Supplementary Material

Organometallic Complexes for Non-Linear Optics. 59. Syntheses and Optical Properties of Some Octupolar (N-Heterocyclic Carbene)gold Complexes

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Syntheses

Synthesis of 1,3,5-(4-I-3,5-Et2C6H2-1-C≡C)3C6H3 (I)

1,3,5-(HC≡C)3C6H3 (0.900 g, 5.99 mmol) and 2,6-Et2-1,4-I2C6H2 (7.32 g, 19.0 mmol) were dissolved in triethylamine (60 mL), and PdCl2(PPh3)2 (0.250 g, 0.360 mmol) and CuI (0.090 g, 0.48 mmol) were added. The mixture was then stirred at 80 °C overnight. The reaction mixture was allowed to cool to room temperature, filtered to remove the precipitate, and the solvent was removed under reduced pressure. The resulting residue was passed through a short pad of silica using hexane as eluent. Removal of the solvent afforded the crude product, and crystallization from hexane provided 1,3,5-(4-I-3,5-Et2C6H2-1-C≡C)3C6H3 (I) as a white solid (4.260 g, 4.61 mmol, 77%). IR (CH2Cl2): ν(C≡C) 2161 cm⁻¹; ¹H NMR (400 MHz, CDCl3): δ 7.65 (s, 3 H, CH aromatic), 7.21 (s, 6 H, CH aromatic), 2.81 (q, J = 7.5 Hz, 12H, CH2CH3), 1.24 (t, J = 7.5 Hz, 18H, CH2CH3) ppm; ¹³C NMR (101 MHz, CDCl3): δ 147.55, 134.04, 128.69, 124.01, 122.57, 108.05, 90.12, 88.22, 35.42, 14.47 ppm; HRMS (ESI): m/z calcd for C42H39I3: 924.0186; found 924.0186. Anal. Calc. for C42H39I3: C 54.57, H 4.25. Found: C 54.61, H 4.20%.

Synthesis of 1,3,5-(4-HC≡C)-3,5-Et2C6H2-1-C≡C)3C6H3 (2)

1,3,5-(4-I-3,5-Et2C6H2-1-C≡C)3C6H3 (I, 2.000 g, 2.16 mmol) was dissolved in NEt3 (60 mL) and Pd(PPh3)4 (0.130 g, 0.11 mmol), CuI (0.030 g, 0.16 mmol) and trimethylsilylacetylene (1.20 mL, 8.57 mmol) were added in sequence under a N₂ atmosphere. After stirring at 50 °C overnight, the reaction mixture was allowed to cool to room temperature, filtered to remove the precipitate, and the solvent was removed under reduced pressure. This product proved difficult to purify by chromatography, and so was reacted on without further purification. The residue was dissolved in THF (30 mL), [¹Bu₄N]F (1.0 M in THF, 8 mL, 8 mmol) was added, and the mixture was stirred at ambient temperature for 15 min. After removal of the solvent, the residue was passed through a short column using hexane/CH2Cl2 (8:1) as eluent. Reduction in volume of the solvent afforded 1,3,5-(4-HC≡C)-3,5-Et2C6H2-1-C≡C)3C6H3 (2) as a light-yellow solid (0.810 g, 1.30 mmol, 60%). IR (CH2Cl2): ν(C≡C) 2097 cm⁻¹; ¹H NMR (400 MHz, CDCl3): δ 7.68 (s, 3H, CH aromatic), 7.28 (s, 6H, CH aromatic), 3.57 (s, 3H, HC≡C), 2.87 (q, J = 7.5 Hz, 12H, CH2CH3), 1.30 (t, J = 7.5 Hz, 18H, CH2CH3) ppm; ¹³C NMR (101 MHz, CDCl3): δ 147.32, 134.10, 128.47, 124.04, 122.57, 108.05, 90.12, 88.78, 86.25, 80.24, 27.74, 14.56 ppm.
Synthesis of 1,3,5-(4-{4-Me3SiC≡CC6H4-1-C≡C}-3,5-Et2C6H2-1-C≡C)3C6H3 (3)

