Journal of Organometallic Chemistry, 249 (1983) C35—C37
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF THE $[Fe_3(CO)_9(\mu_3\text{-}O)]^{2-}$ DIANION: A MODEL COMPOUND FOR AN ADSORBED OXYGEN ATOM

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(Received March 21st, 1983)

Summary

The reaction of $[Fe_3(CO)_{11}]^{2-}$ with oxygen gives an almost quantitative yield of the new red-orange $[Fe_3(CO)_9(\mu_3\text{-}O)]^{2-}$ dianion, which has been isolated in a crystalline state as the trimethylbenzylammonium salt and characterized by an X-ray study. This new cluster may be regarded as model for an oxygen atom adsorbed on a metal surface.

The chemistry of metal carbonyl clusters containing exposed or semi-exposed main group elements such as carbon or nitrogen, as well as small polyatomic fragments derived from them, has received increasing interest in recent years [1—4]; largely as a consequence of the belief that such molecular clusters may provide the most reliable model for the interaction and chemical behaviour of corresponding species adsorbed on a metal surface [5].

Although a low-valent metal cluster* containing an exposed oxygen atom, $Co_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}CO)(\mu_3\text{-}O)$, was isolated and structurally characterized several years ago [7], to our knowledge only two other examples of this kind of clusters have been reported, viz. $[Re_3(CO)_9(\mu_2\text{-}H)_3(\mu_3\text{-}O)]^{2-}$ [8] and the raft-like $Os_6(CO)_{15}(\mu_3\text{-}O)[P(OCH_3)_3]_4$ [9]. We report here the synthesis and structural characterization of an other member of this class of compound, the $[Fe_3(CO)_9(\mu_3\text{-}O)]^{2-}$ dianion, which, in contrast to those mentioned above is readily and quantitatively available.

The $[Fe_3(CO)_9(\mu_3\text{-}O)]^{2-}$ dianion was initially obtained by short exposure to

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*High-valent metal cluster oxides or polynuclear compounds are common [6].

0022-328X/83/$03.00

air of solutions of the red-violet $[Fe_3(CO)_{11}]^-$ radical anion [10] during an attempt to isolate the latter in a crystalline state. Later we found that the dianion was more readily and conveniently produced by exposure to air of solutions of the parent $[Fe_3(CO)_{11}]^{2-}$ dianion, according to reaction 1. IR monitoring of the reaction showed formation of trace amounts $Fe(CO)_5$ and $[Fe_3(CO)_{11}H]^-$ as the

$$[Fe_3(CO)_{11}]^{2-} + O_2 \rightarrow [Fe_3(CO)_9(\mu_3\text{-}O)]^{2-} + CO_2 + CO \qquad (1)$$

only by-products. Concomitant formation of CO_2 was confirmed by GLC analysis of the gas phase when using carbon dioxide-free air. The resulting red-orange $[Fe_3(CO)_9(\mu_3\text{-}O)]^{2-}$ dianion (ν(CO) in THF at 2000w, 1935s, 1905m, 1875mw cm^{-1}) was isolated in the solid state as trimethylbenzylammonium salt in ca. 90% yield, and crystallized from tetrahydrofuran/cyclohexane by slow diffusion. (Calcd.: $[N(CH_3)_3CH_2Ph]^+$, 40.78; Fe, 22.78; CO, 34.26%; $[N(CH_3)_3CH_2Ph]^+/Fe$ = 1/1.5. Found: $[N(CH_3)_3CH_2Ph]^+$, 40.1; Fe, 22.7; $[N(CH_3)_3CH_2Ph]^+/Fe$ = 1/1.52.)

The correct stoichiometry and crystal structure were established by a single crystal X-ray study.

Crystal data: $C_{29}H_{32}Fe_3N_2O_{10}$, M = 736.13, monoclinic, space group $P2_1/n$, a 11.819(1), b 11.402(3), c 24.271(3) Å, β 93.94(2)°, V 3263 Å^3, D_c 1.498 g cm^{-3} for Z = 4, μ(Mo-K_α) 13.7 cm^{-1}.

Intensity data were collected on an Enraf—Nonius CAD-4 diffractometer with graphite monochromated Mo-K_α radiation (λ 0.71073 Å) in the θ range 3—25°. The structure was solved by conventional Patterson and Fourier methods and the

