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## Preliminary communication

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# Thallous tetracarbonylcobaltate; a convenient and versatile source of the tetracarbonylcobaltate anion

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The use of salts of the tetracarbonylcobaltate anion in the synthesis of the organometallic derivatives $RCo(CO)_4$ is a well established technique[1,2]. The most common preparative procedure for formation of $RCo(CO)_4$ employs the reduction of dicobalt octacarbonyl with a 1% sodium amalgam followed by reaction of the resulting $NaCo(CO)_4$ solution with an organic or organometallic halide[3]. The disadvantages in this procedure are the large amounts of mercury required for large scale preparations, occasional formation of $Hg[Co(CO)_4]_2$ as a side product, and the difficulty of preparing solutions containing exact amounts of $Co(CO)_4^-$.

Other preparations suffer from equivalent disadvantages. Reduction of salts of cobalt(II) in a carbon monoxide atmosphere[4] produces aqueous solutions containing a variety of other species in addition to $Co(CO)_4^-$. Reduction of dicobalt octacarbonyl with lithium[5] has proved unreliable in some instances[2]. Use of sodium in liquid ammonia[6] for reduction of dicobalt octacarbonyl requires special facilities for handling the solvent. The cleavage of dicobalt octacarbonyl with bases[7,8] is not a stoichiometrically simple reaction, and yields may vary with conditions.

Our studies of thallous tetracarbonylcobaltate suggest that this compound provides a convenient and versatile source of $Co(CO)_4^-$ which may be used in a variety of synthetic procedures. $TlCo(CO)_4$ forms in about two hours when dicobalt octacarbonyl in benzene or toluene is stirred under nitrogen with a piece of thallium metal. In most of our preparations 2.0 g of $Co_2(CO)_8$ in 15 ml of toluene was stirred with an approximately 3 g piece of thallium rod cleaned by a brief immersion in nitric acid. During the two hours of stirring the inital red solution turned yellow-brown. Following filtration of the reaction mixture to remove the thallium and whatever cobalt carbonate may have been present in the dicobalt octacarbonyl, yellow $TlCo(CO)_4$ was isolated as an 80% yield of a microcrystalline powder* by addition of 15 ml of pentane and cooling to −78°. The product was filtered from the solvent and washed with hexane to remove $Tl[Co(CO)_4]_3$

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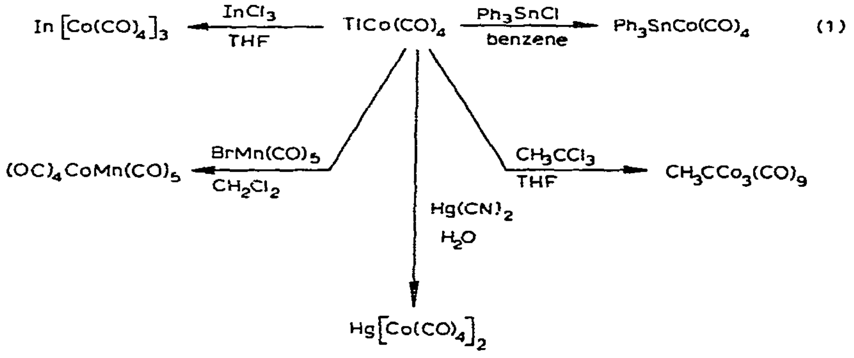
*Found: C, 12.6; Tl, 54.6. $TlCo(CO)_4$ calcd.: C, 12.8; Tl, 54.7%

which forms if small amounts of oxygen are present in the system. Larger crystals of $TlCo(CO)_4$ were isolated from preparations by covering the filtered toluene solution of $TlCo(CO)_4$ with 45 ml of hexane and allowing the two layers to diffuse together over a period of hours.

Solid $TlCo(CO)_4$ is stable in air for brief periods. The larger crystals may be handled in air for about two minutes without appreciable decomposition. $TlCo(CO)_4$ dissolves in all common solvents except saturated hydrocarbons. In solvents of high dielectric constant such as water, dimethylformamide, and dimethylsulfoxide a solution of solvated $Tl^+$ and $Co(CO)_4^-$ ions results[9]. In solvents of low dielectric constant such as benzene, dichloromethane, and tetrahydrofuran covalent molecules containing a weak Tl–Co bond are present.[9] This Tl–Co interaction does not affect the utility of $TlCo(CO)_4$ as a source of $Co(CO)_4^-$ as illustrated by the reactions presented in scheme 1.



The reactions of $TlCo(CO)_4$ with a variety of organic and organometallic halides are analogous to the same reactions with $NaCo(CO)_4$. The reaction of stoichiometric quantities of triphenyltin chloride and $TlCo(CO)_4$ in benzene at room temperature gave an immediate precipitate of TlCl and a solution from which $Ph_3SnCo(CO)_4$[10] could be isolated in 95% yield. A similar yield was obtained from the reaction in tetrahydrofuran, but in this solvent the reaction required about 2 hours to go to completion. From a tetrahydrofuran solution of $InCl_3$ and $TlCo(CO)_4$ a 50% yield of THF · $In[Co(CO)_4]_3$ was isolated. This compound was originally reported[11] as $In[Co(CO)_4]_3$, but subsequent studies[12] have shown that preparation in, or recrystallization from THF gives the THF adduct. $BrMn(CO)_5$ in $CH_2Cl_2$ reacted immediately with $TlCo(CO)_4$ giving a 60% yield of the mixed metal carbonyl $(OC)_4CoMn(CO)_5$[13]. Aqueous solutions of $Hg(CN)_2$ and $TlCo(CO)_4$ gave high yields of $Hg[Co(CO)_4]_2$[3] when mixed. Finally, refluxing $TlCo(CO)_4$ with $CH_3CCl_3$ in THF gave a modest yield of $CH_3CCo_3(CO)_9$ analogous to the reaction of $CH_3CCl_3$ with $NaCo(CO)_4$[14]. In all of these reactions the products were isolated and identified by their infrared spectra and melting points.

As demonstrated by the examples given above, $TlCo(CO)_4$ is a satisfactory source of $Co(CO)_4^-$. The physical and chemical properties of this compound and the simplicity of its preparation make it more convenient to use than the alkali metal or magnesium[15] salts of $Co(CO)_4^-$. The stability of $TlCo(CO)_4$ in air is not great, but crystalline $TlCo(CO)_4$ can be handled in air for short periods simplifying weighing of this reactant. Since $TlCo(CO)_4$ is soluble in non-basic solvents such as $CH_2Cl_2$ and benzene, reactions which are not possible in basic solvents may be run in non-basic media. The metathetical reaction of $TlCo(CO)_4$ and a halide as indicated in eq. 2 produces the insoluble TlX. Since the presence

$$TlCo(CO)_4 + RX \rightarrow RCo(CO)_4 + TlX \qquad (2)$$

of soluble halides as final products in other systems may limit conversion to the desired product[16] by a process analogous to eq. 3, the insolubility of TlX is a particularly useful feature of the $TlCo(CO)_4$ system.

$$RCo(CO)_4 + X^- \rightarrow RX + Co(CO)_4^- \qquad (3)$$

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