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A SIMPLE AND EFFECTIVE PREPARATION OF $(\eta\text{-RC}_5\text{H}_4)_2\text{M}_2(\text{CO})_6$ COMPLEXES (M = Cr, Mo, AND W)

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Summary

Preparation of the readily accessible salts of the $[(\eta\text{-RC}_5\text{H}_4)\text{M}(\text{CO})_3]^-$ anions in diglyme solution and their subsequent oxidation with aqueous ferric sulphate solution provides an efficacious method for preparing $[(\eta\text{-RC}_5\text{H}_4)_2\text{M}_2(\text{CO})_6]$ complexes (M = Cr, Mo, or W). The whole preparation is carried out in a single reaction vessel, and usually gives high yields of pure products. This route may not be used to prepare $[(\eta\text{-indenyl})_2\text{M}_2(\text{CO})_6]$.

Introduction

Although the $[(\eta\text{-C}_5\text{H}_5)_2\text{M}_2(\text{CO})_6]$ complexes of chromium, molybdenum, and tungsten are well-known, their preparations are remarkably tedious. It is only for molybdenum that the direct reaction of the hexacarbonyl with dicyclopentadiene presents a feasible route to the desired compound, but it is fraught with difficulties [1]. For the other two metals, thermal decomposition of $[(\eta\text{-C}_5\text{H}_5)\text{Cr}(\text{CO})_3\text{H}]$ [2] or photochemical decomposition of $[(\eta\text{-C}_5\text{H}_5)\text{W}(\text{CO})_3\text{-CH}_2\text{Ph}]$ [3] have been used successfully.

We report here a synthesis of $[(\eta\text{-RC}_5\text{H}_4)\text{M}_2(\text{CO})_6]$ complexes (M = Cr, Mo or W) by oxidation of salts of their readily obtainable $[(\eta\text{-RC}_5\text{H}_4)\text{M}(\text{CO})_3]^-$ anions. It is simple, straight-forward, and appears to be widely applicable.

Experimental

All chemicals were purchased from the usual sources or obtained by standard methods. Reactions were carried out in dried and deoxygenated solvents under nitrogen.

A typical preparation, that of $[(\eta\text{-MeC}_5\text{H}_4)_2\text{W}_2(\text{CO})_6]$, is described below. The other complexes were obtained similarly.

A solution of sodium methylcyclopentadienide in diglyme (200 ml) was prepared from sodium (1.15 g 0.005 mol) and freshly cracked methylcyclopentadiene (6.0 ml, 0.07 mol). When all of the metal had dissolved, hexacarbonyltungsten (21.0 g, 0.6 mol) was added, and the reaction mixture heated to reflux for 30 minutes. The colour changed from pale pink to yellow. Carbonyltungsten sublimed from the reaction mixture into the reflux condensor and was returned at intervals. When no further reaction took place the excess hexacarbonyl was sublimed into the reflux condensor which was replaced by a clean one. Care should be taken to avoid dropping the unused carbonyltungsten into the flask. The reaction mixture was cooled and stirred. To it was added a solution of hydrated ferric sulphate (20 g) in water (250 ml) and acetic acid (15 ml) over a period of ca. 30 minutes. The colour changed from yellow to purple and fine purple crystals of $[(\eta\text{-MeC}_5H_4)_2W_2(CO)_6]$ precipitated. These were filtered off, washed with water, methanol and pentane, and dried. In this instance the product was both analytically and spectroscopically pure, and was obtained in 98% yield. Further purification could be effected by recrystallization from toluene/pentane mixtures, or from acetone.

The same procedure has been used to prepare $[(\eta\text{-C}_5H_5)_2M_2(CO)_6]$, $[(\eta\text{-MeC}_5H_4)_2M_2(CO)_6]$, and $[(\eta\text{-PhCH}_2C_5H_4)_2M_2(CO)_6]$ (M = Cr, Mo, and W). The product yields and purity were generally comparable to those quoted above except for M = Cr where they are lower, e.g. ca. 60% yields.

Discussion

The preparation of various $[RC_5H_4]^-$ salts in dry diglyme may be accomplished readily starting either from the alkyl- or arylcyclopentadiene [1], or a fulvene [4]. It is straightforward.

These cyclopentadienide salts, like $Na[(C_5H_5)]$ react in refluxing diglyme with $M(CO)_6$ (M = Cr, Mo, or W) to give $[(\eta\text{-dienyl})M(CO)_3]^-$ salts [5]. The reaction times depend on the metal M, but are generally less for molybdenum.

The final stage of the procedure, the oxidation of the carbonyl anion to the dimer $[(\eta\text{-dienyl})_2M_2(CO)_6]$, may be accomplished by a variety of mild oxidising agents. We routinely use an aqueous solution of ferric sulphate to which has been added a small amount of acetic acid. This reagent has an advantage in that the product precipitates from the resulting aqueous diglyme solution and may be filtered off. It has the minor disadvantage that the $M(CO)_6$ should be present in excess in the second stage in the reaction otherwise ferrocene may be formed in the final stage.

The purity of the products is generally high, often above 95% based on their analyses and IR spectra. As the impurities are usually hexacarbonylmetals, it is preferable that these be removed by sublimation at the second stage. Further purification may be effected by recrystallization, but often it is not necessary. The yields of crude products are routinely greater than 90% based on $[M(CO)_6]$ consumed for M = Mo or W, but are lower for M = Cr.

The reaction is generally applicable for the preparation of complexes of substituted cyclopentadienyl ligands. However, it may not be used for $[(\eta\text{-C}_9H_7)_2M_2(CO)_6]$ (C_9H_7 = indenyl) complexes and their derivatives. Although the $[(\eta\text{-C}_9H_7)M(CO)_3]^-$ anions may be obtained, they do not give the dimers on oxidation. Instead small amounts of $M(CO)_6$ are the only products which are insoluble in aqueous diglyme. We feel that this may be due to facile oxidation to $[(\eta\text{-}C_9H_7)M(CO)_2(\text{solvent})_n]^+$ species as has been described by Bottrill and Green using acetonitrile as the solvent [6].

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