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Supporting Information

69451 Weinheim, Germany

Steering the Surprisingly Modular π-Acceptor Properties of N-Heterocyclic Carbenes: Implications for Gold Catalysis**

*Manuel Alcarazo, Timon Stork, Anakuthil Anoop, Walter Thiel, and Alois Fürstner**

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Supporting Information

General : All reactions were carried out in flame-dried glassware under Ar. All the solvents were purified by distillation over the drying agents indicated and were transferred under Ar: THF, Et_2O (Mg-anthracene), CH_2Cl_2 (CaH_2), MeCN, Et_3N (CaH_2), MeOH (Mg), hexane, toluene (Na/K). Flash chromatography: Merck silica gel 60 (230-400 mesh). IR: Nicolet FT-7199 spectrometer, wavenumbers in cm^{-1}. MS (EI): Finnigan MAT 8200 (70 eV), ESI-MS: Finnigan MAT 95, accurate mass determinations: Bruker APEX III FT-MS (7 T magnet). NMR: Spectra were recorded on a Bruker DPX 300 or AV 400 spectrometer in the solvents indicated; ^1H and ^{13}C chemical shifts (δ) are given in ppm relative to TMS, ^{19}F chemical shifts in ppm relative to CF_3COOH, coupling constants (J) in Hz. The solvent signals were used as references and the chemical shifts converted to the TMS scale. Melting points: Büchi melting point apparatus B-540 (corrected). Elemental analyses: H. Kolbe, Mülheim/Ruhr. Unless stated otherwise, all commercially available compounds (Acros, Fluka, Lancaster, Aldrich) were used as received.

Gold Complexes

[Gold chloro 2-mesityl-5-methylimidazo[1,5-a] pyridin-3-ylidene] ([1·AuCl]): A suspension of [2-mesityl-5-methylimidazo[1,5-a] pyridinium chloride (100 mg, 0.35 mmol) in CH_2Cl_2 (3 mL) was treated with Ag_2O (40.4 mg, 0.17 mmol). After stirring for 4 h in the dark, $AuCl(SMe_2)$ (103 mg, 0.35 mmol) was added, causing the formation of a white precipitate. Stirring was continued for 3 h before the AgCl was filtered off over a plug of silica. The filtrate was evaporated to give the title complex as a white solid (168 mg, 99 %). ^1H NMR (400 MHz, CD_2Cl_2): δ = 7.42 (d, J = 9.2 Hz, 1H), 7.37 (s, 1H), 7.07 (s, 2H), 6.96 (t, J = 8.0 Hz, 1H), 6.59 (dd, J = 6.5, 1.0 Hz, 1H), 3.28 (s, 3H), 2.39 (s, 3H), 2.00 ppm (s, 6H); ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 162.5, 140.6, 137.1, 137.0, 135.2, 132.6, 129.8, 123.7, 116.9, 116.0, 113.6, 24.0, 21.6, 18.1 ppm; IR (film): $\tilde{\nu}$ = 3137, 2921, 1655, 1546, 1490, 1420, 1373, 1321, 1287, 1198, 1154, 1071, 1034, 860, 793, 780, 714, 686 cm^{-1}; MS (EI): m/z (%): 482 (61) $[M]^+$, 446 (44), 249 (100), 233 (11), 158 (16), 124 (21), 77 (7), 65 (4), 51 (2), 39 (3); HRMS calcd for $C_{17}H_{18}N_2AuClNa$: 505.07162, found 505.07206.

