Reaction of halfsandwich iridium polychalcogenide complexes with dimethyl acetylenedicarboxylate. Molecular structure of $Cp^*Ir[S_2C_2(COOMe)_2]$

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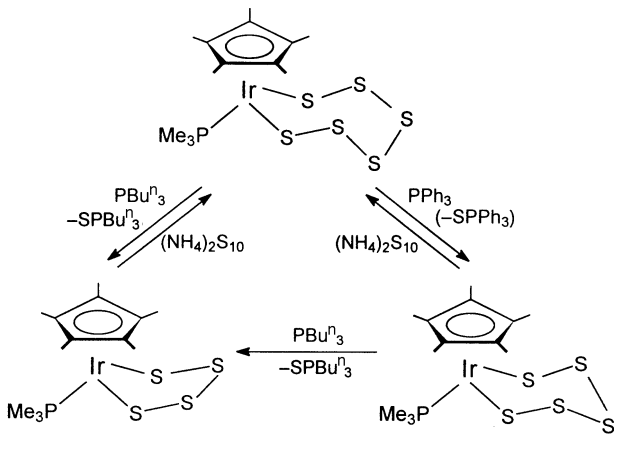
Letter

The pentamethylcyclopentadienyl iridium complexes $Cp^*Ir(PMe_3)(E_n)$ (E = S, n = 4, 5 or 6; E = Se, n = 2 or 4; E = Te, n = 2) react with dimethyl acetylenedicarboxylate to give $Cp^*Ir(PMe_3)[E_2C_2(COOMe)_2]$ compounds which tend to lose the trimethylphosphine ligand; the molecular structure of the dithiolene derivative, $Cp^*Ir[S_2C_2(COOMe)_2]$, has been determined.

The size of the chelating cyclo-oligosulfido ligand in pentamethylcyclopentadienyl iridium halfsandwich complexes, $Cp^*Ir(PMe_3)(S_n)$ (n = 4, 5 or 6), is variable.[1,2] Dechalcogenation of the sulfur-rich complex $Cp^*Ir(PMe_3)(S_6)$ with tertiary phosphines leads reversibly to the ring-shrink derivatives $Cp^*Ir(PMe_3)(S_5)$ and $Cp^*Ir(PMe_3)(S_4)$ (**1a**), which take up chalcogen from polysulfides $(NH_4)_2S_x$ ($x \approx 10$) to reform $Cp^*Ir(PMe_3)(S_6)$ (Scheme 1).[1] A similar equilibrium has been observed between $Cp^*Ir(PMe_3)(Se_4)$ (**1b**) and $Cp^*Ir(PMe_3)(Se_2)$; however, the ditelluride complex, $Cp^*Ir(PMe_3)(Te_2)$ (**1c**) did not take up additional tellurium.†



Scheme 1

In the presence of an excess of dimethyl acetylenedicarboxylate, DMAD, all available cyclooligochalcogenide complexes, $Cp^*Ir(PMe_3)(E_n)$ [E_n = S_6, S_5 or S_4 (**1a**); Se_4 (**1b**), Se_2; Te_2 (**1c**)] uniformly reacted to give ethene–dichalcogenolate derivatives, $Cp^*Ir(PMe_3)[E_2C_2(COOMe)_2]$ [E = S (**2a**), Se (**2b**) or Te (**2c**)], either in refluxing toluene or by adding PBu^n_3 as a potential chalcogen acceptor. Red crystals of **2a**–**2c** were isolated in good yields after column chromatography on silica.‡

The stable 18-electron complex **2a** lost the two-electron ligand PMe_3 to give **3a**§ by either sulfur-induced phosphine

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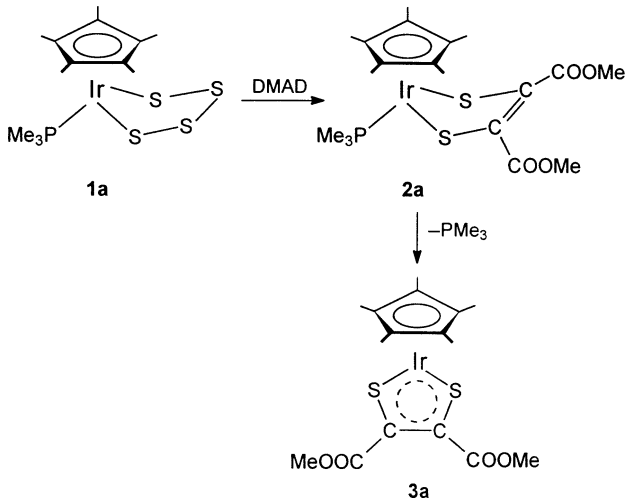
† Synthesis and spectral data of **1c**. A solution containing $Cp^*Ir(PMe_3)Cl_2$ (0.31 g, 0.65 mmol) and $(Bu^n_4N)_2Te_5$ (0.90 g, 0.80 mmol) in 20 ml DMF was kept at 60 °C for 2 h, then the solvent was removed *in vacuo*. The residue was purified by column chromatography (silica, elution with CH_2Cl_2). Crystallization from toluene–hexane (1:3) afforded 0.34 g (79%) black needles of **1c**. IR (CsI) $\nu_{P\text{-}CH3}$ = 950 cm^{-1}; EI-MS (70 eV): 660 (M^+, 52%), 584 ($M^+ - PMe_3$, 100%); ^1H NMR (300 MHz, $CDCl_3$): δ 1.97 (d, 15H, Cp*, J_{PH} = 1.7 Hz), 1.82 (d, 9H, PMe_3, J_{PH} = 10.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 11.0 ($C_5\underline{Me}_5$), 98.0 ($\underline{C}_5Me_5$), 20.7 (d, PMe_3, J_{PC} = 44.3 Hz); ^{31}P NMR (121 MHz, $CDCl_3$): δ − 43.1.

