Radical Anions and other Reduced Species of the Co_3C Cluster

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Summary E.s.r. spectra are reported for the radical anions $YCCo_3(CO)_9^-$ and the preparation of derivatives of the anion $Hg[YCCo_3(CO)_8]_2^{2-}$ is discussed.

IT has been suggested that the 'electron-reservoir' concept most satisfactorily explains the physico-chemical properties of Co_3C derivatives.[1] In an effort to provide quantitative evidence for this effect we have undertaken an investigation of the hitherto unreported radical anions, $YCCo_3(CO)_9^-$ where Y = alkyl, aryl, halogen, $SiMe_3$, *etc.*

The radical anions were prepared by reduction of the appropriate methinyltricobalt enneacarbonyl with sodium in an ether solvent. The purple or brown solutions of the parent compounds turned deep red on contact with the sodium and the latter solutions appeared to be stable for several hours under anaerobic conditions. Replacement of sodium by sodium amalgam as the reducing agent gave no detectable paramagnetic species. The reduction proceeds to $Co(CO)_4^-$ *via* a novel diamagnetic mercury derivative, $Hg[YCCo_3(CO)_8]_2^{2-}$, salts of which have been isolated and characterised by elemental analysis and i.r. spectroscopy. The presence of bridging ν(CO) bands at *ca.* 1808s and *ca.* 1797vs cm^{-1} indicates that a CO-bridged structure is adopted. The parent clusters are readily regenerated from solutions of both the mercury and radical anions by methyl iodide, acids, and iron(III).

Each of the radical anions gave a complex e.s.r. spectrum consisting of hyperfine structure of at least 22 lines (Figure), the g value of $2{\cdot}018 \pm 0{\cdot}005$ being close to the free-electron value. From this hyperfine structure it is clear that there is interaction between the unpaired electron and three equivalent cobalt nuclei ($I = 7/2$). The hyperfine coupling constant a_{Co} was found to be $36{\cdot}0 \pm 0{\cdot}5$ G except when Y = $SiMe_3$ where it decreased slightly to 34·5 G. When Y = F, hyperfine interaction with the single apical fluorine atom splits each of the 22 lines into two with $a_F = 11{\cdot}1$ G. No interaction with other apical groups was observed although the unusual line-shape and large line-width observed in some cases may well be due to unresolved hyperfine structure or second-order effects.

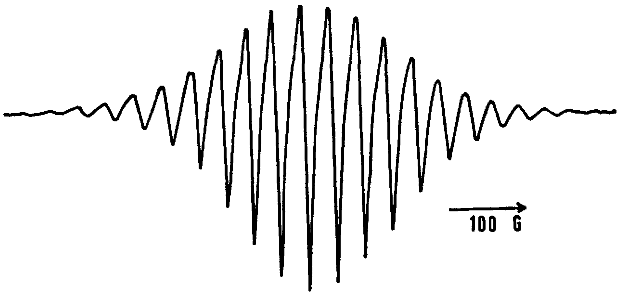

FIGURE. E.s.r. spectrum of $EtCCo_3(CO)_9^-$ in 1,2-dimethoxyethane at 25°.

There have been no reports of paramagnetic metal carbonyl clusters apart from analagous species $Co_3(CO)_9Z$ (Z = S, Se, Te).[2] Poorly resolved solution e.s.r. spectra of these latter compounds gave $a_{Co} = 30{\cdot}9 \pm 0{\cdot}5$ G. The increase in a_{Co} for $YCCo_3(CO)_9^-$ compared with $Co_3(CO)_9Z$

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corresponds to an increase in unpaired spin density at the cobalt nuclei. The fluorine coupling constant (Y = F) is considerably less than that of 64·3 G observed in $\cdot CH_2F$[3] but comparable to 8·61 G in the 4-fluoronitrobenzene radical anion.[4] This suggests that there is no appreciable withdrawal of spin density by the fluorine atom and that the Co_3C cluster is acting as an electron-withdrawing group, in agreement with other physico-chemical data.[1]

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[1] For a general review of the chemistry, structure, etc., of these compounds see B. R. Penfold and B. H. Robinson, *Accounts Chem. Res.*, 1973, **6**, 73.

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[3] M. V. Merritt and R. W. Fessenden, *J. Chem. Phys.*, 1972, **56**, 2353.

[4] M. Kaplan, J. R. Bolton, and G. K. Fraenkel, *J. Chem. Phys.*, 1965, **42**, 955.