[Gold chloro [2](1,4)benzeno[2](5,8)-2-methylimidazo[1,5-a]pyridin-3-ylidenephane] ([2·AuCl]): A suspension of [2](1,4)benzeno[2](5,8)-2-methylimidazo[1,5-a]pyridiniumphane iodide (23.3 mg, 0.06 mmol)[1] in CH_2Cl_2 (1 mL) was treated with Ag_2O (6.9 mg, 0.03 mmol). After stirring for 4 h at ambient temperature in the dark, $AuCl(SMe_2)$ (17.6 mg, 0.06 mmol) was added, which caused the formation of a white precipitate. The mixture was stirred for 3 h at ambient temperature before the AgCl was filtered off over a plug of silica. The filtrate was evaporated to give the title complex as a white solid (29.5 mg, 99 %). ^1H NMR (600 MHz, CD_2Cl_2): δ = 7.05 (s, 1H), 6.65 (dd, J = 7.9, 1.7 Hz, 1H), 6.63 (dd, J = 7.9, 1.6 Hz, 1H), 6.25 (d, J = 7.0 Hz, 1H), 6.14 (dd, J = 7.9, 1.6 Hz, 1H), 6.08 (d, J = 6.9 Hz, 1H), 6.04 (dd, J = 7.9, 1.6 Hz, 1H), 4.96 (dd, J = 14.3, 9.9 Hz, 1H), 4.10 (s, 3H), 3.35 (ddd, J = 13.3, 9.9, 6.9 Hz, 1H), 3.16 (dd, J = 13.3, 10.7 Hz, 1H), 3.10-2.89 ppm (m, 5H); ^{13}C NMR (150 MHz, CD_2Cl_2): δ = 161.96, 137.17, 137.16, 136.41, 136.39, 132.02, 131.73, 129.25, 127.45, 127.18, 124.60, 121.96, 113.11, 40.58, 35.10, 33.82, 32.85, 31.22 ppm; IR (film): $\tilde{\nu}$ = 3113, 2922, 2851, 1641, 1536, 1499, 1429, 1410, 1378, 1306, 1262, 1189, 1096, 1047, 1025, 943, 878, 807, 722 cm^{-1}; MS (EI): m/z (%): 494 (22) $[M]^+$, 458 (16), 355 (9), 324 (3), 262 (7), 221 (1), 157 (3), 130 (4), 104 (100), 78 (6), 51 (2); HRMS calcd for $C_{18}H_{18}N_2AuClNa$: 517.07162, found 517.07205.

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N-((3,6-dimethylpyridin-2-yl)methyl)formamide: A solution of 2-cyano-3,6-dimethylpyridine (470 mg, 3.6 mmol)[2] in acetic acid (60 mL.) was hydrogenated over Pd/C (10 % *w*/*w*, 313 mg) in an autoclave at 10 bar hydrogen pressure for 3 h. The autoclave was vented and the mixture filtered through a pad of Celite which was carefully washed with hot acetic acid (3 x 10 mL). The combined filtrates were evaporated and the residue was dissolved in methyl formiate (20 mL). Et_3N (0.93 mL, 7.2 mmol) was added and the mixture heated at 65 °C for 2 h. Evaporation of all volatile materials and purification of the residue by flash chromatography (EtOAc) gave the title compound as a yellow solid (531 mg, 91 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.38 (bs, 1H), 7.68 (bs, 1H), 7.37 (d, J = 7.6 Hz, 1H), 6.99 (d, J = 7.4 Hz, 1H), 4.49 (d, J = 4.4 Hz, 2H), 2.51 (s, 3H), 2.24 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.1, 154.5, 151.4, 138.3, 127.3, 121.7, 40.4, 23.8, 16.9 ppm; IR (film): $\tilde{\nu}$ = 3287, 5053, 2923, 2887, 1639, 1594, 1577, 1537, 1465, 1385, 1232, 1117, 1036, 1011, 971, 917, 840, 815, 758, 705, 678 cm^{-1}. MS (EI): *m*/*z* (%): 164 (75) [M]$^+$, 147 (3), 135 (100), 120 (28), 108 (21), 92 (5), 77 (22), 65 (8), 51 (12), 41 (9), 39 (20), 30 (24), 27 (13); HRMS calcd for $C_9H_{12}N_2O$: 164.09496, found 164.09491; elemental analysis calcd(%) for $C_9H_{12}N_2O$: C 65.83, H 7.37, N 17.06; found C 65.87, H 7.35, N 16.98.

