

C-H bond activation and C—C bond formation in the reaction of 2,5-dimethylthiophene with Tp^{Me_2} compounds

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Compound 6b

Compound 4 (0.10 g, 0.15 mmol) was dissolved in cyclohexane (5 mL) and PMe_3 (0.38 mL, 1 M solution in THF, 0.38 mmol) was added. The solution was stirred for 3 h at 90 °C. After this period of time, the solvent was evaporated under reduced pressure, pentane (5 mL) was added, and the mixture stirred vigorously for a few minutes. The pale brown solid thus formed was separated by filtration and dissolved in Et_2O (10 mL). Cooling this solution to -20 °C yielded pure compound **6b** (0.09 g, 80%). ^1H NMR (C_6D_6 , 25 °C): δ 6.46 (s, 1 H, CH_{th}), 5.62, 5.59, 5.50 (s, 1 H each, 3 CH_{pz}), 3.81, 3.66 (dd, d, 1 H each, $^2J_{\text{AB}} = 15.8$, $^3J_{\text{HP}} = 5.0$ Hz, IrCH_2C_q), 2.95 (m, 2 H, IrCH_2CH_2), 2.94, 2.63 (m, 1 H each, IrCH_2CH_2), 2.44, 2.32, 2.30, 2.27, 2.08, 1.39, (s, 3 H each, 6 Me_{pz}), 2.18 (s, 3 H, Me_{th}), 1.20 (d, 9 H, $^2J_{\text{HP}} = 10.0$ Hz, PMe_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 25 °C): δ 149.5, 149.2, 148.9, 143.4, 143.1, 142.5 (d, s, s, s, s, d, $J_{\text{CP}} = 3$ and 2 Hz, C_{qpz}), 140.7, 139.4, 132.8 (C_{qth}), 127.9 (CH_{th}), 108.2, 108.1, 108.0 (d, s, s, $J_{\text{CP}} = 4$ Hz, CH_{pz}), 28.3 (IrCH_2CH_2), 17.4 (d, $^1J_{\text{CP}} = 36$ Hz, PMe_3), 16.2, 15.9, 12.3, 13.7, 13.4, 13.3, 13.0 (Me_{pz} and Me_{th}) -16.1, -16.2 (d, $^2J_{\text{CP}} = 8$, IrCH_2 , $^1J_{\text{CH}} = 126$ Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 25 °C): δ -52.2. Anal. Calcd for $\text{C}_{26}\text{H}_{41}\text{BN}_6\text{PSIr}$: C, 44.3; H, 5.8; N, 11.9. Found: C, 43.9; H, 5.9; N, 11.4.

Compound 6c

Compound **4** (0.10 g, 0.16 mmol) was dissolved in cyclohexane (15 mL) and transferred to a Fischer-Porter vessel. The solution was subjected to 3 atm of CO and heated at 100 °C for 3 h. The solvent was evaporated under vacuo and the pale brown residue washed with pentane and dried in vacuo. Compound **6c** was thus isolated in almost quantitative yield. IR (Nujol): $\nu(\text{CO})$ 2005 cm^{-1} . ^1H NMR (C_6D_6 , 25 °C): δ 6.51 (s, 1 H, CH_{th}), 5.50, 5.42, 5.38 (s, 1 H each, 3 CH_{pz}), 4.13, 3.50 (d, 1 H each, $^2J_{\text{AB}} = 15.5$ Hz, IrCH_2C_q), 3.30, 3.07, 2.93, 2.57 (m, 1 H each, IrCH_2CH_2), 2.39, 2.36, 2.30, 2.29, 2.07, 2.05, 1.99 (s, 3 H each, 6 Me_{pz} and Me_{th}). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 25 °C): δ 169.6 (CO), 151.1, 150.0, 149.5, 143.1, 142.9, 142.8 (C_{qpz}), 140.2, 138.7, 133.6 (C_{qth}), 128.2 (CH_{th}), 108.8, 107.1 (1:2, CH_{pz}), 31.5 (IrCH_2CH_2), 14.9, 14.1, 13.8, 13.7, 12.3, 12.1, 12.0 (Me_{pz} and Me_{th}), -4.2, -9.8 (IrCH_2). Anal. Calcd for $\text{C}_{24}\text{H}_{232}\text{BN}_6\text{OSIr}$: C, 43.9; H, 4.8; N, 12.8. Found: C, 44.5; H, 4.9; N, 12.7.

