

Thiophene decorated with Fischer carbene ligands

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Supplimentary Data

Experimental procedure for compounds C, D and E.

[M{(C(OEt))₂-2,3-C₄H₂S}(CO)₄] (M = W (C), Cr (C')). In a typical experiment *n*-butyllithium (1.0 cm³, 1.6 mmol of a 1.6 M hexane solution) was added dropwise to a stirred solution of 3-bromothiophene (0.16 g, 1 mmol) in tetrahydrofuran (30.0 cm³) at -90°C. The colourless solution was stirred for 20 minutes whereafter it turned light yellow. Tungsten hexacarbonyl (0.35 g, 1 mmol) dissolved in THF (30 cm³) was added slowly to the reaction mixture, whereafter the reaction mixture turned red-brown after stirring for 1 h. LDA (a mixture consisting of *di*-*iso*-propylamine (0.154 cm³, 1.1 mmol) and BuLi (0.69 cm³, 1.1 mmol)) prepared in THF was added to the reaction mixture at -78°C and stirring continued for an additional hour. The colour of the solution turned dark brown. The solvent was removed under reduced pressure to leave a red-brown oily residue which was dissolved in cold (-30°C) dichloromethane and alkylated with a dichloromethane solution of triethyloxonium tetrafluoroborate (0.40 g, 2 mmol). The reaction mixture turned blue and was monitored for complete alkylation by thin layer chromatography. The solvent was removed and the components of the residue were separated by column chromatography on silica using hexane as eluent. The first (yellow) fraction to be collected gave [W(CO)₅{C(OEt)Bu}] (0.03 g, 7%). A second (red) fraction was collected and recrystallized from dichloromethane-hexane mixtures to give [W{C(OEt)C₄H₂S}(CO)₅] (0.15 g, 32%). A blue fraction was collected and purified by recrystallization from dichloromethane-hexane mixtures to give **C** (0.24 g, 48%). The analogous reaction with Cr(CO)₆ was done by following the same procedure.

Characterization of C. Blue crystals from dichloromethane-hexane mixtures, Found: C 34.43, H 2.63. C₁₄H₁₂O₆SW requires C 34.17, H 2.46 %. δ_H(400.21 MHz; CDCl₃) 7.60 (1H, d, *J* = 5.1, H5), 6.92 (1H, d, *J* = 5.3 Hz, H4), 4.76 (2H, q, *J* = 7.1, CH₂), 4.74 (2H, q, *J* = 7.1, CH₂), 1.61 (3H, t, *J* = 7.1, CH₃), 1.60 (3H, t, *J* = 7.1, CH₃). δ_C(100.63 MHz; C₆D₆) 313.9, 283.3 (C(carbene)), 201.1, 191.0 (WCO), 78.4, 78.6 (OCH₂), 14.9 (CH₃), 164.7 (C2), 147.5 (C3), 134.7 (C5), 117.7 (C4). IR (ν(CO), cm⁻¹): 2018 (s) A₁⁽¹⁾, 1948 (s) A₁⁽²⁾, 1959 (vs) B₁, 1896 (s) B₂.

Characterization of C' (Chromium analogue of C). Blue crystals from dichloromethane-hexane mixtures, Found: C 46.84, H 3.45. C₁₄H₁₂O₆SCr requires C 46.67, H 3.36 %. δ_H(400.21 MHz; CDCl₃) 8.83 (1H, d, *J* = 5.1, H5), 7.55 (1H, d, *J* = 5.3 Hz, H4), 4.77 (2H, q, *J* = 7.1, CH₂), 4.73 (2H, q, *J* = 7.1, CH₂), 1.64 (3H, t, *J* = 7.1, CH₃), 1.63 (3H, t, *J* = 7.1, CH₃). δ_C(100.63 MHz; CDCl₃) 312.3, 321.0 (C(carbene)), 227.2, 217.5 (CrCO), 76.6, 78.4 (OCH₂), 15.2 (CH₃), 167.3 (C2), 144.9 (C3), 134.6 (C5), 116.7 (C4). IR (ν(CO), cm⁻¹): 2018 (s) A₁⁽¹⁾, 1946 (s) A₁⁽²⁾, 1960 (vs) B₁, 1895 (s) B₂.