‡ Synthesis and characterization of **2a**–**c**: A solution containing 0.3 mmol of the polychalcogenide complex [*e.g.* $Cp^*Ir(PMe_3)(S_4)$ (**1a**)] and a twofold excess of DMAD in 60 ml of toluene was stirred at 60 °C for 3–5 h. Purification by column chromatography over silica (elution with CH_2Cl_2) and recrystallization from hexane–Et_2O (3:1) at −78 °C gave the bis(carbomethoxy)dithiolate complex [*e.g.* $Cp^*Ir(PMe_3)[S_2C_2(COOMe)_2]$ (**2a**)] in 70–80% yield. **2a** (Red crystals, yield 80%), IR (CsI): ν_{CO} = 1714 and 1681 cm^{-1}, $\nu_{P\text{-}CH_3}$ = 964 cm^{-1}; EI-MS (70 eV): m/z 534 ($M^+ - PMe_3$, 100%), 503 ($M^+ - PMe_3 - OMe$, 35%); ^1H NMR ($CDCl_3$): δ 1.76 (d, 15H, Cp*, $J_{(P,H)}$ = 2.0 Hz), 1.59 (d, 9H, PMe_3, $J_{(P,H)}$ = 10.8 Hz), 3.72 (s, 6H, OMe); ^{13}C NMR ($CDCl_3$): δ 8.6 ($C_5\underline{Me}_5$): 96.4 ($\underline{C}_5Me_5$); 14.3 (d, PMe_3, $J_{(P,C)}$ = 41.2 Hz), 52.5 (OMe); ^{31}P NMR ($CDCl_3$): −33.0. **2b** (Red crystals, yield 83%), IR (CsI): ν_{CO} 1713 and 1685 cm^{-1}, $\nu_{P\text{-}CH3}$ = 962 cm^{-1}; EI-MS (70 eV): m/z 704 (M^+, 3%) 628 ($M^+ - PMe_3$, 10%), 485 ($Cp^*IrSe_3^+$, 78%), 156 ($SePMe_3^+$, 100%); FD-MS: m/z 704 (M^+); ^1H NMR ($CDCl_3$): δ 1.77 (d, 15H, Cp*, $J_{(P,H)}$ = 2.0 Hz), 1.68 (d, 9H, PMe_3, $J_{(P,H)}$ = 11.3 Hz), 3.79 (s, 6H, OMe); ^{13}C NMR ($CDCl_3$): δ 9.3 ($C_5\underline{Me}_5$), 96.1 ($\underline{C}_5Me_5$); 16.6 (d, PMe_3, $J_{(P,C)}$ = 34.9 Hz), 52.4 (OMe), 144.1 (C_2), 183.3 ($\underline{C}O_2Me$); ^{31}P NMR ($CDCl_3$): δ −32.2. **2c** (Dark-red crystals, yield 73%), IR (CsI): ν_{CO} = 1708 and 1692 (sh) cm^{-1}, $\nu_{P\text{-}CH3}$ = 953 cm^{-1}; EI-MS (70 eV): m/z 802 (M^+, 30%) 726 ($M^+ - PMe_3$, 18%), 584 ($Cp^*IrTe_2^+$, 100%); ^1H NMR ($CDCl_3$): δ 1.88 (d, 15H, Cp*, $J_{(P,H)}$ = 2.0 Hz), 1.74 (d, 9H PMe_3, $J_{(P,H)}$ = 10.0 Hz), 3.66 (s, 6H, OMe); ^{13}C NMR ($CDCl_3$): δ 10.2 ($C_5\underline{Me}_5$), 112.3 ($\underline{C}_5Me_5$), 19.1 (d, PMe_3, $J_{(P,C)}$ = 45.9 Hz), 52.3 (OMe); ^{31}P NMR ($CDCl_3$): δ −42.4.