1,3,5-{(4-HC≡C)-2,6-Et2C6H2-1-C≡C}3C6H3 (2, 0.440 g, 0.710 mmol) and 4-IC6H4C≡CSiMe3 (0.660 g, 2.20 mmol) were dissolved in NEt3/THF (30 mL/30 mL), and Pd(PPh3)4 (25 mg, 0.022 mmol) and CuI (15 mg, 0.079 mmol) were added. The resulting solution was stirred at 80 °C overnight. The reaction mixture was allowed to cool to room temperature, filtered to remove the precipitate, and the solvent was removed under reduced pressure. The residue was passed through a short column using hexane/CH2Cl2 (5:1) as eluent. Reduction in volume of the solvent afforded 1,3,5-(4-{4-Me3SiC≡CC6H4-1-C≡C}-3,5-Et2C6H2-1-C≡C)3C6H3 (3) as a light yellow solid (0.580 g, 0.510 mmol, 72%). IR (CH2Cl2): ν(C≡C) 2155 cm⁻¹; UV-vis (CH2Cl2): 367 [19.8], 350 [22.2], 343 [22.4]; ¹H NMR (400 MHz, CDCl3): δ 7.67 (s, 3H, CH aromatic), 7.46 (s, 12H, CH aromatic), 7.29 (s, 6H, CH aromatic), 2.90 (q, J = 7.5 Hz, 12H, CH2CH3), 1.33 (t, J = 7.5 Hz, 18H, CH2CH3), 0.27 (s, 27H, Si(CH3)3) ppm; ¹³C NMR (101 MHz, CDCl3): δ 146.69, 134.13, 132.03, 131.19, 128.64, 124.15, 123.71, 123.07, 122.56, 122.04, 104.73, 98.37, 96.43, 91.03, 88.98, 88.41, 27.98, 14.64, 0.01 ppm; HRMS (ESI): m/z calcd for C81H78Si3: 1134.5411; found 1134.5413. Anal. Calc. for C81H78Si3: C 85.66, H 6.92. Found: C 85.50, H 6.98%.

Synthesis of 1,3,5-{4-(4-HC≡C)-CC6H4-1-C≡C}-3,5-Et2C6H2-1-C≡C)3C6H3 (3)

1,3,5-{4-(4-Me3SiC≡CC6H4-1-C≡C)-2,6-Et2C6H2-1-C≡C}3C6H3 (3, 0.570 g, 0.500 mmol) was dissolved in THF (30 mL), [nBu4N]F (1.0 M in THF, 3 mL, 3 mmol) was added, and the resulting solution was stirred at ambient temperature for 1 h. After removing the solvent, the residue was passed through a small pad of silica using hexane/CH2Cl2 (5:1) as eluent. Reduction in volume of the solvent afforded 1,3,5-{4-(4-HC≡CC6H4-1-C≡C)-3,5-Et2C6H2-1-C≡C}3C6H3 (3) as a light-yellow solid (0.430 g, 0.470 mmol, 94%). IR (CH2Cl2): ν(C≡C) 2106 cm⁻¹; UV-vis (CH2Cl2): 363 [16.5], 340 [18.9]; ¹H NMR (400 MHz, CDCl3): δ 7.69 (s, 3H, CH aromatic), 7.51 (s, 12H, CH aromatic), 7.31 (s, 6H, CH aromatic), 3.21 (s, 3H, HCC≡C), 2.93 (q, J = 7.5 Hz, 12H, CH2CH3), 1.35 (t, J = 7.5 Hz, 18H, CH2CH3) ppm; ¹³C NMR (101 MHz, CDCl3): δ 146.66, 134.08, 132.15, 131.23, 128.59, 124.07, 122.55, 121.94, 121.90, 98.07, 90.95, 88.94, 88.42, 83.30, 79.00, 27.93, 14.59 ppm; HRMS (ESI): m/z calcd for C72H54: 918.4226; found 918.4255.
Synthesis of 1,3,5-{4-(4-Me3SiC≡CC6H4-1-C≡C-4-C6H4-1-C≡C)-3,5-Et2C6H2C≡C}3C6H3 (5)

