ANGEWANDTE CHEMIE
A Journal of the Gesellschaft Deutscher Chemiker

Supporting Information

for

Angew. Chem. Int. Ed. Z18810

69451 Weinheim, Germany

Supporting Information for *Angew. Chem.*

$Ir_4(CO)_{12}$-Catalyzed Coupling Reaction of Imidazoles with Aldehydes in the Presence of a Hydrosilane to Give 2-Substituted Imidazoles

Yoshiya Fukumoto, Katsutoshi Sawada, Motoyuki Hagihara, Naoto Chatani, and Shinji Murai*

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565-0871, Japan

General Information. ^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL JMN-270 spectrometer in $CDCl_3$ with tetramethylsilane as an internal standard. Data are recorded as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, sext = sextet, sept = septet, m = multiplet, c = complex), coupling constant (Hz), integration, and interpretation. Infrared spectra (IR) were obtained on a Hitachi IR-400 spectrometer; absorptions are reported in reciprocal centimeters. Mass spectra (MS) were obtained on a Shimadzu GCMS-QP 5000 with an ionization voltage of 70 eV. Elemental Analyses and high resolution mass spectra (HRMS) were performed by the Elemental Analyses Section of Osaka University. Analytical GC was carried out on a Shimadzu GC-14A gas chromatograph equipped with a Shimadzu Hicap CBP-10-M25-025 capillary column. Toluene was distilled over CaH_2. 1-Methylimidazole (**1**), aldehydes (**2**, **5**, **7**, **9**, and **15**), 2,2,2-trifluoroacetophenone (**17**), propyl isocyanate (**19**), and dimethyl acetylenedicarboxylate (DMAD) are commercially available and were purified by distillation before use. $Ir_4(CO)_{12}$ were purchased from Strem Chemicals, Inc. and used as received. Diethylmethylsilane[1] and aldehydes (**11**[2] and **13**[3]) were prepared according to the literature procedures.

General Procedure for $Ir_4(CO)_{12}$-catalyzed coupling of 1-imidazole with aldehydes and diethylmethylsilane. A 10 mL reaction flask equipped with a reflux condenser was flame-dried and then cooled to room temperature. In the flask were placed $Ir_4(CO)_{12}$ (22 mg, 0.02 mmol), 1-methylimidazole (82 mg, 1 mmol), aldehydes (1 mmol), diethylmethylsilane (204 mg, 2 mmol), DMAD (23 mg, 0.16 mmol), and toluene (5 mL). The reaction mixture was refluxed for 1-4 h. After cooling to room temperature, the volatiles were removed in vacuo. The product was isolated by bulb-to-bulb distillation under reduced pressure.

2-[1-(Diethylmethylsiloxy)hexyl]-1-methyl-1*H*-imidazole (3). ^{1}H NMR (270 Hz, $CDCl_3$; TMS): δ -0.05 (s, 3H; CH_3Si), 0.51 (q, ^3J(H,H) = 7.8 Hz, 4H; $SiCH_2$), 0.83 (t, ^3J(H,H) = 7.8 Hz, 3H; $SiCH_2CH_3$), 0.86 (t, ^3J(H,H) = 7.8 Hz, 6H; $SiCH_2CH_3$, CH_3), 1.27-1.50 (c, 6H; $CH_2CH_2CH_2$), 1.80 (m, 2H; $CHCH_2$), 3.74 (s, 3H; NCH_3), 4.88 (dd, ^3J(H,H) = 7.8, 6.2 Hz, 1H; CH), 6.75 (d, ^3J(H,H) = 1.1 Hz, 1H; =CH), 6.88 (d, ^3J(H,H) = 1.1 Hz, 1H; =CH). ^{13}C NMR (68 Hz, $CDCl_3$, TMS): δ -4.89 ($SiCH_3$), 6.22 ($SiCH_2$), 6.33 ($SiCH_2$), 6.51 ($SiCH_2CH_3$), 6.54 ($SiCH_2CH_3$), 13.95 (CH_3), 22.50 (CH_2), 25.52 (CH_2), 31.48 (CH_2), 33.25 (NCH_3), 36.89 (CH_2), 70.51 (CH), 121.64 (=CH), 126.72 (=CH), 148.97 (NCN). IR (neat): ύ = 2932, 1490, 1458, 1411, 1277, 1251, 1067, 1001, 968, 841, 750, 683 cm^{-1}. MS (70 eV): *m*/*z* (%): 282 (8) [M^+], 267 (10) [M^+-Me], 254

(25), 253 (100) [M^+- Et], 225 (11), 212 (13), 211 (47), 165 (15), 101 (14), 73 (11). elemental analysis (%) calcd for $C_{15}H_{30}N_2OSi$: C 63.78, H 10.70, N 9.92; found: C 63.53, H 10.96, N 10.19.

