Supporting information

Facile Synthesis of 4,7-Disubstituted Conjugation-Extended 1,10-Phenanthrolines

Hyungsock Suh, Fernando Hung-Low,[†] Dominick Casadonte,[†] Han-je Kim,[‡] Beomsik Kim, and Taesun Chang[*]

Environment & Resource Research Center, KRICT (Korea Research Institute of Chemical Technology), Daejeon 305-600, Korea
[*]E-mail: tschang@krict.re.kr
[†]Department of Chemistry & Biochemistry, Texas Tech University, Lubbock, TX, 79405, USA
[‡]Department of Science Education, Gongju National University of Education, Gongju 314-711, Korea
Received May 22, 2012, Accepted June 22, 2012

Materials

The reagents were used 1,1'-Bis(diphenylphosphino)-ferrocene palladium (II)dichloride dichloromethane adduct (99%, Acros), copper iodide (99%, Strem), triisopropylsilyl acetylene (99%, Oakwood), phenylacetylene (98%, Acros), *p*-diethynylbenzene (99%, GFS), copper(I)chloride (99%, Acros), copper tetrafluoroborate (98%, Fisher), and triphenylphosphine (99%, Alfa-Aesar). All solvents were degassed and purified by distillation before use.

Instruments

The instruments used in the characterization of the compounds prepared include an INOVA 300 MHz ^{1}H NMR, a Shimadzu UV-2401 PC UV-VIS, an SLM AMINCO emission spectrophotometer with an ELXE-500 light source, and a Thermoquest 2000 Series Trace Ion Trap (MS). Single crystal X-Ray structures were obtained using a Bruker Smart Apex diffractometer with a molybdenum source.

Procedures for Crystal Preparation and X-ray Structure Determinations

2-3 mg of the substituted phenanthrolines or phenanthroline copper phosphines were added into a 1 dram vial and dissolved in 3 mL of dichloromethane:methanol (= 1:1 v/v) solution. The solution was covered with aluminum foil on the top and placed in the refrigerator. Tiny crystals occurred on the vial sidewall in 1-2 days. A spatula was used to push down all of the tiny crystals to the bottom of the vial. The vial was capped and stored in the refrigerator for 2-3 weeks to make suitably large crystals.

Crystal Preparation. Suitable diffraction quality crystals were obtained by isolation on a binocular polarized microscope in chemically inert Paratone-N® oil. Ideal crystals were perfectly single, optically transparent, and displayed dimensions on the order of 0.15 to 0.25 mm^3. The chosen crystal was then immobilized on a polymer-fiber cryoloop in a nitrogen cold stream. The cryoloop was mounted on the goniometer head by means of a magnetic base and centered in the X-ray beam using a digital camera.

Data Collection. Data collection was carried out at 110(2) K to reduce lattice vibrations and prevent sample decomposition on a Bruker X8 Apex using MoKα radiation (λ = 0.71073 Å). Unit cell dimensions were established by indexing reflections collected from a three run matrix set (3 × 12 frames). A data collection strategy was then determined by COSMO that would acquire > 99% of the unique reflections to θ ≥ 25.00° using a combination of φ and ω scans .

Data Reduction. All computations were carried out using the SHELXTL *vs* 6.10 or *vs* 6.3. Data reduction was performed using SAINT PLUS 7.12A. Raw data were corrected for absorption effects using SADABS.

Structure Solution and Refinement. All structures were solved using direct methods. Typically, positional and anisotropic thermal displacement parameters were refined for all non-hydrogen atoms. Carbon-and nitrogen-bound hydrogens were placed in calculated positions (C-H = 0.96 Å; N-H = 0.93 Å) with fixed isotropic parameters [Uiso(H) = 1.2©; Uiso(H) = 1.2(N)].

Synthesis

Compound 1a. 0.30 g (1.2 mmol) of 4,7-dichloro-1,10-phenanthroline, 0.48 g (2.2 eq.) of triisopropylsilyl acetylene, 0.05 g (0.05 eq.) of (dppf)PdCl$_2$·CH$_2$Cl$_2$, 0.24 g (2 eq.) of triethylamine, and 0.14 g (0.6 eq.) of copper iodide were suspended in 10 mL of benzene. This suspension was refluxed for 72 hours under argon. 10 mL of a 10% aqueous KCN solution and 10 mL dichloromethane were then added and the resulting mixture was stirred for 30 min at room temperature. The organic layer was extracted with 50 mL of dichloromethane twice and washed with water three times. The solvent was then evaporated and the solid was purified by column chromatography (Al$_2$O$_3$, DCM:MeOH = 100:1, Rf = 0.4. The middle of the three bands contains the desired product) to obtain a viscous liquid (0.16 g, 25%). ^{1}H NMR (300 MHz, CDCl$_3$): 9.12 (d, 2H), 8.38 (s, 2H), 7.74 (d, 2H), 1.25-1.21 (m, 42H). ^{13}C NMR (75 MHz, CDCl$_3$): 149.71, 146.11, 129.96, 128.48, 126.13, 125.04, 102.63, 102.08,

18.70, 11.28. MS: 541.5 (M, 10%), 303 (M-TIPSMe, 40%), 229 (M-2TIPS, 80%), 73 (TIPS-Me, 100%).

