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Preliminary communication

ELECTRONIC STRUCTURE AND REACTIVITY OF $X_2Co_2(CO)_6$ (X_2 = RC_2R', P_2, As_2) AND $R_xR'_{6-x}C_6Co_2(CO)_4$ RADICAL ANIONS

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Summary

Radical anions of the dinuclear species $X_2Co_2(CO)_6$ (X_2 = P_2, As_2, RC_2R') and $R_xR'_{6-x}C_6Co_2(CO)_4$ have been characterized by electrochemical and ESR methods The frozen solution spectra could be analysed in unusual detail to evaluate the g and hyperfine tensor components and these data allow definitive statements to be made about the directional nature and orbital character of the unpaired electron density Most of the $RC_2R'Co_2(CO)_6^-$ radical anions decay to monomeric paramagnetic species

Detailed descriptions of the redox properties, electronic structure and bonding of $X_2Fe_2(CO)_6$ molecules (X_2 = bridging ligand) have been presented [1,2] and this system is reasonably well understood The analogous cobalt system, where the valence orbitals are all filled [2], is not so amenable to study and the directional nature of the Co—Co bonding interaction is still the subject of some controversy, i e whether it is a 'straight' or 'bent' interaction [1,3] This note presents results on the new radical anions $X_2Co_2(CO)_6^-$ which give significant information on the nature of the orbital containing the unpaired electron, the directional nature of the metal interaction and the redox chemistry of $X_2Co_2(CO)_6$ molecules The formation of the remarkably stable 'flyover' radical anions $R_xR'_{6-x}C_6Co_2(CO)_4^-$ is also described

Acetylene [4], arsenic [5] and phosphorus [6] bridged dimers $X_2Co_2(CO)_6$ (X_2 = RC_2R', As_2, P_2), and 'flyover' acetylene compounds [7] undergo a reversible electrochemical one-electron reduction in THF to the appropriate radical anion. The reduction potentials, ranging from −0 26 to −1 01 V (vs Ag/AgCl), are sensitive to the nature of the bridging group and the type of bridging moiety (Table 1). A second reduction step, close to the first, was observed

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TABLE 1

REPRESENTATIVE RADICAL ANIONS

Radical anion	$E_{1/2}$ (V)^a	$\langle g \rangle$	$\langle a^{Co} \rangle$ (mT)	$\langle a^{X} \rangle$ (mT)
$Ph_2C_2Co_2(CO)_6^-$	−0 81	2 001	−2 82	—
$Bu_2{}^tC_2Co_2(CO)_6^-$	−1 01	2 009	−2 84	—
$CH_3C_2SiMe_3Co_2(CO)_6^-$	—	2 012	−2 86	—
$CF_3C_2SiMe_3Co_2(CO)_6^-$	−0 68	2 013	−2 66	—
$CF_3C_2CF_3Co_2(CO)_6^-$	−0 49	2 015	−2 37	—
$P_2Co_2(CO)_6^-$	−0 56	2 007	−2 80	3 74
$As_2Co_2(CO)_6^-$	−0 52	2 012	−2 81	2 12
$(CF_3)_6C_6Co_2(CO)_4$	−0 26	2 013	−3 11	—

^{a}vs Ag/AgCl in acetone solution

for the acetylene derivatives Chemical reductants such as sodium, sodium naphthalenide and ferrocenium tetrafluoroborate effect reduction to the radical anions in good yields at −70°C The isotropic ESR spectra showed the expected 15 lines resulting from hyperfine coupling with two equivalent cobalt nuclei (I = 7/2) The central lines were noticeably asymmetric as a result of unresolved second-order shifts [8]. In the case of the $P_2Co_2(CO)_6^-$ and $As_2Co_2(CO)_6^-$ species, hyperfine coupling was observed to two equivalent phosphorus or arsenic atoms (Table 1) [2].

