stoichiometric amounts of trityl perchlorate to carry the reactions of these ethers to completion. The four general cyclization reactions are given in Scheme II. Although all cyclizations were successful, the benzyl ethers were always by far the least effective.

Finally, it should be noted that while the intramolecular catalytic cyclizations originally proposed have been successful, this cannot be taken as evidence for free silylenium ions in these reactions. There is no reason to believe that nucleophilic attack by oxygen does not occur before complete loss of hydride, and we suspect that is indeed the case.

Experimental Section

Instrumentation. ^{1}H NMR were recorded on a Nicolet Model NT-300 at 300 MHz in $DCCl_3$. ^{13}C NMR spectra were obtained on the same instrument at 75.5 MHz. IR spectra (not reported but obtained for all products) were taken on an IBM 98 FTIR. GC/MS were taken on a Hewlett-Packard 5970 attached to an HP 5890 GC. Exact mass measurements were made on a Kratos MS-50 at 70 eV. Analytical GC was done on an HP 5790 GC using a 12- or 30-m RSL-150 column. All GC yields were determined with internal standards and predetermined response factors. Preparative GC was performed on a Varian Model 920 GC. Boiling and melting points are uncorrected.

Triphenylmethyl perchlorate was prepared by the method of Dauben.[9]

2,2-Dimethyl-1-oxa-2-silacyclopentane (15). Yields given in Scheme II are by GC analysis. An analytical sample was obtained by preparative GC (8 ft × $^1/_4$ in. 15% SE-30 on Chromosorb W at 90 °C) and identified by GC/MS and ^{1}H NMR comparison with literature values.[10-12]

3,3-Dimethyl-4-oxa-3-silacyclopentene (16). Yields were determined by GC analysis. An analytical sample was obtained by preparative GC (10 ft × $^1/_8$ in. 15% OV-101 column, 50–270 °C/5 °C/min) and identified by GC/MS and ^{1}H NMR comparison with an authentic sample.[13]

2,2-Dimethyl-1-oxa-2-silacyclohexane (17). Yields were determined by GC analysis. An analytical sample was obtained by preparative GC (8 ft × $^1/_4$ in. 15% SE-30 on Chromosorb W at 100 °C) and identified by GC/MS and ^{1}H NMR comparison with literature values.[10-12]

3,3-Dimethyl-4-oxa-3-silacyclohexene (18). GC determined yield. Analytical sample obtained by preparative GC (8 ft × $^1/_4$ in. 15% SE-30 Chromosorb W at 100 °C): ^{1}H NMR δ 0.17 (s, 6 H), 2.25 (tdd, 5.3, 4.0, and 2.0 Hz, 2 H), 3.95 (t, 5.3 Hz, 2 H), 5.74 (dt, 14.2 and 2.0 Hz, 1 H), 6.82 (dt, 14.2 and 4.0 Hz, 1 H); ^{13}C NMR δ −0.62, 31.12, 61.73, 127.23, 147.76; IR 2974, 2931, 1585, 1261, 1087, 1050 cm^{-1}; calcd for $C_6H_{12}OSi$ m/e 128.0658, measd m/e 128.0660. Anal. Calcd for $C_6H_{12}OSi$: C, 56.19; H, 9.43. Found: C, 56.50; H, 9.36.

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Registry No. 5A, 82816-38-4; **5B**, 16314-18-4; **5C**, 4039-82-1; **6A**, 75014-48-1; **6B**, 59574-66-2; **6C**, 22273-77-4; **7A**, 110827-10-6; **7B**, 110827-11-7; **7C**, 110827-12-8; **8A**, 110827-13-9; **8B**, 110827-14-0; **8C**, 110827-15-1; **9A**, 110827-16-2; **9B**, 110827-17-3; **9C**, 110827-18-4; **10A**, 110827-19-5; **10B**, 110827-20-8; **10C**, 110827-21-9; **11A**, 110827-22-0; **11B**, 110827-23-1; **11C**, 110827-24-2; **12A**, 110827-28-6; **12B**, 110827-29-7; **12C**, 110827-30-0; **13A**, 110827-25-3; **13B**, 110827-26-4; **13C**, 110827-27-5; **14A**, 110827-31-1; **14B**, 110827-32-2; **14C**, 110827-33-3; **15**, 3292-88-4; **16**, 110827-34-4; **17**, 5833-47-6; **18**, 110827-35-5; Me_2HSiCl, 1066-35-9; $Ph_3C^+ClO_4^-$, 3058-33-1.