1,3,5-(4-HC≡C-3,5-Et2C6H2-1-C≡C)3C6H3 (2, 0.440 g, 0.710 mmol) and 4-Me3SiC≡CC6H4-1-C≡C-4-C6H4-1-I (0.880 g, 2.20 mmol) were dissolved in NEt3/THF (30 mL/30 mL), and Pd(PPh3)4 (25 mg, 0.022 mmol) and CuI (15 mg, 0.079 mmol) were added. The mixture was stirred at 80 °C overnight. The reaction mixture was allowed to cool to room temperature, filtered to remove the precipitate, and the solvent was then removed under reduced pressure. The residue was passed through a short column using hexane/CH2Cl2 (4:1) as eluent. Reduction in volume of the solvent afforded 1,3,5-{4-(4-Me3SiC≡CC6H4-1-C≡C-4-C6H4-1-C≡C)-3,5-Et2C6H2C≡C}3C6H3 (5) as a light-yellow solid (0.660 g, 0.460 mmol, 64%). IR (CH2Cl2): ν(C≡C) 2159 cm⁻¹; UV-vis (CH2Cl2): 356 [30.5]; 1H NMR (400 MHz, CDCl3): δ 7.68 (s, 3H, CH aromatic), 7.52-7.44 (m, 24H, CH aromatic), 7.30 (s, 6H, CH aromatic), 2.92 (q, J = 7.5 Hz, 12H, CH2CH3), 1.34 (t, J = 7.5 Hz, 18H, CH2C3) ppm; 13C NMR (101 MHz, CDCl3): δ 146.71, 134.16, 132.02, 131.70, 131.50, 131.40, 128.66, 124.15, 123.71, 123.23, 123.14, 122.94, 122.59, 122.04, 104.68, 98.42, 96.57, 91.12, 91.06, 89.03, 88.54, 28.01, 14.68, 0.01 ppm; HRMS (ESI): m/z calcd for C105H90Si3: 1434.6350; found 1434.6359.

Synthesis of 1,3,5-{4-(4-Me3SiC≡CC6H4-1-C≡C-4-C6H4-1-C≡C)-3,5-Et2C6H2-1-C≡C}3C6H3 (6)

1,3,5-{4-(4-Me3SiC≡CC6H4-1-C≡C-4-C6H4-1-C≡C)-3,5-Et2C6H2-1-C≡C}3C6H3 (5, 0.660 g, 0.460 mmol) was dissolved in THF (30 mL) and [nBu4N]+F⁻ (1.0 M in THF, 3 mL, 3.0 mmol) was added. The resulting solution was stirred at ambient temperature for 3 h. After removing the solvent, the residue was passed through a short pad of silica using hexane/CH2Cl2 (4:1) as eluent. Reduction in volume of the solvent afforded 1,3,5-{4-(4-Me3SiC≡CC6H4-1-C≡C-4-C6H4-1-C≡C)-3,5-Et2C6H2-1-C≡C}3C6H3 (6) as a light-yellow solid (0.540 g, 0.440 mmol, 96%). IR (CH2Cl2): ν(C≡C) 2108 cm⁻¹; UV-vis (CH2Cl2): 354 [25.5]; 1H NMR (400 MHz, CDCl3): δ 7.68 (s, 3H, CH aromatic), 7.52 (s, 12H, CH aromatic), 7.49 (s, 12H, CH aromatic), 7.30 (s, 6H, CH aromatic), 3.19 (s, 3H, CH aromatic), 2.92 (q, J = 7.5 Hz, 12H, CH2CH3), 1.34 (t, J = 7.5 Hz, 18H, CH2C3) ppm; 13C NMR (101 MHz, CDCl3): δ 146.65, 134.08, 132.12, 131.65, 131.50, 131.32, 128.60, 124.09, 123.71, 123.51, 122.81, 122.53, 122.14, 121.97, 98.32, 91.10, 90.97, 90.77, 88.94, 88.50, 83.25, 79.05, 27.94, 14.59 ppm.
Preparation of aniline compounds 7 - 10

