Journal of Organometallic Chemistry, 288 (1985) 219–223
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

THE REACTIONS OF [Co(η-C_5H_5)(CO)(X)(SnX_3)] COMPLEXES WITH NUCLEOPHILES

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(Received December 10th, 1984)

Summary

The extent of the reaction of [Co(η-C_5H_5)(CO)(X)(SnX_3)] with CO in chloroform at ca. 20°C and 1 atmosphere pressure is markedly dependent on X. Thus when X = Cl the reductive elimination of the tin(IV) halide, $SnCl_4$, is complete within 30 minutes and [Co(η-C_5H_5)$(CO)_2$] is formed almost quantitatively but reversibly. When X = I no detectable reaction takes place, but when X = Br an intermediate situation is observed, with both reagent and product present in the reaction mixture. On the other hand, the principal reactions of [Co(η-C_5H_5)(CO)(X)(SnX_3)] with both $(PhO)_3P$ and Ph_3P (L) are CO substitutions to give [Co(η-C_5H_5)(L)(X)(SnX_3)]. A limited amount of reductive elimination to give [Co(η-C_5H_5)$(CO)_2$] and [Co(η-C_5H_5)(CO)(L)] may occur, but because it is reversible these side-products soon disappear. The course of the reactions of [Co(η-C_5H_5)(L)(X)(SnX_3)] with CO depends on the P^{III} ligand L, and on X. Thus when L = $(PhO)_3P$ and X = Br the sole product is [Co(η-C_5H_5)$(CO)_2$] but when L = Ph_3P and X = Br [Co(η-C_5H_5)(CO)(Br)($SnBr_3$)] and then some [Co(η-C_5H_5)$(CO)_2$] are formed. [Co(η-C_5H_5)(PPh_3)(Cl)($SnCl_3$)] does not appear to react with CO. When [Co(η-C_5H_5)(CO)(X)(SnX_3)] (X = Cl or Br) are dissolved in donor solvents such as tetrahydrofuran, acetone or acetonitrile, some reversible formation of [Co(η-C_5H_5)$(CO)_2$] takes place, but the sole isolable products have the empirical formulae [Co(η-C_5H_5)$(\text{solvent})_2$(X)(SnX_3)]. With pyridine (py) or 2,2′-bipyridyl (bipy), these last give blue [Co$(py)_4$(X)(SnX_3)] and brown [Co$(bipy)_2$(OC_4H_8)(X)(SnX_3)] respectively.

Introduction

Recent publications on the reactions of $Pt^{II}SnCl_3$ complexes with carbon monoxide [1] prompts us to report our work on the reactions of [Co(η-C_5H_5)(CO)(X)(SnX_3)] derivatives (X = Cl, Br, or I) with nucleophiles such as CO, phosphines, phosphites, donor solvents such as tetrahydrofuran, acetone or

0022-328X/85/$03.30

acetonitrile, and the strong nitrogen bases pyridine or 2,2′-bipyridyl. The behaviour that we observed is often fundamentally quite different from that reported for other systems, since it often involves the reductive elimination of SnX_4, especially under the influence of soft nucleophiles such as CO.

The origin of this work lies in our studies of the reactions of $[Co(\eta\text{-}C_5H_5)(L)X_2]$ and $[Fe(CO)_3(L)X_2]$ complexes with tin(II) halides SnY_2 (X and Y = halogens; L = CO or Ph_3P). Some $[Fe(CO)_3(PPh_3)(X)(SnXY_2)]$ derivatives reacted with Ph_3P to give *trans*-$[Fe(PPh_3)_2(CO)_3]$, and some of the $[Co(\eta\text{-}C_5H_5)(CO)(X)(SnXY_2)]$ complexes decomposed in solution in ways that we did not understand [2].

Experimental

Previously published methods were used to prepare $[Co(\eta\text{-}C_5H_5)(CO)_2]$ [3] and $[Co(\eta\text{-}C_5H_5)(CO)(X)(SnX_3)]$ (X = Cl, Br, or I) [4]. Other chemicals were purchased.

Unless otherwise stated, reactions were carried out at room temperature under nitrogen. Tetrahydrofuran, benzene or chloroform were purified by refluxing over calcium hydride and, for tetrahydrofuran also over sodium benzophenone. Acetonitrile was refluxed over calcium sulfate. All solvents were distilled before use.

IR spectra were measured on a Perkin–Elmer 337 spectrometer between 400 and 4000 cm^{-1}, and analyses were carried out in the Analytical Laboratory of University College, Dublin.