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Strained Palladium(II) Complexes:[1] Synthesis and Complexation of Functionalized 8,8′-Dimethyl-2,2′-biquinolines

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The syntheses of several new 2,2′-biquinoline derivatives are described. Active metal coupling of 2-bromo-8-methylquinoline gave 8,8′-dimethyl-2,2′-biquinoline. Application of α-methyl functionalization techniques gave the derivatized 8,8′-dimethyl-2,2′-biquinolines. Formation of an N,N-coordinated Pd(II) complex with either 8,8′-bis(cyanomethyl)- or 8,8′-bis[2,2-bis(methoxycarbonyl)ethyl]-2,2′-biquinoline proved unsuccessful; however, a monometalated C,N,N complex was obtained with 8,8′-dimethyl-2,2′-biquinoline.

Introduction

Our interest in the structural features of novel strained metallacycles of the platinum metals has led us to the synthesis of diverse ligands containing varying functionalities.[2] The primary purpose has been to determine which structural features of the ligand cause those subtle changes in the binding locus so that either a metal selectivity or molecular inclusion of a neutral guest can be achieved. To this end, we herein report the expansion of our series to include a highly sterically hindered N,N-coordination site in order to determine the problems caused by molecular crowding at the binding locus.

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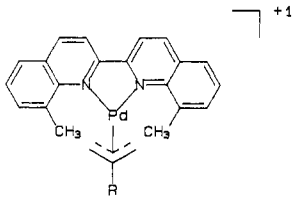
Even before our reported[8] acute bonding deviation in square-planar d^8 palladium(II) dipyridine complexes, Deeming and Rothwell[4] attempted the formation of an N,N′-coordinated complex with **2** and $PdCl_2$, $[Pd(OAc)_2]_3$, and $Rh_2Cl_2(CO)_4$. The only successful metal source and reaction conditions were **2** with $[PdCl(\eta^3\text{-allyl})]_2$/$AgClO_4$/acetone to give an N,N′-coordinated Pd(II) η-allyl perchlorate complex **3**, which also contained severe dis-



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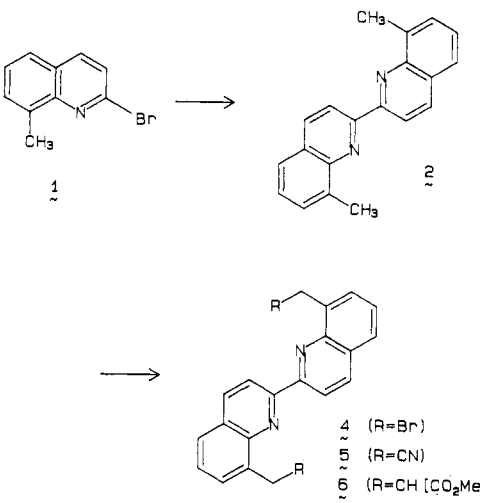
tortion within the coordination sphere. X-ray analysis of **3** showed an out-of-plane distortion of 1.097 Å of the Pd(II) with a torsion angle of 30.5°. Despite this severe distortion, the Pd–N bond lengths were nearly normal (2.125 and 2.216 Å versus the normal range of 2.0–2.2 Å). The results of our study indicate that despite the extreme steric hindrance in initial N,N′-coordination, suitable conditions can lead to carbon–metal bond formation.