General procedure: the octupolar alkyne (1 mmol) and 4-iodo-\(N,N'\)-diphenylaniline (1.450 g, 4.00 mmol) were dissolved in NEt\(_3/\)THF (30 mL/30 mL) and Pd(PPh\(_3\))\(_4\) (0.092 g, 0.080 mmol) and CuI (0.019 g, 0.10 mmol) were added. The resulting solution was stirred at 80 °C overnight. The reaction mixture was allowed to cool to room temperature, filtered to remove the precipitate, and the solvent was then removed under reduced pressure. The residue was passed through a short column using hexane/CH\(_2\)Cl\(_2\) (2:1) as eluent. Reduction in volume of the solvent afforded a yellow-green solid. Compounds 7-10 decomposed slowly over a period of days, precluding elemental analysis.

**Synthesis of 1,3,5-(4-Ph\(_2\)NC\(_6\)H\(_4\)-1-\(\equiv\)C)\(_3\)C\(_6\)H\(_3\) (7)**

7 was prepared by the general procedure. Yield: (0.220 g, 0.250 mmol, 25%). IR (CH\(_2\)Cl\(_2\)): \(\nu\) (C\(\equiv\)C) 2203 cm\(^{-1}\); UV-vis (CH\(_2\)Cl\(_2\)): 370 [12.4]; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.57 (s, 3H, core CH aromatic), 7.37-7.28 (m, 18H, CH aromatic), 7.13-6.99 (m, 24H, CH aromatic); \(^13\)C NMR (101 MHz, CDCl\(_3\)): \(\delta\) 148.21, 147.17, 133.42, 132.65, 129.43, 125.10, 124.29, 123.67, 122.16, 115.61, 90.74, 87.33; HRMS (ESI): \(m/z\) calcd for C\(_{66}\)H\(_{45}\)N\(_3\): 879.3613; found: 879.3608.

**Synthesis of 1,3,5-(4-Ph\(_2\)NC\(_6\)H\(_4\)-1-\(\equiv\)C-4-C\(_6\)H\(_4\)-1-\(\equiv\)C)\(_3\)C\(_6\)H\(_3\) (8)**

8 was prepared by the general procedure. Yield: (0.190 g, 0.160 mmol, 16%). IR (CH\(_2\)Cl\(_2\)): \(\nu\) (C\(\equiv\)C) 2202 cm\(^{-1}\); UV-vis (CH\(_2\)Cl\(_2\)): 382 [15.4], 307 [11.6]; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.65 (s, 3H, core CH aromatic), 7.50 (s, 12H, CH aromatic), 7.39-7.26 (m, 18H, CH aromatic), 7.13-7.00 (m, 24H, CH aromatic) ppm; \(^13\)C NMR (101 MHz, CDCl\(_3\)): \(\delta\) 148.17, 147.17, 133.42, 132.65, 129.43, 125.10, 124.29, 123.67, 122.16, 115.61, 90.74, 87.33; HRMS (ESI): \(m/z\) calcd for C\(_{69}\)H\(_{46}\)N\(_3\): 914.3758; found: 914.3754.
129.42, 125.08, 123.98, 123.66, 122.72, 122.09, 115.64, 91.97, 90.48, 89.41, 88.35 ppm; HRMS (ESI): m/z calcd for C₉₀H₅₇N₃: 1179.4552; found: 1179.4590.

**Synthesis** of 1,3,5-{4-(4-Ph₂NC₆H₄-1-C≡C-4-C₆H₄-1-C≡C-4-C₆H₄-1-C≡C)-3,5-Et₂C₆H₂-1-C≡C}₃C₆H₃ (10)

10 was prepared by the general procedure. Yield: (0.310 g, 0.159 mmol, 16%). IR (CH₂Cl₂): ν(C≡C) 2206 cm⁻¹; UV-vis (CH₂Cl₂): 378 [30.1]; ¹H NMR (400 MHz, CDCl₃): δ 7.67 (s, 3H, core CH aromatic), 7.52-7.28 (m, 48H, CH aromatic), 7.15-6.98 (m, 24H, CH aromatic), 2.92 (q, J = 7.5 Hz, 12H, CH₂CH₃), 1.34 (t, J = 7.5 Hz, 18H, CH₂CH₃) ppm; ¹³C NMR (101 MHz, CDCl₃): δ 148.14, 147.12, 146.62, 134.06, 132.58, 131.61, 131.54, 131.40, 131.32, 129.42, 128.58, 125.07, 124.07, 123.77, 123.65, 123.54, 122.97, 122.50, 122.37, 122.13, 121.99, 115.65, 98.39, 91.91, 91.22, 90.99, 90.87, 88.95, 88.41, 88.44, 27.93, 14.60 ppm; MS (MALDI) m/z calcd for C₁₅₀H₁₀₅N₃: 1947.83; found: 1947.77.