5,8-Dimethylimidazo[1,5-a]pyridine: $POCl_3$ (54.6 µl, 0.6 mmol) was added to a solution of N-((3,6-dimethylpyridin-2-yl)methyl)formamide (500 mg, 3.0 mmol) in toluene (12 mL) and the mixture was stirred at 80 ºC for 3 h. After cooling to ambient temperature the solvents were evaporated, the residue suspended in $CHCl_3$ (25 mL), the organic phase was washed with NaOH (2 M, 2 x 5 mL) and dried over Na_2SO_4. Evaporation of the solvent and purification of the residue by flash chromatography (EtOAc) afforded the title compound as a yellow solid (350 mg, 75 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.02 (s, 1H), 7.47 (s, 1H), 6.47 (d, J = 6.6 Hz, 1H), 6.31 (d, J = 6.6 Hz, 1H), 2.53 (s, 3H), 2.42 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 132.1, 128.5, 125.8, 125.6, 119.6, 118.1, 111.6, 17.8, 17.6 ppm; IR (film): $\tilde{\nu}$ = 3137, 2919, 1637, 1563, 1527, 1446, 1394, 1355, 1299, 1262, 1227, 1119, 1064, 1044, 915, 825, 786, 752, 711 cm^{-1}; MS (EI): *m*/*z* (%): 146 (100) [M]$^+$, 131 (6), 119 (16), 104 (9), 91 (12), 77 (8), 65 (7), 58 (3), 51 (13), 39 (13), 27 (7); HRMS calcd for $C_9H_{10}N_2$: 146.08440, found 146.08451; elemental analysis calcd(%) for $C_9H_{10}N_2$: C 73.94 H 6.89, N 19.16; found C 73.86, H 6.91, N 19.07.

2,5,8-Trimethylimidazo[1,5-a]pyridin-2-ium iodide: MeI (60 µL, 0.98 mmol) was added to a solution of 5,8-dimethylimidazo[1,5-a]pyridine (28.5 mg, 0.20 mmol) in THF (2.0 mL) and the mixture was stirred at 60 ºC for 18 h. After removal of the solvent, the residue was washed with pentane (3 x 5 mL) and dried in vacuo to afford the title compound as a yellow solid (44 mg, 78 %). ^{1}H NMR (400 MHz, d_6-DMSO): δ = 9.78 (d, J = 1.0 Hz, 1H), 8.38 (d, J = 1.5 Hz, 1H), 7.06 (dd, J = 6.9, 1.1 Hz, 1H), 6.98 (dd, J = 6.9, 1.0 Hz, 1H), 4.17 (s, 3H), 2.60 (s, 3H), 2.43 ppm (s, 3H); ^{13}C NMR (100 MHz, d_6-DMSO): δ = 131.0, 130.3, 126.1, 125.0, 123.3, 116.0, 114.2, 37.0, 17.1, 16.7 ppm; IR (film): $\tilde{\nu}$ = 3029, 2985, 1651, 1548, 1530, 1443, 1400, 1348, 1324, 1305, 1268, 1236, 1186, 1129, 1090, 1061, 1030, 849, 823 cm^{-1}; MS (ESI): *m*/*z* (%): 161 (100) [M^+ - I].

(2,5,8-Trimethyl-2,3-dihydroimidazo[1,5-a]pyridin-3-yl)gold(I) chloride ([1b·AuCl]): A suspension of 2,5,8-trimethylimidazo[1,5-a]pyridin-2-ium iodide (31 mg, 108 mmol) in CH_2Cl_2 (3 mL) was treated with Ag_2O (124 mg, 54 mmol). After stirring for 3 h at ambient temperature in the dark, AuCl(SMe_2) (32 mg, 108 mmol) was introduced, which caused the formation of a white precipitate. The mixture was stirred for 3 h at ambient temperature before the formed AgCl was filtered off over a plug of silica. The filtrate was evaporated to give the title complex as a white solid (21.1 mg, 50 %). ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.37 (s, 1H), 6.66 (dd, J = 6.6, 1.1 Hz, 1H), 6.45 (dd, J = 6.7, 0.8 Hz, 1H), 4.20 (s, 3H), 3.18 (s, 3H), 2.34 ppm (s, 3H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 162.0, 134.1, 134.0, 126.1, 122.2, 115.9, 112.4, 41.3, 23.7, 17.8 ppm; IR (film): $\tilde{\nu}$ = 3101, 1651, 1462, 1418, 1365, 1292, 1203, 1099, 1034, 831,

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778, 717 cm^{-1}; MS (EI): *m*/*z* (%): 392 (70) $[M]^+$, 356 (100), 159 (61), 145 (19), 132 (8), 117 (13), 106 (6), 91 (15), 77 (9), 65 (7), 51 (7), 39 (6); HRMS calcd for $C_{10}H_{12}N_2AuClNa$: 415.02467, found 415.02499.

