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NOTE

RHENIUM DIIRON DODECACARBONYL DIMER

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Anions of the type $[MFe_2(CO)_{12}]^-$, where M = Mn or Re, have been prepared previously by several methods. Addition of $[Mn(CO)_5]^-$ to $Fe(CO)_5$ in diglyme[1] or to $Fe_2(CO)_9$ in refluxing tetrahydrofuran (THF)[2] has given $[MnFe_2(CO)_{12}]^-$, and irradiation of $Re_2(CO)_{10}$ and $Fe(CO)_5$ in diethyl ether[3] yielded $[ReFe_2(CO)_{12}]^-$. The anions have been considered to be derived from $Fe_3(CO)_{12}$[4], with which they are isoelectronic, by replacing the $Fe(CO)_4$ group with $[M(CO)_4]^-$. It was thought that the direct reaction of a variety of organometallic anions with $Fe_3(CO)_{12}$ might give a wide range of trinuclear anions based on the $Fe_3(CO)_{12}$ structure. Such a series of reactions has been undertaken and, although the anionic products are in the main extremely unstable, the method has proved useful in the synthesis of the novel polynuclear mixed metal carbonyl, $[ReFe_2(CO)_{12}]_2$.

EXPERIMENTAL

An analogous procedure to that described below for $[Re(CO)_5]^-$ was used to investigate the reaction of $Fe_3(CO)_{12}$ with the other organometallic anions listed in the discussion. All reactions were performed under a N_2 atmosphere using solvents distilled under N_2 from $LiAlH_4$ immediately before use. IR spectra were recorded on a Beckman IR 12 spectrophotometer. Microanalyses were carried out by Dr. A. Bernhardt, 5251 Elbach über Engelskirchen, Fritz-Pregl-Strasse 14–16 (West Germany).

$[Et_4N]^+[ReFe_2(CO)_{12}]^-$

A solution of $Re_2(CO)_{10}$ (3.0 g, 4.6 mmoles) in THF (100 ml) was added to sodium amalgam [Na (0.6 g, 26.1 mmoles) in mercury (15 ml)] and the mixture stirred vigorously for 20 min. Excess amalgam was removed through a tap in the base of the flask, the $NaRe(CO)_5$ solution washed with mercury (5 ml) and then added dropwise to a stirred solution of $Fe_3(CO)_{12}$ (4.5 g, 9.0 mmoles) in THF (150 ml) at room temperature, the solution rapidly acquiring the deep red colouration characteristic of the anion $[ReFe_2(CO)_{12}]^-$. After 1 h, Et_4NCl (1.48 g, 9.0 mmoles) was added, the solution stirred for a further 1 h, filtered and solvent removed under high vacuum. The resultant solid was dissolved in dichloromethane, the solution filtered and heptane added slowly to precipitate the required maroon coloured complex

(4.88 g, 71.5% yield). (Found: C, 31.23; H, 2.71; Fe, 14.29; N, 1.98; O, 25.08. $C_{20}H_{20}Fe_2NO_{12}Re$ calcd.: C, 31.42; H, 2.62; Fe, 14.66; N, 1.83; O, 25.13%.)

[ReFe$_2$(CO)$_{12}$]$_2$

A solution of $Na[ReFe_2(CO)_{12}]$ in THF (or, less expeditiously, of the tetraethylammonium salt) prepared as above was treated with tropylium bromide (1.5 g, 8.8 mmoles) and the mixture stirred for 1 h. Solvent was removed under high vacuum, the residue washed with heptane (2 × 100 ml) to remove bitropyl (characterised by m.p. 61–61.5°, parent ion *m/e* 182) then dissolved in a minimum of THF and divided into three equal portions, each portion being chromatographed twice under N_2 on a 2.5 × 35 cm "Florisil" column. On elution with THF two different coloured bands appeared. A green band eluted first was shown to be a mixture of $Fe_3(CO)_{12}$ and $Re_2(CO)_{10}$ by IR spectroscopy. Further development of the column gave, as the main component, a deep red-violet solution from which solvent was removed in high vacuum. The resulting deep red-violet, air-sensitive complex, $[ReFe_2(CO)_{12}]_2$, was pumped for 3 days under high vacuum to remove traces of $Fe_3(CO)_{12}$ and $Re_2(CO)_{10}$. Yield 2.08 g, 39% based on $Fe_3(CO)_{12}$. (Found: C, 22.42; H, 0.23; Fe, 17.37; O, 30.54. $C_{24}Fe_4O_{24}Re_2$ calcd.: C, 22.71; H, 0.0; Fe, 17.66; O, 30.28%.)

