Single crystals of **9a**·0.5Et_2O were grown by slow recrystallization from CH_2Cl_2/Et_2O.

Synthesis of [Pd(ToNq^{t}Bu)I(CN^{t}Bu)(PPh$_3$)] (10a′; ToNq^{t}Bu = 3-*tert*-Butyl-2-[(4-methylphenyl)imino]-2,3-dihydroquinazolin-4-yl). ^{t}BuNC (73 μL, 0.63 mmol) was added to a solution of **4a** (150 mg, 0.15 mmol) in CH_2Cl_2 (5 mL), giving a purple solution that was stirred for 20 min. The solution was filtered through Celite, the filtrate was concentrated to dryness, and the residue was triturated with *n*-pentane/Et_2O 2:1 (10 mL). The resulting solid was collected by filtration, washed with *n*-pentane/Et_2O 2:1 (3 × 3 mL), and dried to give purple **10a′**. Yield: 110 mg, 85%. Mp: 146−148 °C. IR (Nujol, cm^{-1}): ν 2216 (C≡N). ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.29 (d, 1 H, H5 or H6, $^3J_{HH}$ = 8 Hz), 7.70−7.25 (m, 15 H, PPh$_3$), 7.09 (d, 2 H, To, $^3J_{HH}$ = 8 Hz), 6.99 (d, 2 H, To, $^3J_{HH}$ = 8 Hz), 6.85 (t, 1 H, H6 or H7, $^3J_{HH}$ = 8 Hz), 6.67 (d, 1 H, H5 or H8, $^3J_{HH}$ = 8 Hz), 6.04 (t, 1 H, H6 or H7, $^3J_{HH}$ = 8 Hz), 2.25 (s, 3 H, Me), 1.99 (s, 9 H, ^{t}Bu), 1.19 (s, 9 H, ^{t}Bu). ^{13}C{^{1}H} NMR: the compound decomposes during the experiment; however, a three-bond CH correlation (HMBC) permits the assignment of the signal at 190.09 ppm to C−Pd. ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ 15.10 (s, PPh$_3$). Anal. Calcd for $C_{42}H_{49}IN_4PPd$: C, 58.04; H, 5.10; N, 6.54. Found: C, 57.65; H, 5.09; N, 6.23.

Synthesis of *trans*-[Pd(ToNHq)(CN^{t}Bu)(PPh$_3$)$_2$]TfO (11; ToNHq = 2-[(4-Methylphenyl)amino]quinazolin-4-yl). PPh$_3$ (37 mg, 0.14 mmol) and Tl(TfO) (42 mg, 0.12 mmol) were added to a solution of **10a′** (100 mg, 0.12 mmol) in Me_2CO (10 mL), and the resulting suspension was stirred for 30 min. The solvent was removed, during which the color of the reaction mixture changed from red to yellow. The residue was treated with CH_2Cl_2 (5 mL), and the mixture was filtered through Celite, giving a clear solution which was concentrated to dryness. The residue was triturated with Et_2O to give a solid which was filtered, washed with Et_2O (3 × 3 mL), and dried to give **11** as a pale yellow solid. Yield: 105 mg, 83%. This solid was recrystallized from CH_2Cl_2/*n*-pentane to give crystals of **11**, some of which were suitable for an X-ray diffraction study. Yield: 87 mg, 70%. Mp: 162−164 °C. Λ_M = 127 Ω^{-1} cm^2 mol^{-1}. IR (Nujol, cm^{-1}): ν 3320 (N−H), 2213 (C≡N), 1030 (OTf). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.80 (d, 1 H, H5 or H8, C_6H_4, $^3J_{HH}$ = 7.5 Hz). 7.50−7.25 (m, 33 H), 7.11 (d, 2 H, To, $^3J_{HH}$ = 8.5 Hz), 7.04−6.97 (m, 2 H), 6.52 (b s, 1 H, NH), 2.38 (s, 3 H, Me), 0.78 (s, 9 H, ^{t}Bu). ^{13}C{^{1}H} NMR: decomposes during the experiment. ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ 23.12 (s, PPh$_3$). Anal. Calcd for $C_{57}H_{51}F_3N_4O_3P_2PdS$: C, 62.38; H, 4.68; N, 5.11; S, 2.92. Found: C, 62.20; H, 4.77; N, 5.09; S, 2.58.

Synthesis of 3,4-Bis(carboxymethyl)-2-[(4-methylphenyl)amino]quinoline (12a). Method A. Complex **4a** (250 mg, 0.26 mmol) and $MeO_2CC{\equiv}CCO_2Me$ (95 μL, 0.78 mmol) were mixed in Me_2CO (10 mL) in a Carius tube, and the resulting mixture was heated at 150 °C for 30 min. The reaction mixture was cooled to room temperature and filtered through Celite. The filtrate was concentrated (ca. 1 mL) and applied to a silica gel chromatographic column. Elution with *n*-hexane/Et_2O gave a yellow fraction, which was concentrated to dryness; the residue was recrystallized from Et_2O/*n*-hexane, giving yellow **12a**. Yield: 61 mg, 70%.

Method B. **12a** was obtained similarly, from complex **5a** (150 mg, 0.25 mmol), $MeO_2CC{\equiv}CCO_2Me$ (179 mg, 1.26 mmol), and Tl(TfO) (88 mg, 0.25 mmol). Yield: 34 mg, 40%. Mp: 98−100 °C. IR (Nujol, cm^{-1}): ν 3342 (N−H), 1732, 1704 (C═O). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.83 (s, 1 H, NH), 7.77−7.73 (several m, 3 H, H2 and H6, To, H8), 7.64 (td, 1 H, H7, $^3J_{H,H}$ = 7.6 Hz, $^4J_{H,H}$ = 1.6 Hz), 7.55 (dd, 1 H, H5, $^3J_{H,H}$ = 7.6 Hz, $^4J_{H,H}$ = 1.6 Hz), 7.29 (td, 1 H, H6, $^3J_{H,H}$ = 7.6 Hz, $^4J_{H,H}$ = 1.6 Hz), 7.17 (d, 2 H, H3 and H5, To, $^3J_{HH}$ = 8 Hz), 4.04 (s, 3 H, OMe), 3.96 (s, 3 H, OMe), 2.35 (s, 3 H, Me). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 167.73 (C═O), 166.65 (C═O), 151.58 (C2 or C3), 149.50 (C8a), 145.12 (C4), 137.09 (CN, To), 132.70 (C7H), 132.49 (*C*Me), 129.26 (C3H and C5H, To), 127.28 (C8H), 125.89 (C5H), 123.98 (C6H), 120.62 (C2H and C6H, To), 118.81 (C4a), 107.23 (C3 or C2), 53.12 (OMe), 52.78 (OMe), 20.87 (Me). EI MS *m*/*z*: 350 (M$^+$, 90%), 317 (M$^+$ − OMe, 32%), 287.15 (M$^+$ − 2OMe, 13%), 232 (M$^+$ − 2CO_2Me, 100%), 91 (To$^+$, 14%). Anal. Calcd for $C_{20}H_{18}N_2O_4$: C, 68.56; H, 5.18; N, 8.00. Found: C, 68.38; H, 5.15; N, 7.90. Single crystals of **12a** suitable for the X-ray diffraction study were obtained by cooling a concentrated *n*-hexane solution of the amorphous solid.