Results and Discussion

A. Ligand Synthesis. The initial problem to overcome in the synthesis of 2,2′-biquinolines was the coupling of suitable quinoline precursors. Even though there are several quinoline coupling procedures cited in the literature,[5] most gave low (and unpredictable) conversions resulting from the formation of troublesome byproducts, the use of highly reactive coupling reagents, and competitive reductions from the presence of protonic source[6] (e.g. proton–metal exchange). The present synthesis has overcome these difficulties by using the modified procedure of Tiecco et al.,[7] in which a stoichiometric amount of a nickel coupling reagent was used. The generation of $[(C_6H_5)_3P]_4Ni^0$ was conducted by the Zn(0) reduction of $NiCl_2{\cdot}6H_2O$ in the presence of $(C_6H_5)_3P$. Use of a stoichiometric amount of catalyst required a large quantity of $(C_6H_5)_3P$, which subsequently made the purification of **2** difficult; however, when a catalytic amount of the Ni(0) reagent was used, low conversions were reported.[7] Tiecco's experiments involved the presence of catalytic amounts of $NiCl_2{\cdot}6H_2O$ and stoichiometric amounts of Zn(0). To be noted is the well-known competitive reduction of related haloheterocycles by Zn(0) in the presence of a proton source (e.g. H_2O).[8] Therefore to circumvent these pitfalls, $NiCl_2{\cdot}6H_2O$ in catalytic amounts (typically 0.25 equiv) with the proportional addition of Zn(0) catalyzed the coupling of 2-bromo-8-methylquinoline (**1**) to give (65–85%) **2**.

The ^1H NMR spectrum of **2** indicates that the quinoline rings are in an anti conformation, since H-3 is shifted downfield by about 1.5 ppm (from δ 7.31 in quinoline[9] to δ 8.91 in **2**) due to the juxtaposed *N* electrons to H-3. This effect has been estimated[10] to cause a 0.4–0.6 ppm downfield shift for H-3 in the related bipyridines whereas the additional 1.0 ppm shift can be attributed to the presence of the quinoline ring at the 2-position. A similar *N* lone pair effect can be seen in the shift of the quinoline 8-methyl group (δ 2.92): similar to that shown in the methylquinoline series,[11] in which the 8-methyl signal appears at δ 2.75. This downfield shift is even greater than that experienced by either the quinoline 2-methyl or 4-methyl group (δ 2.67 and 2.70, respectively), where the electron density on C-2 and C-4 is reduced via electron withdrawal by the ring heteroatom.

Bromination[12] of **2** with NBS in CCl_4 gave (70%) the desired bromomethyl derivative **4**. The product distribution in the reaction mixture showed that **4** is the major product [^1H NMR δ 5.39 (CH_2Br)] with a small amount of unchanged starting material and bis(dibromomethyl) derivative [δ 7.62 ($CHBr_2$)]. Reaction of **4** with KCN in either DMF or DMSO at 25 °C afforded (90%) acetonitrile **5**. The upfield shift of the methylene protons from δ 5.39 to δ 4.45 clearly supported cyanide substitution. When KCN was replaced by dimethyl potassiomalonate, generated by stirring a slurry of dimethyl malonate and anhydrous K_2CO_3 in acetonitrile at 25 °C, **6** was formed in good yields (80–85%). In the ^1H NMR spectrum, the characteristic pattern for monosubstituted malonates [doublet (δ 3.68) and triplet (δ 4.39)] verified this structure.



B. Complex Formation. This series (**2**, **5**, and **6**) was synthesized in order to evaluate the steric congestion at the (N,N)-binding locus. Ligand **2** is the least sterically hindered and **6** is the most with **5** being intermediate. Conversely, the order of increasing acidity of the α-alkyl hydrogens is **2** < **6** < **5**. The comparative acidity of the 2-alkyl hydrogen is usually an important factor in determining the ease of C–Pd bond formation,[1] however, the unsuccessful attempts to generate a new stable $C(sp^3)$–Pd bond with **5** (or **6**) would indicate that the increased steric factors are more critical. The inherent steric congestion was previously noted[2b] with the 1,10-phenanthroline ligand **7**, which contains a rigid central five-membered ring in a potential 5.5.5-fused ring system; however, only the monometalated Pd(II) complex **8** was obtained. With **2**, a similar side-ring rigidity is found in this potential 5.5.5-

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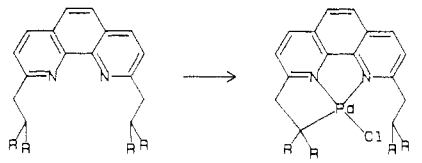