(5-Methyl-2-phenyl-[1,2,4]triazolo[4,3-a]pyridin-3(2H)-ylidene)gold(I) chloride ([5·AuCl]): NEt_3 (65 µl, 0.47 mmol) was added to a suspension of 5-methyl-2-phenyl-[1,2,4]triazolo[4,3-a]pyridin-2-ium tetrafluoroborate (127 mg, 0.43 mmol)[3] and $AuCl(SMe_2)$ (126 mg, 0.43 mmol) in THF (4 mL) and the resulting mixture was stirred for 1.5 h. Evaporation of all volatile materials and purification of the residue by flash chromatography (CH_2Cl_2) provided the title complex as a yellow solid (174 mg, 92 %). ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 8.08-8.03 (m, 2H), 7.67-7.59 (m, 4H), 7.48 (dd, *J* = 9.0, 6.8 Hz, 1H), 6.82 (dpent, *J* = 6.8, 1.1 Hz, 1H), 3.36 ppm (s, 3H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 165.7, 149.8, 140.8, 139.1, 132.3, 130.7, 129.9, 125.7, 116.9, 114.1, 23.5 ppm; IR (film): $\tilde{\nu}$ = 3056, 2978, 1652, 1597, 1542, 1536, 1503, 1462, 1423, 1391, 1379, 1351, 1306, 1264, 1231, 1146, 1103, 1079, 1008, 965, 782, 767, 748, 739, 693, 680, 660 cm^{-1}; MS (EI): *m*/*z* (%): 441 (33) $[M]^+$, 405 (72), 209 (100), 182 (11), 168 (22), 154 (2), 118 (14), 103 (8), 91 (15), 77 (29), 65 (14), 51 (12), 39 (8); HRMS calcd for $C_{13}H_{11}N_3AuClNa$: 464.01992, found 464.02035.

Complex [6·AuCl]: A solution of KHMDS (89.5 mg, 0.43 mmol) in THF (3 mL) was added dropwise over a period of 30 min to a suspension of the parent azolium tetrafluoroborate salt (200 mg, 0.41 mmol)[4] and $AuCl(SMe_2)$ (126 mg, 0.43 mmol) in THF (4 mL) at -78 °C. After 1 h, the mixture was allowed to reach ambient temperature and stirring was continued overnight, causing the formation of a grey precipitate. The solvent was evaporated and the residue was suspended in CH_2Cl_2 (2 mL). The mixture was filtered through a short pad of Celite which was carefully washed with CH_2Cl_2 (5 x 1mL) and the combined filtrates were evaporated to give the title complex as a grey solid (150.0 mg, 58 %). ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 8.23-8.19 (m, 2H), 7.93-7.85 (m, 8H), 7.79-7.72 (m, 7H), 7.65 (s, 1H), 7.58-7.51 (m, 2H), 7.49-7.43 ppm (m, 1H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 168.8 (d, *J* = 31.3 Hz), 145.8 (d, *J* = 18.8 Hz), 144.3, 134.8 (d, *J* = 10.7 Hz), 132, 130.2 (d, *J* = 14.1 Hz), 129.1, 127.8, 124.4, 122.0 (d, *J* = 93.3 Hz), 101.9 ppm (d, *J* = 127.3 Hz). ^{31}P NMR (162 MHz, CD_2Cl_2): δ = 15.13 ppm; IR (film): $\tilde{\nu}$ = 3093, 1595, 1492, 1481, 1468, 1450, 1435, 1349, 1330, 1207, 1162, 1109, 948, 771, 758, 749, 720, 710, 697, 687 cm^{-1}; MS (ESI): *m*/*z* (%): 675 (11) $[M^+ + K]$, 659 (63) $[M^+ + Na]$, 637 (15) $[M^+ + H]$, 405 (23), 242 (100), 186 (12), 142 (25); HRMS calcd for $C_{27}H_{21}N_2AuClPNa$: 659.06886, found 659.06896.