Synthesis of 3,4-Diphenyl-2-[(4-methylphenyl)amino]-quinoline (12a′). Complex **5a** (150 mg, 0.25 mmol), Tl(TfO) (90 mg, 0.25 mmol), and PhC≡CPh (223 mg, 1.25 mmol) were mixed in Me_2CO (5 mL) in a Carius tube, and the resulting mixture was heated at 150 °C for 5 h. The reaction mixture was cooled to room temperature and filtered over Celite. The resulting solution was concentrated to dryness, and the residue was treated with Et_2O (5 mL) and applied to a silica gel preparative TLC plate. Elution with *n*-hexane/Et_2O (5:1) gave a yellow fraction (R_f = 0.45), which was extracted with CH_2Cl_2 (15 mL). The extract was dried with anhydrous $MgSO_4$ and filtered and the filtrate concentrated to dryness, giving a solid which was dried in vacuo to give **12a′** as a yellow solid. Yield: 40 mg, 41%. Mp: 168−170 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.91 (d, 1 H, H5 or H8, $^3J_{H,H}$ = 8 Hz), 7.62 (d, 2 H, H2 and H6, To, $^3J_{H,H}$ = 8.5 Hz), 7.56 (td, 1 H, H6 or H7, $^3J_{H,H}$ = 8 Hz, $^4J_{H,H}$ = 1.5 Hz), 7.40−7.10 (several m, 14 H), 6.41 (s, 1 H, NH), 2.31 (s, 3 H, Me). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 151.81 (C), 147.29 (C), 147.03 (C), 137.89 (C), 137.00 (C), 135.62 (C), 131.62 (C), 130.76 (CH), 130.04 (CH), 129.22 (CH),

Table 1. Crystallographic Data for Complexes 6, 8a·CDCl$_3$, and 9a·0.5OEt$_2$

	6	**8a**·$CDCl_3$	**9a**·$0.5OEt_2$
formula	$C_{43}H_{34}INP_2PdS$	$C_{35}H_{32}Cl_3DF_3N_5O_3PdS$	$C_{43}H_{43}IN_5O_{0.5}Pd$
M_r	892.01	874.47	871.12
habit	yellow tablet	pale yellow lath	dark red tablet
cryst size (mm)	0.37 × 0.23 × 0.10	0.40 × 0.18 × 0.08	0.28 × 0.17 × 0.05
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$C2/c$	$P2_1/n$
cell constants			
a (Å)	18.6773(11)	19.4435(12)	11.6858(11)
b (Å)	10.1129(7)	17.2646(12)	12.4756(12)
c (Å)	21.2647(12)	23.0688(12)	27.123(2)
α (deg)	90	90	90
β (deg)	109.686(4)	107.358(3)	99.538(3)
γ (deg)	90	90	90
V (Å^3)	3781.8	7391.2	3899.5
Z	4	8	4
D_{exptl} (Mg m^{-3})	1.567	1.572	1.484
μ (mm^{-1})	1.48	0.83	1.31
$F(000)$	1776	3536	1756
T (°C)	−140	−140	−140
$2\theta_{max}$	60	56.6	56.6
no. of rflns measd	77 534	63 723	61 700
no. of indep rflns	11 066	9177	9688
transmissions	0.66−0.80	0.77−0.93	0.71−0.92
R_{int}	0.026	0.041	0.055
no. of params	442	464	460
no. of restraints	89	116	419
$R_w(F^2$, all reflns)	0.055	0.077	0.137
$R(F, >4\sigma(F))$	0.021	0.028	0.052
S	1.03	1.04	1.05
max $\Delta\rho$ (e Å^{-3})	1.3	0.58	2.8

Table 2. Crystallographic Data for Complexes 11, 12a, and 12a′

	11	**12a**	**12a′**
formula	$C_{57}H_{51}F_3N_4O_3P_2PdS$	$C_{20}H_{18}N_2O_4$	$C_{28}H_{22}N_2$
M_r	1097.42	350.36	386.48
habit	colorless prism	yellow lath	colorless, irregular
cryst size (mm)	0.40 × 0.30 × 0.25	0.5 × 0.2 × 0.1	0.34 × 0.24 × 0.16
cryst syst	monoclinic	monoclinic	triclinic
space group	Cc	$P2_1/n$	$P\bar{1}$
cell constants			
a (Å)	19.3279(12)	6.2487(6)	12.7148(16)
b (Å)	17.2145(11)	23.830(2)	14.3523(18)
c (Å)	15.9880(11)	11.5383(11)	17.725(3)
α (deg)	90	90	105.899(3)
β (deg)	98.850(3)	93.920(3)	98.506(3)
γ (deg)	90	90	92.791(3)
V (Å^3)	5256.2	1714.1	3063.1
Z	4	4	6
D_{exptl} (Mg m^{-3})	1.387	1.358	1.257
μ (mm^{-1})	0.51	0.10	0.07
$F(000)$	2256	736	1224
T (°C)	−140	−140	−140
$2\theta_{max}$	60	60	56.6
no. of rflns measd	49 173	27 081	27 880
no. of indep rflns	15 097	5001	14 793
transmissions	0.83−0.96		
R_{int}	0.018	0.042	0.030
no. of params	648	242	826
no. of restraints	58	0	0
$R_w(F^2$, all reflns)	0.049	0.116	0.063
$R(F, >4\sigma(F))$	0.019	0.039	0.043
S	1.03	1.03	1.33
max $\Delta\rho$ (e Å^{-3})	0.65	0.40	0.25

129.21 (CH), 128.88 (CH), 127.88 (CH), 127.72 (CH), 127.17 (CH), 127.14 (CH), 126.46 (CH), 124.47 (C), 123.84 (C), 122.86 (CH), 119.44 (CH), 20.78 (Me). Anal. Calcd for $C_{28}H_{22}N_2$: C, 87.01; H, 5.74; N, 7.25. Found: C, 87.03; H, 5.86; N, 7.37. Single crystals were grown from concentrated solutions of **12a′** in Et_2O.

Synthesis of 3,4-Bis(carboxymethyl)-6-methyl-2-[(4-methylphenyl)amino]quinoline (12c). Complex **4c** (150 mg, 0.16 mmol) and $MeO_2CC{\equiv}CCO_2Me$ (98 μL, 0.81 mmol) were mixed in Me_2CO (5 mL) in a Carius tube, and the resulting mixture was heated at 150 °C for 3 h. The reaction mixture was cooled to room temperature and filtered through $MgSO_4$. The filtrate was concentrated to dryness, and the residue was redissolved in Et_2O and applied to a silica gel TLC plate. Elution with *n*-pentane/Et_2O 1:1 gave a yellow band (R_f = 0.45), which was extracted with CH_2Cl_2. This solution was treated with anhydrous $MgSO_4$ for 30 min, the suspension was filtered, and the filtrate was concentrated to dryness, giving a solid. Cooling a concentrated solution in *n*-hexane gives yellow crystals of **12c**. Yield: 37 mg, 65%. Mp: 118−120 °C. IR (Nujol, cm^{-1}): ν 1732, 1704 (C═O). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.78 (s, 1 H, NH), 7.74 (d, 2 H, H2 and H6, To, $^3J_{H,H}$ = 8.5 Hz), 7.67 (d, 1 H, H8, $^3J_{H,H}$ = 8.6 Hz), 7.48 (dd, 1 H, H7, $^3J_{H,H}$ = 8.6 Hz, $^4J_{H,H}$ = 1.8 Hz), 7.22 (d, 1 H, H5, $^4J_{H,H}$ = 1.8 Hz), 7.17 (d, 2 H, H4 and H5, To, $^3J_{H,H}$ = 8.5 Hz), 4.05 (s, 3 H, OMe), 3.97 (s, 3 H, OMe), 2.45 (s, 3 H, Me), 2.35 (3 H, Me, To). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 167.82 (C═O), 166.75 (C═O), 151.19 (C3), 148.04 (C8a), 144.42 (C4), 137.26 (C1, To), 135.03 (C7H), 133.75 (C6), 132.26 (C4, To), 129.25 (C3H and C5H, To), 127.08 (C8H), 124.55 (C5H), 120.48 (C2H and C6H, To), 118.72 (C4a), 107.10 (C, C2), 53.08 (MeO), 52.77 (MeO), 21.44 (Me), 20.86 (Me, To). HR EI-MS: calcd for $C_{21}H_{20}N_2O_4$, *m/e* 364.142 (100), 365.146 (19.08), 366.148 (2.96); found, *m/e* 364.143 (100), 365.147 (24.88).

