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Preliminary communication

PHASE TRANSFER CATALYZED REDUCTIONS OF METAL CARBONYLS

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Summary

Reductions of metal carbonyl halides and some metal carbonyls by quaternary ammonium borohydrides in phase transfer catalyzed reactions are described. The method provides an efficient synthetic route to metal carbonyl anions from $BrMn(CO)_5$, $C_5H_5Mo(CO)_3Cl$, $Fe_3(CO)_{12}$ and $Co_2(CO)_8$ and yields the corresponding hydrides from $BrMn(CO)_4Ph_3$ and $C_5H_5Ru(CO)_2Br$.

Transition metal anions play a central role in the formation of metal—carbon and metal—metal bonds [1]. The conventional preparations of the anions have utilized sodium amalgam reductions of metal carbonyl dimers or metal carbonyl halides [2]; however, this method has sometimes led to products contaminated with mercury-containing side products [3]. In recent years, several new methods have been developed for anion syntheses. Thus, Ellis [4] has employed sodium—potassium alloy in combination with a metal carbonyl dimer whereas Shore [5] and Glaydsz [6] have used active metal hydrides with the dimers (or metal carbonyl halides [6]) to generate anions. The newer methods work efficiently and well, however all require the use of special equipment for handling moisture-sensitive reagents and all result in highly reactive alkali metal salts of the anions.

Prior to the use of sodium amalgam for anion synthesis, methods involving aqueous hydroxide were frequently used [7]. It is thus clear that, in many cases, the metal carbonyl anion is not readily converted to the corresponding hydride by exposure to water.

Noting that quaternary ammonium (Q) or bis(triphenylphosphine) iminium (PPN) cations have been effective in stabilizing reactive anions [4,8], we sought to develop a synthetic route to metal carbonyl anions which would yield Q salts directly. We have determined that two phase reactions in which $Q^+BH_4^-$ is generated in the aqueous phase and transferred to the organic phase (CH_2Cl_2) are effective methods for generating some metal carbonyl anions from metal carbonyls or metal carbonyl halides. Our results, to the present time, are summarized in Table 1. Although phase transfer catalyzed borohydride reductions of organic carbonyl compounds have been known for some time [9], this appears to be the first instance in which the technique has been applied to the reduction of metal carbonyls. Phase transfer of OH^- has recently been shown to be a useful way of generating some reduced metal carbonyl species [10].

Since the metal carbonyls and metal carbonyl halides are relatively stable in air and the Q salts are much less air sensitive than their alkali metal counterparts, the reactions can be performed without the necessity for either vacuum lines or dry boxes. Furthermore, the method is quite economical.

The phase transfer method compares well in reaction time and product yield with other synthetic routes to the anions. The cobalt anion is generated as rapidly and in as good yield by this method as by those of Shore [5] and Gladysz [6], but not quite as efficiently as the method of Ellis [4]. Generation of $Mn(CO)_5^-$ by our method requires more time than the method of Gladysz, but provides a nearly quantitative yield of product (determined as the triphenyltin derivative). The procedures of Shore, Ellis and Gladysz which employ $Mn_2(CO)_{10}$ are also faster, but not better in yield. The best previous synthesis of $HFe_3(CO)_{11}^-$ is the recent report [11] which described the preparation of the tetraethylammonium salt from $Fe(CO)_5$; the method requires about 15 h for completion and must be followed by cation exchange in order to obtain the quaternary ammonium salt (in 81% yield). Our method is not directly comparable since the starting materials are different; previous preparations of the anion from $Fe_3(CO)_{12}$ have resulted in very low yields [7]. Conversion of $C_5H_5Mo(CO)_3Cl$ to the anion by our method is somewhat slower than the method of Gladysz, but the yield (determined as the Ph_3Sn derivative) is somewhat better.

Many of the neutral metal carbonyl hydrides have been difficult to obtain and have usually been prepared by protonation of an alkali metal salt of the corresponding anion [12]; *cis*-$HMn(CO)_4PPh_3$ was prepared by this route [13] some years ago and also by ligand substitution of $HMn(CO)_5$ [14]. Both routes are rather long and proceed in low yields. Darensbourg [15] has recently prepared this hydride by reaction of the cation $Mn(CO)_5PPh_3^+$ with NaSH; the hydride was formed quickly but the yield was only moderate (50%). Reduction of the related cation *cis*-$Mn(CO)_4(OH_2)PPh_3^+$ by $NaBH_4$ also yields this hydride [16] (no yield was reported). Phase transfer catalyzed reduction of $C_5H_5Ru(CO)_2Br$ [17] also yields the hydride [18].

