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Preliminary communication

SYNTHESIS AND CHARACTERIZATION OF THE $[(OC)_3M(P_3O_9)]^{2-}$ ANIONS, M = Re AND Mn

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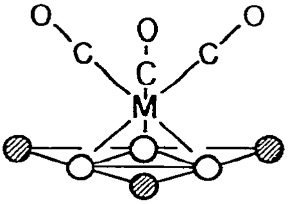
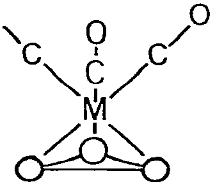
Summary

Reaction of $[(OC)_3M(NCCH_3)_3](PF_6)$ (M = Re or Mn) with $[(n\text{-}C_4H_9)_4N]_3(P_3O_9)$ in 1,2-$C_2H_4Cl_2$ yields $[(n\text{-}C_4H_9)_4N]_2[(OC)_3M(P_3O_9)]$, shown to contain an anion whose structure is related to the P_4O_{10} structure by replacement of an OP^{3+} unit by $(OC)_3M^+$.

The $[(OC)_3M(Nb_2W_4O_{19})]^{3-}$ anions [1], M = Re and Mn, contain metal tricarbonyl groups bonded to a triangle of oxygen atoms occupying the center of a rigid, close-packed layer of six oxygens (structure **a**). Since each of the peripheral oxygens in this layer, hatched in **a**, is in close proximity to a carbonyl group, the set of peripheral oxygens could play a key steric role in determining the chemical reactivity of the metal tricarbonyl groups. A metal tricarbonyl binding site lacking these three peripheral oxygens (structure **b**) would provide an opportunity for investigating this effect through comparative reactivity studies. The $[(OC)_3M(P_3O_9)]^{2-}$ anions reported here, M = Re and Mn, utilize the trimetaphosphate ligand to create such a binding site. These complexes are, to the best of our knowledge, the first isolable metal trimetaphosphate complexes to be reported in the chemical literature.



a



b

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Addition of $[(n\text{-}C_4H_9)_4N]_3(P_3O_9)$ [2], prepared from aqueous $Na_3(P_3O_9)$ using an ion exchange resin, to one equivalent of $[(OC)_3M(NCCH_3)_3](PF_6)$ [3], M = Re or Mn, in 1,2-$C_2H_4Cl_2$ under N_2 at 79°C followed by precipitation with ether and recrystallization by cooling a hot saturated THF/$CH_3C_6H_5$ solution to —30°C yields microcrystalline $[(n\text{-}C_4H_9)_4N]_2[(OC)_3M(P_3O_9)]$, M = Re (1) or Mn (2). The Mn compound is light-sensitive and its preparation must be carried out in darkness. Compounds 1 and 2 are formulated as indicated on the basis of satisfactory C, H, N, P and M analyses and conductivity measurements in CH_3CN which characterize then as 2/1 electrolytes. The structure shown in Fig. 1 is consistent with IR and ^{31}P NMR spectroscopic data obtained from CH_3CN solutions. Infrared absorptions in the CO stretching region (1: 2018 cm^{-1} (s), 1885 cm^{-1} (s, br); 2: 2034 cm^{-1} (s), 1913 cm^{-1} (s, br) are in accord with a C_{3v} metal tricarbonyl unit [4]. ^{31}P NMR spectra, which in each case display a single resonance (for 0.1 *M* solutions, 11.1 (1) and 9.8 (2) ppm upfield from 85% H_3PO_4), similarly support a C_{3v} structure.

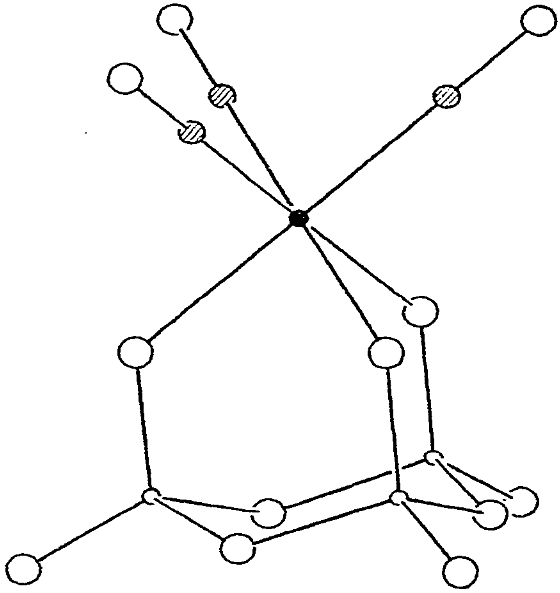

Fig. 1. Proposed C_{3v} structure of the $[(OC)_3(P_3O_9)]^{2-}$ anions. Large open circles represent oxygen atoms, small open circles represent phosphorus atoms, hatched circles represent carbon atoms, and the filled circle represents the M atom.

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