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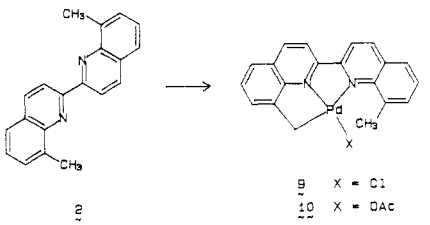
fused ring system. Thus, not surprisingly, the inability to form the second C–Pd bond was observed; both **9** and **10** were inert to tandem bond formation. Even under rigorous reaction conditions, such as added $AgNO_3$ or $AgClO_4$, or with excess BuLi, **9** could not be driven to the desired bis-metalated complex.

A modified procedure of von Zelewshi and co-workers[13] was initially used to generate the first C–Pd bond. When **2** was treated with 2.2 equiv of BuLi in THF, followed by $(Et_2S)_2PdCl_2$ at −40 °C, the monometalated complex **9** was formed in moderate (35–45%) yields, whereas treatment of **2** in warm (55 ± 5 °C) glacial AcOH in the presence of $[Pd(OAc)_2]_3$ gave the monometalated complex **10** in fair (30–35%) yield. The presence of the monometalated complexes **9** and **10** was readily detected by ^1H NMR, in which the methylene bound to Pd(II) shifts downfield an average of 2.27 ppm (δ 2.92 for **2**, 4.17 for **9**, and 4.21 for **10**). This large shift compares to a range of 0.50–1.20 ppm for cyclometalated (8-methylquinoline)palladium(II) complexes.[14] The subtle differences probably are attributed to the strain of the cyclometalated ring. The free methyl group shifts very slightly (0.17 and 0.19 ppm for **9** and **10**, respectively), presumably due to the nearness of Cl (for **9**) or O (for **10**). A characteristic of monometalated com-



2 9 X = Cl 10 X = OAc

plexes, previously noted,[2b] is the collapsing of the symmetrical patterns normally seen in bis-metalated complexes into a complex, overlapping pattern. This is again the case for both **9** and **10**. In addition, the downfield shift of H-3, noted earlier for **2** and **4–6**, is eliminated due to the mandatory syn configuration of the C,N,N complexes. No evidence for the formation of the bis-metalated complex could be found in any case.

Further support for the structure of **10** can be found in the ^{13}C NMR spectral data. The metalated carbon shows a downfield shift (5.4 ppm) whereas the free methyl carbon also experiences a slight downfield shift (3.5 ppm), indicative of its juxtaposition near the apical position of the Pd(II) atom.[14b] A better indication of the apparent strains involved in **10** can be seen in the shifts for C8, C8′, C2, and C2′. For C8′, the methylenic carbon is shifted (59.4 ppm) when compared to C2 and the related 2,2′-bipyridine ligands upon cyclometalation,[2b] which has been previously correlated to ring strain. In these systems, downfield shifts on the order of 5–15 ppm are normally observed. This large observed shift of C8′ suggests that unusually large strains are involved. On the non-metalated side of **10**, C8 shifts +5.6 ppm, which is larger than expected for a carbon bound to a noninteracting methyl moiety. For the coupled C2 and C2′, shifts of −5.0 and −4.9 ppm, respectively, are observed and are larger than the −2 to −3 ppm shifts observed for the related bipyridines. On the basis of these NMR data, it would appear that the extreme steric congestion of this system forces the second methyl to distort sufficiently out of the plane to prevent a bonding interaction to occur.

Conclusion

The synthesis of **2** shows the utility of Ni(0) coupling reagents, specifically $[(C_6H_5)_3P]_4Ni^0$. The greatly increased yields observed with this reagent are far superior to those normally encountered.[4] α-Methyl functionalization of **2** is readily achieved via nucleophilic substitution of the corresponding bromomethyl derivative **4**, obtained in good yield via free radical bromination[11] of **2**.

