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A TETRAIRIDIUM CLUSTER WITH A BRIDGING SO_2: THE SYNTHESIS, FLUXIONAL BEHAVIOUR, AND CRYSTAL STRUCTURE OF $Ir_4(CO)_9(\mu_2\text{-}CO)_2(\mu_2\text{-}SO_2)$

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Summary

The reaction of SO_2 with $Ir_4(CO)_{11}$(norborn-2-ene) yields $Ir_4(CO)_9(\mu_2\text{-}CO)_2(\mu_2\text{-}SO_2)$ (i). X-ray diffraction shows that I contains a sulphur dioxide ligand and two CO groups, all three bridging between two basal metal atoms. The lowest-energy CO scrambling process for I has been determined by ^{13}C NMR studies. The thermal stability and high solubility of I (compared to $Ir_4(CO)_{12}$) make it a good starting material for the synthesis of other tetrairidium clusters.

Although the coordination chemistry of SO_2 has been extensively studied [1], only a few cluster compounds containing this ligand have been reported [2—4]. In such carbonyl clusters the SO_2 acts as a bridging rather than a terminal two-electron ligand. In the bridged arrangement SO_2 seems to withdraw more negative charge than CO from the clusters, causing considerable lengthening [5] and, in one case [4], scission of the bridged M—M bond (M = Rh).

Pursuing our interest in the relative reactivities of substituted and unsubstituted iridium carbonyl clusters, we describe here the first example of an iridium cluster containing SO_2. When SO_2 is bubbled through a solution of $Ir_4(CO)_{11}$(norborn-2-ene) [6] in isopentane/dimethyl ether (2:1) at −30°C for 15 min, subsequent evaporation of excess SO_2 and dimethyl ether (at −30 to +20°C) gives a precipitate of an air-stable yellow microcrystalline solid (> 85% yield) analysing as $Ir_4(CO)_{11}(SO_2)$ (I). IR and low-temperature ^{13}C NMR data are consistent with the presence of bridging CO and SO_2 ligands: ν(CO), CH_2Cl_2, 2118vw, 2084 vs, 2070sh, 2053vs, 2029m, 1908s, 1866vs cm^{-1} ; $\nu(SO_2)$, Nujol, 1265s, 1096vs cm^{-1}. ^{13}C NMR (90.55 MHz, 190 K, CD_2Cl_2), δ_C 190.6, 169.3, 165.7, 155.6, 155.3, 151.6, 149.3 ppm; ratios 2/1/2/1/2/2/1. The assignments in Fig. 2 follow those reported for $Rh_4(CO)_9(\mu\text{-}CO)_3$ [7] and for $Ir_4(CO)_8(\mu\text{-}CO)_3(PR_3)$ [8] [9].

The structure of I has been established by single crystal X-ray diffraction. Crystal data for $Ir_4(CO)_{11}(SO_2)$ (I): Single crystals obtained by recrystallization from CH_2Cl_2/hexane, m.p. 120—145°C (dec.); $C_{11}Ir_4O_{13}S$; $M = 1140.97$, orthorhombic space group $Pna2_1$, no. 33, a 17.773(1), b 9.238(3), c 12.152(3) Å, U 1995.2 $Å^3$, D_c 3.8 g cm^{-3}, $F(000) = 1920$, $Z = 4$, Mo-K_α radiation, λ 0.71069 Å, μ(Mo-K_α) 258.5 cm^{-1}. Intensity measurements: CAD 4 diffractometer, 4186 reflections collected by the $\omega/2\theta$ method in the range $2.5 < \theta < 27°$, scan angle 0.7°, 1478 independent reflections. Final R value (0.035 (R_w = 0.027) for 1415 reflections with $F_o > 5\sigma(F_o)$) corrected for absorption. The crystal was disordered with two molecular orientations related by an idealized two-fold axis passing through Ir(1) and the center of the opposite triangular face of the tetrahedron (a similar disorder has been observed in crystals of $Co_4(CO)_{12}$ [10]). Joint refinement of the occupancy factors for the two orientations of the molecule converged to 0.66 and 0.34, respectively*. The molecular symmetry (Fig. 1) is C_s and the mirror plane passes through the SO_2 ligand and the two opposite Ir atoms. The SO_2 ligand bridges symmetrically through the S atom across an Ir—Ir edge, and two CO groups

