

### Preliminary communication

## SYNTHESIS AND CRYSTAL STRUCTURE OF A HETERODINUCLEAR COMPLEX WITH A BRIDGED ETHENYL LIGAND $\text{FeCo}(\text{CO})_7(\mu\text{-CH=CPhH})$

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### Summary

$[\text{Fe}_2(\text{CO})_6(\mu\text{-CO})(\mu\text{-CH=CPhH})]^-$  reacts with  $\text{Co}_2(\text{CO})_8$  at room temperature to give the neutral heterodinuclear complex  $\text{FeCo}(\text{CO})_7(\mu\text{-CH=CPhH})$ , which has been characterized by elemental analysis and spectroscopic (mass, IR and  $^1\text{H}$  NMR) methods and by determination of its structure by X-ray diffraction.

The chemistry of dinuclear metal complexes containing  $\mu$ -alkylidene,  $\mu$ -alkylidyne or  $\mu$ -ethenyl fragments is of interest because of their probable involvement in some heterogeneous metal-catalyzed processes [1]. Furthermore, dinuclear mixed complexes containing metal-metal bonds can be important in selective activation of organic substrates [2].

We recently showed that the  $[\text{Fe}_2(\text{CO})_6(\mu\text{-CO})(\mu\text{-CH=CH}_2)]^-$  (I) anion reacts with  $\text{Co}_2(\text{CO})_8$  at room temperature to give a mixed Fe-Co complex containing a vinyl bridge,  $\text{FeCo}(\text{CO})_7(\mu\text{-CH=CH}_2)$  (II) [3].

It was not possible to determine the structure of this complex because of its low melting point but it was characterized by infrared, NMR, and mass spectroscopy.

With the aim of isolating a solid, crystalline analogue of II we examined the same

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reaction with  $[\text{Fe}_2(\text{CO})_6(\mu\text{-CO})(\mu\text{-CH}=\text{CPhH})]^-$  (III). Complex III did indeed react rapidly with a stoichiometric amount of  $\text{Co}_2(\text{CO})_8$  in dichloromethane solution at room temperature and evaporation of the solution, followed by extraction with hexane gave a green-black solution containing a solid which was recrystallized from  $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$ , however complex IV was isolated as black crystals in 40% yield.

The infrared spectrum of IV in cyclohexane solution shows only four terminal CO stretching frequencies: 2100m, 2047s, 2020s and 1992m  $\text{cm}^{-1}$ . The proton NMR spectrum in  $\text{CDCl}_3$  solution shows two doublets at 4.95(1H) and 8.63(1H) ppm ( $J$  12.3 Hz) and a complex multiplet centered at 7.3(5H) ppm consistent with a  $\sigma$ - $\pi$ -2-phenylethenyl bridge having the protons in a *trans* configuration. The mass spectrum shows the parent ion with  $m/z = 414$  and subsequent loss of seven CO ligands. The elemental analysis (Found: C, 43.70; H, 1.70.  $\text{FeCoC}_{15}\text{H}_7\text{O}_7$  calcd.: C, 43.51; H, 1.79%) and the spectral data of complex IV support the mixed Fe-Co dinuclear ethenyl bridged formulation. Complete characterization of IV was determined by an X-ray diffraction study.

*Crystal data:*  $\text{C}_{15}\text{H}_7\text{O}_7\text{FeCo}$ ,  $M = 414.0$ , monoclinic, space group  $P2_1/a$ ,  $a$  14.304(3),  $b$  12.461(3),  $c$  8.918(2) Å,  $\beta$  92.36(2)°,  $D_{\text{calc}}$  1.731  $\text{g cm}^{-3}$ ,  $Z = 4$ . A suitable crystal was mounted on a Philips PW-1100 four circle diffractometer and reflections between  $4^\circ \leq \theta \leq 9^\circ$  were measured using the  $\omega$ -scan technique with graphite monochromated  $\text{Mo-K}_\alpha$  radiation. 3337 reflections were measured in the range  $2 \leq \theta \leq 30^\circ$ ; 3295 of which were assumed as observed applying the condition  $I \geq 2.5\sigma(I)$ . The Fe and Co atoms were located from a Patterson synthesis and the remaining non-hydrogen atoms from a weighted Fourier synthesis. The structure was refined by full-matrix least-squares method using the SHELX 76 computer program [4]. The function minimized was  $w = ||F_0| - |F_c||^2$ , where  $w = |\sigma^2 |F_0| + 0.021 |F_0|^2|^{-1}$ ,  $f$ ,  $f'$  and  $f''$  were taken from International Tables of