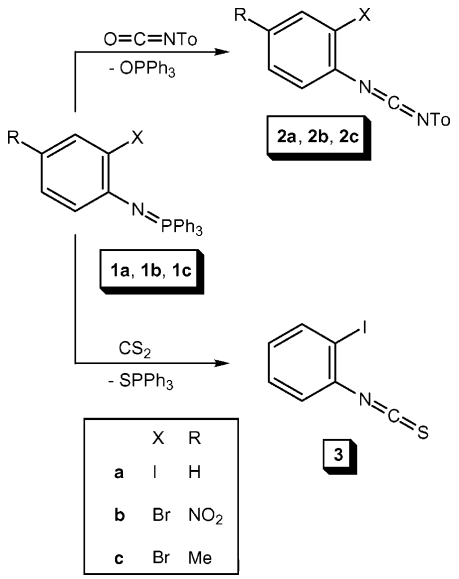
X-ray Structure Determinations. Numerical details are presented in Tables 1 and 2. Data were recorded at low temperature on a Bruker SMART 1000 CCD diffractometer using Mo Kα radiation (λ = 0.710 73 Å). Absorption corrections were based on face indexing (**8a**, **9a**) or multiple scans (program SADABS; **6a**, **11**); no correction was applied to **12a** or **12a′**. Structures were refined anisotropically on F^2 using the program SHELXL-97 (Prof. G. M. Sheldrick, University of Göttingen). Hydrogen atoms of NH groups were refined freely and methyls as rigid methyl groups; others were refined using a riding model. Special features of refinement: **9a**, the ether molecule is disordered over an inversion center; **11**, the Flack parameter was refined to −0.015(7).

Results and Discussion

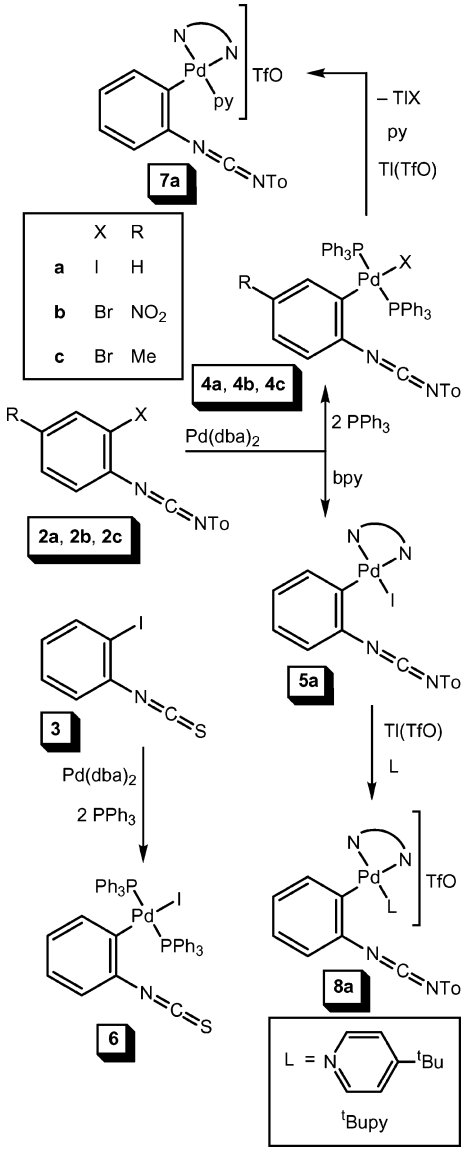
Synthesis of Ortho-Palladated Arylcarbodiimides and of an Ortho-Palladated Aryl Isothiocyanate. The reactions of [(2-haloaryl)imino]phosphoranes $Ph_3P{=}NC_6H_3X$-2-R-4 (X = I, R = H (**1a**); X = Br, R = NO_2 (**1b**), Me (**1c**))[11] with *p*-tolyl isocyanate gave good yields of (2-iodoaryl)- and (2-bromoaryl)carbodiimides $ToN{=}C{=}NC_6H_3X$-2-R-4 (To = C_6H_4Me-4; X = I, R = H (**2a**); X = Br, R = NO_2 (**2b**); X = Br, R = Me (**2c**)) (Scheme 1). Similarly, **1a** was reacted with CS_2 to give the isothiocyanate $S{=}C{=}NC_6H_4$I-2 (**3**). This compound was always contaminated with small amounts of the symmetric carbodiimide 2-$C(=NC_6H_4I\text{-}2)_2$ (approximately 10%). This mixture proved difficult to separate but could be used successfully for further reactions of **3**, because neither the impurities nor their potential reaction products had any significant negative effect.

The (iodoaryl)carbodiimide **2a** oxidatively adds at room temperature to $Pd(dba)_2$ ([$Pd_2(dba)_3$]·dba, dba = dibenzylideneacetone), in the presence of PPh_3 or 2,2′-bipyridine (bpy), to give [$Pd(C_6H_4N{=}C{=}NTo\text{-}2)IL_2$] (L = PPh_3 (**4a**), L_2 = bpy (**5a**)) (Scheme 2). The same reaction using *N*,*N*,*N*′,*N*′ tetramethylethylenediamine as the neutral ligand failed to give a homologue of **5a**. The reactions of the bromoarylcarbodiimides **2b**,**c** with $Pd(dba)_2$ and PPh_3 required refluxing in toluene in order

Scheme 1

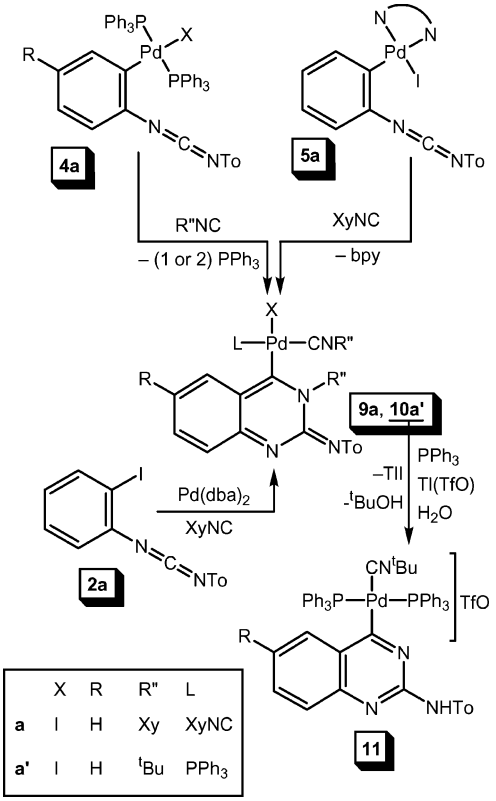


Scheme 2



to obtain the complexes *trans*-[Pd(C_6H_3N═C═NTo-2-R-5)Br(PPh_3)$_2$] (R = NO_2 (**4b**), Me (**4c**)), because of the lower reactivity of the bromoarenes with respect to the iodoarenes; the corresponding reactions in the presence of bpy did not take place at room temperature or resulted in decomposition on heating. A complex mixture containing a small amount of **5a** was obtained by reacting [Pd(C_6H_4N═PPh_3)I(bpy)][11] with *p*-tolyl isocyanate.