Compound 6d

Compound **4** (0.10 g, 0.16 mmol) was dissolved in cyclohexane (5 mL) and CNBu^t was added (1.60 mL of a solution 0.1 M in cyclohexane, 0.16 mmol). The solution was stirred for 3 h at 90 °C. After this period of time, the solvent was evaporated under reduced pressure, pentane (5 mL) added, and the mixture stirred vigorously for a few minutes. The white solid formed was separated by filtration, dissolved in Et_2O (5 mL), and the solution cooled to -20 °C, to yield compound **6d** (0.09 g, 80%). IR (Nujol): $\nu(\text{CN})$ 2126 cm^{-1} . ^1H NMR (C_6D_6 , 25 °C): δ 6.54 (s, 1 H, CH_{th}), 5.67, 5.58, 5.48 (s, 1 H each, 3 CH_{pz}), 3.97, 3.64 (d, 1 H each, $^2J_{\text{AB}} = 15.9$ Hz, IrCH_2C_q), 3.13, 2.90, 2.80, 2.75 (m, 1 H each, IrCH_2CH_2), 2.52, 2.50, 2.46, 2.33, 2.16, 2.14, 2.09 (s, 3 H each, 6 Me_{pz} and Me_{th}), 0.95 (s, 9 H, CMe_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 25 °C): δ 150.5, 149.5, 149.1, 142.5, 142.4, 142.3 (C_{qpz}), 141.2, 140.1, 132.4 (C_{qth}), 128.1 (CH_{th}), 108.4, 106.6, 106.6 (CH_{pz}), 56.0 (CMe_3), 31.6 (IrCH_2CH_2), 29.8 (CMe_3), 15.2, 14.5, 14.2, 14.0, 12.5, 12.3, 12.2 (Me_{pz} and Me_{th}), -9.6, -12.9 (IrCH_2). Anal. Calcd for $\text{C}_{28}\text{H}_{41}\text{BN}_7\text{SIr}\cdot 0.5\text{Et}_2\text{O}$: C, 48.1; H, 6.1; N, 13.1. Found: C, 48.3; H, 6.0; N, 13.0.

Reaction of compound 4 with thiophene

Compound 4 was heated in neat thiophene for 6 h, at 60 °C. ¹H NMR analysis of the crude of the reaction reveals formation of the known compound Tp^{Me2}Ir(2-SC₄H₃)₂(SC₄H₄) together with 2,5-dimethyl-3-ethylthiophene. Albeit not isolated, this product is characterized, among others, by a single resonance at 6.47 ppm, in the ¹H NMR spectrum.

Compound 7

Solid samples of compound 3 (0.02 g, 0.036 mmol) and the acid [H(OEt₂)₂][(3,5-(F₃C)₂C₆H₃)₄B] (0.037 g, 0.036 mmol) were mixed, degassed and dissolved into CH₂Cl₂ (8 mL) cooled at -70 °C, a brown solution being formed. After 10 min the mixture was slowly warmed to room temperature, and after 15 min stirring under these conditions, the solvent was evaporated in vacuo, petroleum ether was added (10 mL), and the suspension stirred vigorously. Compound 7 was isolated as a brown powder (0.05 g, 95%). IR (Nujol): ν(IrH) 2181 cm⁻¹. ¹H NMR (CDCl₃, 25 °C): δ 6.78, 6.63 (d, 2 H each, ³J_{HH} = 1.9 Hz, 4 CH_{th}), 6.01, 5.68 (s, 2:1, 3 CH_{pz}), 2.56, 1.03 (s, 6 H each, 4 Me_{th}), 2.49, 2.37, 2.33, 1.58 (s, 1:1:2:2, 6 Me_{pz}), -19.80 (s, 1 H, IrH). ¹³C{¹H} NMR (CDCl₃, 25 °C): δ 153.6, 153.1, 146.5, 146.3 (1:2:2:1, C_{qpz}), 143.9, 143.8 (C_{qth}), 130.7, 130.6 (CH_{th}), 108.6, 107.3 (1:2, CH_{pz}), 16.4 (Me_{th}), 14.1, 13.9, 13.5, 13.1, 12.6, 12.2 (1:2:2:2:1, Me_{pz} and Me_{th}). Anal. Calcd for C₅₉H₅₁B₂N₆F₂₄S₂Ir: C, 44.8; H, 3.2; N, 5.3. Found: C, 44.7; H, 3.3; N, 5.9.

Compound 8

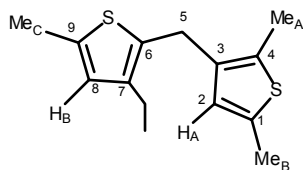
A mixture of solid samples of Tp^{Me2}Ir(H)(2-SC₄H₃)(NCMe) (0.02 g, 0.033 mmol) and the acid [H(OEt₂)₂][(3,5-(F₃C)₂C₆H₃)₄B] (0.033 g, 0.035 mmol) was dissolved in a mixture of Et₂O:MeOH (10 mL, 1:1) at -70 °C, a brown solution being formed. After 15 min at low temperature, the mixture was warmed to room temperature and stirred for 24 h. The solvent was then evaporated under vacuum, petroleum ether (10 mL) was added and the suspension was cooled again to -70 °C to provide compound 8 as a greenish solid (0.046 g, 95%). IR (Nujol): ν(IrH) 2169 cm⁻¹. ¹H NMR (CDCl₃, 25 °C): δ 7.44,

