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THE REACTION OF $Cp_2M(CO)H$ (M = Nb OR Ta) COMPLEXES WITH ACYL CHLORIDES, A NEW WAY TO TRANSFORM ACYL CHLORIDES INTO ALDEHYDES *

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Summary

$Cp_2M(CO)H$ complexes react immediately with acyl chlorides to give the chloro complexes $Cp_2M(CO)Cl$ and aldehydes. This reaction can also be applied to dichlorides.

It is known that dicarbonyldi-η^5-cyclopentadienyltitanium(II), $Cp_2Ti(CO)_2$, reacts with acyl chlorides at room temperature, in toluene solution, losing the two CO groups to give the corresponding acylchlorotitanium(IV) derivatives [1].

$$Cp_2Ti(CO)_2 + RCOCl \xrightarrow{-2CO} Cp_2Ti(COR)Cl$$

This reaction has been interpreted by Fachinetti as an S_N2 like substitution involving nucleophilic attack by the titanium(II) species on the electrophilic carbon of the acyl chloride. Such nucleophilic behaviour can be understood only via the "coordinative assistance" of the two CO groups in the rate-limiting step of the reaction. This reaction can also be considered as an insertion of the 14-electron unit "Cp_2Ti" acting as a carbenoid reagent. The electronic arrangement of carbonyldi-η^5-cyclopentadienyl-tantalum or -niobium hydride, $Cp_2M(CO)H$, has a formal analogy with that of $Cp_2Ti(CO)_2$. But the two 18-electron species $Cp_2M(CO)H$ (M = Ta or Nb) must have more typical nucleophilic or basic properties. We have effectively characterized the salts of the $Cp_2M(CO)H_2^+$ cation [2]. In some ways, $Cp_2Ti(CO)_2$ and $Cp_2Ta(CO)H$ have a formal analogy with carbenes and amines, respectively.

Moreover, we have now found that the behaviour of $Cp_2M(CO)H$ (M = Ta or Nb) towards acyl chlorides is quite different to the behaviour of $Cp_2Ti(CO)_2$ towards the same electrophiles.

The $Cp_2M(CO)H$ complexes are easily prepared through carbonylation of the

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trihydrides Cp_2MH_3 [3]. They react immediately with acyl chlorides to give the chloro complex $Cp_2M(CO)Cl$ and aldehydes according to the following equation:

$$Cp_2M(CO)H + RCOCl \rightarrow Cp_2M(CO)Cl + RCHO \tag{1}$$

The reaction takes place in most of the usual solvents, but diethyl ether appears to be the most suitable. Many acyl chlorides and aldehydes are soluble in this solvent and $Cp_2M(CO)Cl$ precipitates.

Interest, scope and mechanism of the reaction

Several methods are available for the partial reduction of acyl chlorides to aldehydes. The classical Rosenmund method has some drawbacks: it is not applicable to dichlorides; the chemiselectivity is low and the yields are variable.

The reduction can also be carried out with lithium tri-t-butoxylammonium hydride [4] with sodium or copper tetrahydroborate or with the complex copper cyanotrihydroborate [5]. The same conversion to aldehydes has also been achieved with anionic carbonyliron complexes [6]. Many of these methods are not exempt from disadvantages (limited scope of applicability, contamination of the aldehyde, or incompatibility with the presence of other reducible groups).

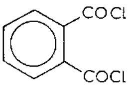
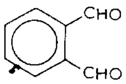
The palladium-catalysed reaction of tributyltin hydride with acyl chlorides gives a mild, selective and more general route to aldehydes [7]. However, for the reduction of α,β-unsaturated acyl chlorides it is necessary to use strictly the equivalent amount of tributyltin hydride to avoid the formation of the saturated aldehyde. Moreover, this recent method is not applicable to dichlorides which are capable of undergoing ring-chain tautomerism. For example, succinyl dichloride affords exclusively 4-chloro-4-butyrolactone. It must also be pointed out that this method is inexpensive only if the catalyst is recovered.

To date, we have found that the transformation reaction 1 may be applied to acid chlorides of different types (aliphatic, aromatic and metallocenic). It tolerates the presence of other reducible functions, such as NO_2 or CH=CH, and can also be used to synthesize *o*-phthalaldehyde, starting from the corresponding dichloride (Table 1).