Scheme 3

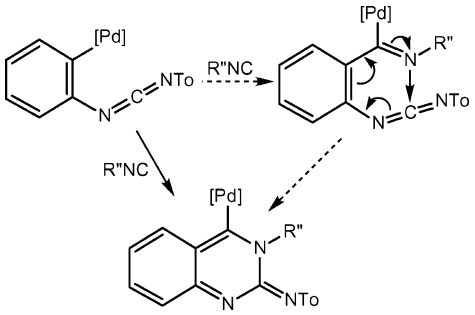


The isothiocyanate S═C═NC_6H_4I-2 (**3**) adds oxidatively to Pd(dba)$_2$ in the presence of PPh_3 to give the complex *trans*-[Pd(C_6H_4N═C═S-2)I(PPh_3)$_2$] (**6**). As far as we are aware, complexes **2** and **3** are the first arylpalladium complexes having a carbodiimine or an isothiocyanate substituent (Scheme 2).

Complex **4a** was reacted with pyridine (py) in the presence of Tl(TfO) to give the cationic complex *trans*-[Pd(C_6H_4N═C═NTo-2)(py)(PPh_3)$_2$]TfO (**7a**). Similarly, the complex [Pd(C_6H_4N═C═NTo-2)(^{t}Bupy)(bpy)]TfO (**8a**) was obtained from **5a**, Tl(TfO), and 4-*tert*-butylpyridine (^{t}Bupy). We attempted the reactions of **4a** and **5a** with Tl(TfO) without added ligand, to see if the ortho substituent could be coordinated to palladium to give di- or polynuclear complexes, but they gave TlI and a complex mixture.

Reactions with Isocyanides. Complexes **4** and **5a** react with isocyanides R″NC (R″ = Xy (2,6-dimethylphenyl), ^{t}Bu), to give C-palladated quinazolines (Scheme 3). Thus, **4a** or **5a** was reacted with XyNC in a 1:4 molar ratio to give *trans*-[Pd(ToNqXy)I($CNXy)_2$] (**9a**; ToNqXy = 3-(2,6-dimethylphenyl)-2-[(4-methylphenyl)imino]-2,3-dihydroquinazolin-4-yl). When a stoichiometric molar ratio was used, instead of an excess of isocyanide, complex mixtures were obtained; the same occurred for the other reactions with isocyanides described in this work. The complex **9a** was also prepared by the oxidative addition of **2a** to Pd(dba)$_2$ in the presence of XyNC

Scheme 4



(1.3:1:4.3). This procedure did not give good results when other (2-haloaryl)carbodiimides or isocyanides were used.

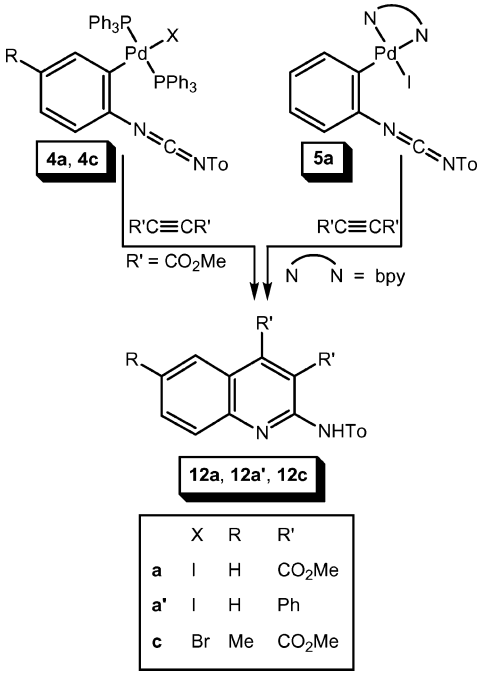
The reaction of **5a** with ^{t}BuNC resulted in the formation of the analogous *trans*-[Pd(ToNq^{t}Bu)I(CN^{t}Bu)$_2$] (**9a′**; ToNq^{t}Bu = 3-*tert*-butyl-2-[(4-methylphenyl)-imino]-2,3-dihydroquinazolin-4-yl). The low stability of this compound prevented us from isolating it in a satisfactorily pure state, as shown by NMR and elemental analyses (see the Supporting Information). However, the reaction of **4a** with ^{t}BuNC (1:4 molar ratio) gave the complex [Pd(ToNq^{t}Bu)I(CN^{t}Bu)(PPh$_3$)] (**10a′**), in which one PPh$_3$ ligand remained coordinated to the palladium atom in a trans position with respect to the coordinated isocyanide. A similar result was achieved from **4b** and XyNC but, in this case, the isolated complex [Pd(ToNO$_2$NqXy)Br(CNXy)(PPh$_3$)] (ToNO$_2$-NqXy = 3-(2,6-dimethylphenyl)-2-[(4-methylphenyl)-imino]-6-nitro-2,3-dihydroquinazolin-4-yl) (**10b**) showed in its NMR spectra the presence of small amounts of unidentified impurities which affected the elemental analysis (see the Supporting Information). The difficulties in the purification of this complex may be also due to its low stability. The reaction of **4c** with XyNC gives a complex mixture in which the compound [Pd(ToMe-NqXy)Br(CNXy)(PPh$_3$)] (ToMeNqXy = 3-(2,6-dimethylphenyl)-2-[(4-methylphenyl)imino]-6-methyl-2,3-dihydroquinazolin-4-yl) seems to be present, as shown by ^{1}H and ^{31}P NMR.

We propose a pathway for the formation of the quinazoline ring in Scheme 4. We believe that the isocyanide inserts into the Pd−C bond to give an iminoacyl intermediate;[6,7,9,11,19−21] this species should undergo a cyclization process to give the palladated quinazoline. Compounds **9** and **10** exhibit intense red or purple colors that could be due to extensive electronic delocalization within the benzoheterocyclic rings and imine group (see below). To the best of our knowledge, there is only one precedent for a C-palladated quinazoline: a product we unexpectedly isolated, whose structure was determined by an X-ray diffraction study but whose synthesis could not be repeated.[9] Very few examples of palladium-catalyzed syntheses of quinazolines are known; one example is the reaction of 2-nitroaryl ketones with formamide and carbon monoxide in the presence of [PdCl$_2$(PPh$_3$)$_2$] and MoCl$_5$.[43]

We tried several reactions of compounds **9** and **10** with Tl(TfO) or strong acids in order to depalladate them to give the free quinazoline, but all attempts resulted in the formation of intractable mixtures. However, the reaction of **10a′** with Tl(TfO) and PPh$_3$ resulted in the formation of the new complex *trans*-[Pd(ToNHq)-(CN^{t}Bu)(PPh$_3$)$_2$]TfO (**11**; ToNHq = 2-[(4-methylphenyl)-amino]quinazolin-4-yl) (Scheme 3), in which the iodo ligand has been replaced by another PPh$_3$ ligand. Although two isomers are possible, only one was obtained; this may be due to the higher transphobia[8,44] exhibited by the pair of ligands C-quinazoline/PPh$_3$ with respect to that of C-quinazoline/CNXy. Additionally, the heterocyclic ring lost the ^{t}Bu substituent and protonation of the NTo nitrogen took place; we believe this is due to a hydrolytic process caused by the water present in the reaction mixture. The change of color of complexes **9** and **10** from purple to colorless in complex **11** is probably due to the absence in **11** of the electronic delocalization present in **9** and **10**; this is also confirmed by the X-ray diffraction studies of **9a** and **11** (see below).