IR Spectra

Principal absorptions in the ν(CO) region were observed in THF solution for $[Et_4N]^+[ReFe_2(CO)_{12}]^-$ at 2075, 2047, 2009, 1996, 1983, 1951, 1910, 1874, 1819, 1789 cm^{-1} and for $[ReFe_2(CO)_{12}]_2$ at 2074, 2035, 2009, 1997, 1983, 1951, 1910, 1820, 1790 cm^{-1}.

DISCUSSION

Reactions of $Fe_3(CO)_{12}$ with the series of organometallic ions $[Mn(CO)_5]^-$, $[Re(CO)_5]^-$, $[Co(CO)_4]^-$, $[C_5H_5Mo(CO)_3]^-$, $[C_5H_5Fe(CO)_2]^-$, $[C_5H_5Ni(CO)]^-$, give stable products only with the first two anions listed. The trinuclear ions, $[MnFe_2(CO)_{12}]^-$ and $[ReFe_2(CO)_{12}]^-$, which are obtained by reaction in solution at ambient temperature, are identical with those formed in earlier, less direct procedures[1-3] but, contrary to a previous suggestion[2], are isolated in superior yields by this method. Despite the definite colour change which occurs on addition of a THF solution of each of the other anions to $Fe_3(CO)_{12}$, subsequent removal of solvent gives solids which are unstable at room temperature even under high vacuum.

The method is convenient when further *in situ* reaction of the trinuclear anion is desired. Thus, tropylium bromide, a one-electron oxidizing agent used previously in the dimerisation of $[C_5H_5Cr(CO)_3]^-$ to $[C_5H_5Cr(CO)_3]_2$[5] and of $[Mn(CO)_5]^-$ to $Mn_2(CO)_{10}$[6], when added to $[ReFe_2(CO)_{12}]^-$ gives the novel hexanuclear complex, $[ReFe_2(CO)_{12}]_2$. Although in the solid state the complex rapidly decomposes on exposure to air, a solution in THF, acetone, ether, ethanol or water is comparatively air stable. That this may be attributed to a strongly solvent co-ordinated species may be inferred from the anomalous values for the mol.wt. which were obtained osmometrically.

The complex, $[ReFe_2(CO)_{12}]_2$, was shown to be diamagnetic by the NMR spectroscopic method of Evans[7] (see also Kaesz *et al.*[8]) but an attempt to obtain

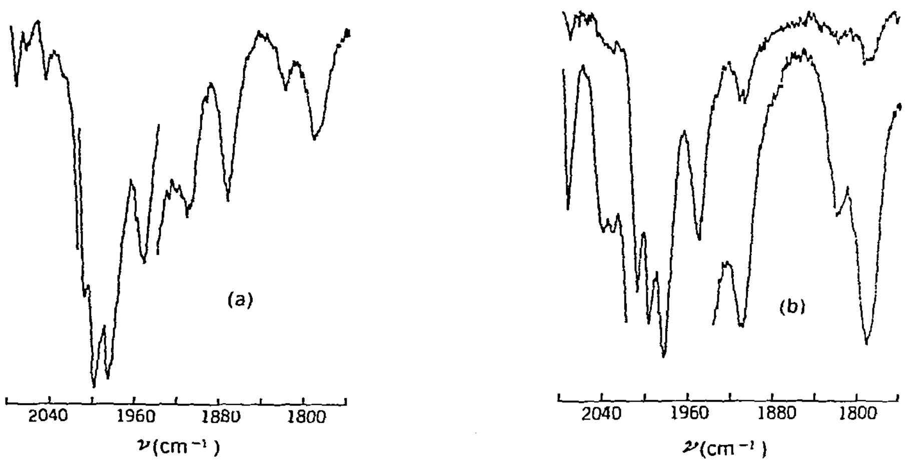

Fig. 1. IR spectra in the ν(CO) region of (a) $[Et_4N]^+[ReFe_2(CO)_{12}]^-$ and (b) $[ReFe_2(CO)_{12}]_2$ in THF solution.

direct evidence for the presence of a Re–Re bond using Raman spectroscopy [128 cm^{-1} in $Re_2(CO)_{10}$[9]] was thwarted by the rapid decomposition of the sample in the He/Ne laser beam. However, the overal similarity (Fig. 1) between the infrared spectra of the complex and its anionic precursor strongly suggests a straight forward coupling of two $[ReFe_2(CO)_{12}]$ groups via the Re atoms. Confirmation of structure is awaited from an X-ray crystallographic structure determination.

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