

Expeditious synthesis of $\text{Re}_3(\mu\text{-H})_3(\text{CO})_{11}(\text{NCMe})$

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Abstract

The cluster hydride $\text{Re}_3(\mu\text{-H})_3(\text{CO})_{11}(\text{NCMe})$ can be prepared in ca. 90% isolated yield by passing hydrogen into a toluene solution of $\text{Re}_2(\text{CO})_8(\text{NCMe})_2$ at 80°C.

Keywords: Rhenium; Carbonyl; Acetonitrile; Cluster

1. Introduction

The development of the chemistry of metal cluster carbonyls such as $\text{M}_3(\text{CO})_{12}$ ($\text{M} = \text{Ru}, \text{Os}$), $\text{M}_4(\text{CO})_{12}$ ($\text{M} = \text{Rh}, \text{Ir}$) and $\text{Re}_3(\mu\text{-H})_3(\text{CO})_{12}$ has been closely related to the availability of suitably substituted derivatives containing ligands other than CO. The lack of reactivity of the parent carbonyls (or their high activation energy towards CO substitution) has been ascribed to their high symmetry which does not offer a readily accessible site of attack by incoming reagents [1]. A useful ligand to replace one or two CO groups is acetonitrile, and high yield syntheses of mono- and disubstituted derivatives of the ruthenium and osmium carbonyls by trimethylamine *N*-oxide (TMNO) initiated displacement of CO are well documented [2].

In the rhenium case, several reports of the synthesis of $\text{Re}_3(\mu\text{-H})_3(\text{CO})_{12}$ in moderate yield from $\text{Re}_2(\text{CO})_{10}$ have appeared. First prepared by reduction of $\text{Re}_2(\text{CO})_{10}$ with NaBH_4 , followed by acidification (H_3PO_4), which gave a 50% yield in a rather tedious procedure [3], this cluster hydride was obtained more conveniently albeit in similar yield by direct hydrogenation of $\text{Re}_2(\text{CO})_{10}$ in decalin or dodecane (120–170°C) [4]. Subsequent reactions of this dodecacarbonyl require conditions under which mixtures of products, some derived by alteration and/or fragmentation of ligands on the cluster core, or even of the cluster core itself, are often obtained [5].

Application of the TMNO method to the replacement of CO by MeCN in the rhenium dodecacarbonyl results in the formation of a mixture of mono-, di- and trisubstitution products in varying ratios [6]. Other preparations of these complexes include acidification of the unsaturated cluster anion $[\text{Re}_3(\mu\text{-H})_4(\text{CO})_{10}]^-$ in acetonitrile to give $\text{Re}_3(\mu\text{-H})_3(\text{CO})_{10}(\text{NCMe})_2$ (yield not reported), which could be successively converted to the mono-MeCN derivative and the dodecacarbonyl by adding CO [7]. Later, the acetonitrile-substituted anion $[\text{Re}_3(\mu\text{-H})_4(\text{CO})_9(\text{NCMe})_3]^-$ was similarly treated to give the neutral trisubstituted complex (73%) [6]. The series of complexes $\text{Re}_3(\mu\text{-H})_3(\text{CO})_{12-n}(\text{NCMe})_n$ can be interconverted by addition of CO or TMNO respectively in acetonitrile solution. In addition, all these routes use $\text{Re}_3(\mu\text{-H})_3(\text{CO})_{12}$ as starting material, which can be obtained from $\text{Re}_2(\text{CO})_{10}$ in only moderate yield at best [4].

2. Results

In the course of attempts to extend our earlier studies of Re_3 clusters containing acetylenic tertiary phosphines and related ligands [8], we have developed a method of making $\text{Re}_3(\mu\text{-H})_3(\text{CO})_{11}(\text{NCMe})$ in 90% isolated yield, on a half-gram scale, directly from $\text{Re}_2(\text{CO})_8(\text{NCMe})_2$ and hydrogen. The reaction takes between 8 and 20 h (dependent on scale) and isolation is achieved by simple evaporation and recrystallisation from tetrahydrofuran/hexane mixtures. The binuclear complex [9–11]

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can be prepared directly from $\text{Re}_2(\text{CO})_{10}$ in 80% yield by the improved procedure described below.

In conclusion, this synthesis makes this useful cluster hydride readily available in larger quantities, large enough to facilitate further development of its chemistry [12].

3. Experimental

3.1. Synthesis of $\text{Re}_2(\text{CO})_8(\text{NCMe})_2$

A Schlenk flask equipped with a pressure-equalising dropping funnel was flushed with nitrogen and charged with $\text{Re}_2(\text{CO})_{10}$ (2.0 g, 3.0 mmol), CH_2Cl_2 (10 ml) and MeCN (10 ml). Freshly sublimed Me_3NO (0.45 g, 6.0 mmol) in CH_2Cl_2 (5 ml) was added dropwise (over 1 h) and the reaction stirred at room temperature until complete conversion had occurred (5–7 h; monitored by IR). Evaporation of the solvent and recrystallisation (Et_2O /hexane containing a few drops of MeCN) gave pure $\text{Re}_2(\text{CO})_8(\text{NCMe})_2$ (1.7 g, 80%). IR ($\text{CH}_2\text{Cl}_2/\text{MeCN}$): $\nu(\text{CN})$ 2076w, 2071w; $\nu(\text{CO})$ 2016s, 2001s, 1965(br), 1904(br) cm^{-1} [Lit. [11] (MeCN): $\nu(\text{CN})$ 2075w, 2070w; $\nu(\text{CO})$ 2015m, 2001s, 1962s, 1909m cm^{-1}].

3.2. Synthesis of $\text{Re}_3(\mu\text{-H})_3(\text{CO})_{11}(\text{NCMe})$

A four-necked Schlenk flask was equipped with a magnetic stir bar, fine porosity glass frit, thermometer, rubber septum and reflux condenser. A solution of $\text{Re}_2(\text{CO})_8(\text{NCMe})_2$ (500 mg, 0.74 mmol) in toluene (40 ml) was warmed to 80°C in an oil bath while hydrogen was bubbled through the solution. The reaction was monitored by IR spectroscopy until complete conversion to $\text{Re}_3(\mu\text{-H})_3(\text{CO})_{11}(\text{NCMe})$ had been achieved (the band at 2015 cm^{-1} was observed). After cooling and removal of solvent, the pale brown residue was dissolved in CH_2Cl_2 and filtered through a pad of silica gel to give a pale yellow filtrate. Evaporation and

recrystallisation (THF/heptane containing a few drops of MeCN) afforded white crystals of $\text{Re}_3(\mu\text{-H})_3(\text{CO})_{11}(\text{NCMe})$ (350–400 mg, 80–90%). IR (toluene): $\nu(\text{CN})$ 2114w; $\nu(\text{CO})$ 2090m, 2037s, 2021s, 2001vs, 1972s, 1933m cm^{-1} . ^1H NMR: $\delta(\text{CDCl}_3)$ –17.20 (Re–H), –14.51 (Re–H), 2.36 (NCMe) [Lit. [6]: $\nu(\text{CN})$ 2113mw; $\nu(\text{CO})$ 2090mw, 2038m, 2022s, 2003vs, 1971m, 1936m, 1921(sh) cm^{-1} . ^1H NMR: $\delta(\text{CDCl}_3)$ –17.00, –14.37, 2.61].

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