[{W(CO)₄(C(OEt))₂-2,3,4,5-C₄S} (D). 2.0 cm³ (3.2 mmol) of a 1.6 M hexane solution of *n*-butyllithium was added dropwise to a stirred solution of tetrabromothiophene (0.40 g, 1 mmol) in tetrahydrofuran (30.0 cm³) at -90°C. The colourless solution was stirred for 40 minutes

whereafter it turned light yellow. Tungsten hexacarbonyl (0.70 g, 2 mmol) dissolved in THF (100 cm³, -90°C) was added slowly to the reaction mixture, whereafter the reaction mixture turned red-brown. After stirring for 1h, BuLi (1.25 cm³, 2 mmol) was added and stirring continued for an additional hour. The colour of the solution turned dark brown. The solvent was removed under reduced pressure to leave a red-brown oily residue which was dissolved in cold (-30°C) dichloromethane and alkylated with a dichloromethane solution of triethyloxonium tetrafluoroborate (1.00 g, 5 mmol). The reaction mixture turned black and was monitored for complete alkylation by thin layer chromatography. The solvent was removed and the components of the residue were separated by column chromatography on silica using hexane as eluent. The first (yellow) fraction to be collected gave [W(CO)₅{C(OEt)Bu}] (0.03 g, 3.4%). A second (red) fraction was collected and represented a mixture of six monocarbene complexes (0.14 g, ca 10-15% of the total yield. Note: H/Br exchange had occurred on the thiophene ring and the complexes were identified by NMR spectroscopy). A blue fraction was collected and purified to give **C** (0.22 g, 22%). The eluent was changed to a 10:1 mixture of hexane:dichloromethane and a purple-black fraction was collected to give **D** (0.65 g, 36%). Unstable products of very low yields collected after **D** were discarded.

Characterization of D. Purple-black crystals from dichloromethane-hexane mixtures. Found: C 32.28, H 2.36. C₂₄H₂₀O₁₂SW₂ requires C 32.02, H 2.24 %. δ_H(400.21 MHz; CDCl₃) 4.90 (2H, q, *J* = 7.1, CH₂), 4.86 (2H, q, *J* = 7.1, CH₂), 1.59 (3H, t, *J* = 7.1, CH₃), 1.57 (3H, t, *J* = 7.1, CH₃). δ_C(100.63 MHz; C₆D₆) 283.7, 317.8 (C(carbene)), 212.4, 209.1, 195.1, 194.8 (WCO), 81.2, 79.9 (OCH₂), 14.8, 14.7 (CH₃), 165.4 (C2, C5), 158.3 (C3, C4). IR (ν(CO), cm⁻¹): 2018 (s) A₁⁽¹⁾, 1948 (s) A₁⁽²⁾, 1959 (vs) B₁, 1896 (s) B₂.

[Cr{C(OEt)C(NH₂)-2,3-C₄H₂S}(CO)₄] (E). In a typical experiment **C'** (0.36 g, 1 mmol) was dissolved in diethylether (30 cm³) and a slow stream of ammonia was bubbled through the solution. The conversion of **C'** was monitored by thin layer chromatography (eluent 1:1 mixture of dichloromethane-hexane). With only a little **C'** left, bubbling was stopped. The precursor blue compound was almost completely displaced by a second, much more polar, blue compound (duration 10-15 minutes). To remove excess ammonia, nitrogen (HP) was bubbled through the solution for 3 minutes, the solvent was concentrated and layered by an equal volume of hexane. This mixture was left to crystallize at 0°C to give **E** (0.30 g, 91%) as blue crystals.

Characterization of E. Blue crystals from dichloromethane-hexane mixtures. Found: C 43.71, H 2.82. C₁₂H₉O₅SNCr requires C 43.51, H 2.74 %. δ_H(400.21 MHz; CDCl₃) 8.45 (1H, br, NH₂), 8.09 (1H, br, NH₂) 7.54 (1H, d, *J* = 4.1, H5), 6.80 (1H, d, *J* = 4.0, H4), 4.74 (2H, q, *J* = 6.8, CH₂), 1.59 (3H, br, CH₃). δ_C(100.63 MHz; CDCl₃) 312.1, 320.8 (C(carbene)), 226.9, 218.5 (CrCO), 76.7, (OCH₂), 15.0 (CH₃), 168.0 (C2), 166.0 (C3), 134.4 (C5), 113.9 (C4). IR (ν(CO), cm⁻¹): 017 (s) A₁⁽¹⁾, 1934 (s) A₁⁽²⁾, 1958 (vs) B₁, 1894 (s) B₂.