With the complexes which yield hydride products, we thought that water might be responsible for the alternate course of the reactions. However, reduction of $BrMn(CO)_4PPh_3$ by $Et_4N^+BH_4^-$ in non-aqueous media also provides the hydride. That the borohydride reductions of these halides yield hydride products whereas the halides reduced by $LiEt_3BH$ [6] yield anions is probably due to two factors: the lower basicity [19] of BH_4^- as compared to Et_3BH^- and the strongly basic nature [20] of $Mn(CO)_4PPh_3^-$ and $C_5H_5Ru(CO)_2^-$.

The reactions require an excess of $NaBH_4$ in order to proceed to completion at a reasonable rate. Gas evolution is observed in the PTC reactions and also when $BrMn(CO)_4PPh_3$ is converted to $HMn(CO)_4PPh_3$ by $Et_4N^+BH_4^-$ in non-aqueous media; the gas is probably B_2H_6 (together with H_2 in those reactions which yield non-hydridic products). Although we note that Parshall [21] obtained borane derivatives of some metal carbonyl anions (including $Mn(CO)_5^-$), such complexes are not stable in solution at ambient temperatures and are not observed in our reactions.

Work is continuing to establish the full scope of this simple and convenient technique.

General procedure for reductions

The phase transfer catalyst (benzyltriethylammonium chloride or tetraethylammonium bromide, see Table 1), 1.5 mmol, and sodium borohydride, 10.0 mmol, were dissolved in 50 ml of water and stirred with a solution of the metal carbonyl complex* (1 mmol) in CH_2Cl_2 (60—80 ml) under prepurified nitrogen. The progress of each reaction was determined by monitoring the disappearance of the carbonyl bands (in the IR spectrum) due to starting material. After the reaction was complete, the organic layer was separated, washed with three 60 ml portions of water and then dried over $MgSO_4$.

TABLE 1

REDUCTIONS OF METAL CARBONYL COMPLEXES [a]

Starting carbonyl	Reaction time (h)	Product formed	Product isolated	Yield (%)
$BrMn(CO)_5$	7	$BzEt_3N^+Mn(CO)_5^-$	$Ph_3SnMn(CO)_5$	95
$BrMn(CO)_4PPh_3$ [b]	3	$HMn(CO)_4PPh_3$	same	88
$Fe_3(CO)_{12}$	½	$Et_4N^+HFe_3(CO)_{11}^-$	same	90
$Co_2(CO)_8$	½	$Et_4N^+Co(CO)_4^-$ [c]	same	74
$Co_2(CO)_8$	½	$Et_4N^+Co(CO)_4^-$	$Ph_3SnCo(CO)_4$	83
$C_5H_5Ru(CO)_2Br$ [b]	17	$C_5H_5Ru(CO)_2H$	same	74
$C_5H_5Mo(CO)_3Cl$	2	$BzEt_3N^+C_5H_5Mo(CO)_3^-$	$C_5H_5Mo(CO)_3SnPh_3$	81

[a] All reactions were conducted at room temperature except that of $C_5H_5Ru(CO)_2Br$ which was at 40°C. [b] The catalyst was benzyltriethylammonium chloride. [c] This compound has been prepared previously [22] but its properties were not reported. The pale green solid has m.p. 145—146.5° and IR (ν(CO), CH_2Cl_2) 1890 cm^{-1} (broad). Found: C, 47.65; H, 6.68; N, 4.61. $C_{12}H_{20}O_4NCo$ calcd.: C, 47.85; H, 6.69; N, 4.65%.

Conversions to triphenyltin derivatives were accomplished by direct reaction of the CH_2Cl_2 solutions with Ph_3SnCl. Quaternary ammonium salts were purified by recrystallization from CH_2Cl_2/hexane or CH_2Cl_2/ether. All products had physical and spectral properties in accord with published data.

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*Solutions of $BrMn(CO)_5$ and $C_5H_5Mo(CO)_3Cl$ in CH_2Cl_2 were added dropwise to the PTC reagent and $NaBH_4$ in water.

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