Functionalized cobalt clusters. Properties of carboxylate clusters (CO)6Co2HCC-COOH and (CO)10Co 4HCC-COOH as related to their structures

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Reaction of propiolic acid (HCCCOOH) with dicobalt octacarbonyl (Co 2(CO)8) and tetracobalt dodecacarbonyl (Co 4(CO)12) leads to the organometallic carboxylic acids (CO)6Co2HCC-COOH (1) and (CO)10Co 4HCC-COOH (2) in good yield. Both organometallic compounds show a cobalt carbonyl core bonded to a carboxylate function. The structure of the acetylene-carboxylic group in both clusters deviates from that of ethylene. The C(1)-C(2)-C(3) fragment is half way between acrylic and acetylene-carboxylic acid. The comparative acidity of the carboxylic group measured in methanol reveals that (1) is a stronger acid than (2), but less acidic than propiolic acid. Both organometallic carboxylic acids are thermally decomposed into phases with high metal content at relatively low temperatures. Fenske-Hall calculations on this series of cobaltocarbonyl cluster carboxylic acids confirm that the Co(CO)3 donates electron density to the HCC-COOH fragment, thus decreasing the acidity of the carboxylic function.