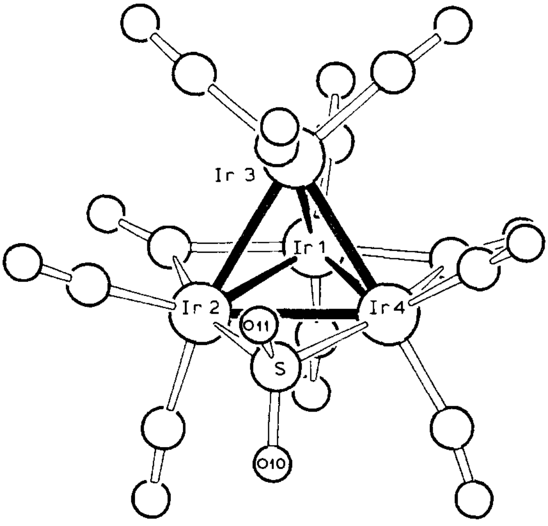

Fig. 1. The molecular structure of $Ir_4(CO)_9(\mu_2\text{-}CO)_2(\mu_2\text{-}SO_2)$ (I). The Ir—Ir bond lengths (Å) are: 1—2 2.729, 1—3 2.683, 1—4 2.733, 2—3 2.707, 2—4 2.765, 3—4 2.692; maximum e.s.d.'s are 0.003. Other important bond lengths (Å) are: mean Ir—S 2.34(1), S—O 1.43(2), Ir—C 2.11(2) (bridge), 1.93 (terminal).

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*The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

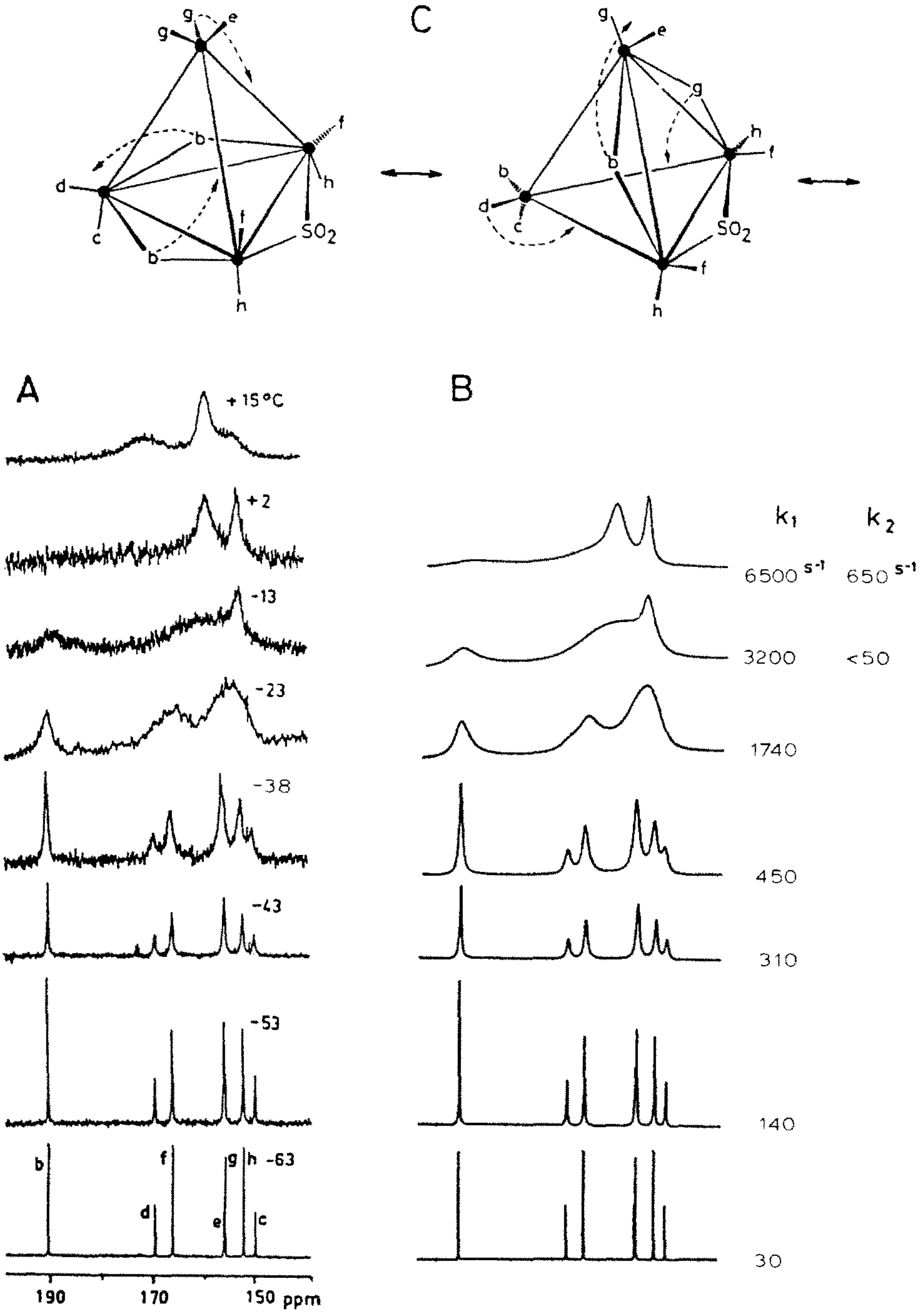

Fig. 2. Variable temperature ^{13}C NMR spectra of I in CD_2Cl_2 (A experimental, B calculated), and proposed mechanism for the lowest-energy carbonyl scrambling process (C).

