

## Functionalized cobalt clusters. Properties of carboxylate clusters (CO)<sub>6</sub>Co<sub>2</sub>HCC-COOH and (CO)<sub>10</sub>Co<sub>4</sub>HCC-COOH as related to their structures

Calvo-Perez, Víctor

Vega C., Andrés

Cortes, Piedad

Spodine, Evgenia

Reaction of propiolic acid (HCCCOOH) with dicobalt octacarbonyl (Co<sub>2</sub>(CO)<sub>8</sub>) and tetracobalt dodecacarbonyl (Co<sub>4</sub>(CO)<sub>12</sub>) leads to the organometallic carboxylic acids (CO)<sub>6</sub>Co<sub>2</sub>HCC-COOH (1) and (CO)<sub>10</sub>Co<sub>4</sub>HCC-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)<sub>3</sub> donates electron density to the HCC-COOH fragment, thus decreasing the acidity of the carboxylic function