§ Characterization of **3a** (dark-red prismatic crystals). IR (CsI): ν_{CO} = 1730 and 1689 cm^{-1}; EI-MS (70 eV): m/z 534 (M^+, 100%), 503 ($M^+ - OMe$, 19%), 502 (21%), 414 ($Cp^*IrS_2^+$, 14%); ^1H NMR ($CDCl_3$): δ 1.84 (s 15H, Cp*), 3.76 (s 6H, OMe): ^{13}NMR ($CDCl_3$): δ 8.9 ($C_5\underline{Me}_5$), 93.4 ($\underline{C}_5Me_5$); 52.2 (OMe).

abstraction or prolonged thermolysis in refluxing toluene (Scheme 2). The phosphine-free iridium–diselenolene and –ditellurolene analogues, $Cp^*Ir[E_2C_2(COOMe)_2]$ [M = Se (**3b**) or Te (**3c**)], were obtained similarly, although not free of side-products; the EI-MS spectra contained the molecular ions of **3b** and **3c**, respectively, as the peaks of highest mass. Cyclopentadienyl metal ethene–dithiolate complexes of the lighter Group 9 homologues, $CpM[S_2C_2(COOMe)_2]$ (M = Co[3], Rh[4,5]) have been synthesized earlier by a one-pot reaction of the cycloocta-1,5-diene precursors, $CpM(C_8H_{12})$, with DMAD and elemental sulfur.



Scheme 2

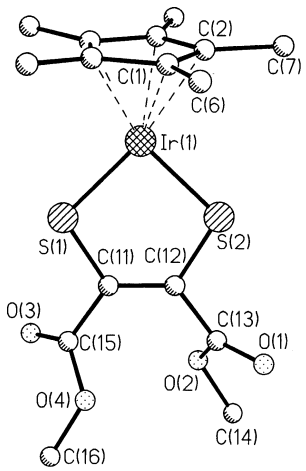


Fig. 1 Molecular geometry of **3a** in the crystal. Selected bond lengths (pm) and angles (°): Ir(1)—S(1) 223.27(18), Ir(1)—S(2) 223.42(15), Ir(1)—Cp*(center) 181.9, S(1)—C(11) 173.6(6), S(2)—C(12) 174.4(5), C(11)—C(12) 134.1(7), S(1)—Ir—S(2) 87.70(5), Ir(1)—S(1)—C(11) 105.9(2), Ir(1)—S(2)—C(12) 105.91(19)

The molecular structure of $Cp^*Ir[S_2C_2(COOMe)_2]$ (**3a**)¶ combines two essentially planar five-membered rings, Cp* and IrS_2C_2, which are arranged perpendicular to each other (dihedral angle 87.7°). The Ir—S bond lengths (223.35 pm av. in **3a**) are significantly shorter than in the 18-electron oligosulfido precursor complexes $Cp^*Ir(PMe_3)(S_n)$ [$n = 6$, 235.8(2) and 234.5(3) pm;[1] $n = 4$ (**2a**),[2] 237.6(2) and 237.2(2) pm], and in $Cp^*Ir(PMe_3)(SH)_2$ [6] [238.0(2) and 237.0(2) pm], but comparable with the corresponding Ir—S bond distances in the benzene-1,2-dithiolate $Cp^*Ir[S_2C_6H_4]$ [225.3(4) and 224.4(4) pm][7] and in the iridathiabenzene complex $Cp^*Ir[SC_4H_2Me_2]$ [220.3(2) pm].[8] This indicates that the metal in **3a** is integrated into a "pseudo-aromatic" dithiolene ring involving considerable Ir—S multiple bonding, probably as a result of sulfur-to-metal electron transfer (as discussed for benzene-1,2-dithiolate complexes[7,9,10]). The intra-annular S—C and C—C distances in **3a** are observed in the range expected for complexes containing ethene-1,2-dithiolate ligands. Intermolecular bonding interactions are absent.

¶ Crystal structure of **3a**: dark red block, 0.20 × 0.40 × 0.60 mm, monoclinic, space group $P2_1/n$; $a = 11.849(2)$, $b = 11.491(2)$, $c = 15.100(3)$ Å, $\beta = 111.86(3)°$, $U = 1908.1(6)$ Å^3, $Z = 4$, $D_c = 1.858$ g cm^{-3}, $F(000) = 1032$. Siemens P4 diffractometer Mo-Kα radiation ($\lambda = 0.71073$ Å), 293(2) K, 2θ range 4.0–52.0°, index ranges $0 \leqslant h \leqslant 14$, $0 \leqslant k \leqslant 14$, $-18 \leqslant l \leqslant 17$; 4149 reflections collected, 3754 independent ($R_{int} = 0.0306$), 3072 observed [$F^2 > 2.06(F^2)$], 209 refined parameters. Siemens, SHELX97 direct methods, (SHELXS97). Final R indices (observed data), $R1 = 0.0292$, $wR2 = 0.0637$, goodness-of-fit 1.161; max./min. residual electron density 0.80/−0.83 e Å^{-3}. CCDC reference number 440/057.

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