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Preliminary communication

LIGAND TRANSFER REACTIONS BETWEEN DIFFERENT METALLIC SITES. CRYSTAL STRUCTURE OF $[(C_5H_5)_2Co_4(CO)_5(F_3CC{\equiv}CCF_3)]$

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Summary

Direct reactions between organometallic complexes of iron and of cobalt are described in which an exchange of ligands (hexafluorobut-2-yne, cyclopentadienyl or carbonyl) takes place. The reaction between $[Cp(CO)Fe\{\mu\text{-}C(CF_3){=}C(CF_3)SMe\}_2Fe(CO)Cp]$ and $Co_2(CO)_8$ affords a new tetracobalt cluster compound which has been characterized by X-ray analysis.

It is known that the catalytic activity of metals involves the mobility of species chemisorbed on metallic surfaces or the transfer of ligands between metal atoms in cluster compounds [1]. This phenomenon occurs either by a dissociative process, with the rupture of metal—ligand bonds, or by a non-dissociative process, with migration of a molecule or radical over the surface of the metal or cluster. In cluster chemistry the non-dissociative mechanism is more frequently encountered and is well known for both neutral and anionic ligands such as carbonyl, halide and hydride.

In this communication we describe new reactions in which organic ligands are transferred between two metallic centres. Thus the addition of $Co_2(CO)_8$ to the dimeric iron complex $[Cp(CO)Fe\{\mu\text{-}C(CF_3){=}C(CF_3)SMe\}_2Fe(CO)Cp]$ (I) ($Cp = \eta^5\text{-}C_5H_5$)* leads to the transfer of cyclopentadienyl and hexafluoro-

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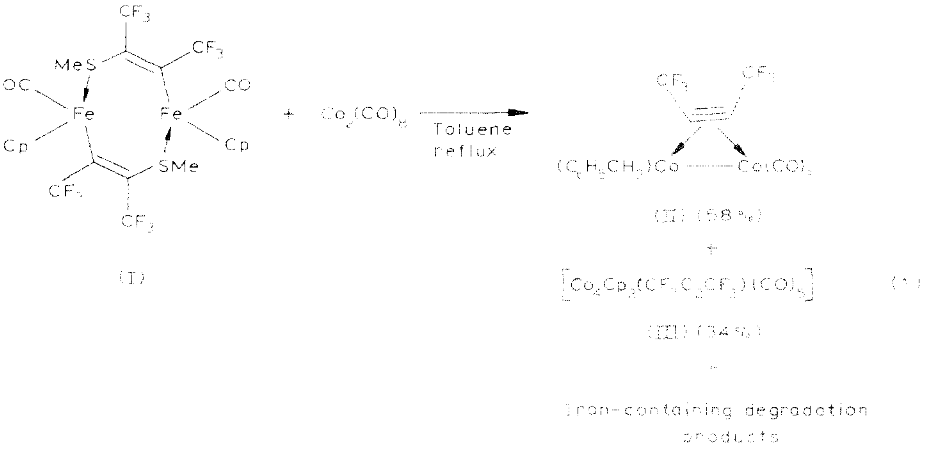
*Complex I was originally formulated as a monomer [2] but X-ray analysis has now established that it is dimeric, at least in the solid state [3].

but-2-yne ligands from iron to cobalt with the formation of two new cobalt complexes, II and III (reaction 1).



Reaction 1 is rather surprising in that $Co_2(CO)_8$, used generally as a reagent for the synthesis of polynuclear complexes [4], here selectively extracts all the ligands of the iron dimer I with the exception of the thiolato group. Usually $Co_2(CO)_8$ is considered to have a strong affinity for sulphur-containing molecules [5]. The detailed mechanism of reaction 1 has not at present been elucidated, but it could involve the formation of an intermediate iron-cobalt complex which might explain the disruption of the vinylthiolato bridging unit in I and the subsequent alkyne transfer process. Note that complex I is stable when heated alone in refluxing toluene. The incorporation of toluene in II is also significant.

It might be supposed that the transfer of hexafluorobut-2-yne from iron to cobalt was due to specific properties of the latter metal and should occur only in the direction Fe → Co. To verify this we have treated $[(CO)_3CoC_2(CF_3)_2Co(CO)_3]$, a derivative in which the alkyne is complexed to cobalt, with the iron thiolate dimer $[Cp(CO)Fe(\mu\text{-}SMe)_2Fe(CO)Cp]$ (reaction 2). This reaction also gives rise to a transfer of ligands, but in this case from cobalt to iron, i.e. in the inverse sense to that observed in reaction 1. The complexes IV and V, products of reaction 2, appear to arise from loss of the iron-bound sulphur and rupture of the iron dimer during transfer of carbonyl and hexafluorobut-2-yne from cobalt to iron, followed by insertion of the alkyne into an $Fe{-}CH_3$ bond.