The complex **6** was reacted with isocyanides, but only complex mixtures were obtained.

Scheme 5



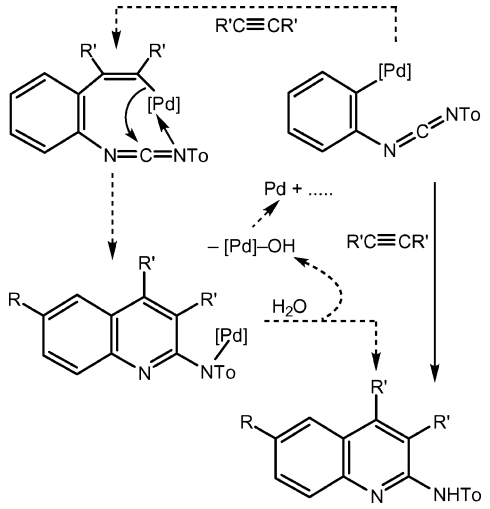
	X	R	R'
a	I	H	CO_2Me
a'	I	H	Ph
c	Br	Me	CO_2Me

Reactions with Alkynes. Complexes **4** and **5a** were reacted in Me$_2$CO at different temperatures with an excess of alkynes (1:3−5), with and without 1 equiv of Tl(TfO) (Scheme 5). 2-Aminoquinolines were obtained at high temperatures (150 °C) in a Carius tube. Thus, the reaction of **5a** with MeO$_2$CC≡CCO$_2$Me gave 3,4-bis-(carboxymethyl)-2-[(4-methylphenyl)amino]quinoline (**12a**) in moderate yield (40−45%). A better result (70%) was obtained by starting from **4a**. The reaction between **5a** and PhC≡CPh required the presence of Tl(TfO), giving 3,4-diphenyl-2-[(4-methylphenyl)amino]quinoline (**12a′**). **4b**, Tl(TfO), and MeO$_2$CC≡CCO$_2$Me gave slightly impure 3,4-bis(carboxymethyl)-6-nitro-2-[(4-methylphenyl)amino]quinoline (**12b**), which could not be purified (see the Supporting Information), while from **4c** and MeO$_2$CC≡CCO$_2$Me, but without Tl(TfO), pure 3,4-bis-

(43) Akazome, M.; Yamamoto, J.; Kondo, T.; Watanabe, Y. *J. Organomet. Chem.* **1995**, *494*, 229.

(44) Vicente, J.; Abad, J. A.; Hernandez-Mata, F. S.; Jones, P. G. *J. Am. Chem. Soc.* **2002**, *124*, 3848. Vicente, J.; Arcas, A.; Bautista, D.; Jones, P. G. *Organometallics* **1997**, *16*, 2127.

Scheme 6



(carboxymethyl)-6-methyl-2-[(4-methylphenyl)amino]-quinoline (**12c**) (Scheme 5) was obtained.

We propose a pathway for the formation of these 2-aminoquinolines, involving in the first step an alkenylpalladium intermediate, resulting from the insertion of the corresponding alkyne into the carbon−palladium bond (Scheme 6). Such an intermediate is plausible, since many monoinserted palladium complexes have been isolated (or proposed as intermediates in palladium-mediated organic synthesis[12,45]) as the product of the reaction between an arylpalladium complex and an alkyne.[5,6,11,46] This species should undergo a cyclization process, giving a palladium amide containing the quinoline ring. Finally, traces of water present in the reaction mixture would hydrolyze the last intermediate to give the quinoline and a hydroxopalladium complex, which would decompose under the reaction conditions to give metallic palladium and other products. However, **12a** and **12a′** were not detected when **2a** was reacted with an excess of the corresponding alkyne using as catalyst $Pd(dba)_2$ (with or without PPh_3) or $[Pd(PPh_3)_4]$, in the presence or absence of a base such as Na_2CO_3 or Et_3N, at room or higher temperatures (100−150 °C).

Spectroscopic Data. The infrared spectra of the compounds **1a**−**c**, **4a**−**c**, **5a**, **7a**, and **8a** show at least one very strong band at about 2150 cm^{-1} corresponding to ν(N═C═N) of the carbodiimide grouping. In some cases (**4b**, **7a**, and **8a**), two bands appear. Complex **6** shows two bands at 2146 and 2100 cm^{-1} assignable to the ν(S═C═N) group. The complexes **9a**, **9a′**, **10a′**, **10b**, and **11** show bands assignable to the ν(C≡N) mode of the isocyanide ligands in the range 2180−2300 cm^{-1}.

The NMR spectra of the new compounds are in accordance with the proposed structures. We have been able to determine the chemical shift of the carbons bound to palladium of the quinazoline complexes **9a**, **9a′**, and **10a** by means of HMBC techniques. The resonances appear at 191.27, 181.67, and 190.09 ppm, frequencies higher than those usually observed in arylpalladium complexes; for example, this signal appears at frequencies not higher than 160 ppm in the aryl complexes **4**−**8**. Such a high frequency is typical of N-heterocyclic carbenes bonded to palladium (see below).[47] The quinoline **12a′** shows a resonance in its ^1H NMR spectrum at 6.41 ppm assignable to the NH proton shifted upfield with respect to the signal for complexes **12a** (9.38 ppm), **12b** (10.06 ppm), and **12c** (9.78 ppm), presumably because of the presence in these complexes of an intramolecular hydrogen bond involving this proton and the C═O oxygen of the 3-CO_2Me substituent, as occurs for **12a** in the solid state (see below).[10,48]

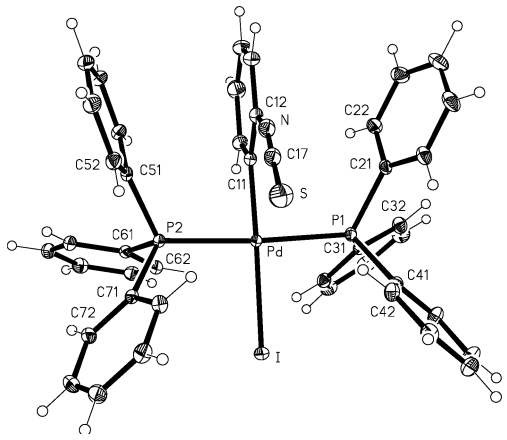


Figure 1. Ellipsoid representation of **6a** (30% probability). Selected bond lengths (Å) and angles (deg): Pd−C(11) = 2.0157(14), Pd−P(2) = 2.3259(4), Pd−P(1) = 2.3292(4), Pd−I = 2.68242(19), S−C(17) = 1.5936(19), N−C(17) = 1.167(2), N−C(12) = 1.392(2); C(11)−Pd−P(2) = 87.37(4), C(11)−Pd−P(1) = 88.27(4), P(2)−Pd−I = 92.130(11), P(1)−Pd−I = 92.039(11), C(17)−N-C(12) = 159.58(16), N−C(17)−S = 176.84(16).

X-ray Structure Determinations. The crystal and molecular structures of the compounds **6** (Figure 1), **8a**·$CDCl_3$ (Figure 2), **9a**·0.5OEt_2 (Figure 3), **11** (Figure 4), **12a** (Figure 5), and **12a′** (Figure 6) have been determined by X-ray diffraction studies. The palladium complexes **6**, **8a**·$CDCl_3$, **9a**·0.5OEt_2 and **11** show slightly distorted square planar structures. In complexes **6** and **8a** the N═C═S and N═C═N groups, respectively, lie above the palladium atom. For **6**, the S···Pd (4.3345(5) Å) and C(17)···Pd (3.442(2) Å) distances are greater than the sum of van der Waals radii (S···Pd = 3.37 Å, C···Pd

(45) Spencer, J.; Pfeffer, M. *Tetrahedron: Asymmetry* **1995**, *6*, 419. Tian, Q. P.; Larock, R. C. *Org. Lett.* **2000**, *2*, 3329. Larock, R. C.; Reddy, C. K. *Org. Lett.* **2000**, *2*, 3325. Roesch, K. R.; Larock, R. C. *J. Org. Chem.* **2001**, *66*, 412.