2-[1-(Diethylmethylsiloxy)-2-methylpropyl]-1-methyl-1*H*-imidazole (6). ^{1}H NMR (270 Hz, $CDCl_3$, TMS): δ -0.07 (s, 3H; CH_3Si), 0.46 (q, ^3J(H,H) = 7.8 Hz, 2H; $SiCH_2$), 0.50 (q, ^3J(H,H) = 7.8 Hz, 2H; $SiCH_2$), 0.69 (d, ^3J(H,H) = 6.6 Hz, 3H; CH_3), 0.81 (t, ^3J(H,H) = 7.8 Hz, 3H; $SiCH_2CH_3$), 0.86 (t, ^3J(H,H) = 7.8 Hz, 3H; $SiCH_2CH_3$), 1.06 (d, ^3J(H,H) = 6.6 Hz, 3H; CH_3), 2.05 (d of sept, ^3J(H,H) = 9.2, 6.6 Hz, 1H; CH), 3.73 (s, 3H; NCH_3), 4.45 (d, ^3J(H,H) = 9.2 Hz, 1H; OCH), 6.75 (d, ^3J(H,H) = 1.3 Hz, 1H; =CH), 6.88 (d, ^3J(H,H) = 1.3 Hz, 1H; =CH). ^{13}C NMR (68 Hz, $CDCl_3$, TMS): δ -5.03 ($SiCH_3$), 6.04 ($SiCH_2$), 6.22 ($SiCH_2$), 6.45 ($SiCH_2CH_3$), 6.53 ($SiCH_2CH_3$), 18.64 (CH_3), 19.82 (CH_3), 33.28 (CH), 34.45 (NCH_3), 76.53 (OCH), 121.53 (=CH), 126.81 (=CH), 148.34 (NCN). IR (neat): ύ = 2958, 2882, 1499, 1468, 1411, 1251, 1211, 1068, 1003, 960, 837, 794, 764, 683 cm^{-1}. MS (70 eV): *m*/*z* (%): 254 (3) [M^+], 239 (4) [M^+-Me], 225 (36) [M^+-Et], 212 (18), 211 (100) [M^+-*i*Pr], 183 (10), 139 (20), 137 (19), 101 (71), 95 (12), 73 (93), 61 (19), 55 (10). elemental analysis (%) calcd for $C_{13}H_{26}N_2OSi$: C 61.37, H 10.30, N 11.01; found: C 61.33, H 10.27, N 11.14.

2-[1-(Diethylmethylsiloxy)-2,2-dimethylpropyl]-1-methyl-1*H*-imidazole (8). ^{1}H NMR (270 Hz, $CDCl_3$, TMS): δ -0.07 (s, 3H; CH_3Si), 0.46 (q, ^3J(H,H) = 7.8 Hz, 2H; $SiCH_2$), 0.52 (q, ^3J(H,H) = 7.8 Hz, 2H; $SiCH_2$), 0.79 (t, ^3J(H,H) = 7.8 Hz, 3H; $SiCH_2CH_3$), 0.88 (t, ^3J(H,H) = 7.8 Hz, 3H; $SiCH_2CH_3$), 0.93 (s, 9H; CCH_3), 3.74 (s, 3H; NCH_3), 4.62 (s, 1H; OCH), 6.73 (s, 1H; =CH), 6.91 (s, 1H; =CH). ^{13}C NMR (68 Hz, $CDCl_3$, TMS): δ -5.12 ($SiCH_3$), 6.02 ($SiCH_2$), 6.26 ($SiCH_2$), 6.49 ($SiCH_2CH_3$), 6.63 ($SiCH_2CH_3$), 26.44 (CCH_3), 34.32 (NCH_3), 37.40 (CCH_3), 78.49 (OCH), 121.35 (=CH), 126.99 (=CH), 147.31 (NCN). IR (neat): ύ = 2958, 2880, 1486, 1408, 1393, 1362, 1275, 1252, 1074, 1004, 850, 796, 764, 738 cm^{-1}. MS (70 eV): *m*/*z* (%): 268 (2) [M^+], 253 (3) [M^+-Me], 239 (11) [M^+-Et], 212 (19), 211 (100) [M^+-*t*Bu], 139 (14), 101 (49), 95 (10), 73 (68). elemental analysis (%) calcd for $C_{12}H_{28}N_2OSi$: C 62.63, H 10.51, N 10.43; found: C 62.64, H 10.49, N 10.59.