Preparation of the Substrates and Gold-Catalyzed Transformations

Dimethyl 2-cinnamyl-2-(4-methylpenta-2,3-dienyl)malonate (**7**)[5] and (E)-dimethyl 2-(4-methylpenta-2,3-dienyl)-2-(penta-2,4-dienyl)malonate (**15**)[6] were prepared according to the cited literature procedures.

2-(3-(Trimethylsilyl)prop-2-ynyl)cyclopentanone: *n*BuLi (1.6 M in hexane, 8 mL, 12.8 mmol) was added to a solution of iPr_2NH (2 mL, 14.1 mmol) in THF (100 mL) at 0 °C and the resulting mixture was stirred at 0 °C for 1 h and then cooled to –40 °C. A solution of 2-cyclopentylidene-1,1-dimethylhydrazine (1.62 g, 12.8 mmol)[7] in THF (20 mL) was slowly added and the mixture stirred at –40 °C for 3 h. A solution of (3-iodo-1-ynyl)trimethylsilane (3.35 g, 14.1 mmol)[8] in THF (20 mL) was then introduced and the resulting mixture stirred at the same temperature overnight. The reaction was quenched with water (3 mL) and the mixture concentrated under reduced pressure. The residue was dissolved in diethyl

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ether (150 mL), the organic phase was washed with H_2O (2 x 50 mL) and brine (2 x 50 mL), dried over Na_2SO_4 and evaporated. The residue was dissolved in THF (50 mL), mixed with aq. oxalic acid solution (4.55 g in 25 mL H_2O, 50.5 mmol) and the resulting heterogeneous mixture was stirred under reflux for 6 h. A standard extractive work up followed by distillation of the crude product under reduced pressure (0.6 mbar, 75 °C) afforded the title compound as a colorless oil (1.86 g, 75 %). The analytical and spectral properties match those previously reported in the literature.[9]

1-(Prop-1-en-2-yl)-2-(3-(trimethylsilyl)prop-2-ynyl)cyclopentanol: A slurry of anhydrous $CeCl_3$ (801 mg, 4.24 mmol) in THF (25 mL) was stirred for 1 h at ambient temperature before it was cooled to –78 °C. A pre-cooled (–78 °C) solution of isopropenylmagnesium bromide (0.162 M in THF, 20 mL, 3.24 mmol) was transferred via canula to the cold $CeCl_3$-slurry. After the resulting yellow suspension had been stirred for 2 h at –78 °C, a solution of 2-(3-(trimethylsilyl)prop-2-ynyl)cyclopentanone (210 mg, 1.08 mmol) in THF (10 mL) was slowly added and the mixture allowed to reach ambient temperature overnight. Treatment with aq. sat. NH_4Cl (30 mL) followed by a standard extractive workup and purification of the crude material by flash chromatography (hexanes/*tert*-butyl methyl ether, 15:1) gave the title compound as a colorless oil (221 mg, 87 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.10 (dd, J = 1.5, 0.8 Hz, 1H), 4.90 (t, J = 1.5 Hz, 1H), 2.33-2.18 (m, 2H), 2.17-2.07 (m, 1H), 2.02-1.90 (m, 2H), 1.89-1.80 (m, 1H), 1.78 (d, J = 0.8 Hz, 3H), 1.73-1.57 (m, 4H), 0.13 ppm (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.3, 110.8, 106.6, 85.8, 84.6, 44.9, 39.6, 29.6, 21.4, 19.8, 18.8, 0.2 ppm; IR (neat) $\tilde{\nu}$ = 3521, 2959, 2873, 2173, 1248, 1025, 899, 837, 758, 697 cm^{-1}; MS (EI): *m*/*z* (%): 236 (4) [*M*]$^+$, 221 (62), 207 (12), 193 (15), 179 (8), 163 (7), 145 (18), 131 (30), 107 (10), 91 (10), 79 (9), 73 (100), 69 (10), 59 (10), 41 (14), 29 (3); HRMS calcd for $C_{14}H_{24}OSi$: 236.15965, found 236.15953.