(46) Maassarani, F.; Pfeffer, M.; Le Borgne, G. *Organometallics* **1987**, *6*, 2029. Pfeffer, M. *Recl. Trav. Chim. Pays-Bas* **1990**, *109*, 567. Yagyu, T.; Osakada, K.; Brookhart, M. *Organometallics* **2000**, *19*, 2125. Yagyu, T.; Hamada, M.; Osakada, K.; Yamamoto, T. *Organometallics* **2001**, *20*, 1087. Zhao, G.; Wang, Q.-G.; Mak, T. C. W. *J. Organomet. Chem.* **1999**, *574*, 311. Kelly, A. E.; Macgregor, S. A.; Willis, A. C.; Nelson, J. H.; Wenger, E. *Inorg. Chim. Acta* **2003**, *352*, 79.

(47) Herrmann, W. A.; Elison, M.; Fischer, J.; Kocher, C.; Artus, G. R. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2371. Gründemann, S.; Albrecht, M.; Loch, J. A.; Faller, J. W.; Crabtree, R. H. *Organometallics* **2001**, *20*, 5485. Loch, J. A.; Albrecht, M.; Peris, E.; Mata, J.; Faller, J. W.; Crabtree, R. H. *Organometallics* **2002**, *21*, 700. Gstöttmayr, C. W. K.; Böhm, V. P. W.; Herdtweck, E.; Grosche, M.; Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **2002**, *41*, 1363. Chamizo, J. A.; Morgado, J.; Castro, M.; Bernès, S. *Organometallics* **2002**, *21*, 5428. Fürstner, A.; Seidel, G.; Kremzow, D.; Lehman, C. W. *Organometallics* **2003**, *22*, 907. Danopoulos, A. A.; Tulloch, A. A. D.; Winston, S.; Eastham, G.; Hursthouse, M. B. *Dalton* **2003**, 1009. Pytkowicz, J.; Roland, S.; Mangeney, P.; Meyer, G.; Jutand, A. *J. Organomet. Chem.* **2003**, *678*, 166.

(48) Günther, H. *NMR Spectroscopy. Basic Principles, Concepts, and Applications in Chemistry*; Wiley: Chichester, U.K., 1995. Alajarin, M.; López-Lázaro, A.; Pastor, A.; Prince, P. D.; Steed, J. W.; Arakawa, R. *Chem. Commun.* **2001**, 169.

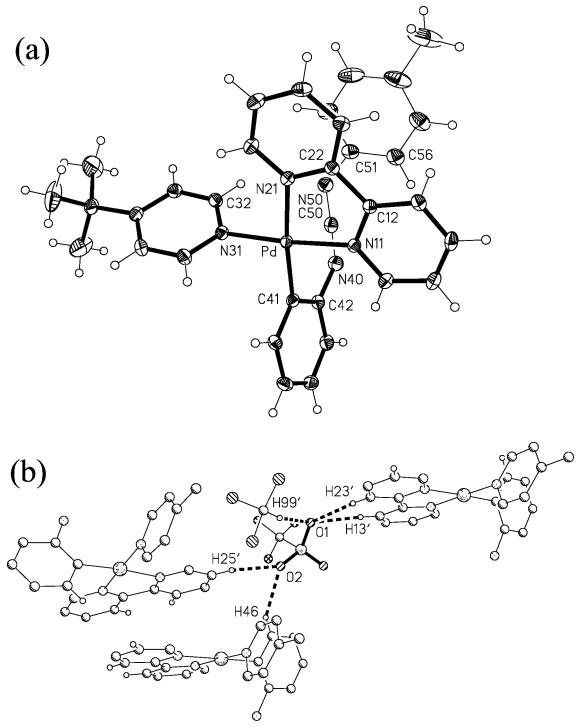


Figure 2. (a) Ellipsoid representation of **8a**·$CDCl_3$ (50% probability). The anion and the solvent are omitted. Selected bond lengths (Å) and angles (deg): Pd−C(41) = 1.9897(18), Pd−N(11) = 2.0289(15), Pd−N(31) = 2.0375(15), Pd−N(21) = 2.1035(16), N(40)−C(50) = 1.209(3), N(40)−C(42) = 1.427(2), N(50)−C(50) = 1.223(3), N(50)−C(51) = 1.425(3); C(41)−Pd−N(11) = 93.62(6), C(41)−Pd−N(31) = 90.22(6), N(11)−Pd−N(21) = 79.47(6), C(50)−N(40)−C(42) = 128.73(18), C(50)−N(50)−C(51) = 127.83(19), N(40)−C(50)−N(50) = 168.8(2). (b) Hydrogen-bonding environment of the triflate ion in **8a**·$CDCl_3$. The dashed lines represent hydrogen bonds. The following were omitted for clarity: H atoms not involved in H bonding; methyl groups; carbodiimide group. Details (including symmetry operators) are given in the Supporting Information.

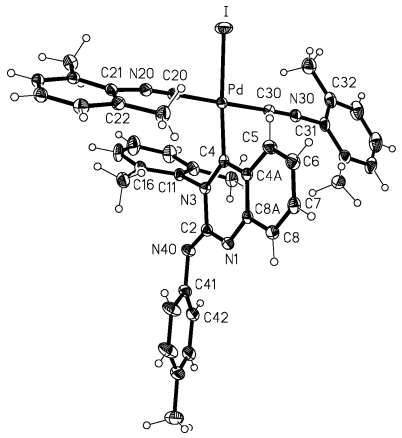


Figure 3. Ellipsoid representation of **9a**·0.5OEt_2 (50% probability). The solvent is omitted. Selected bond lengths (Å) and angles (deg): I−Pd = 2.6207(5), Pd−C(30) = 1.959(4), Pd−C(20) = 1.973(4), Pd−C(4) = 2.032(4), N(1)−C(2) = 1.335(6), N(1)−C(8A) = 1.336(6), C(2)−N(40) = 1.304(6), C(2)−N(3) = 1.451(6), N(3)−C(4) = 1.332(6), N(3)−C(11) = 1.472(6), C(4)−C(4A) = 1.404(6), C(4A)-C(8A) = 1.421(6), C(4A)-C(5) = 1.428(6), C(5)−C(6) = 1.347(7), C(6)−C(7) = 1.396(7), C(7)−C(8) = 1.350(7), C(8)−C(8A) = 1.445(6), N(20)−C(20) = 1.142(6), N(20)−C(21) = 1.402(5), N(30)−C(30) = 1.146(6), N(30)−C(31) = 1.402(6), N(40)−C(41) = 1.423(6); C(30)−Pd−C(4) = 88.88(17), C(20)−Pd−C(4) = 90.71(17), C(30)−Pd−I = 89.35(13), C(20)−Pd−I = 90.85(13), C(2)−N(1)−C(8A) = 119.3(4), N(40)−C(2)-N(1) = 127.5(4), N(40)−C(2)−N(3) = 114.5(4), N(1)−C(2)−N(3) = 118.0(4), C(4)−N(3)−C(2) = 123.7(4), C(4)−N(3)−C(11) = 118.2(4), C(2)−N(3)−C(11) = 117.9(3), N(3)−C(4)−C(4A) = 117.7(4), N(3)−C(4)−Pd = 122.3(3), C(4A)−C(4)−Pd = 120.0(3), C(4)−C(4A)−C(8A) = 117.1(4), C(4)−C(4A)−C(5) = 123.5(4), C(8A)−C(4A)−C(5) = 119.4(4), C(6)−C(5)−C(4A) = 121.1(5), C(5)−C(6)−C(7) = 120.0(5), C(8)−C(7)−C(6) = 121.9(5), C(7)−C(8)−C(8A) = 120.5(4), N(1)−C(8A)−C(4A) = 124.2(4), N(1)−C(8A)−C(8) = 118.6(4), C(4A)−C(8A)−C(8) = 117.2(4), C(20)−N(20)−C(21) = 171.9(5), N(20)−C(20)−Pd = 177.2(4), C(30)−N(30)−C(31) = 174.4(5), N(30)−C(30)−Pd = 178.6(4), C(2)−N(40)−C(41) = 117.7(4).