2-[1-(Diethylmethylsiloxy)-3-phenylpropyl]-1-methyl-1*H*-imidazole (10). ^{1}H NMR (270 Hz, $CDCl_3$, TMS): δ -0.05 (s, 3H; CH_3Si), 0.48 (q, ^3J(H,H) = 7.8 Hz, 2H; $SiCH_2$), 0.52 (q, ^3J(H,H) = 7.8 Hz, 2H; $SiCH_2$), 0.84 (t, ^3J(H,H) = 7.8 Hz, 3H; $SiCH_2CH_3$), 0.88 (t, ^3J(H,H) = 7.8 Hz, 3H; $SiCH_2CH_3$), 2.15 (m, 2H; $PhCH_2$), 2.57 (m, 1H; CH_2CH), 2.78 (m, 1H; CH_2CH), 3.73 (s, 3H; NCH_3), 4.95 (t, ^3J(H,H) = 7.0 Hz, 1H; OCH), 6.76 (s, 1H; =CH), 6.91 (s, 1H; =CH), 7.16-7.29 (c, 5H; Ph). ^{13}C NMR (68 Hz, $CDCl_3$, TMS): δ -4.87 ($SiCH_3$), 6.22 ($SiCH_2$), 6.35 ($SiCH_2$), 6.53 ($SiCH_2CH_3$), 6.58 ($SiCH_2CH_3$), 32.17 ($PhCH_2$), 33.21 (NCH_3), 38.49 (CH_2CH), 69.88 (OCH), 121.76 (=CH), 125.80 (=CH), 126.92 (Ph), 128.30 (Ph), 128.34 (Ph), 141.55 (Ph), 148.50 (NCN). IR (neat): ύ = 3030, 2954, 2880, 1498, 1456, 1412, 1270, 1251, 1084, 1003, 967, 797, 746, 697 cm^{-1}. MS (70 eV): *m*/*z* (%): 316 (4) [M^+], 301 (6) [M^+-Me], 288 (24), 287 (76) [M^+-Et], 225 (12), 213 (13), 212 (71), 211 (31), 199 (20), 181 (10), 156 (10), 139 (15), 125 (10), 109 (56), 107 (15), 101 (47), 96 (11), 95 (22), 92 (10), 91 (100) [$C_7H_7^+$], 83 (14), 73 (92), 65 (18), 61 (27), 54 (14). elemental analysis (%) calcd for $C_{18}H_{28}N_2OSi$: C 68.31, H 8.92, N 8.85; found: C 68.27, H 8.91, N 9.10.

2-[1-(Diethylmethylsiloxy)-3-[1.3]dioxolan-2-ylpropyl]-1-methyl-1*H*-imidazole (12). ^{1}H NMR (270 Hz, $CDCl_3$, TMS): δ -0.06 (s, 3H; CH_3Si), 0.47 (q, ^3J(H,H) = 8.1 Hz, 2H; $SiCH_2$), 0.50 (q, ^3J(H,H) = 8.1 Hz, 2H; $SiCH_2$), 0.82 (t, ^3J(H,H) = 8.1 Hz, 3H; $SiCH_2CH_3$), 0.85 (t, ^3J(H,H) = 8.1 Hz, 3H; $SiCH_2CH_3$), 1.58 (m, 1H;

