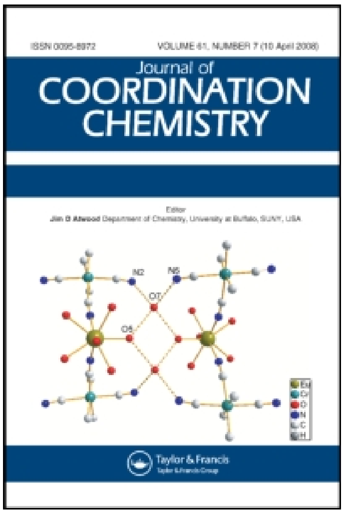

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NOTE

A NEW ROUTE TO MANGANESE AND RHENIUM CARBONYL TETRAFLUOROBORATE SALTS AND AN IMPROVED PROCEDURE FOR PREPARING THEIR PRECURSOR HYDRIDES

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Tetrafluoroborate salts of substituted Mn and Re carbonyls can be prepared in almost quantitative yield from their corresponding hydrides by the following reaction:

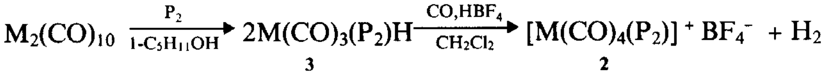
$$fac\text{-}(CO)_3M(P_2)H + HBF_4 + CO \longrightarrow [(CO)_4M(P_2)]^+BF_4^- + H_2$$

where P_2 are either the chelating phosphines, 1,2-bis(diphenylphosphino)ethane or 1,3-bis(diphenylphosphino)propane, or triphenylphosphine. The hydrides may be prepared from $M_2(CO)_{10}$ in a single reaction by refluxing the decacarbonyl in 1-pentanol in the presence of the desired phosphine.

KEYWORDS: hydride, manganese carbonyl, rhenium carbonyl, tetrafluoroborate, 1-pentanol

INTRODUCTION

In connection with our long term goal of comparing the properties and reactions of functional groups attached to the transition metals Mn and Re with those of the same functional groups bonded to carbon, we have sought routes to the preparation of the complexes *fac*-$M(CO)_3(P_2)Z$,**1**, where Z is one of a variety of functional groups, *viz.*, -CHO, -CO_2H, -CO_2R, -CH_2OR, CH_2X, etc. We have now developed a new methodology for preparing the cationic salts $[(CO)_4M(P_2)]^+BF_4^-$,**2**, which we[1] and others[2] have shown, react with various nucleophiles to give the desired complexes, **1**. We have also developed an improved synthesis of the hydrides **3** (the precursors of the cationic salts) from their corresponding decacarbonyls. The relevant reactions are shown in Scheme 1.



$$M_2(CO)_{10} \xrightarrow[\text{1-}C_5H_{11}OH]{P_2} \underset{\mathbf{3}}{2M(CO)_3(P_2)H} \xrightarrow[CH_2Cl_2]{CO,HBF_4} \underset{\mathbf{2}}{[M(CO)_4(P_2)]^+BF_4^-} + H_2$$

a, M = Mn; $P_2 = Ph_2P(CH_2)_2PPh_2$
b, M = Mn; $P_2 = Ph_2P(CH_2)_3PPh_2$
c, M = Re; $P_2 = Ph_2P(CH_2)_3PPh_2$
d, M = Mn; $P_2 = (PPh_3)_2$