The steric congestion of the N,N′-coordination sites caused by the methyl groups prevents protonation even in 6 M HCl, let alone coordination to a much larger transition metal.[4] Thus, complexes **9** and **10** demonstrate the great propensity on the part of Pd(II) to form C–Pd bonds. Only in example **3**, where perchlorate is the only available ligand to complete the Pd(II) coordination sphere, does **2** coordinate and then only with severe acute bonding distortion. Yet, not only does Pd(II) N,N′-coordination occur, but also a C–Pd bond is formed. This is one of the most intriguing examples of a cyclometalated complex with Pd(II) due to these anomalies. The inability of ligand **5** or **6** to undergo even N,N′-complexation appears to underline the subtleties involved in the complex chemistry of 8,8′-dimethyl-2,2′-biquinoline derivatives.

Experimental Section

General Comments. All melting points were taken in capillary tubes with a Thomas-Hoover Uni-Melt apparatus and are uncorrected. ^1H and ^{13}C NMR spectra were determined on either an IBM NR/80 or AF/100 NMR spectrometer using $CDCl_3$, solvent, with TMS (0.01%), as the internal standard; prime marks denote metalated side. Mass spectral (MS) data (70 eV) were determined by D. Patterson or H. Land on a Hewlett-Packard HP5985 gas chromatograph/mass spectometer in these laboratories and presented as *m/e* (relative intensity, assignment). Preparative thick-layer chromatography (ThLC) was performed on 20 × 40 cm glass plates coated with a 2-mm layer of Brinkmann silica gel PF-254-366. "Dry-Column" flash chromatography (FC) was performed by using the technique of Harwood[15] with TLC grade silica gel.

Solvents. Anhydrous *N,N*-dimethylformamide (DMF) was purified to remove traces of HCN, which has been demonstrated to form by its photolytic decomposition upon standing.[16] Anhydrous carbon tetrachloride (CCl_4) was prepared by distillation from P_2O_5 under an argon atmosphere. Anhydrous tetrahydrofuran (THF) was prepared by distillation from Na(Pb) amalgam with benzophenone, as indicator.

2-Bromo-8-methylquinoline (1) was prepared by a literature procedure[14a] via PBr_5 bromination of 1,8-dimethyl-2-quinolone: mp 78–79 °C (lit.[14a] mp 77–78 °C).

8,8′-Dimethyl-2,2′-biquinoline (2) was prepared by a modification of the procedure of Tiecco and co-workers.[7] Freshly activated Zn powder[17] (1.31 g, 20 mmol) was added in four equal portions at 8-h intervals to a solution of $NiCl_2 \cdot 6H_2O$ (1.19 g, 5.0 mmol) and $(C_6H_5)_3P$ (5.24 g, 20 mmol) in degassed DMF (100 mL) at 50 ± 5 °C under argon. After ca. 15 min,[18] the time necessary

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for Ni(0) formation (color change: deep blue to red-brown), **1** (4.44 g, 20 mmol) was added to the solution and the temperature maintained for 8 h after the last portion of Zn had been added. (Note: A stoichiometric amount of Ni catalyst may be used with a shortening of the reaction time, but the workup becomes much more difficult!) Upon cooling to 25 °C, the DMF was evaporated in vacuo and the dark brown residue dissolved in hot MeOH, which decomposes the Ni(II) and Zn(II) phosphine complexes. Addition of H_2O (100 mL) and extraction with CH_2Cl_2 (4 × 50 mL) yielded a mixture of $(C_6H_5)_3P$ and crude product.

Concentration of the dried (anhydrous $MgSO_4$) combined organic layer and trituration with Et_2O gave (83%) pure **2**: mp 209–210 °C (lit.[15a] mp 210–211 °C; ^1H NMR δ 2.92 (s, CH_3, 6 H), 7.2–7.8 (m, 5,5′,6,6′,7,7′-biquin*H*, 6H), 8.25 (d, 4,4′-biquin*H*, J = 8.6 Hz, 2 H), 8.91 (d, 3,3′-biquin*H*, J = 8.6 Hz, 2 H); ^{13}C NMR δ 17.9 (CH_3), 119.0 (C3), 125.6 (C5), 126.6 (C6), 128.4 (C4a), 129.5 (C7), 136.8 (C4), 137.9 (C8), 146.8 (C8a), 155.2 (C2).

