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Preliminary communication

THE USE OF SO_2Cl_2 IN ORGANOMETALLIC CHEMISTRY. CONVENIENT HIGH YIELD SYNTHESES OF $[Fe(\eta\text{-}C_5H_5)(CO)_3][FeCl_4]$ AND $[M(CO)_5Cl]$ (M = Mn or Re)

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Summary

Depending on the substrate and the reaction conditions, SO_2Cl_2 is a useful reagent which brings about either chlorination or the formation of cationic species on reaction with transition metal carbonyl complexes.

During the course of our studies of the reactions of transition metal carbonyl complexes with electrophiles [1], we have investigated the properties of sulphur chlorides and have found that SO_2Cl_2 is a very useful reagent. It is a mild chlorinating agent under some circumstances, but under others it brings about the formation of cationic species which are often difficult to prepare by other routes.

Thus, freshly distilled SO_2Cl_2 reacts instantaneously with $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$ (mole ratio 1/1) in dichloromethane solution at room temperature to give $[Fe(\eta\text{-}C_5H_5)(CO)_2Cl]$ in high yield. In benzene solution and with a reactant mole ratio of 1.7/1 the products are $[Fe(\eta\text{-}C_5H_5)(CO)_2Cl]$ (35% of Fe) and $[Fe(\eta\text{-}C_5H_5)(CO)_3][FeCl_4]$ (60% of Fe) which are readily separable. If this last reaction is carried out in the presence of one mole of Ph_3P the purification of the crude $[Fe(\eta\text{-}C_5H_5)(CO)_3][FeCl_4]$ by recrystallization from acetonitrile is facilitated. The role of the Ph_3P is not clear but it is converted to Ph_3PO. The fate of the SO_2 moiety is not known, but it is not released as the free gas. The simplicity of this reaction makes it a very attractive method for preparing $[Fe(\eta\text{-}C_5H_5)(CO)_3]^+$ salts (and their MeC_5H_4 or C_9H_7 counterparts) although the presence of $[FeCl_4]^-$ as the counter-anion may be disadvantageous.

Similar results have been obtained with derivatives of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$ containing one or more phosphite or isocyanide ligands, and with

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$[Ru_2(\eta\text{-}C_5H_5)_2(CO)_4]$ which with SO_2Cl_2 in benzene solution gives a salt of the $[Ru(\eta\text{-}C_5H_5)(CO)_3]^+$ cation. However we have not been able to identify the anion.

Somewhat different results are obtained from the reactions of SO_2Cl_2 with $[M_2(CO)_{10}]$ (M = Mn or Re) which in either dichloromethane or benzene solutions give high yields of $[M(CO)_5Cl]$ (91–97%) as the sole products. This represents a much simpler procedure for the preparation of these halide complexes than that normally employed [2].

$[Re_2(CO)_8(PPh_3)_2]$ gives a mixture of *cis*- and *trans*-$[Re(PPh_3)(CO)_4Cl]$ with the *trans*-isomer increasing in importance when the reaction is carried out at 0°C rather than room temperature, or in benzene or toluene solutions rather than dichloromethane. Although this *cis*/*trans* mixture may be converted to pure *cis*-$[Re(PPh_3)(CO)_4Cl]$ on refluxing in chloroform for 2 h, its recrystallization from benzene/petroleum ether mixtures affords the *trans*-isomer as the predominant product. This represents the first report of *trans*-$[Re(PPh_3)(CO)_4Cl]$. The *cis*-isomer has been obtained by an alternative route [3] and both *cis*- and *trans*-$[Re(PPh_3)(CO)_4Br]$ have been prepared [4].

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