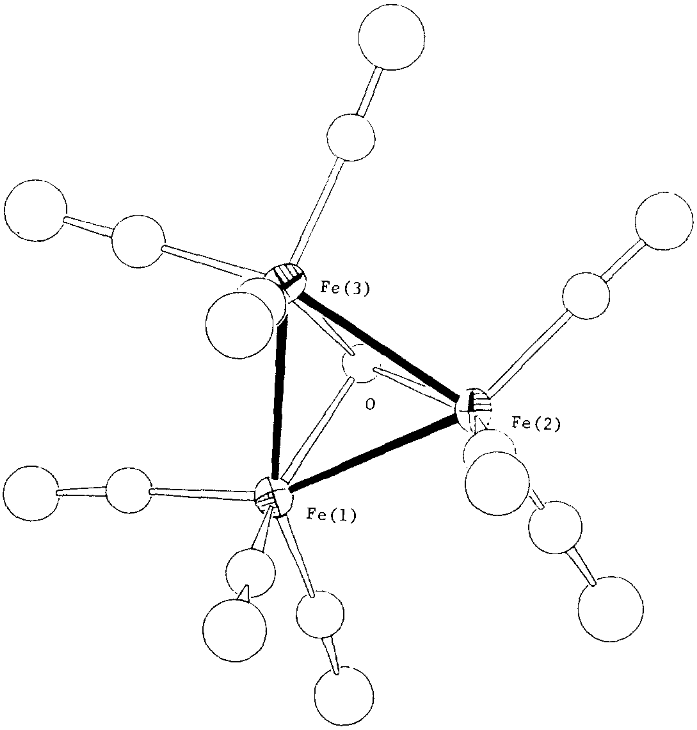

Fig. 1. Structure of $[Fe_3(CO)_9(\mu_3\text{-}O)]^{2-}$. Bond lengths (Å): Fe(1)—Fe(2) 2.480(1), Fe(1)—Fe(3) 2.492(1), Fe(2)—Fe(3) 2.480(1), Fe(1)—O 1.895(3), Fe(2)—O 1.891(3), Fe(3)—O 1.890(3); Fe—C_{av} 1.771, C—O_{av} 1.152.

refinement carried out by full-matrix least-squares using 1798 independent absorption-corrected reflections having $I \geqslant 3\sigma(I)$, led to current R and R_W values of 0.041 and 0.051, respectively. Typical e.s.d.'s on single distances are: Fe—Fe 0.001, Fe—C 0.007, Fe—O 0.003, C—O 0.007 Å.

The structure derives from the packing of $[N(CH_3)_3CH_2Ph]^+$ cations and $[Fe_3(CO)_9(\mu_3\text{-}O)]^{2-}$ dianions; a perspective view of the latter is given in Fig. 1, the legend to which presents the most significant molecular parameters.

The cluster of idealized C_{3v} symmetry is made up of an almost perfectly equilateral triangle of iron atoms. Each iron atom is bonded to three terminal carbonyl ligands. A unique oxygen atom sits on the top of the Fe_3 triangle and shows essentially equivalent interatomic separations from the three iron atoms (see Figure caption). Through the contribution of four valence electrons from the triply-bridging oxygen atom the dianion achieves a closed shell configuration.

The average Fe—Fe bond distance (2.484 Å) is shorter than in the parent $[Fe_3(CO)_{11}]^{2-}$ dianion (2.596 Å) [11], whereas it is comparable with the nitrogen-bridged Fe—Fe bond distances in $Fe_3(CO)_9(\mu_3\text{-}NR)_2$ (2.462 Å) [12]. This feature is in keeping with previous finding that M—M interactions in ligand-bridged clusters are mainly affected by the size and effective electronegativity of the bridging atom [13,14].

The calculated covalent radius of the oxygen atom in $[Fe_3(CO)_9(\mu_3\text{-}O)]^{2-}$ (0.65 Å) is close to that in $[Re_3(CO)_9(\mu_2\text{-}H)_3(\mu_3\text{-}O)]^{2-}$ [8] (0.64 Å).

The residual nucleophilicity of the oxygen atom of $[Fe_3(CO)_9(\mu_3\text{-}O)]^{2-}$ is shown by the ready reaction with acids and alkyl halides (eq. 2). The resulting red-orange hydroxy- and alkoxy-derivatives have infrared spectra identical in

$$[Fe_3(CO)_9(\mu_3\text{-}O)]^{2-} + R^+ \rightleftarrows [Fe_3(CO)_9(\mu_3\text{-}OR)]^- \qquad (2)$$

$$(R = H, CH_3, CH_2CH{=}CH_2)$$

pattern to that of the parent dianion, but shifted ca. 30 cm^{-1} to higher frequencies. Their formulation is based on their spectra and chemical behaviour.

Similar reactivity is shown by the structurally related $[Re_3(CO)_9(\mu_2\text{-}H)_3\text{-}(\mu_3\text{-}O)]^{2-}$ [15].

References

1 M. Tachikawa and E.L. Muetterties, J. Am. Chem. Soc., 102 (1980) 4541.
2 J.W. Kolis, E.M. Holt, M. Drezdzen, K.H. Whitmire and D.F. Shriver, J. Am. Chem. Soc., 104 (1982) 6134.
3 J.S. Bradley, Phil. Trans. R. Soc. London, A 308 (1982) 103.
4 M. Tachikawa, J. Stein, E.L. Muetterties, R.G. Teller, M.A. Beno, E. Gebert and J.M. Williams, J. Am Chem. Soc., 102 (1980) 6648.
5 E.L. Muetterties and J. Stein, Chem. Rev., 79 (1979) 479.
6 E.L. Muetterties, Chem. Eng. News, 28, Aug. 30, 1982.
7 V.A. Uchtman and L.F. Dahl, J. Am. Chem. Soc., 91 (1969) 3763.
8 A. Bertolucci, M. Freni, P. Romiti, G. Ciani, A. Sironi and V.G. Albano, J. Organomet. Chem., 113 (1976) C61.
9 B.F.G. Johnson, Phil. Trans. R. Soc. London, A 308 (1982) 5.
10 P.J. Kruzic, J. San Filippo, B. Hutchinson, R.L. Hance and L.M. Daniels, J. Am. Chem. Soc., 103 (1981) 2129.
11 F. Yip-Kwai Lo, G. Longoni, P. Chini, L.D. Lower and L.F. Dahl, J. Am. Chem. Soc., 102 (1980) 7691.
12 R.S. Doedens, Inorg. Chem., 8 (1969) 570.
13 L.F. Dahl, E.R. de Gil and R.D. Feltham, J. Am. Chem. Soc., 91 (1969) 1653.
14 L.F. Dahl, W.R. Costello and R.B. King, J. Am. Chem. Soc., 90 (1968) 5422.
15 G. D'Alfonso, personal communication.