**Preparation of NHC-Au acetylide complexes 11 - 14**

General procedure: the alkyne (1 eq., 0.100 mmol) was dissolved in THF (50 mL) and potassium tert-butoxide (0.138 g, 1.00 mmol) was added. The solution was then stirred at 80 °C for 0.5 h. AuCl(NHC-Pr) (0.186 g, 0.300 mmol) was added, and the solution was stirred at 80 °C overnight. The reaction mixture was filtered to remove the precipitate and the solvent was removed under reduced pressure. The residue was dissolved in CH₂Cl₂ (2 mL) and the solution was slowly added dropwise to
stirring hexane (200 mL). The mixture was filtered and the white solid collected, washed with hexane, and dried.

**Synthesis of 1,3,5-{(NHC-iPr)Au}C≡C\(_3\)C\(_6\)H\(_3\) (11)**

The compound 1,3,5-{(NHC-iPr)Au}C≡C\(_3\)C\(_6\)H\(_3\) (11) has been reported previously, prepared from the Au(OH)(NHC-iPr) precursor (84%). In the present case, 11 was prepared by the general procedure with a similar yield to the earlier report. Yield: (0.150 g, 0.080 mmol, 80%). IR (CH\(_2\)Cl\(_2\)): \(\nu\) (C≡C) 2106 cm\(^{-1}\); UV-vis (CH\(_2\)Cl\(_2\)): 290 [7.7]; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.47 (t, J = 8.0 Hz, 6H, CH aromatic), 7.27 (d, J = 8.0 Hz, 12H, CH aromatic), 7.10 (s, 6H, CH imidazole), 6.96 (s, 3H, core CH aromatic), 2.59 (m, 12H, CH(CH\(_3\))\(_2\)), 1.34 (d, J = 7.0 Hz, 36H, CH(C\(_6\)H\(_3\))(CH\(_3\))\(_2\)), 1.20 (d, J = 6.9 Hz, 36H, CH(CH\(_3\))\(_2\)) ppm; \(^{13}\)C NMR (101 MHz, CDCl\(_3\)): \(\delta\) 191.59, 145.57, 134.31, 133.88, 130.41, 127.47, 124.63, 124.12, 122.97, 103.92, 28.78, 24.54, 24.06 ppm; HRMS (ESI): m/z calcd for C\(_{93}\)H\(_{111}\)Au\(_3\)N\(_6\): 1903.7945 [M+H]+; found: 1903.7944.

**Synthesis of 1,3,5-{(NHC-iPr)Au}C≡C-4-C\(_6\)H\(_4\)-1-C≡C\(_3\)C\(_6\)H\(_3\) (12)**

12 was prepared by the general procedure. Yield: (0.165 g, 0.075 mmol, 75%). IR (CH\(_2\)Cl\(_2\)): \(\nu\) (C≡C) 2109 cm\(^{-1}\); UV-vis (CH\(_2\)Cl\(_2\)): 294 [14.1], 325 [16.2]; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.49 (t, J = 8.0 Hz, 6H, CH aromatic), 7.47 (s, 3H, core CH aromatic), 7.29 (d, J = 8.0 Hz, 12H, CH aromatic), 7.25 (s, 12H, CH aromatic), 7.12 (s, 3H, CH imidazole), 2.59 (m, 12H, CH(CH\(_3\))\(_2\)), 1.34 (d, J = 7.0 Hz, 36H, CH(CH\(_3\))\(_2\)), 1.20 (d, J = 6.9 Hz, 36H, CH(CH\(_3\))\(_2\)) ppm; \(^{13}\)C NMR (101 MHz, CDCl\(_3\)): \(\delta\) 190.91, 145.62, 134.27, 133.57, 132.66, 132.18, 130.97, 130.51, 126.47, 124.18, 124.06, 123.20, 119.75, 103.59, 90.85, 88.52, 28.83, 24.61, 24.03 ppm; HRMS (ESI): m/z calcd for C\(_{117}\)H\(_{123}\)Au\(_3\)N\(_6\): 2203.8884 [M+H]+; found: 2203.9502.