= 3.33 Å).[49] The N−C(17) (1.167(2) Å) distance and the N−C(17)−S (168.8(2)°) and C(12)−N−C(17) (159.58(2)°) angles lie in the ranges found in the three reported crystal structures (*R* factor <5%) of free isothiocyanates (1.151−1.178 Å and 173.7−178.0 and 163.5−175.0°, respectively); however, the C(17)−S distance (1.5936-(19) Å) is significantly longer than all the corresponding reported values (1.540-1.571 Å),[50] perhaps because the low-temperature measurement reduces the appreciable libration effects. In **8a** the short contacts C(50)···Pd (3.246(2) Å) and N(50)···Pd (2.916(2) Å), smaller than the sum of van der Waals radii (C···Pd = 3.33 Å, N···Pd = 3.18 Å),[49] are observed. However, the small lengthening of the C(50)−N(50) distance (1.223(3) Å) with respect to C(50)−N(40) (1.209(3) Å) may not be highly significant, and these distances and the angles N(40)−C(50)−N(50) (168.8(2)°), C(50)−N(50)−C(51) (127.83(19)°), and C(50)−N(40)−C(42) (128.73(18)°) are not significantly different from those observed in the only crystal structure reported (*R* factor <5%) of a free carbodiimide (1.226, 1.213 Å and 169.0, 129.8, and 128.8°, respectively).[51] The N−Pd bond distances of the bpy ligand in **8a**, Pd−N(11) = 2.0289(15) Å and Pd−N(21) = 2.1035(16) Å, indicate the greater trans influence of the aryl group with respect to ^{t}Bupy. In the absence of good hydrogen bond acceptors, the crystal packing of compound **6** is unexceptional, with just two C−H···I contacts. In contrast, the triflate ion of compound **8a** accepts five hydrogen bonds, some of which are extremely short (normalized H(99)···O(1) = 2.19 Å, H(25)···O(2) = 2.14 Å) (Figure 2a). The net effect is to connect the residues to form a broad layer parallel to the *xy* plane.

The structure of **9a**·0.5OEt_2 (Figure 3) confirms the trans disposition of the isocyanide ligands and the presence of a palladated quinazoline, which lies almost perpendicular to the coordination plane (interplanar angle 88.3°). The bonding distances within the heterocyclic moiety indicate extensive electron delocalization, this being probably responsible for the intense purple

(49) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.
(50) Hardgrove, G. L., Jr.; Einstein, J. R.; Wei, C. H. *Acta Crystallogr., Sect. C* **1983**, *39*, 616. Rudolf, B.; Makowska, M.; Domagala, A.; Rybarczyk-Pirek, A.; Zakrzewski, J. *J. Organomet. Chem.* **2003**, *668*, 95. Byrn, M. P.; Curtis, C. J.; Hsiou, Y.; Khan, S. I.; Sawin, P. A.; Tendick, S. K.; Terzis, A.; Strouse, C. E. *J. Am. Chem. Soc.* **1993**, *115*, 9480. Klapotke, T. M.; Krumm, B.; Mayer, P.; Piotrowski, H. *Z. Anorg. Allg. Chem.* **2001**, *627*, 1983.
(51) Irngartinger, H.; Jager, H.-U. *Acta Crystallogr., Sect. B* **1978**, *34*, 3262.

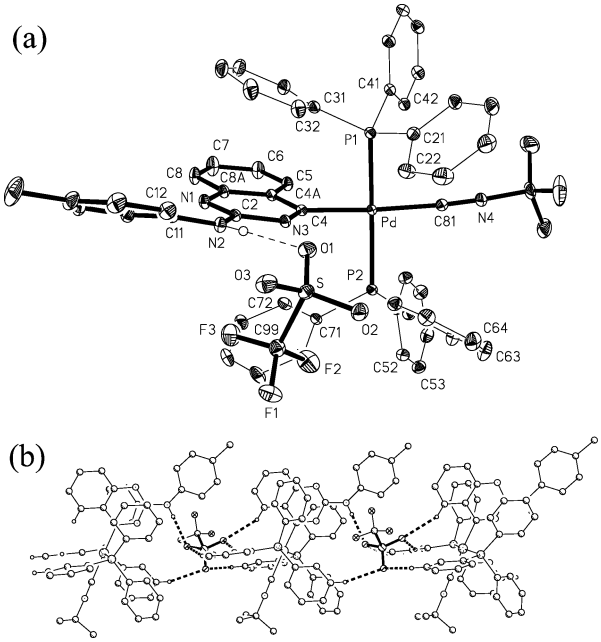


Figure 4. (a) Ellipsoid representation of **11** (30% probability). The anion is omitted. Selected bond lengths (Å) and angles (deg): Pd−C(4) = 2.0112(15), Pd−C(81) = 2.0350(17), Pd−P(2) = 2.3224(3), Pd−P(1) = 2.3259(3), N(1)−C(2) = 1.3155(16), N(1)−C(8A) = 1.3641(17), N(2)−C(2) = 1.3681(17), N(2)−C(11) = 1.4011(17), N(3)−C(4) = 1.3081(19), N(3)−C(2) = 1.3833(16), N(4)−C(81) = 1.151(2), N(4)−C(82) = 1.461(2), C(4)−C(4A) = 1.4365(18), C(4A)−C(5) = 1.4119(17), C(4A)−C(8A) = 1.4129(17), C(5)−C(6) = 1.3758(18), C(6)−C(7) = 1.416(2), C(7)−C(8) = 1.366(2), C(8A)−C(8) = 1.4158(18); C(4)−Pd−P(2) = 91.56(4), C(81)−Pd−P(2) = 92.29(4), C(4)−Pd−P(1) = 85.26(4), C(81)−Pd−P(1) = 90.81(4), C(2)−N(1)−C(8A) = 115.78(11), C(2)−N(2)−C(11) = 128.55(12), C(4)−N(3)−C(2) = 117.23(12), C(81)−N(4)−C(82) = 176.76(16), N(1)−C(2)−N(2) = 120.95(12), N(1)−C(2)−N(3) = 127.02(12), N(2)−C(2)−N(3) = 112.00(11), N(3)−C(4)−C(4A) = 121.55(13), N(3)−C(4)−Pd = 118.11(10), C(4A)−C(4)−Pd = 120.05(10), C(5)−C(4A)−C(8A) = 120.32(11), C(5)−C(4A)−C(4) = 123.66(12), C(8A)−C(4A)−C(4) = 116.00(12), C(6)−C(5)−C(4A) = 120.12(12), C(5)−C(6)−C(7) = 119.49(13), C(8)−C(7)−C(6) = 121.20(13), N(1)−C(8A)−C(4A) = 122.38(11), N(1)−C(8A)−C(8) = 119.14(12), C(4A)−C(8A)−C(8) = 118.46(12), C(7)−C(8)−C(8A) = 120.40(13), N(4)−C(81)−Pd = 176.26(12). (b) Packing diagram for **11**, showing the chain of residues generated by hydrogen bonding (dashed lines). Details are given in the Supporting Information.