Compound 1b. 0.30 g (1.1 mmol) of 2,9-dimethyl-4,7-dichloro-1,10-phenanthroline, 0.44 g (2.2 eq.) of triisopropylsilyl acetylene, 0.04 g (0.05 eq.) of (dppf)PdCl$_2$·CH$_2$Cl$_2$, 0.22 g (2 eq.) of triethylamine, and 0.12 g (0.6 eq.) of copper iodide were suspended in 10 mL of benzene. This suspension was refluxed for 72 hours under argon. 10 mL of a 10% aqueous KCN solution and 10 mL dichloromethane were then added and the resulting mixture was stirred for 30 min at room temperature. The organic layer was extracted with 50 mL of dichloromethane twice and washed with water three times. The solvent was then evaporated and the solid was purified by alumina column chromatography (dichloromethane and gradient with methanol; the middle of the three bands is the desired product) to obtain a viscous liquid (0.18 g, 30%). ^{1}H NMR (300 MHz, CDCl$_3$): 8.32 (s, 2H), 7.66 (s, 2H), 2.95 (s, 6H), 1.27-1.24 (m, 42H). ^{13}C NMR NMR (75 MHz, CDCl$_3$): 158.86, 146.28, 129.99, 126.65, 126.63, 123.92, 102.41, 101.45, 25.74, 18.70, 11.28. MS: 568.5 (M, 40%), 544 (M-2C, 80%), 527 (M-IP, 100%).

Compound 2a. 0.30 g (0.55 mmol) of (**1a**) and 0.36 g (2.5 eq.) of tetrabutylammonium fluoride were added to 10 mL of THF. The mixture was stirred for 30 min at room temperature. 10 mL of water was added and the organic layer was extracted with 50 mL of dichloromethane twice. The product was washed with 50 mL of water twice and the solvent was then evaporated. The solid was purified by alumina column chromatography (dichloromethane and gradient with methanol; the middle of the three bands is the desired product) to obtain an ivory solid (0.11 g, 90%). ^{1}H NMR (300 MHz, CDCl$_3$): 9.17 (d, 2H), 8.38 (s, 2H), 7.78 (d, 2H), 3.74 (s, 6H). ^{13}C NMR (75 MHz, CDCl$_3$): 149.81, 146.09, 128.79, 128.63, 126.41, 125.02, 86.98, 79.17. MS: 228.1 (M, 100%).

Compound 2b. 0.30 g (0.53 mmol) of (**1b**) and 0.34 g (2.5 eq.) of tetrabutylammonium fluoride were added to 10 mL of THF. The mixture was stirred for 30 min at room temperature. 10 mL of water was added and the organic layer was extracted with 50 mL of dichloromethane twice. The product was washed with 50 mL of water twice and the solvent was then evaporated. The solid was purified by alumina column chromatography (dichloromethane and gradient with methanol; the middle of the three bands is the

desired product) to obtain an ivory solid (0.12 g, 91%). ^{1}H NMR (300 MHz, CDCl$_3$): 8.31 (s, 2H), 7.70 (s, 2H), 3.71 (s, 2H), 2.96 (s, 6H). ^{13}C NMR (75 MHz, CDCl$_3$): 159.24, 145.48, 129.10, 127.13, 127.01, 124.12, 86.36, 79.69, 26.01. MS: 256.2 (M, 100%).

Compound 3a. 0.30 g (1.2 mmol) of 4,7-dichloro-1,10-phenanthroline, 0.27 g (2.2 eq.) of phenylacetylene, 0.05 g (0.05 eq.) of (dppf)PdCl$_2$·CH$_2$Cl$_2$, 0.24 g (2 eq.) of triethylamine, and 0.14 g (0.6 eq.) of copper iodide were suspended in 10 mL of benzene. This suspension was refluxed for 72 hours under argon. 10 mL of a 10% aqueous KCN solution and 10 mL dichloromethane were then added and the resulting mixture was stirred for 30 min at room temperature. The organic layer was extracted with 50 mL of dichloromethane twice and washed with water three times. The solvent was then evaporated and the solid was purified by alumina column chromatography (dichloromethane and gradient with methanol; the middle of the three bands is the desired product) to obtain an ivory solid (0.36 g, 78%). ^{1}H NMR (300 MHz, CDCl$_3$): 9.18 (d, 2H), 8.48 (s, 2H), 7.80 (d, 2H), 7.70 (m, 4H), 7.45 (m, 6H). ^{13}C NMR (75 MHz, CDCl$_3$): 149.83, 146.27, 131.98, 129.96, 129.51, 128.64, 128.37, 125.47, 125.02, 122.10, 99.21, 85.04. MS: 380.6 (M, 100%).

Compound 3b. 0.30 g (1.1 mmol) of 2,9-dimethyl-4,7-dichloro-1,10-phenanthroline, 0.24 g (2.2 eq.) of phenylacetylene, 0.04 g (0.05 eq.) of (dppf)PdCl$_2$·CH$_2$Cl$_2$, 0.22 g (2 eq.) of triethylamine, and 0.12 g (0.6 eq.) of copper iodide were suspended in 10 mL of benzene. This suspension was refluxed for 72 hours under argon. 10 mL of a 10% aqueous KCN solution and 10 mL dichloromethane were then added and the resulting mixture was stirred for 30 min at room temperature. The organic layer was extracted with 50 mL of dichloromethane twice and washed with water three times. The solvent was then evaporated and the solid was purified by alumina column chromatography (dichloromethane and gradient with methanol; the middle of the three bands is the desired product) to obtain an ivory solid (0.33 g, 75%). ^{1}H NMR (300 MHz, CDCl$_3$): 8.43 (s, 2H), 7.74 (s, 2H), 7.72 (m,4H), 7.48 (m, 6H), 2.99 (2, 6H). ^{13}C NMR (75 MHz, CDCl$_3$): 158.95, 145.32, 131.93, 129.98, 129.36, 128.60, 126.52, 125.92, 123.89, 122.21, 98.33, 85.27, 25.83. MS: 408.5 (M, 100%).