**Synthesis of 1,3,5-4-{(NHC-iPr)Au}C≡C-4-C\(_6\)H\(_4\)-1-C≡C\(_3\)C\(_6\)H\(_3\) (13)**

13 was prepared by the general procedure. Yield: (0.192 g, 0.072 mmol, 72%). IR (CH\(_2\)Cl\(_2\)): \(\nu\) (C≡C) 2109 cm\(^{-1}\); UV-vis (CH\(_2\)Cl\(_2\)): 362 [20.1], 348 [21.3]; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.62 (s, 3H, core CH aromatic), 7.50 (t, J = 8.0 Hz, 6H, CH aromatic), 7.30 (d, J = 8.0 Hz, 12H, CH aromatic), 7.28-7.27 (m, 12H, CH aromatic), 7.23 (s, 6H, CH aromatic), 7.13 (s, 3H, CH imidazole), 2.59 (m, 12H, CH(CH\(_3\))\(_2\)), 1.34 (d, J = 7.0 Hz, 36H, CH(CH\(_3\))\(_2\)), 1.20 (d, J = 6.9 Hz, 36H, CH(CH\(_3\))\(_2\)) ppm; \(^{13}\)C NMR (101 MHz, CDCl\(_3\)): \(\delta\) 190.83, 146.36, 145.63, 134.29, 133.94, 132.55, 132.25, 130.64, 130.52, 128.44, 126.26, 124.20, 124.08, 123.24, 122.49, 121.92, 120.56, 103.66, 99.33, 91.03, 88.67, 86.97, 84.84, 78.86, 24.64, 24.04, 14.54 ppm.
NMR spectra

$\text{I,3,5-}(4\text{-I}\text{-3,5-Et}_2\text{C}_6\text{H}_2\text{-1-C≡C})_3\text{C}_6\text{H}_3 \ (1)$
$1,3,5-(4-HC≡C-3,5-Et_2C_6H_2-1-C≡C)C_6H_3 (2)$
1,3,5-{4-(4-Me₃SiC≡CC₆H₄-1-C≡C)-3,5-Et₂C₆H₂-1-C≡C}₃C₆H₃ (3)
1,3,5-{4-(4-\(\text{HC} \equiv \text{C} \_\text{C}_8\text{H}_4\_1 \_\text{C} \equiv \text{C}\))}-3,5-\(\text{Et}_2\text{C}_8\text{H}_2\_1 \_\text{C} \equiv \text{C}\)}\(\text{C}_6\text{H}_3\) (4)
$\text{1,3,5-}\{4-(4-\text{Me}_3\text{SiC≡CC}_6\text{H}_4-1-\text{C≡C}-4-\text{C}_6\text{H}_4-1-\text{C≡C})-3,5-\text{Et}_2\text{C}_6\text{H}_2-1-\text{C≡C}\}_3\text{C}_6\text{H}_3$ (5)
$1,3,5\{4-(4-HC\equiv C_C_6H_4-1-C\equiv C_4-C_6H_4-1-C\equiv C)-3,5-Et_2C_6H_2-1-C\equiv C\}_3C_6H_3$ (6)
$1,3,5$-(4-$\text{Ph}_2$N$\text{C}_6\text{H}_4$-1-$\text{C}≡\text{C})_3\text{C}_6\text{H}_3$ (7)
1,3,5-(4-Ph₂NC₆H₄-1-C≡C-4-C₆H₄-1-C≡C)₃C₆H₃ (8)
$1,3,5\{-4-(4-\text{Ph}_2\text{NC}_6\text{H}_4\text{-}1\text{-}C\equiv C\text{-}4\text{-}C_6\text{H}_4\text{-}1\text{-}C\equiv C\} - 3,5\text{-Et}_2\text{C}_6\text{H}_2\text{-}1\text{-}C\equiv C\}_3\text{C}_6\text{H}_3$ (9)
$1,3,5\{-4-(4-\text{Ph}_2\text{NC}_6\text{H}_4-1-C\equiv C-4-\text{C}_6\text{H}_4-1-C\equiv C-4-\text{C}_6\text{H}_4-1-C\equiv C)-3,5-\text{Et}_2\text{C}_6\text{H}_2-1-C\equiv C\}_3 \text{C}_6\text{H}_3 (10)$
1,3,5-\{[(NHC\textsuperscript{t}Pr)Au]C≡C\textsubscript{3}C\textsubscript{6}H\textsubscript{3}\} (11)
1,3,5-\{[(NHC\text{Pr})Au]C≡C-4-C_6H_4-1-C≡C\}_3C_6H_3 (12)
$1,3,5-\{4-\[(\text{NHCPr})Au\]C≡C-4-C_6H_4-1-C≡C\}-3,5-\text{Et}_2C_6H_2-1-C≡C\}_3C_6H_3$ (13)
$1,3,5-\{4-[(\text{NHC}^\text{Pr})\text{Au}]C≡C-4-C_6H_4-1-C≡C-4-C_6H_4-1-C≡C\}-3,5-$Et$_2C_6H_2-1-C≡C\}_3C$