bridge the remaining edges of the basal face. The S atom is almost coplanar with the cluster base and the O—S—O angle is, as expected, smaller (114.1(2)) than that in free SO_2 (119.0 (5)°). The main effect of coordination of SO_2 to the tetrahedral cluster seems to be a shortening of the opposite Ir(1)—Ir(3) bond (with respect to $Ir_4(CO)_{12}$) [11].

Cluster I is fluxional in solution on the ^{13}C NMR time scale (Fig. 2, A), all CO's becoming equivalent above ca. 50°C. The mechanism of the lowest-energy carbonyl scrambling was investigated at —60°C using selective 180° pulses generated by the DANTE pulse sequence [9] [12]. A selective 180° pulse was first applied to the carbonyls labelled b at δ 190.6 ppm, then an observing 90° pulse was applied at time τ ranging from 0.01 to 0.6 s. Under these conditions the recovery of the signal assigned to b was found to be due principally to chemical exchange bringing unperturbed nuclei from sites d at δ 169.3 and g at δ 155.3 ppm into site b. This exchange occurred with maximum transfer after ca. 0.3 s, and the inverted magnetization was apparently not transferred to other carbonyls at $\tau > 0.3$ s, Additional information was obtained from the ^{13}C NMR spectra above —63°C. At 2°C two peaks, at δ 158 and 153 ppm, were found at the arithmetic means of the signals of carbonyls f and h, and e and c, respectively. Thus, the lowest-energy scrambling process involving b, d and g must involve interconversion of f and h, and of c and e. Furthermore, a higher-energy scrambling process evidently becomes operative above ca. —20°C and has to be taken into account in calculating the rate constant for low temperature process. A first exchange matrix (related to rate constant k_1) was constructed for exchanges b $\leftrightarrow$ d $\leftrightarrow$ g, f $\leftrightarrow$ h and c $\leftrightarrow$ e, and a second matrix (related to k_2) was constructed by assuming local apical exchanges g $\leftrightarrow$ e $\leftrightarrow$ h. The program used was EXCHIT [13]. The good fit between the experimental and calculated spectra confirms the interpretation of the DANTE experiments and the assumption that the SO_2 bridge remains fixed during CO exchange. The proposed concerted mechanism for the lowest-energy CO scrambling process is shown in Fig. 2,C.

As a starting material for the synthesis of other tetrairidium clusters the thermal stability of I (no decomposition took place when the solid was left in air for 6 months or when a solution in CH_2Cl_2 was kept under SO_2) makes it superior to $Ir_4(CO)_{11}$(norborn-2-ene). Relative to $Ir_4(CO)_{12}$ its higher solubility in polar organic solvents (20 and 60 g/l at 25°C in CH_3OH and CH_2Cl_2, respectively) is advantageous. Moreover, the SO_2 is easily replaced by various ligands (in contrast to the bridging CO's) giving $Ir_4(CO)_{11}L$ (L = PPh_3, $AsPh_3$ [14] or CO) or $Ir_4(CO)_{10}L$ (L = $Ph_2PCH_2CH_2PPh_2$ [14] or diolefins) [6]. The SO_2 ligand undergoes selective nucleophilic attack by CH_3O^- in methanol giving, after addition of an aqueous solution of $[(Ph_3P)_2N]Cl$, the new cluster $(Ph_3P)_2N[Ir_4(CO)_8(\mu_2\text{-}CO)_3(SO_2OCH_3)]$ (II); the IR and ^1H NMR data for this cluster are consistent with the presence of a methoxysulfonyl moiety S-bonded to a basal Ir atom in the axial position: ν(CO), Nujol, 2087w, 2058sh, 2051vs, 2025s, 2009vs, 1994w, 1985s, 1884w, 1829s cm^{-1}; ν_{as}(S=O) 1227s, ν_s(S=O) 1090s, ν(S—O) 975s, δ(O—S—O) 672s cm^{-1}. ^1H NMR (80 MHz, 300 K, $CDCl_3$), δ(H) 7.70—7.30 (m, 30 H), 3.45 ppm (s, 3 H). For comparison, see data of $[Ir_4(CO)_8(\mu\text{-}CO)_3(COOCH_3)]^-$ [15] and of Pt^{II}- and Pd^{II}-SO_2OCH_3 derivatives [16]. The reaction of I with H_2 and with various carbanions is under study.

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