8,8′-Bis(bromomethyl)-2,2′-biquinoline (4). A slurry of **2** (570 mg, 2.0 mmol), freshly recrystallized NBS[19] (710 mg, 4.0 mmol), and a trace of $[(C_6H_5)CO_2]_2$ in CCl_4 (50 mL) was refluxed for 2.5 h under argon with irradiation by a 150-W bulb. The CCl_4 was evaporated in vacuo and the residue taken up into CH_2Cl_2 (50 mL). The resulting solution was extracted with 2 N NaOH (2 × 25 mL), dried over anhydrous $MgSO_4$, and concentrated to give crude **4**, which was recrystallized from $CHCl_3/C_6H_{12}$ to give (71%) **4**, as bright orange-yellow crystals: 630 mg; mp 238–240 °C; ^1H NMR δ 5.39 (s, CH_2Br, 4 H), 7.4–8.0 (m, 5,5′,6,6′,7,7′-biquin*H*, 6 H), 8.34 (d, 4,4′-biquin*H*, J = 8.4 Hz, 2 H), 8.97 (d, 3,3′-biquin*H*, J = 8.4 Hz, 2 H); MS, m/e 444 (12, M^+), 442 (22.5, M^+), 440 (13.9, M^+), 363 (26.7, $M^+ - Br$), 282 (39.8, $M^+ - 2Br$), 141 [100, $^1/_2(M^+ - Br)$]. Anal. Calcd for $C_{20}H_{14}N_2Br_2$: C, 54.33; H, 3.19; N, 6.34. Found: C, 54.08; H, 2.97; N, 6.15.

8,8′-Bis(cyanomethyl)-2,2′-biquinoline (5). A solution of **4** (221 mg, 0.5 mmol) and anhydrous KCN (130 mg, 2.00 mmol) in DMF (60 mL) was stirred at 25 °C for 24 h. The solvent was evaporated in vacuo and the residue dissolved in CH_2Cl_2 (50 mL), filtered, and concentrated to give crude **5**. Purification is achieved by recrystallization from $CHCl_3/C_6H_{12}$ to give (92%) **5**, as orange-yellow crystals: 153 mg; mp 208–210 °C; ^1H NMR δ 4.45 (s, CH_2CN, 4 H), 7.3–8.1 (m, 5,5′,6,6′,7,7′-biquin*H*,6 H), 8.24 (d, 4,4′-biquin*H*, J = 8.5 Hz, 2 H), 8.83 (d, 3,3′-buquin*H*, J = 8.5 Hz, 2 H); MS, m/e 334 (100, M^+), 333 (99, $M^+ - H$), 306 (26, $M^+ -$ HCN), 279 (34, $M^+ -$ NCN). Anal. Calcd for $C_{22}H_{14}N_4$: C, 79.02; H, 4.22; N, 16.76. Found: C, 79.07; H, 4.36; N, 16.54.

8,8′-Bis[2,2-bis(methoxycarbonyl)ethyl]-2,2′-biquinoline (6). A slurry of **4** (660 mg, 1.5 mmol), $CH_2(CO_2CH_3)_2$ (790 mg, 6.0 mmol), and anhydrous K_2CO_3 (830 mg, 6.0 mmol) in DMF (75 mL) was stirred at 25 °C for 18 h. The solvent was evaporated in vacuo and the residue dissolved in CH_2Cl_2. After filtration, the solution was concentrated and the residue distilled [70 °C (1 mm)] to give the crude product, which was recrystallized from C_6H_{12} to afford (85%) pure **6**, as a white solid: 700 mg; mp 171–173 °C; ^1H NMR δ 3.68 (s, CO_2CH_3, 12 H), 3.98 (d, CH_2CH, J = 7.1 Hz, 4 H), 4.39 (t, CH_2C*H*, J = 7.1 Hz, 2 H), 7.3–7.9 (m, 5,5′,6,6′,7,7′-biquin*H*, 6 H), 8.31 (d, 4,4′-biquin*H*, J = 8.6 Hz, 2 H), 8.93 (d, 3,3′-biquin*H*, J = 8.6 Hz, 2 H); MS, m/e 544 (13, M^+), 486 [12, $M^+ - CO_2CH_3$], 427 [11, $M^+ - 2(CO_2CH_3)$], 295 [24, $M^+ - [CH(CO_2CH_3)_2 + 2(CO_2CH_3)]$], 94 (100). Anal. Calcd for $C_{30}H_{28}N_2O_8$: C, 66.17; H, 5.18; N, 5.15. Found: C, 66.03; H, 4.99; N, 5.08.