The complexes II—V have been identified by NMR (^1H, ^{13}C, ^{19}F), infrared, and mass spectroscopy*. Analysis of the mass spectrum of III indicated that four cobalt atoms were incorporated in the molecule. To confirm this we carried out an X-ray analysis of a single crystal of III, obtained from a 2/1 mixture of hexane/dichloromethane. Eight $C_{19}H_{10}F_6O_5Co_4$ molecular units occupy an orthorhombic cell of dimensions a 15.933(6), b 15.306(9), c 17.089(12) Å, space group $Pbca$, d(calcd) 2.129 g cm^{-3}. Intensity measurements to θ(Mo-K_α) 22° were made on an Enraf—Nonius CAD4F diffractometer

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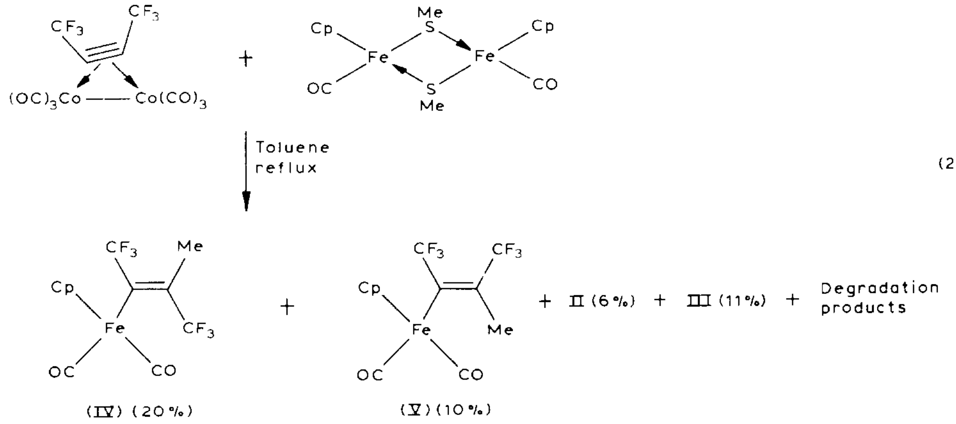
*All compounds have satisfactory elemental analyses.



(2)

using Mo X-rays and a graphite monochromator. The structure was solved by Patterson and difference synthesis techniques and has been refined by full-matrix least-squares methods to $R(R_w) = 0.052(0.055)$ using 1155 independent reflections ($I > 3\sigma(I)$). All calculations were carried out on a GOULD SEL 3227 computer using the GX program system [6]*.

A view of the molecule is shown in Fig. 1. III is tetranuclear with the four cobalt atoms in a butterfly configuration. The hexafluorobut-2-yne is σ-bonded to Co(3) and Co(4) and π-bonded to Co(1) and Co(2). The C(7)—C(8) axis is nearly parallel to the Co(3)—Co(4) bond so that the $Co_4C(7)C(8)$ unit defines

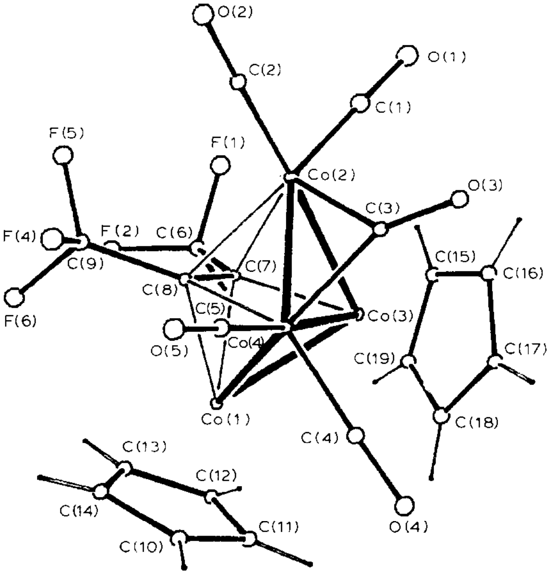


Fig. 1. A perspective view of a molecule of III. Selected bond lengths are: Co(1)—Co(3) 2. 419(4), Co(1)—Co(4) 2.404(4), Co(2)—Co(3) 2.398(4), Co(2)—Co(4) 2.387(4), Co(3)—Co(4) 2.471(4), Co(1)—C(7) 1.970(17), Co(2)—C(7) 2.112(17), Co(3)—C(7) 1.904(17), Co(1)—C(8) 1.912(16), Co(2)—C(8) 2.064(16), Co(4)—C(8) 2.016(15), C(7)—C(8) 1.44(2) Å.

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*Atomic coordinates for this work can be obtained from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should include the full literature citation of this communication.

a somewhat distorted octahedron. The structure of III is thus derived from those of the complexes $[\mathrm{Co_4(CO)_{10}(C_2R_2)}]$ (R = H [7], $\mathrm{C_2H_5}$ [8]) by replacement of five carbonyl ligands by two cyclopentadienyl groups. In III only the Co(2)—Co(4) bond is edge-bridged by carbonyl.

The migration of ligands from one metal centre to another has been previously described in the cases of carbonyl, halide, hydride [9], and, less frequently, cyclopentadienyl [10], but so far as we are aware it is observed here for the first time in the case of alkynes.

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