Triethyl(1-(prop-1-en-2-yl)-2-(prop-2-ynyl)cyclopentyloxy)silane (19): K_2CO_3 (1.0 g, 7.3 mmol) was added to a solution of 1-(prop-1-en-2-yl)-2-(3-(trimethylsilyl)prop-2-ynyl)cyclopentanol (216 mg, 0.91 mmol) in MeOH (7 mL) and the resulting mixture stirred for 2 h. The mixture was then diluted with diethyl ether (25 mL), the organic phase was washed with aq. sat. NH_4Cl (10 mL) and brine (10 mL), dried over Na_2SO_4 and evaporated. TESOTf (2 mL, 3 mmol) was added dropwise to a solution of the residue and 2,6-lutidine (1.9 mL, 8.2 mmol) in CH_2Cl_2 (2 mL) at 0 °C and the mixture was stirred at 0 °C for 1.5 h. The reaction was quenched with aq. sat. $NaHCO_3$, the aqueous phase was extracted with CH_2Cl_2 (2 x 20 mL), and the combined organic phases were dried over Na_2SO_4. Evaporation of the solvent and purification of the residue by flash chromatography (hexanes/EtOAc, 10:1) afforded the title compound as a colorless oil (185 mg, 73 %). ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 4.99 (d, J = 1.5 Hz, 1H), 4.89-4.87 (m, 1H), 2.28 (ddd, J = 17.1, 3.3, 3.0 Hz, 1H), 2.16-1.86 (m, 5H), 1.83-1.69 (m, 5H), 1.68-1.54 (m, 2H), 0.94 (t, J = 8.0 Hz, 9H), 0.61 ppm (q, J = 7.8 Hz, 6H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 148.6, 111.9, 87.0, 85.8, 68.1, 48.6, 37.5, 30.1, 22.3, 20.2, 18.3, 7.6, 7.1 ppm; IR (neat) $\tilde{\nu}$ = 3313, 2954, 2912, 2876, 2118, 1641, 1457, 1237, 1165, 1121, 1084, 1051, 1007, 900, 721 cm^{-1}; MS (EI): *m*/*z* (%): 278 (12) [*M*]$^+$, 263 (14), 249 (92), 237 (18), 223 (14), 207 (11), 193 (19), 175 (6), 145 (20), 131 (7), 115 (32), 103 (100), 87 (48), 75 (71), 59 (31), 47 (15); HRMS calcd for $C_{17}H_{30}OSi$: 278.20660, found 278.20626.

Representative Procedure for the Gold(I)-Catalyzed Reactions: A solution of $(Ph_3P)AuCl$ (2.5 mg, 5 mmol) in CH_2Cl_2 (0.75 mL) was added to a solution of $AgSbF_6$ (1.7 mg, 5 mmol) in CH_2Cl_2 (0.75 mL) at –5 °C. The mixture was stirred for 5 min before a solution of dimethyl 2-cinnamyl-2-(4-methylpenta-2,3-dienyl)malonate **7** (33 mg, 0.1 mmol)[5] in CH_2Cl_2 (1.5 mL) was introduced.[10] The reaction was stirred at –5 °C and monitored by GC-MS analysis. Upon full conversion of the substrate, NEt_3 (0.05 mL) was added and the mixture was filtered through a short pad of silica, which was carefully washed with CH_2Cl_2. The combined filtrates were evaporated and the residue purified by flash chromatography (hexanes/EtOAc, 10:1) to give a mixture of isomers as a transparent oil (27.4 mg, 83 %). The ratio of the isomers was determined by ^{1}H NMR to be **10**:**13**:**14** = 50:32:18. The individual compounds were obtained in pure form by HPLC (Chiralpak IC, *n*-heptane/*i*-propanol, 99:1). The

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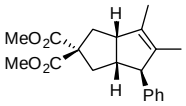
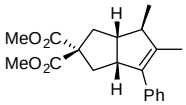
10 For the reactions shown in Table 3 of the paper, the precipitated silver salts were filtered off prior to the addition of the substrate.

recorded analytical and spectral data of dimethyl 6-phenyl-7-(propan-2-ylidene)bicyclo[3.2.0]heptane-3,3-dicarboxylate **10**[5] match those reported in the literature. The analytical and spectral properties of the [3+2] adducts are compiled below. All other gold catalyzed reactions were performed analogously, with the resulting products matching the reported data: **17** and **18** (ref. [6]), **22** and **24** (ref [11]).