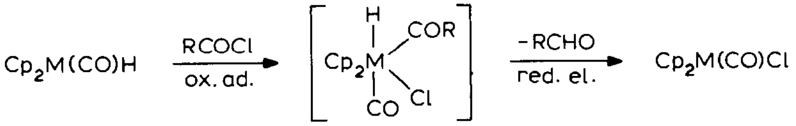
Several mechanisms for reaction 1 can be suggested. The simplest one would be to consider this reaction as the resultant of two classical, elementary processes of

TABLE 1

REDUCTION OF RCOCl WITH $Cp_2M(CO)H$ (M = Nb or Ta)

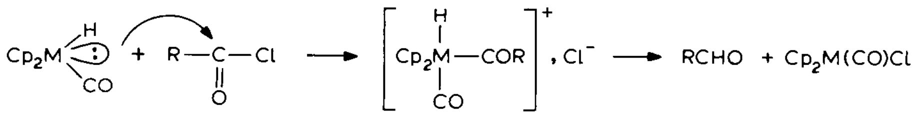
RCOCl	RCHO	ν(CO) (cm^{-1})
$(CH_3)_3CCOCl$	$(CH_3)_3CCHO$	1742
$C_6H_5CH_2COCl$	$C_6H_5CH_2CHO$	1734
C_6H_5COCl	C_6H_5CHO	1713
(2) $4\text{-}NO_2C_6H_4COCl$	$4\text{-}NO_2C_6H_4CHO$	1713
$C_6H_5CH{=}CHCOCl$	$C_6H_5CH{=}CHCHO$	1787
$(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4COCl)Fe$	$(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4CHO)Fe$	1786
		1701, 1720

organometallic chemistry: an oxidative addition followed by reductive elimination:



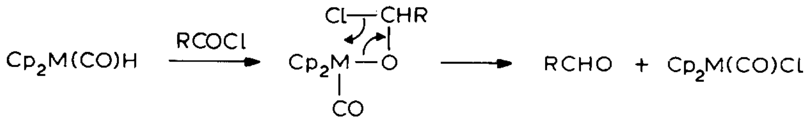
The first step seems unlikely from both steric and electronic considerations, since the intermediate state would be a 20-electron species and highly congested from a coordinative point of view.

It is more likely that the rate-determining step involves nucleophilic attack on the carbonyl to generate a cationic species, which then undergoes reductive elimination with formation of the aldehyde:



Alternatively, one may suggest the intermediate formation of $Cp_2M(CO)COR$ with subsequent cleavage of the metal–COR bond by HCl. The first step of the reaction is then formally analogous to the reaction of an acyl chloride with an amine (cf. suggestion above.)

A final possibility would be a heterohydrometallation followed by a halogeno β-elimination:



One elementary process analogous to the first step has been proposed by Sato et al. [8], to rationalize the catalytic cycle observed in the reduction of carboxylic acids to aldehydes by Cp_2TiCl_2-catalysed Grignard reactions:

The second step is rather unlikely since it assumes cleavage of the metal–oxygen bond. However, it has recently been suggested for the analogous (α-chloroalkoxy)tin species ($R'_3SnOCHRCl$) [9].

We are currently studying the scope and the exact mechanism of this reaction.

Experimental

The carbonyl complexes $Cp_2M(CO)H$ (M = Ta [3a], Nb [3b]) were prepared by literature methods. All operations were carried out in an argon atmosphere with exclusion of molecular oxygen. Infrared spectra were recorded on a Perkin–Elmer 580 B spectrometer. NMR spectra were obtained with a JEOL FX 100 spectrometer.

In a typical reaction, a solution of acyl chloride (1 mmol) in 20 ml of diethyl ether was added, dropwise, to a solution of $Cp_2M(CO)H$ (1 mmol) in 40 ml of diethyl ether. The solution changed colour immediately from violet to greenish; the green, fine, crystalline precipitate obtained was separated by filtration and identified as $Cp_2M(CO)Cl$: M = Nb: ν(CO) 1926 cm^{-1} (toluene; ^1H NMR: 4.81 ppm (C_6D_6); M = Ta: ν(CO) 1908 cm^{-1} (toluene); ^1H NMR: 4.72 ppm (C_6D_6).

The mother liquid was evaporated under atmosphere pressure; the crude aldehyde was isolated in 90% yield and characterized by its spectroscopic data (IR, ^1H NMR, mass spectrometry).

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References

1 G. Fachinetti and C. Floriani, J. Chem. Soc. Dalton Trans., (1977) 2297.
2 To be published.
3 (a) M.L.H. Green and J. Jousseaume, J. Organomet. Chem., 193 (1980) 339; (b) J. Labinger, Adv. Chem. Ser., 149 (1978) 167.
4 H.C. Brown and B.C. Subba Rao, J. Am. Chem. Soc., 80 (1958) 5377.
5 G.W.J. Fleet and P.J.C. Harding, Tetrahedron Lett., (1979) 975; T.N. Sorrel and P.S. Pearlman, J. Org. Chem., 45 (1980) 3449; R.O. Hutchins and M. Markowitz, Tetrahedron Lett., 21 (1980) 813.
6 T.E. Cole and R. Petit, Tetrahedron Lett., (1977) 781.
7 P. Four and F. Guibe, J. Org. Chem., 46 (1981) 4439.
8 F. Sato, T. Jinbo and M. Sato, Synthesis, (1981) 871.
9 J. Lusztyk, E. Lusztyk, B. Maillard and K.U. Ingold, J. Am. Chem. Soc., 106 (1984) 2293.