CHCH_2), 1.72-2.03 (c, 3H; CHCH_2, SiOCHCH_2), 2.78 (m, 1H; CH_2CH), 3.74 (s, 3H; NCH_3), 3.75-3.97 (c, 4H; OCH_2), 4.85 (t, ^3J(H,H) = 4.3 Hz, 1H; OCHO), 4.92 (dd, ^3J(H,H) = 8.1, 6.2 Hz, 1H; SiOCH), 6.74 (s, 1H; =CH), 6.86 (s, 1H; =CH). ^{13}C NMR (68 Hz, $CDCl_3$, TMS): δ -5.01 ($SiCH_3$), 6.06 ($SiCH_2$), 6.17 ($SiCH_2$), 6.40 ($SiCH_2CH_3$), 6.45 ($SiCH_2CH_3$), 30.05 (CHCH_2), 30.93 (SiOCHCH_2), 33.16 (NCH_3), 64.73 (OCH_2), 70.45 (SiOCH), 103.92 (OCH), 121.65 (=CH), 126.63 (=CH), 148.34 (NCN). IR (neat): ύ = 2956, 2882, 1499, 1455, 1278, 1252, 1137, 1091, 1062, 1004, 909, 799, 729 cm^{-1}. MS (70 eV): *m*/*z* (%): 312 (3) [M^+], 283 (6) [M^+-Et], 225 (10), 212 (41), 211 (30), 211 (31), 152 (11), 151 (100) [$C_8H_{11}N_2O^+$], 139 (14), 133 (22), 123 (34), 122 (10), 121 (13), 109 (35), 107 (13), 101 (36), 99 (12), 96 (28), 95 (13), 89 (43), 86 (18), 83 (13), 77 (13), 73 (96), 61 (51), 55 (21), 54 (10). elemental analysis (%) calcd for $C_{15}H_{28}N_2O_3Si$: C 57.66, H 9.03, N 8.97; found: C 57.48, H 9.05, N 8.72.

4-(Diethylmethylsiloxy)-4-(1-methyl-1*H*-imidazol-2-yl)butyric acid methyl Ester (14) ^{1}H NMR (270 Hz, $CDCl_3$, TMS): δ 0.05 (s, 3H; CH_3Si), 0.47 (q, ^3J(H,H) = 7.8 Hz, 2H; $SiCH_2$), 0.53 (q, ^3J(H,H) = 7.8 Hz, 2H; $SiCH_2$), 0.85 (t, ^3J(H,H) = 7.8 Hz, 6H; $SiCH_2CH_3$), 2.09-2.23 (m, 2H; CH_2), 2.30-2.46 (m, 2H; CH_2), 3.64 (s, 3H; NCH_3), 3.75 (s, 3H, OCH_3), 4.92 (dd, ^3J(H,H) = 8.1, 6.8 Hz, 1H; CH), 6.78 (s, 1H; =CH), 6.88 (s, 1H; =CH). ^{13}C NMR (68 Hz, $CDCl_3$, TMS): δ -5.01 ($SiCH_3$), 6.06 ($SiCH_2$), 6.17 ($SiCH_2$), 6.51 ($SiCH_2CH_3$), 30.37 (CHCH_2), 31.68 (SiOCHCH_2), 33.21 (NCH_3), 51.54 (OCH_3), 69.40 (SiOCH), 121.89 (=CH), 126.92 (=CH), 147.80 (NCN), 173.48 (C=O). IR (neat): ύ = 2914, 2880, 1736 (C=O), 1498, 1443, 1416, 1359, 1278, 1250, 1198, 1160, 1137, 1088, 1078, 1005, 882, 837, 800, 754 cm^{-1}. MS (70 eV): *m*/*z* (%): 298 (9) [M^+], 270 (11), 269 (57) [M^+-Et], 225 (52), 211 (22), 195 (10), 181 (20), 149 (57), 139 (16), 122 (13), 121 (100), 109 (14), 107 (19), 101 (40), 82 (11), 77 (23), 75 (18), 73 (73), 61 (36), 59 (11), 54 (11), 53 (11). HRMS calcd for $C_{14}H_{26}N_2O_3Si$ (M^+): 298.1712; found: 298.1696.