Reactions of $[Co(\eta\text{-}C_5H_5)(L)(X)(SnX_3)]$ (L = CO, $(PhO)_3P$, or Ph_3P; X = Cl, Br, or I) with L in chloroform solution

CO gas was bubbled through a solution of $[Co(\eta\text{-}C_5H_5)(CO)(X)(SnX_3)]$ (0.5 g; X = Cl, Br, or I) in chloroform (20 ml). The reactions were monitored by IR spectroscopy, but no products were isolated. The reactions between CO and other $[Co(\eta\text{-}C_5H_5)(L)(X)(SnX_3)]$ complexes were studied similarly for L = $(PhO)_3P$ when X = Br, and for L = Ph_3P with X = Cl and Br.

Equimolar amounts of $[Co(\eta\text{-}C_5H_5)(CO)(X)(SnX_3)]$ (0.2 g; X = Cl, Br or I) and the phosphorus ligand L = $(PhO)_3P$ or Ph_3P were dissolved in chloroform (20 ml). The reactions, which were fast, were monitored by IR spectroscopy until they were complete. Then the mixtures were filtered and the solvents removed at reduced pressures. Recrystallization of the residues from dichloromethane/hexane mixtures gave high yields (60–80%) of the known $[Co(\eta\text{-}C_5H_5)(PPh_3)(X)(SnX_3)]$ [2] (X = Cl, Br, or I) and a 45% yield of $[Co(\eta\text{-}C_5H_5)\{P(OPh)_3\}(Br)(SnBr_3)]$ (black crystals; dec. pt. 162°C; Anal. Found: C, 31.5; H, 2.6. $C_{23}H_{20}Br_4CoO_3PSn$ calcd.: C, 31.6; H. 2.3%.

Reactions of $[Co(\eta\text{-}C_5H_5)(CO)(X)(SnX_3)]$ with nucleophilic solvents

$[Co(\eta\text{-}C_5H_5)(CO)(X)(SnX_3)]$ (0.5 g; X = Cl or Br) were dissolved in 20 ml of the solvent (tetrahydrofuran, acetonitrile, or acetone). The reactions were monitored by IR spectroscopy until they were complete and no CO-containing species were present. The mixtures were then filtered and the solvents removed at reduced pressure. The residues were recrystallized from dichloromethane/hexane mixtures to give the green products. Unfortunately, high yields of analytically pure samples could only be obtained for "$[Co(\eta\text{-}C_5H_5)(OC_4H_8)_2(Br)(SnBr_3)]$" (dec. pt. 162°C. Anal. Found: C, 22.4; H, 2.8; Br, 45.3. $C_{13}H_{21}Br_4CoO_2Sn$ calcd.: C, 22.1; H, 3.0;

Br, 45.3%). and "[Co(η-C_5H_5)($OCMe_2$)$_2$(Br)($SnBr_3$)]" (dec. pt. 154°C. Anal. Found: C, 20.0; H, 1.8; Br, 47.0. $C_{11}H_{17}Br_4CoO_2Sn$ calcd.: C, 19.5; H, 1.6; Br, 47.2%.

If, when the above reactions were complete, pyridine (py 2 mol) or 2,2′-bipyridyl (bipy 2 mol) were added to the reaction mixtures, blue crystals of [Co(py)$_4$(X)(SnX_3)] and brown [Co(bipy)$_2$(solvent)(X)(SnX_3)] were obtained, but the only ones which were analytically pure were [Co(py)$_4$(Br)($SnBr_3$)] (blue crystals, dec. pt. 188°C, Anal. Found: C, 29.4; H, 2.5; N, 6.6; Br, 39.9. $C_{20}H_{20}Br_4CoN_4Sn$ calcd.: C, 29.5; H, 2.5; N, 6.9; Br, 39.4%). [Co(bipy)$_2$(OC_4H_8)(Br)($SnBr_3$)] (brown crystals, dec. pt. 171°C, Anal. Found: C, 33.1; H, 3.0; N, 6.4; Br, 36.0. $C_{24}H_{28}Br_4O_4N_4OSn$ calcd.: C, 32.7; H, 2.7; N, 6.4; Br, 36.3%) and [Co(bipy)$_2$(OC_4H_8)(Cl)($SnCl_3$)] (brown crystals, dec. pt. 174°C, Anal. Found: C, 39.9; H, 3.7; N, 7.9; Cl, 21.4. $C_{24}H_{24}Cl_4CoN_4OSn$ calcd.: C, 41.0; H, 3.4; N, 7.9; Cl, 20.2%).