color of **9a** and the other related compounds (see above). Thus, the C(2)−N(40) (1.304(6) Å), C(5)−C(6) (1.347(7) Å), and C(7)−C(8) (1.350(7) Å) distances correspond to C═N or C═C double bonds and the N(1)−C(8A) (1.336(6) Å), N(3)−C(4) (1.332(6) Å), N(1)−C(2) (1.335(6) Å), C(6)−C(7) (1.396(7) Å), and C(4)−C(4A) (1.404(6) Å) lengths to an intermediate situation between single C−N or C−C and double C═N or C═C bonds, while the C(2)−N(3) (1.451(6) Å), N(3)−C(11) (1.472(6) Å), C(4A)−C(8A) (1.421(6) Å), C(4A)−C(5) (1.428(6) Å), and C(8)−C(8A) (1.445(6) Å) distances correspond to single C−N or C−C bonds. Therefore, the delocalization of electron density in this ligand can be represented as shown in Chart 1, in which the quinazoline is viewed as a carbene ligand. This is consistent with the fact that the carbon nuclei bonded to palladium appear in the ^{13}C NMR

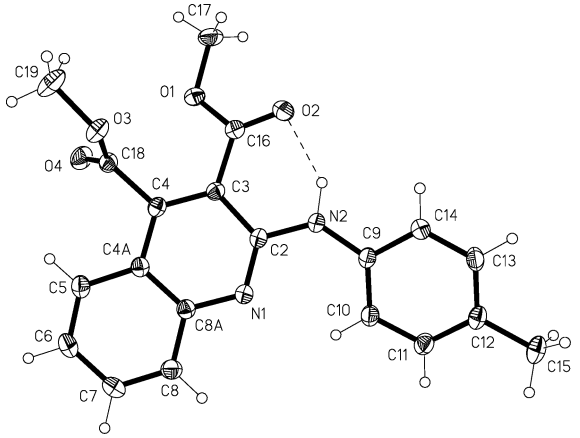


Figure 5. Ellipsoid representation of **12a** (50% probability). Selected bond lengths (Å) and angles (deg): C(2)−N(1) = 1.3173(12), C(2)−N(2) = 1.3627(12), C(2)−C(3) = 1.4570(12), C(3)−C(4) = 1.3804(13), C(3)−C(16) = 1.4898(13), C(4)−C(4A) = 1.4206(13), C(4)−C(18) = 1.5069(12), C(4A)−C(5) = 1.4201(13), C(4A)−C(8A) = 1.4217(12), C(5)−C(6) = 1.3687(15), C(6)−C(7) = 1.4117(15), C(7)−C(8) = 1.3716(14), C(8)−C(8A) = 1.4144(14), C(8A)−N(1) = 1.3657(12), C(16)−O(2) = 1.2134(12), C(16)−O(1) = 1.3346(11), C(17)−O(1) = 1.4523(12), C(18)−O(4) = 1.2054(12), C(18)−O(3) = 1.3322(12), C(19)−O(3) = 1.4439(12); C(2)−N(2)−C(9) = 130.52(9).

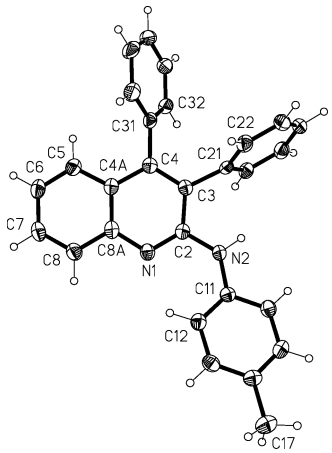


Figure 6. Ellipsoid representation of **12a′** (XX% probability). Selected bond lengths (Å) and angles (deg) for this molecule: N(1)−C(2) = 1.3165(15), N(1)−C(8A) = 1.3793(15), N(2)−C(2) = 1.3802(15), N(2)−C(11) = 1.4120(15), C(2)−C(3) = 1.4457(17), C(3)−C(4) = 1.3716(16), C(4)−C(4A) = 1.4338(17), C(4A)−C(8A) = 1.4128(17), C(4A)−C(5) = 1.4164(16), C(5)−C(6) = 1.3652(18), C(6)−C(7) = 1.4026(18), C(7)−C(8) = 1.3664(17), C(8)−C(8A) = 1.4166(17); C(2)−N(2)−C(11) = 130.93(12).

spectra of **9a**, **9a′**, and **10a′** at chemical shifts (180−190 ppm) characteristic of N-heterocyclic carbenes (see above).[47]

The structure of **11** (Figure 4) shows the presence of the quinazolinyl ligand and the trans disposition of the phosphine ligands. A bond order pattern different from that of **9a** is observed: the heterocyclic part shows double (N(3)−C(4) = 1.3081(19) Å, N(1)−C(2) = 1.3155(16) Å) and single bonds (N(1)−C(8A) = 1.3641(17) Å, N(2)−C(2) = 1.3681(17) Å, N(3)−C(2) = 1.3833(16) Å, C(4)−C(4A) = 1.4365(18) Å), while delocalization through C−C bonds intermediate between single- and double-bond order (1.366(2)−1.416(2) Å) is restricted to the

benzo component (Chart 1). This could explain the change of color from the intense purple of **9a** and related compounds to pale yellow **11**. The triflate anion accepts a classical hydrogen bond from the N(2)−H group (Figure 4). Additionally, it acts as acceptor for four C−H···O contacts, one within the asymmetric unit and three to the same cation generated by the *n* glide plane, involving four C−H phenyl groups and one C−H quinazolinyl group. The net effect is to form a chain of residues parallel to the diagonal [101] (Figure 4a). Except for H(56)···O(3), all these C−H···O contacts are, with H···O = ca. 2.6 Å, much longer than in compound **8a**.

The structures of **12a** (Figure 5) and **12a′** (Figure 6) are similar to those found for other quinolines.[52] In **12a**, O(2) forms a classical but intramolecular hydrogen bond with the N−H group; O(2) is also acceptor for one and O(4) for two C−H···O interactions (for details see the Supporting Information), leading to a three-dimensional packing. The structure of **12a′** involves three independent molecules, which differ in the orientations of the substituent rings; in all cases, however, the moiety N(1)−C(2)−N(2)−C(11) is approximately synperiplanar. None of the NH groups are involved in hydrogen bonding, presumably because of the lack of suitable acceptors.

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Supporting Information Available: Text giving experimental details of the preparation of **9a′**, **10b**, and **12b**, listings of all refined and calculated atomic coordinates, anisotropic thermal parameters, and bond lengths and angles, and CIF files for **6**, **8a**·$CDCl_3$, **9a**·0.5OEt_2, **11**, **12a**, and **12a′**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(52) Moya Argilagos, D.; Linden, A.; Heimgartner, H. *Helv. Chim. Acta* **1999**, *82*, 238. Katritzky, A. R.; Huang, T.-B.; Voronkov, M. V.; Steel, P. J. *J. Org. Chem.* **2000**, *65*, 8069. Kempe, R.; Hillebrand, G. Z. *Z. Kristallogr.-New Cryst. Struct.* **2000**, *215*, 281.