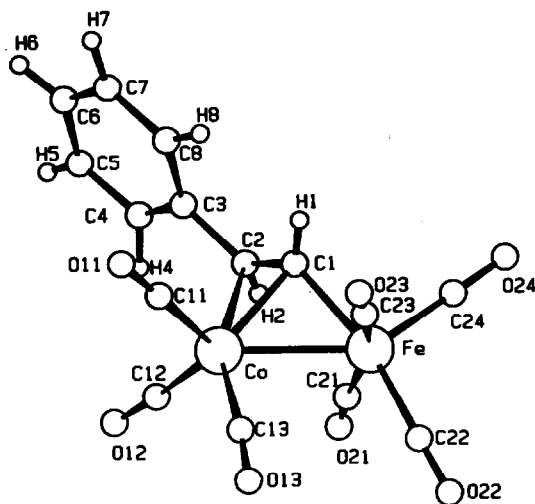


Fig. 1. Molecular structure of complex IV,  $\text{FeCo}(\text{CO})_7(\mu\text{-CH}=\text{C}(\text{C}_6\text{H}_5)\text{H})$ . Bond lengths: Fe-Co 2.563(1), C(1)-Co 2.014(3), C(2)-Co 2.178(3), C(1)-Fe 1.983(3), C(11)-Co 1.805(3), C(12)-Co 1.809, C(13)-Co 1.769(3), C(21)-Fe 1.833(3), C(22)-Fe 1.815(3), C(23)-Fe 1.821(3), C(24)-Fe 1.790(3), C(2)-C(1) 1.391(4), C(3)-C(2) 1.488 (Å).

X-ray Crystallography [5]. All hydrogen atoms were located from a difference synthesis and refined with an overall isotropic temperature coefficient. The final  $R$  was 0.044 ( $R_w = 0.053$ ) for all observed reflections.

The structure of IV is represented in Fig. 1, together with the most important bond parameters. The molecule contains two units:  $\text{Fe}(\text{CO})_4$  and  $\text{Co}(\text{CO})_3$  linked by a bridging 2-phenylethenyl ligand. The Fe–Co distance of 2.563(3) Å is a normal value for a Fe–Co single bond [6]. The organic bridge is  $\sigma$ -bonded to Fe and unsymmetrically  $\pi$ -bonded to Co and the hydrogens are in a *trans* configuration. The bridging  $\sigma, \pi$ -vinyl ligands are usually unsymmetric, as observed recently, in dinuclear iron complexes [7]. Another feature of the molecule is that the iron atom lies in the plane of the 2-phenylethenyl ligand, indicating that there is  $\pi$ -delocalization. The geometry around the Fe atom is a distorted octahedra formed by four CO, C(1) and the Co atom. The shortest Fe–CO bond distance is for the carbonyl nearly *trans* to the Fe–Co bond. The Co atom displays a very distorted polyhedron of coordination containing three CO groups, the vinyl system and the Fe atom. The Co–CO distance for the carbonyl *trans* to the Fe–Co bond is also the shortest.

This study confirms the ethenyl bridged dinuclear Fe–Co structure of the complexes obtained from the reaction of  $[\text{Fe}_2(\text{CO})_6(\mu\text{-CO})(\mu\text{-CH=CRH})]^-$  (I: R = H; and III, R = Ph) with  $\text{Co}_2(\text{CO})_8$ . Another fact of interest is that the hydrogens of the ethenyl bridge in the mixed complex IV are in *trans* configuration as well as in the dinuclear anionic complex III of departure. Thus, the opening of the  $\mu$ -ethenyl ligand in the metal–exchange reaction do not modify the configuration of the organic bridge.

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