Scheme 1

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EXPERIMENTAL AND RESULTS

Preparation of the tetrafluoroborate salts, **2a-d**: A stream of CO was bubbled through a solution of 2 mmol of **3a-d** in 100 ml of CH_2Cl_2 for about 0.5 h. Then 10 equivalents of $HBF_4 \cdot Et_2O$ was added to the solution and the CO bubbling continued while the solution was stirred vigorously. The progress of the reaction was monitored by IR and the reaction was complete after about 2 h. The solution was concentrated to about 25 ml and then diluted with 100 ml of diethyl ether. On cooling, the white microcrystalline salts, **2a-d**, precipitated; these were filtered and washed with 5 x 5 ml of diethyl ether. Yields were 96–98%. The melting points and spectral characteristics of compounds **2a-d** were consistent with those previously reported.[3] Monitoring with IR during the course of the reaction showed small quantities of the covalent tetrafluoroborate $M(CO)_3(P_2)F \cdot BF_3$ being formed, analagous to related complexes observed with Re;[4] however prolonged bubbling of CO converted these to the desired salts, **2**. Preparation of the hydrides, **3a-d**: To 100 ml of 1-pentanol were added five mmol of $M_2(CO)_{10}$, and ten mmol of P_2 (20 mmol of PPh_3) and the solution brought to reflux temperature (137°C) under an inert atmosphere. Periodic monitoring with IR showed the presence, in the case of the diphosphines, of the dimers $[M(CO)_3P_2]_2$,[5] and in the case of PPh_3, the dimer $]Mn(CO)_4PPh_3]_2$ as intermediate.[6] The reflux times requried for complete conversion to the hydrides **3a**, **3b**, **3c**, and **3d** were respectively, 2.5, 1.0, 8.0, and 10 h. On cooling to 0°C, the hydrides precipitated; these were filtered, then washed, first with 2 x 5 ml of 1-pentanol followed by 2 x 5 ml of hexane. No further purification was necessary for **3b** and **3c**. The yields of **3b** and **3c** were greater than 95%. Impure **3a** was dissolved in 100 ml of C_6H_6 and stirred with 1 g silica gel for about 15 min. The mixture was filtered and the filtrate was evaporated to dryness. The solid was recrystallized from 120 ml of 1-propanol. The light pink crystals were filtered, washed with 2 x 5 ml portions of hexane and air-dried giving a yield of 75% of **3a**. The impure hydride **3d** was dissolved in 200 ml of CH_2Cl_2 and the solution was filtered through a pad of Celite. The filtrate was concentrated to 50 ml, diluted with 50 ml of hexane and the solution cooled to 0°C. The pale yellow microcrystalline **3d** which precipitated was filtered, washed with 5 ml of hexane and air dried to give a yield of 50%. The melting points and spectral properties of the hydrides were consistent with those previously reported.[7]

DISCUSSION

Past preparations of the cationic BF_4 salts, **2**, involved the reaction of covalent halides $M(CO)_3P_2X$ with expensive $AgBF_4$ in the presence of CO.[1c,3b] We have found that the hydrides **3** can be treated with the more readily available and relatively inexpensive HBF_4 to liberate dihydrogen and give the desired **2** in almost quantitative yield, Scheme 1. Thus this important intermediate in the synthesis of functional groups bonded to Mn and Re is now available in two steps in good yield from the commercially available decacarbonyls of Mn and Re.

The improvement in the preparation of hydrides **3a** involves the substitution of 1-pentanol for 1-propanol, the previous alcohol of choice.[8] We have extended the use of pentanol to the preparation of the other hydrides, **3b-d**. The advantage of conducting the reaction at the boiling point of the 1-pentanol is that the relatively high reflux temperature shortens the reaction time, but more importantly, both the yield and purity of the hydrides are greater when 1-pentanol is used. The primary alcohol provides the hydrogen necessary for the reduction of the decacarbonyl and we have been able on occasion to identify pentanal (GLC) as the oxidation product although at the high temperatures it rapidly undergoes the aldol reaction as well as polymerization. The preparation of **3d** has been achieved previously by three less desirable methods. One method involved the ligand substitution of $HMn(CO)_5$ by PPh_3.[7a] A second preparation made use of metallic sodium to reduce $Mn_2(CO)_{10}$ in the presence of PPh_3.[9] A third synthesis[7d] consisted of refluxing a xylene solution of $Mn_2(CO)_{10}$ in the presence of PPh_3; it would be of interest to determine the source of hydrogen in this case. The relatively poor yield observed in the preparation of the hydride **3d** is probably due to decomposition and the formation of paramagnetic species.[6a] Similar but more severe difficulties were encountered in the preparation of Re $(CO)_3$(dppe)H.

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