$\text{dH}_2$ (14)
DFT calculations

We undertook density functional theory (DFT) and time-dependent (TD-DFT) calculations to rationalize the experimental optical properties. All models were constrained to either D_3 (organic compounds) or D_{3h} (organometallic complexes) symmetry. In addition, isopropyl (iPr) groups of the NHC ligand in the laboratory gold complexes and ethyl substituents used as an aid to mitigate solubility issue in the laboratory compounds 9, 10, 13, and 14 were replaced with hydrogens for computational expediency. We constrained the dihedral angle between the planes of a substituted phenyl and the NHC group to 90°. Initial geometries were optimized using hybrid B3LYP\textsuperscript{1,2} functional. For TD-DFT calculations, the hybrid PBE1PBE\textsuperscript{3,4} (or PBE0) functional was employed. The 6-31G(d) (for optimization) and 6-31G(d,p) (for TD-DFT studies) basis sets were employed for main group elements. Gold was modelled using the SDD\textsuperscript{5} basis set and associated pseudopotential. All calculations were performed using the Gaussian09\textsuperscript{6} program package.
**Figure S1.** Calculated UV-Vis spectra of two different model conformations of 7, namely, $7^*$ (all phenylene rings including core are co-planar) and $7'(45)$ (dihedral angle between two planes of adjacent phenylene rings is constrained to $45^\circ$). The solid (red) lines show the experimental absorption spectra. Abbreviations: $\varepsilon$, molar extinction coefficient ($10^4 \text{M}^{-1} \text{cm}^{-1}$). $\nu$, wavenumbers (cm$^{-1}$). $f$, relative oscillator strengths.

**Figure S2.** Comparison of calculated UV-Vis data between two different conformations of $11^*$, namely, $11^*(0)$ (core ring and all NHC groups are co-planar) and $11^*(90)$ (dihedral angle between the planes of the core and each NHC ring is constrained to $90^\circ$). The solid (maroon) lines show the experimental absorption spectra and the vertical sticks display the calculated oscillator strengths. Abbreviation: $\varepsilon$, molar extinction coefficients ($10^4 \text{M}^{-1} \text{cm}^{-1}$). $\nu$, wavenumbers (cm$^{-1}$). $f$, relative oscillator strengths.
**Figure S3.** Selected frontier molecular orbital plots (0.015 e bohr$^3$) for $7^*$ to $10^*$ (top to bottom). Abbreviations: H, HOMO; L, LUMO.
Figure S4. Selected frontier molecular orbital plots (0.02 e bohr$^3$) for 11$^+$ - 14$^+$ (top to bottom). Abbreviations: H, HOMO, L, LUMO.
References