Results and discussion

If a solution of [Co(η-C_5H_5)(CO)(Cl)($SnCl_3$)] in chloroform is kept at room temperature the absorption band due to its ν(CO) vibration ($\sim$ 2170 cm^{-1}) disappears during ca. 90 mins. At first it is partially replaced by those due to [Co(η-C_5H_5)(CO)$_2$] ($\sim$ 1955 and 2020 cm^{-1}), but these also finally disappear. CO loss also takes place in the solid state, but more slowly. When CO gas is passed through this aged solution, the adsorption bands due to [Co(η-C_5H_5)(CO)(Cl)($SnCl_3$)] are regenerated rapidly and then replaced by those due to [Co(η-C_5H_5)(CO)$_2$]. This last reaction is complete within ca. 70 mins. It involves the reductive elimination of $SnCl_4$ and is the reverse of that used to prepare [Co(η-C_5H_5)(CO)(Cl)($SnCl_3$)] [4]. It is possible that the CO-free complex is a polymer similar to [Co_2(η-C_5Me_4Et)$_2$(μ-Cl)$_2Cl_2$] [5]. Our observations may be summarised by the following interconnected equilibria:

$$[\mathrm{Co}(\eta\text{-}\mathrm{C_5H_5})(\mathrm{CO})_2] + \mathrm{SnCl_4} \rightleftharpoons [\mathrm{Co}(\eta\text{-}\mathrm{C_5H_5})(\mathrm{CO})(\mathrm{Cl})(\mathrm{SnCl_3})] + \mathrm{CO} \rightleftharpoons \frac{1}{n}[\{\mathrm{Co}(\eta\text{-}\mathrm{C_5H_5})(\mathrm{Cl})(\mathrm{SnCl_3})\}_n] + 2\mathrm{CO}$$

The complexes [Co(η-C_5H_5)(CO)(X)(SnX_3)] are much more stable towards dissociative loss of CO when X = Br or I than when X = Cl. They are also more stable towards reductive elimination of SnX_4. Thus there is no detectable reaction between [Co(η-C_5H_5)(CO)(I)(SnI_3)] and CO, and CO does not convert [Co(η-C_5H_5)(CO)(Br)($SnBr_3$)] completely to [Co(η-C_5H_5)(CO)$_2$] so that these two complexes co-exist in equilibrium in the reaction mixture.

The susceptibility of [Co(η-C_5H_5)(CO)(X)(SnX_3)] to CO-induced reductive elimination of SnX_4 decreases along the series X = Cl > Br > I. It has been shown that the susceptibility of [Fe(PPh_3)(CO)$_3$(X)(SnY_2X)] to the Ph_3P-induced reductive elimination of SnX_2Y_2 also increases as the electron-withdrawing nature of X and Y increases [2]. It was suggested that there may be a Lewis acid–Lewis base interaction between the SnX_3 ligand and the X ligand *cis* to it which facilitates the loss of SnX_4 (or SnX_2Y_2). Such an interaction would account for our present observations, as the Lewis acid strength of the tin centre would be expected to decrease for X = Cl > Br > I.

On the other hand the dominant reactions between [Co(η-C_5H_5)(CO)(X)(SnX_3)]

and L = $(PhO)_3P$ (for X = Br only) and Ph_3P (for X = Cl, Br, or I) are CO-substitutions which are rapid and complete within ca. 15 minutes to give $[Co(\eta\text{-}C_5H_5)(L)(X)(SnX_3)]$ derivatives, normally in high yields. In all instances except when X = I small amounts of $[Co(\eta\text{-}C_5H_5)(CO)_2]$ were observed, and the formation of $[Co(\eta\text{-}C_5H_5)(PPh_3)(Cl)(SnCl_3)]$ was also accompanied by the appearance of even smaller amounts of $[Co(\eta\text{-}C_5H_5)(CO)(PPh_3)]$. The side products, which were detected by monitoring the reactions using IR spectroscopy, disappeared during the reaction. Also, they are formed in relatively greater amounts if the reactions are carried out using higher reactant concentrations. Their most probable source is the reversible reductive elimination of SnX_4 induced by liberated CO and added Ph_3P which give $[Co(\eta\text{-}C_5H_5)(CO)_2]$ and $[Co(\eta\text{-}C_5H_5)(CO)(PPh_3)]$ respectively.

The difference in behaviour between $(PhO)_3P$ or Ph_3P and CO in their reactions with $[Co(\eta\text{-}C_5H_5)(CO)(X)(SnX_3)]$ may be more apparent than real. The CO ligands of the $[Co(\eta\text{-}C_5H_5)(CO)(X)(SnX_3)]$ appear to be very labile and are probably replaced readily by a wide range of nucleophiles. However, it is only in the case of CO that reductive elimination can take place as well as the inevitable CO exchange. Both $(PhO)_3P$ and Ph_3P are probably too bulky to bring about both processes and the final products, $[Co(\eta\text{-}C_5H_5)(L)_2]$, are probably very crowded with their two *cis*-phosphorus(III) ligands. On the other hand, Ph_3P does bring about the reductive elimination of $SnBr_2Cl_2$ from $[Fe(PPh_3)(CO)_3(Br)(SnCl_2Br)]$ as the final product $[Fe(PPh_3)_2(CO)_3]$ has two phosphine ligands mutually *trans* and is not overcrowded [2].