Dimethyl 4,5-dimethyl-6-phenyl-3,3a,6,6a-tetrahydropentalene-2,2(1H)-dicarboxylate (13): 

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.26 (t, J = 7.0 Hz, 2H), 7.17 (tt, J = 7.8, 1.4 Hz, 1H), 7.05 (d, J = 7.0 Hz, 2H), 3.69 (s, 3H), 3.69 (s, 3H), 3.37-3.29 (m, 2H), 2.54 (tdd, J = 8.3, 7.2, 2.0 Hz, 1H), 2.49 (ddd, J = 12.5, 8.8, 1.0 Hz, 1H), 2.46 (ddd, J = 12.8, 8.4, 1.0 Hz, 1H), 2.19 (dd, J = 12.8, 6.3 Hz, 1H), 2.11 (dd, J = 13.2, 4.8 Hz, 1H), 1.64 (s, 3H), 1.37 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=172.6, 171.9, 146.1, 134.0, 133.6, 128.4, 127.3, 126.0, 63.5, 61.2, 53.7, 52.7, 52.4, 49.0, 41.8, 38.7, 12.6, 12.3 ppm; IR (film): $\tilde{\nu}$ = 3024, 2951, 2875, 1730, 1452, 1434, 1258, 1227, 1200, 1162, 1085, 1058, 753, 700 cm^{-1}; MS (EI): *m*/*z* (%): 328 (26) $[M]^+$, 297 (10), 268 (100), 253 (5), 236 (7), 221 (4), 209 (15), 193 (9), 169 (24), 145 (7), 115 (4), 77 (2), 59 (2); HRMS calcd for $C_{20}H_{24}O_4Na$: 351.15668, found 351.15639.

Dimethyl 5,6-dimethyl-4-phenyl-3,3a,6,6a-tetrahydropentalene-2,2(1H)-dicarboxylate (14): 

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33 (t, J = 7.4 Hz, 2H), 7.24 (d, J = 8.0 Hz, 2H), 7.21 (t, J = 7.4 Hz, 1H), 3.73-3.80 (m, 1H), 3.72 (s, 3H), 3.62 (s, 3H), 2.50 (ddd, J = 13.6, 8.7, 1.6 Hz, 1H), 2.49 (ddd, J = 12.8, 8.2, 1.6 Hz, 1H), 2.44-2.51 (m, 1H), 2.33 (dq, J = 2.0, 8.6 Hz, 1H), 2.06 (dd, J = 12.8, 9.0 Hz, 1H), 1.78 (dd, J = 13.6, 6.0 Hz, 1H), 1.71 (dd, J = 2.0, 0.9 Hz, 3H), 1.10 ppm (d, 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.8, 172.1, 138.2, 137.7, 136.9, 128.4, 128.0, 126.3, 61.5, 52.6, 52.4, 51.4, 50.9, 47.8, 40.7, 38.8, 19.8, 13.5 ppm; IR (film): $\tilde{\nu}$ = 2962, 1732, 1435, 1295, 1202, 1086, 1015, 864, 795, 700 cm^{-1}; MS (EI): *m*/*z* (%): 328 (22) $[M]^+$, 313 (2), 297 (9), 268 (100), 253 (6), 236 (7), 221 (4), 209 (17), 193 (10), 169 (23), 145 (8), 115 (4), 91 (7), 77 (2), 59 (2); HRMS calcd for $C_{20}H_{24}O_4Na$: 351.15668, found 351.15703.

X-Ray Crystallographic Study

Data were recorded using an Bruker-AXS KappaCCD-diffractometer with graphite-monochromated Mo-K_α-radiation (λ = 0.71073 Å). The crystal was mounted in a stream of cold nitrogen gas and measured at 100 K. The structures were solved by direct methods (SHELXS-97)[12] and refined by full-matrix least-squares techniques against F^2 (SHELXL-97).[13] Hydrogen atoms were inserted from geometry consideration using the HFIX option of the program.

