Preparation, Reactions, and Crystal Structures of Some Ligand-bridged Manganese and Rhenium Carbonyl Derivatives

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Summary. The synthesis, reactivity, and structure of some ligand-bridged derivatives of dimanganese and dirhenium decacarbonyls are discussed.

BIDENTATE ligands are known to react with dimanganese and dirhenium decacarbonyls under a variety of conditions to give essentially two types of substitution products; paramagnetic complexes such as $LM(CO)_3$,[1] (M = Mn, Re) and diamagnetic complexes such as $M_2(CO)_8L$[2,3] which retain the metal–metal bond. In both types of complex the ligand is thought to be chelated to one metal atom. We have prepared a new series of complexes $M_2(CO)_8L$ which contain a metal–metal bond, and a bidentate ligand that is bridging the two metal atoms. We have also found that under certain conditions these bridged complexes isomerise.

The ligand $f_4$fars, $Me_2AsC{=}CAsMe_2CF_2CF_2$, and dimanganese decacarbonyl react under u.v. irradiation in acetone solution to give $f_4farsMn_2(CO)_8$ (I). The ligands $f_4$fars and $f_4$fos, $Ph_2PC{=}CPPh_2CF_2CF_2$, react with dirhenium decacarbonyl in refluxing xylene to give the compounds $f_4farsRe_2(CO)_8$ (II) and $f_4fosRe_2(CO)_8$ (III). The compounds (I)—(III) were purified by chromatography and crystallization. They analyse correctly for C, H, and F, and show a parent ion followed by loss of eight carbonyl groups in their mass spectra. The ^{19}F n.m.r. spectra of (I), (II), and (III) and the ^1H n.m.r. spectra of (I) and (II) show one single peak indicating that the methyl and CF_2 groups in these molecules are equivalent. Treatment of these compounds with iodine at room temperature in dichloromethane causes immediate fission of the metal–metal bond and gives only the compounds $L[M(CO)_4I]_2$. On the basis of this n.m.r. and chemical evidence a bridged structure as shown in the Figure is suggested for (I), (II), and (III). This has now been confirmed by an *X*-ray study on $f_4farsMn_2(CO)_8$ (I).

Orange crystals of (I) were obtained by slow cooling of an acetone solution, they are orthorhombic with a = 7·479(3), b = 12·713(3), c = 10·273(3) Å, space group $Pna2_1$, Z = 4. 1439 observed reflections within the Mo-K_α sphere ($2\theta < 45°$) give a current R of 3·8%. In (I) the distorted octahedral arrangement about the manganese atoms is such that the carbonyl groups are perfectly staggered as in dimanganese decacarbonyl.[4] The Mn–Mn bond length is increased from 2·923(3) to 2·971(3) Å, other variations are not significant.

The structure of $f_4fars[Mn(CO)_4I]_2$ has also been determined. Crystals are monoclinic a = 13·85(2), b = 14·79(1), c = 13·96(2) Å, β = 102·2(1)°, space group $P2_1/c$, Z = 4. 943 observed reflections give a current R value of 15·3%. The rapid fall-off of intensity with Bragg angle indicates that an accurate structure will be difficult to obtain. In $f_4fars[Mn(CO)_4I]_2$ there is no Mn–Mn bond. The dimethylarsenic groups are rotated so that the $Mn(CO)_4I$ moieties on each arsenic atom are situated on opposite sides of the cyclobutene plane. The iodine atoms are co-ordinated *cis* to the ligand. A highly significant change in the ligand geometry takes place, the As ··· As distance increasing from 4·02 [in (I)] to 4·31 Å. This type of increase has also been observed in changes from bidentate to monodentate co-ordination in systems of a similar type.[5]

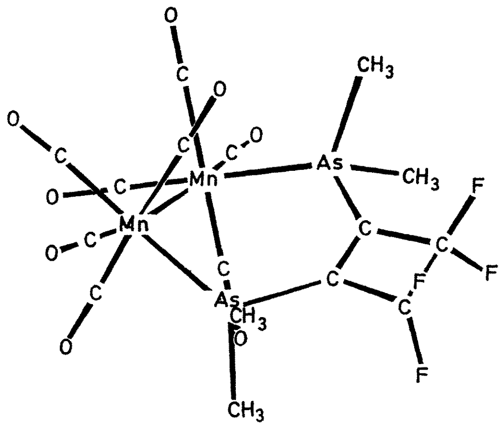

FIGURE. *Structure of* $f_4farsMn_2(CO)_8$ (I) *as plotted from the atomic co-ordinates.*

In refluxing xylene, $f_4$fars and dimanganese decacarbonyl react to give $f_4farsMn_2(CO)_9$ (I); on further heating this is converted into another complex (IV), which by elemental analysis (C, H, F) and mass spectroscopy has been shown to be an isomer of (I). The ^1H n.m.r. spectrum of (IV), however, shows two singlets due to inequivalent dimethylarsenic groups. Manganese carbonyl and $f_4$fos also react in refluxing toluene to give a compound analogous to (IV).

Other bidentate ligands form bridged complexes with dirhenium decacarbonyl, this and their surprisingly ready iodine cleavage reactions are the subject of further study.

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