Alternatively the reaction between the phosphorus(III) ligands L and $[Co(\eta\text{-}C_5H_5)(CO)(X)(SnX_3)]$ may proceed via the initial displacement of X^- or SnX_3^- to give $[Co(\eta\text{-}C_5H_5)(CO)(L)(Y)]Z$ (Y^- or $Z^- = X^-$ or SnX_3^-) which cannot undergo reductive elimination (see below). This then undergoes Z^- displacement of CO to give $[Co(\eta\text{-}C_5H_5)(L)(X)(SnX_3)]$. There are many examples of each of these reactions to be found in the literature [6,7,8]. However, in view of the lability of the CO ligand in the $[Co(\eta\text{-}C_5H_5)(CO(X)(SnX_3)]$ complexes, we feel that this is probably not an important reaction pathway.

If CO (1 atm.) is passed through a chloroform solution of the $[Co(\eta\text{-}C_5H_5)(L)(X)(SnX_3)]$ complexes, the course of the reaction depends on both L and X. Thus when L = $(PhO)_3P$ and X = Br a rapid reaction takes place to give $[Co(\eta\text{-}C_5H_5)(CO)_2]$ as the sole detectable product. In the light of our other results, it is clear that this can only take place if the CO-induced reductive-elimination of $SnBr_4$ precedes $(PhO)_3P$/CO exchange giving, in turn, $[Co(\eta\text{-}C_5H_5)(CO)\{P(OPh)_3\}]$ and $[Co(\eta\text{-}C_5H_5)(CO)_2]$. The phosphorus(III) ligands, L, in $[Co(\eta\text{-}C_5H_5)(CO)(L)]$ are labile and can be displaced by CO at 1 atm/20°C e.g. when L = Ph_3P conversion to $[Co(\eta\text{-}C_5H_5)(CO)_2]$ is complete within ca. 25 minutes. On the other hand $[Co(\eta\text{-}C_5H_5)(PPh_3)(Br)(SnBr_3)]$ reacts with CO by a rapid CO/Ph_3P exchange to give $[Co(\eta\text{-}C_5H_5)(CO)(Br)(SnBr_3)]$, which then undergoes a slower, partial reductive elimination of $SnBr_4$ (see above). $[Co(\eta\text{-}C_5H_5)(PPh_3)(Cl)(SnCl_3)]$ fails to react with CO; perhaps the more strongly electron-withdrawing Cl and $SnCl_3$ ligands decrease the lability of the Co–P bond. It is noteworthy that CO is able to bring about the reductive elimination from $[Co(\eta\text{-}C_5H_5)(L)(Br)(SnBr_3)]$ when L = $(PhO)_3P$ or CO, but not when L = Ph_3P. The reasons for this are not clear at the present time.

The dissolution of $[Co(\eta\text{-}C_5H_5)(CO)(X)(SnX_3)]$ in donor solvents such as tetrahydrofuran, acetone, or acetonitrile results in a colour change from brown to green. Some [Co(η-C_5H_5)(CO)$_2$], detectable by IR spectroscopy, is formed at high substrate concentrations but not at low ones. It probably arises from the reversible attack of liberated CO on the unreacted substrate and it slowly disappears as all of the liberated CO is carried off in the nitrogen gas flow. From the reaction solutions could be isolated green solids which analysed as [Co(η-C_5H_5)(solvent)$_2$(X)(SnX_3)] when X = Br and solvent = tetrahydrofuran or acetone. When X = Cl or the solvent is acetonitrile, the products are not very stable and did not give consistent analyses. It is possible that in this reaction the solvent has displaced CO and either $[SnX_3]^-$ or X^- ions to give $[Co(\eta\text{-}C_5H_5)(\text{solvent})_2Y]^+ Z^-$ salts (Y or Z = X or SnX_3) in which the cobalt atom has an 18-electron configuration (cf. the reaction of [Co(η-C_5H_5)(CO)X_2] with 2,2′-bipyridyl (bipy) which gives [Co(η-C_5H_5)(bipy)(X)(SnX_3)] [7]). However in view of the known disproportionation of [Co_2(η-C_5H_5)$_2I_4$] in weakly coordinating solvents such as tetrahydrofuran or acetone [9] it is equally possible that we observed the formation of similar salts which contained the $[Co(\eta\text{-}C_5H_5)_2]^+$ ions. The colour changes during the reactions are consistent with this second suggestion, as is the formation of blue [Co(py)$_4$(X)(SnX_3)] and brown [Co(bipy)$_2$(tetrahydrofuran)(X)(SnX_3)] on the addition of pyridine and 2,2′-bipyridyl to the reaction mixtures. These reactions were not investigated further.

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