2-[(Diethylmethylsiloxy)-phenylmethyl]-1-methyl-1*H*-imidazole (16). ^{1}H NMR (270 Hz, $CDCl_3$, TMS): δ 0.04 (s, 3H; CH_3Si), 0.60 (q, *J* = 8.1 Hz, 2H; $SiCH_2$), 0.62 (q, *J* = 8.1 Hz, 2H; $SiCH_2$), 0.89 (t, *J* = 8.1 Hz, 3H; $SiCH_2CH_3$), 0.92 (t, *J* = 8.1 Hz, 3H; $SiCH_2CH_3$), 3.37 (s, 3H; NCH_3), 6.13 (s, 1H; CH), 6.74 (s, 1H, =CH), 6.94 (s, 1H, =CH), 7.23-7.37 (c, 5H; Ph). ^{13}C NMR (68 Hz, $CDCl_3$, TMS): δ -4.98 ($SiCH_3$), 6.18 ($SiCH_2$), 6.24 ($SiCH_2$), 6.54 ($SiCH_2CH_3$), 6.58 ($SiCH_2CH_3$), 33.12 (NCH_3), 70.89 (CH), 122.14 (=CH), 125.27 (Ph), 126.77 (=CH), 127.04 (Ph), 128.14 (Ph), 141.22 (Ph), 148.25 (NCN). IR (neat): ύ = 3064, 3028, 2956, 2880, 1497, 1454, 1413, 1253, 1186, 1129, 1084, 1059, 1004, 965, 840, 799, 767, 720, 692 cm^{-1}. MS (70 eV): *m*/*z* (%): 288 (10) [M^+], 260 (22), 259 (100) [M^+-Et], 172 (11), 171 (17), 170 (54), 169 (12), 155 (12), 153 (20), 130 (21), 125 (19), 115 (17), 109 (20), 106 (15), 103 (13), 77 (22), 73 (34), 61 (15). elemental analysis (%) calcd for $C_{16}H_{24}N_2OSi$: C 66.62, H 8.39, N 9.71; found: C 66.72, H 8.51, N 9.94.

2-[1-(Diethylmethylsiloxy)-2,2,2-trifluoro-1-phenylethyl]-1-methyl-1*H*-imidazole (18). ^{1}H NMR (270 Hz, $CDCl_3$, TMS): δ -0.10 (s, 3H; CH_3Si), 0.40-0.77 (c, 4H, $SiCH_2$), 0.91 (q, ^3J(H,H) = 8.0 Hz, 2H; $SiCH_2$), 0.96 (t, ^3J(H,H) = 8.0 Hz, 3H; $SiCH_2CH_3$), 3.09 (s, 3H; NCH_3), 6.82 (d, ^3J(H,H) = 1.1 Hz, 1H; =CH), 7.09 (d, ^3J(H,H) = 1.1 Hz, 1H; =CH). ^{13}C NMR (68 Hz, $CDCl_3$, TMS): δ -4.98 ($SiCH_3$), 6.18 ($SiCH_2$), 6.24 ($SiCH_2$), 6.54 ($SiCH_2CH_3$), 6.58 ($SiCH_2CH_3$), 33.12 (NCH_3), 70.89 (q, ^2J(F,C) = 28.0 Hz; COSi), 122.14 (=CH), 124.20 (q, ^1J(F,C) = 287.2 Hz; CF_3), 125.27 (Ph), 126.77 (=CH), 127.04 (Ph), 128.14 (Ph), 141.22 (Ph), 148.25 (NCN). IR (neat): ύ = 2964, 2938, 2912, 2882, 1488, 1453, 1409, 1284, 1270, 1186, 1166, 1112, 1075, 1013,

1000, 957, 947, 905, 853, 803, 753, 724 cm^{-1}. MS (70 eV): *m*/*z* (%): 356 (4) [M^+], 328 (22), 327 (100) [M^+-Et], 217 (16), 170 (23), 169 (11), 155 (15), 129 (25), 108 (25), 104 (20), 77 (26), 73 (21), 61 (15). HRMS calcd for $C_{17}H_{23}F_3N_2OSi$ (M^+): 356.1532; found: 356.1544.

