

Preliminary communication

SYNTHESIS OF $P(C_6H_5)_4[HF_e_3(CO)_{10}(\mu_2-CHCOOC_2H_5)]$ BY REACTION OF ETHYL DIAZOACETATE WITH $P(C_6H_5)_4[HF_e_3(CO)_{11}]$

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Summary

The compound $[HF_e_3(CO)_{10}(\mu_2-CHCOOC_2H_5)]^-$ has been synthesized by the reaction of ethyldiazoacetate with $[HF_e_3(CO)_{11}]^-$ at room temperature. Spectroscopic data show that the alkylidene ligand has replaced the bridging CO of the starting molecule and that the CO ligands are fluxional.

The chemistry of cluster complexes containing bridging alkylidene and alkylidyne ligands is a developing field [1] and the recent report of the $HF_e_3(CO)_{10}(\mu_2-CNR_2)$ compound [2] prompts me to publish the synthesis of a new triiron cluster complex containing a μ_2 -alkylidene ligand.

One method of forming a bridging alkylidene ligand is by the action of a diazoalkane compound [3]. This method was applied with success by Shapley et al. in the synthesis of the cluster containing the μ_2 -methylene ligand $H_2Os_3(CO)_{10}(\mu-CH_2)$ by the action of diazomethane on $H_2Os_3(CO)_{10}$ [4, 5]. While this method is much used for dinuclear complexes [1, 6–9], its extension to cluster chemistry has been rather limited. I now report an example of the use of the ligand to incorporate a bridging alkylidene into the $[HF_e_3(CO)_{11}]^-$ cluster.

Upon adding a two-fold excess of ethyldiazoacetate to a solution of $P(C_6H_5)_4[HF_e_3(CO)_{11}]$ in dichloromethane at room temperature, the dark red solution slowly turns dark brown. After 15 h the dichloromethane is evaporated to dryness and the residue is dissolved in a minimum of methanol. Crystallisation at $-20^\circ C$ gives air stable black crystals (52% yield). The infrared spectrum in CH_2Cl_2 solution shows five terminal carbon monoxide stretching frequencies (2050w, 2011s, 1980s, 1962m cm^{-1}), and one weak band at 1695 cm^{-1} attributed to the ester group. The proton NMR spectrum in $(CD_3)_2CO$ shows resonances at: δ (ppm) 1.28 (t, 3 H (CH_3), J 7.2 Hz); 4.25 (q, 2H, (OCH_2), J 7.2 Hz); 7.82

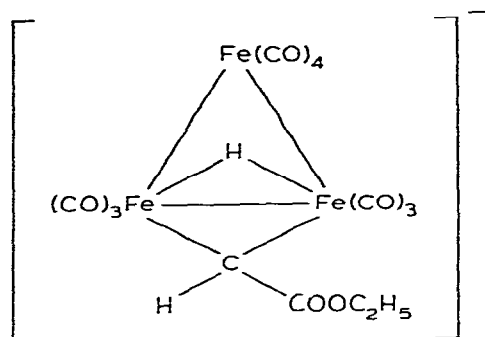


Fig. 1.

(s, 1 H, (CH)), the expected result for a μ -CH(COOC₂H₅) ligand [6–8] with the P(C₆H₅)₄ resonances appearing as two complex multiplets centered at 7.61 and 8.22 (20 H) ppm. A hydride resonance with intensity equivalent to 1 proton appears at δ -20.51 ppm.

The ¹³C {¹H} NMR spectrum shows signals relative to (CH₃)₄Si at δ (ppm) 14.1 (CH₃); 60.9 (OCH₂); 142.4 (CHCOOC₂H₅); 164.3 (-C(O)OC₂H₅) and 213.4 (CO) in good agreement, with values for the rhodium complex [C₅(CH₃)₅Rh(CO)]₂(μ -CH(COOC₂H₅)) [8]. The elemental analysis shows that the trinuclear unit is preserved: Found: C, 51.99; H, 3.28; Fe, 19.34. P(C₆H₅)₄-[HFe₃(CO)₁₀CHCOOC₂H₅] calcd.: C, 52.17; H, 3.08; Fe, 19.22%.

We conclude that this compound has a structure in which the bridging carbonyl has been replaced by the bridging alkylidene ligand (Fig. 1). The ¹³C NMR spectrum shows only one signal for the carbonyl ligands and, as is the case for the HFe₃(CO)₁₀CNR₂ compound [2] the CO ligands must be involved in a fluxional process, which is being investigated.

The reactivity of [HFe₃(CO)₁₀(μ -CH(COOC₂H₅))] and the generality of this synthetic method are also being studied.

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