ESR spectra of frozen THF solutions at −160°C of $X_2Co_2(CO)_6^-$ were sufficiently well-resolved to unambiguously determine the largest hyperfine tensor component a_1. In some cases other features were also resolved, which enable us to analyse the spectra in detail [9]. The magnitude of the anisotropic hyperfine tensor components (e g $X_2 = CF_3C_2SiMe_3$, $g_1 = 2.02$, $g_2 = 2\ 012$, $g_3 = 2\ 007$, $a_1 = 2\ 7$ mT, $a_2 = -4\ 2$ mT, $a_3 = -6.49$ mT) suggests that the unpaired electron occupies a molecular orbital largely cobalt 3d in character [10] If the Co—Co and X—X vectors respectively define the molecular z and x axes, then under C_{2v} symmetry only linear combinations of d_{z^2}, d_{yz} and $d_{x^2-y^2}$ orbitals are of the required* A_1 and B_2 symmetry Since the A_1 orbitals are strongly bonding we conclude that the unpaired electron is in a B_2 orbital. An orbital having 72% d_{z^2} and 28% d_{yz} character is required by the experimental anisotropic parameters, in good agreement with the ratio derived from molecular orbital calculations on $X_2Fe_2(CO)_6$ molecules [1]. With respect to the directional nature of the Co—Co interaction the analysis of the $X_2 = CF_3C_2SiMe_3$ spectrum shows that the major hyperfine tensor axes are oriented at $\alpha \sim \pm 15°$ relative to the Co—Co vector The 72% d_{z^2}, 28% d_{yz} combination requires that the principal hyperfine tensor axes be displaced from the local z and y axes on each cobalt by $\beta \sim \pm 10°$. Thus, as shown in the diagram, the local z axes are aligned at ca 25° relative to the Co—Co vector, in good agreement with the orientation of the axial carbonyl ligand (32° in the case of $(C_6H_5)_2C_2(CO)_6$) [11] and with the angles utilized by Dahl and co-workers in their theoretical analysis of $X_2Fe_2(CO)_6$ compounds [1]. The angle α may be identified with the orientation of the bonding interaction in the metal—metal bond [1]

All of the 'flyover' radical anions, $R_xR'_{6-x}C_6Co_2(CO)_4^-$, have half-lives of at

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*It is found that two tensor components are negative and only A_1 and B_2 combinations give this result. Orbitals of B_1 and A_2 symmetry (cobalt d_{xy} and d_{yz}) lead to two positive and one negative tensor.

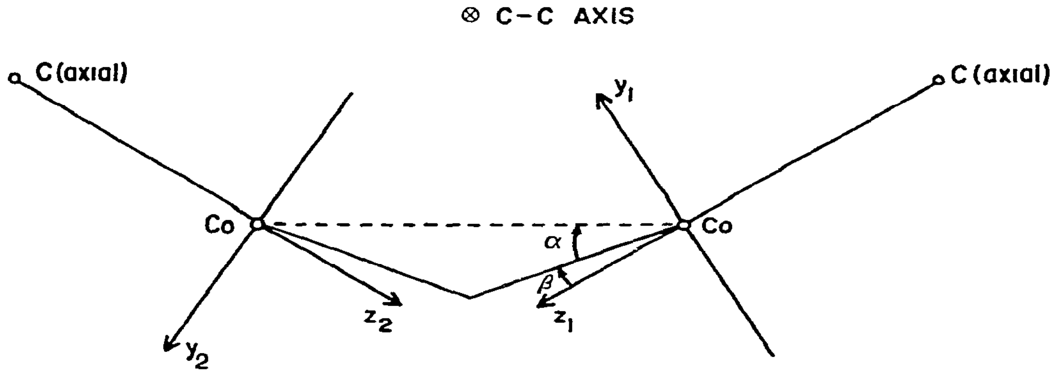

Fig 1 View down C—C bond axis of acetylenedicobalt

least several hours at room temperature In contrast, the half-life of $Ph_2C_2Co_2(CO)_6^-$ is less than 1 min at −60°C A novel feature of the chemistry of the $X_2Co_2(CO)_6^{-\cdot}$ ($X_2 = RC_2R'$) species was the rapid decay to monomeric paramagnetic species at temperatures above −60°C except when $R = R' = CF_3$ Typical of the ESR parameters are $\langle g \rangle = 2.058$ and $\langle a^{Co} \rangle = 5.22$ mT for the monomer derived from $Ph_2C_2Co_2(CO)_6^-$ Reduction of $RC_2R'Co_2(CO)_6$ compounds in the presence of phosphite or phosphine ligands accelerates the formation of monomers (which in this case show hyperfine coupling to phosphorus of $\sim\langle a^P \rangle = 10\ 9$ mT) such that $RC_2R'Co_2(CO)_6^-$ species are not observed, even at −70°C It is known [12] that radical anions derived from uncoordinated alkynes slowly dimerize in THF to produce butadiene dianions A similar process accelerated by the template and electronic effect of the metal can be visualized for our system

Further work is in hand to extend the series of acetylene- and phosphorus-bridged radical anions, to confirm the theoretical analysis, to establish the exact nature of the monomeric species and to isolate some of the more stable radical anions

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