7.34 (d, 2 H each, $^3J_{\text{HH}} = 3.9$ Hz, 4 CH_{th}), 6.00, 5.90, 5.82 (s, 1 H each, 3 CH_{pz}), 2.63, 2.49, 2.42, 2.38, 2.27 (s, 2:1:1:1:1, 6 Me_{pz}), 2.01 (s, 3 H, NCMe), -19.63 (s, 1 H, IrH). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 25 °C): δ 153.1, 151.3, 150.6, 146.2, 145.6, 145.5 (C_{qpz}), 134.0, 132.0 (CH_{th}), 119.3 (NCMe), 107.7, 107.3, 107.1 (CH_{pz}), 14.7, 14.7, 13.4, 12.7, 12.5, 12.1 (Me_{pz}), 3.0 (NCMe). Anal. Calcd for $\text{C}_{53}\text{H}_{42}\text{B}_2\text{N}_7\text{F}_{24}\text{SIr}$: C, 43.0; H, 2.8; N, 6.6. Found: C, 43.4; H, 3.2; N, 6.2.

Compound 15

Compound **5** (0.017 g, 0.023 mmol) and the acid $[\text{H}(\text{OEt}_2)_2][(\text{3,5-(F}_3\text{C)}_2\text{C}_6\text{H}_3)_4\text{B}]$ (0.025 g, 0.023 mmol) were mixed and dissolved in acetonitrile (8 mL) cooled to -50 °C. After 10 min stirring the temperature was slowly raised to 25 °C and the solution stirred for 20 further minutes. The solvent was then evaporated under reduced pressure, petroleum ether added (10 mL) and the mixture stirred vigorously at -70 °C to yield a brown powder of compound **15** in almost quantitative yield. IR (Nujol): $\nu(\text{IrH})$ 2171 cm^{-1} . ^1H NMR (CDCl_3 , 25 °C): δ 6.74, 6.36 (s, 1 H each, 2 CH_{th}), 5.92, 5.81, 5.69 (s, 1 H each, 3 CH_{pz}), 4.13, 3.37 (d, 1 H each, $^2J_{\text{HH}} = 13$ Hz, CH_2), 2.50, 2.20 (m, 1 H each, CH_2Me), 2.44, 2.43, 2.35, 2.32, 2.20, 2.18, 1.53 (s, 1:1:2:3:1:1:1, 6 Me_{pz} , NCMe and 3 Me_{th}), 1.09 (t, 3 H, $^3J_{\text{HH}} = 7.6$ Hz, CH_2Me), -19.83 (s, 1 H, IrH). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 25 °C): δ 153.0, 151.3, 150.2, 146.0, 145.6, 145.4 (C_{qpz}), 145.7, 142.3, 138.3, 136.0, 134.0, 130.7 (C_{qth}), 132.8, 126.2 (CH_{th}), 119.1 (NCMe), 107.8, 107.0, 107.0 (CH_{pz}), 25.2 (CH_2Me), 22.8 (CH_2), 15.0, 14.7, 13.8, 13.5, 13.3, 13.0, 12.6, 12.5, 12.1 (Me_{pz} , Me_{th} and CH_2Me), 2.9 (NCMe). Anal. Calc for: $\text{C}_{63}\text{H}_{42}\text{B}_2\text{N}_7\text{F}_{24}\text{S}_2\text{Ir}$: C, 46.1; H, 2.6; N, 5.9. Found: C, 46.7; H, 3.1; N, 5.6.

Isolation of the dithienyl derivative



Compound **14** (0.05 g, 0.03 mmol) was dissolved in acetonitrile (10 mL) and the solution stirred for 48 h at 85 °C. After this period of time the solvent was evaporated under vacuo, petroleum ether added (15 mL) and the mixture stirred vigorously for 2 h, to separate a green solid. The solution obtained after filtration was concentrated and eluted through a column of silica gel (1:9 CH₂Cl₂:petroleum ether). The organic derivative was isolated as a colorless oil in almost quantitative yield. ¹H NMR (CDCl₃, 25 °C): δ 6.52 (s, 1 H, H_B), 6.44 (s, 1 H, H_A), 3.80 (s, 2 H, C⁵H₂), 2.53 (q, 2 H, ³J_{HMe} = 7.3 Hz, CH₂Me), 2.39, 2.37, 2.36 (s, 3 H each, Me_C, Me_B and Me_A resp.), 1.17 (t, 3 H, CH₂Me). ¹³C{¹H} NMR (CDCl₃, 25 °C): δ 138.9 (C⁷), 136.1 (C⁹), 135.7 (C¹), 135.2 (C⁴), 134.3 (C⁶), 130.7 (C³), 127.1 (C²), 126.5 (C⁸), 26.3 (C⁵), 21.5 (CH₂Me), 15.3 (Me_A), 15.2 (Me_B), 15.0 (CH₂Me), 12.9 (Me_C).