Selected X-ray crystallographic data for complex [2·AuCl]: $C_{18}H_{18}AuClN_2$, M_r = 494.76 g · mol^{-1}, colorless block, crystal size 0.12 x 0.06 x 0.04 mm, orthorhombic, space group *Pnma*, a = 21.6308(8) Å, b = 9.3463(3) Å, c = 7.7429(3) Å, V = 1565.37(10) Å^3, Z = 4, D_{calc} = 2.099 g · cm^3, μ(*Mo-K*$_\alpha$) = 9.566 mm^{-1}, semi-empirical absorption correction ($T_{min.}$= 0.46/$T_{max.}$= 0.69), 4.35 < θ < 25.03, 15560 measured reflections, 1469 independent reflections, 1436 reflections with $I > 2\sigma(I)$, R_1 = 0.098 [$I > 2\sigma(I)$], wR_2 = 0.209, 96 parameters, S = 1.457, residual electron density +2.1 / -3.3 e · Å^{-3}.

Selected X-ray crystallographic data for complex [5·AuCl]: $C_{13}H_{11}AuClN_3$, M_r = 441.66 g · mol^{-1}, colorless block, crystal size 0.09 x 0.04 x 0.03 mm, orthorhombic, space group $P2_12_12_1$, a = 6.6980(12) Å, b = 10.0354(17) Å, c = 19.281(3) Å, V = 1296.0(4) Å^3, Z = 4, D_{calc} = 2.264 g · cm^3, μ(*Mo-K*$_\alpha$) = 11.541 mm^{-1}, Gaussian absorption correction ($T_{min.}$= 0.46/$T_{max.}$= 0.72), 3.66 < θ < 36.39, 43521 measured reflections, 6153 independent reflections, 6071 reflections with $I > 2\sigma(I)$, R_1 = 0.026 [$I > 2\sigma(I)$], wR_2 = 0.065, 134 parameters, S =

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1.064, absolute structure parameter 0.322(8), residual electron density +2.9 / -2.0 e · Å^{-3}.

Selected X-ray crystallographic data for complex [6·AuCl]: C_{27} H_{21} Au Cl N_2 P, M_r = 636.84 g · mol^{-1}, colorless plate, crystal size 0.16 x 0.07 x 0.04 mm, monoclinic, space group $P2_1n$, a = 10.5155(12) Å, b = 13.9952(16) Å, c = 15.8114(18) Å, β = 102.126(2)°, V = 2275.0(4) Å^3, Z = 4, D_{calc} = 1.859 g · cm^3, μ(*Mo-K*$_\alpha$) = 6.673 mm^{-1}, Gaussian absorption correction ($T_{min.}$= 0.98/$T_{max.}$= 0.98), 1.96 < θ < 35.25, 70140 measured reflections, 10183 independent reflections, 8708 reflections with $I > 2\sigma(I)$, R_1 = 0.034 [$I > 2\sigma(I)$], wR_2 = 0.092, 289 parameters, S = 1.036, residual electron density +4.1 / -2.5 e · Å^{-3}.

Selected X-ray crystallographic data for compound 13: C_{20} H_{24} O_4, M_r = 328.39 g · mol^{-1}, colorless plate, crystal size 0.22 x 0.08 x 0.06 mm, monoclinic, space group $P2_1$, a = 10.9252(5) Å, b = 5.8661(3) Å, c = 13.8471(6) Å, β = 96.464(2)°, V = 881.80(7) Å^3, Z = 2, D_{calc} = 1.237 g · cm^3, μ(*Mo-K*$_\alpha$) = 0.085 mm^{-1}, Gaussian absorption correction ($T_{min.}$= 0.98/$T_{max.}$= 1.00), 2.96 < θ < 33.20, 13256 measured reflections, 6558 independent reflections, 4924 reflections with $I > 2\sigma(I)$, R_1 = 0.063 [$I > 2\sigma(I)$], wR_2 = 0.157, 222 parameters, S = 1.030, absolute structure parameter 0.1(11), residual electron density +0.4 / -0.3 e · Å^{-3}.

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 774776 ([**2**·AuCl]), 743804 ([**5**·AuCl]), 743802 ([**6**·AuCl]) and 743803 (**13**). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1 EZ, UK (fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

Computational Studies

Density functional theory (DFT) calculations were carried out using Turbomole 5.91.[14] The BP86 functional[15,16] was employed in combination with the def-TZVP basis set.[17] The resolution-of-identity (RI) approximation was applied in conjunction with the appropriate auxiliary basis sets to speed up the calculations.[18,19,20] All geometries were fully optimized without symmetry constraints.

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