Chloro[[[(8-methyl-2,2′-biquinolin)-8′-yl]methyl]-*C*,*N*,*N*′]palladium(II) (9). BuLi (0.69 mL, 1.6 M, 1.1 mmol) was added to a stirred solution of **2** (142 mg, 0.5 mmol) in anhydrous THF (50 mL) at −40°C under argon. This temperature was maintained for 30 min; then a solution of $(Et_2S)_2PdCl_2$ (196 mg, 0.55 mmol) in THF (25 mL) was added dropwise over ca. 15 min. The temperature was warmed to 25 °C and stirring continued for 12 h. The solvent was evaporated in vacuo to give the crude product, which was purified by flash chromatography ($CHCl_3$) affording (45%) **9**, as a yellow crystalline solid: 87 mg; mp 211–213 °C; ^1H NMR δ 3.09 (s, CH_3, 3 H), 4.17 (s, CH_2Pd, 2 H), 7.3–7.8 (m, 5,5′,6,6′,7,7′-biquin*H*, 6 H), 8.0–8.4 (m, 3,3′,4,4′-biquin*H*, 4 H). Anal. Calcd for $C_{20}H_{15}N_2PdCl$: C, 56.49; H, 3.56; H, 6.59. Found: C, 56.07; H, 3.24; N, 6.30.

(Acetato)[[[(8-methyl-2,2′-biquinolin)-8′-yl]methyl]-*C*,*N*,*N*′]palladium(II) (10). A stirred solution of **2** (38.2 mg, 0.13 mmol) and $[Pd(OAc)_2]_3$ (29.3 mg, 0.13 mmol) in glacial AcHO (5 mL) was warmed to 55 ± 5 °C under argon for 20 h. The AcOH was evaporated in vacuo; the residue triturated with C_6H_6 and then filtered to give crude **10**, as a red-brown solid. Recrystallization from $CHCl_3/Et_2O$/petroleum ether (bp 30–60 °C) gave (34%) **10**, as yellow-orange microcrystals: 20 mg; mp 226–228 °C; ^1H NMR δ 3.1 (s, CH_3, 3 H), 4.21 (s, CH_2Pd, 2 H), 7.3–7.8 (m, 5,5′,6,6′,7,7′-biquin*H*, 6 H) 8.0–8.4 (m, 3,3′,4,4′-biquin*H*, 4 H); ^{13}C NMR δ 21.4 (CH_3), 23.3 (CH_2Pd), 119.8 (C3), 120.3 (C3′), 127.1 (C6), 127.4 (C6′), 128.1 (C5), 128.3 (C5′), 129.1 (C4a), 129.2 (C4a′), 131.2 (C7), 131.4 (C7′), 138.4 (C4), 138.6 (C4′), 143.5 (C8), 143.7 (C8a′), 144.9 (C8a), 150.2 (C2), 150.3 (C2′), 159.3 (C8′). Anal. Calcd for $C_{22}H_{18}N_2O_2Pd$: C, 58.88; H, 4.04; N, 6.24. Found: C, 58.51; H, 3.87; N, 6.05.

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Registry No. **1**, 99073-81-1; **2**, 1160-86-7; **4**, 110589-45-2; **5**, 110589-46-3; **6**, 110589-47-4; **9**, 110589-49-6; **10**, 110589-50-9; $(Et_2S)_2PdCl_2$, 14873-91-7; $[Pd(OAc)_2]$, 33571-36-7; $CH_2(CO_2CH_3)_2$, 108-59-8; 8,8′-bis(dibromomethyl)-2,2′-biquinoline, 110589-48-5.

(18) The time necessary for formation of $[C_6H_5)_3P]_4Ni^0$ is dependent on the efficiency of the degassing of the DMF solution, prior to the addition of Zn(0).

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