Methyl-1*H*-imidazole-2-carboxylic acid propyl amide (20). ^1H NMR (270 Hz, $CDCl_3$, TMS): δ 0.96 (t, ^3J(H,H) = 7.3 Hz, 3H; CH_3), 1.59 (sext, ^3J(H,H) = 7.2 Hz, 2H; CH_2CH_3), 3.33 (t, ^3J(H,H) = 7.2 Hz, 2H; NCH_2), 4.05 (s, 3H; NCH_3), 3.75-3.97 (c, 4H; OCH_2), 4.85 (t, ^3J(H,H) = 4.3 Hz, 1H; OCHO), 4.92 (dd, ^3J(H,H) = 8.1, 6.2 Hz, 1H; SiOCH), 6.94 (s, 1H; =CH), 6.97 (s, 1H; =CH), 7.39 (bs, 1H; NH). ^{13}C NMR (68 Hz, $CDCl_3$, TMS): δ 11.40 (CH_3), 22.84 (CH_2CH_3), 40.65 (NCH_3), 125.30 (=CH), 127.40 (=CH), 139.17 (NCN), 159.23 (C=O). IR (neat): ύ = 3304, 3110, 2966, 2936, 2876, 1668, 1551, 1506, 1479, 1440, 1411, 1288, 1268, 1166, 1152, 1084, 927, 750, 693, 653, 620 cm^{-1}. MS (70 eV): *m*/*z* (%): 167 (5) [M^+], 138 (33) [M^+-Et], 110 (20), 109 (100) [M^+-C_3H_8N], 82 (32), 81 (14), 58 (12), 54 (21). elemental analysis (%) calcd for $C_8H_{13}N_3O$: C 57.47, H 7.84, N 25.13; found: C 57.31, H 7.75, N 25.04.

2-[1-(Diethylmethylsiloxy)hexyl]-1-methyl-1*H*-benzimidazole (22). ^1H NMR (270 Hz, $CDCl_3$; TMS): δ -0.01 (s, 3H; CH_3Si), 0.47-0.60 (c, 4H; $SiCH_2$), 0.80-0.91 (c, 6H; CH_3, $SiCH_2CH_3$), 1.28-1.30 (c, 4H; $CH_2CH_2CH_3$), 1.42-1.70 (c, 2H; $CHCH_2CH_2$), 1.80-1.92 (m, 2H; $CHCH_2$), 3.93 (s, 3H; NCH_3), 5.09 (dd, ^3J(H,H) = 7.8, 6.2 Hz, 1H; CH), 7.24-7.35 (c, 3H; Ar), 7.71-7.34 (c, 1H; Ar). ^{13}C NMR (68 Hz, $CDCl_3$, TMS): δ -4.78 ($SiCH_3$), 6.22 ($SiCH_2CH_3$), 6.29 ($SiCH_2$), 6.56 ($SiCH_2CH_3$), 13.95 (CH_3), 22.48 (CH_2), 25.47 (CH_2), 30.66 (CH_2), 31.45 (NCH_3), 37.09 (CH_2), 71.41 (CH), 108.95 (Ar), 119.68 (Ar), 121.80 (Ar), 122.34 (Ar), 136.57 (Ar), 142.05 (NCN), 155.36 (Ar). IR (neat): ύ = 3056, 2948, 2878, 1511, 1466, 1441, 1393, 1318, 1241, 1081, 1003, 962, 851, 797, 740 cm^{-1}. MS (70 eV): *m*/*z* (%): 332 (21) [M^+], 317 (11) [M^+-Me], 304 (30), 303 (100) [M^+- Et], 275 (22), 262 (24), 261 (14), 231 (14), 215 (10), 189 (23), 187 (16), 173 (16), 160 (16), 159 (63), 157 (17), 146 (29), 145 (16), 131 (12), 102 (14), 101 (37), 77 (13), 73 (95), 61 (30). elemental analysis (%) calcd for $C_{19}H_{32}N_2OSi$: C 68.62, H 9.70, N 8.42; found: C 68.60, H 9.85, N 8.44.

References

[1] O. W. Steward, O. R. Pierce, *J. Am. Chem. Soc.* **1961**, *83*, 1916-1921.

[2] F. Lucchesini, *Tetrahedron* **1992**, *48*, 9951-9966.

[3] P. M. Gannett, D. L. Nagel, P. J. Reilly, T. Lawson, J. Sharpe, B. Toth, *J. Org. Chem.* **1988**, *53*, 1064-1071.