Journal of Organometallic Chemistry, 221 (1981) C21—C24
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

PHOTOCHEMICALLY INDUCED TRANSMETHYLATION IN TRANSITION METAL COMPOUNDS USING METHYLTITANOCENES

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(Received July 21st, 1981)

Summary

Photolysis of dimethyltitanocene and chloromethyltitanocene in the presence of another transition metal complex leads to methyl transfer from titanium to the transition metal and to other ligand transfer reactions. These reactions are thought to proceed by a free radical pathway.

Previous studies on the photolytic degradation of Cp_2TiR_2 (Cp = cyclopentadienyl, C_5H_5; R = methyl or phenyl group) have shown that the initial step involves homolytic cleavage of the Ti—C σ bond with loss of alkyl radicals in recombination reactions to give hydrocarbons [1], in the case of $Cp_2Ti(CH_3)_2$ (I) the methyl radicals formed abstract hydrogen from the medium to give methane and other gaseous products. Cp radicals were produced by photolysis of Cp_2TiCl_2 also [2]. All these radicals have been characterized by their spin adduct spectra, but no useful reactions involving them have been reported so far. We show below that irradiation of I or Cp_2TiCH_3Cl (II) in presence of another transition metal compound leads to methyl transfer from titanium to the transition metal.

The transition metal compounds we found suitable for accepting the alkyl groups and the alkylated products formed are shown in Table 1. They fall into three classes according to the chemical processes involved:

(a) Transition metal halogen compounds. With these compounds, methyl transfer proceeds by simple metathetical exchange. We postulate for these reactions the following mechanism:

$$Cp_2Ti(CH_3)_2 \xrightarrow{h\nu} Cp_2Ti(CH_3) + CH_3^{\bullet} \qquad (1)$$

$$(M)Cl + CH_3^{\bullet} \rightarrow (M)CH_3 + Cl^{\bullet} \qquad (2)$$

TABLE 1

TRANSITION METAL COMPOUNDS AND THEIR METHYL DERIVATIVES PRODUCED PHOTOCHEMICALLY BY TRANSMETHYLATION WITH DIMETHYLTITANOCENE (For cationic compounds, $[BPh_4]^-$ as counterion, L = trimethylphosphine; L′ = triethylphosphine)

Compound	Methylation product	$\nu(CO)$ (cm^{-1})	Solvent	$\delta(M—CH_3)$[a] (ppm)
(a) Halogen—methyl exchange				
$MnBr(CO)_5$	$MnCH_3(CO)_5$			
$ReBr(CO)_5$	$ReCH_3(CO)_5$			
mer-trans-$MnBr(CO)_3L'_2$	$MnCH_3(CO)_3L'_2$	1998vw, 1904.5 vs, 1878s	Hexane	-0.50(t)
cis-cis-trans-$FeCl_2(CO)_2L_2$	$Fe(CH_3)Cl(CO)_2L_2$			
	$Fe(CH_3)_2(CO)_2L_2$			
$FeCl_2(CO)_2L'_2$	$Fe(CH_3)Cl(CO)_2L'_2$			
$RuCl_2(CO)_2L_2$	$Ru(CH_3)Cl(CO)_2L_2$	2021s, 1951s	Hexane	0.18(t)
mer-trans-$IrCl_3(CO)(P\phi_3)_2$	$Ir(CH_3)Cl_2(CO)(P\phi_3)_2$			
	$Ir(CH_3)_2Cl(CO)(P\phi_3)_2$	1952s	CH_2Cl_2	-0.12 (d of t)
$[FeCl(CO)_3L_2]^+$	$[Fe(CH_3)(CO)_3L_2]^+$	2084s, 2021vs	CH_2Cl_2	
cis-mer-$[FeI(CO)_2L_3]^+$	$[Fe(CH_3)(CO)_2L_3]^+$	2020s, 1963s	CH_2Cl_2	
trans-$PdCl_2L_2$	*trans*-$Pd(CH_3)ClL_2$			
trans-$NiCl_2L_2$	*trans*-$Ni(CH_3)ClL_2$			
(b) M—M bond cleavage				
$Cp_2Fe_2(CO)_4$	$CpFe(CO)_2CH_3$			
$Mn_2(CO)_{10}$	$Mn(CO)_5CH_3$ + $CpMn(CO)_3$			
(c) Oxydative addition				
trans-$Fe(CO)_3L_2$	*cis-cis-trans*-$Fe(CH_3)Cl(CO)_2L_2$			
trans-$IrCl(CO)(P\Phi_3)_2$	$Ir(CH_3)Cl_2(CO)(P\Phi_3)_2$			

[a] For spectroscopic data of the other compounds, see references 3 to 7 or literature.

$$Cp_2TiCH_3 + Cl^{\bullet} \rightarrow Cp_2Ti(CH_3)Cl \quad (3)$$

where (M) stands for a transition metal compound moiety. $Cp_2Ti(CH_3)Cl$ was identified from its proton NMR signal. The fact that such chloride—methyl exchange occurs even in cationic compounds (see Table 1) excludes a mechanism involving carbanion attack on the metal center.

(b) Compounds containing M—M bond. The reaction can be written as follows:

$$(M{-}M) \xrightarrow{h\nu} 2\,(M)^{\bullet} \quad (4)$$

$$(M)^{\bullet} + CH_3^{\bullet} \rightarrow (M)CH_3 \quad (5)$$

Light-induced homolytic cleavage of M—M bonds as in eq. 5 is now fairly well established [8]. Interestingly in this example, another reaction takes place, involving transfer of Cp radicals to the metal:

$$Cp_2Ti(CH_3)_2 + Mn_2(CO)_{10} \xrightarrow{h\nu} CpMn(CO)_3 \quad (6)$$

(c) Oxidative addition. The reactions shown in Table 1 which involve Cp_2TiCH_3Cl are thought to proceed as follows:

$$Cp_2Ti(CH_3)Cl \xrightarrow{h\nu} Cp_2TiCl + CH_3^{\bullet} \quad (7)$$

$$CH_3^{\bullet} + [M] \rightarrow [M]CH_3 \text{ intermediate} \quad (8)$$

$$Cp_2TiCl + [M]CH_3 \rightarrow [M]CH_3Cl + \text{“}Cp_2Ti\text{”} \quad (9)$$

where [M] is a low-valent subcoordinate transition metal complex. Reaction 9 is a thermal process involving a photochemically generated Cp_2TiCl monomer, and gives the hexacoordinate methyl-transition metal compound.

The photostability of the methylmetal compounds formed is probably due to the fact that in most cases they are colorless and therefore do not absorb in the wavelength range of the radiation source used.

The results noted above call for a few remarks. First, in the case of dihalocarbonylruthenium alkylation is selective, and only one halide group is exchanged whereas a mixture of mono- and di-methyl compounds is obtained from the iron analogs. Secondly, methylation of $Mn(CO)_5Br$ and $Re(CO)_5Br$ proceeds smoothly and no attack on the carbonyl group occurs, as is the case with alkyllithium reagents which give the acetylhalo compound [9].

The transmethylation reactions described in this work cover a wide range of transition metals and may be of importance in the study of the reactivity of metal sites in polymetallic homogeneous systems.

Experimental

Solutions containing I or II and the relevant transition metal complex were irradiated for 3 to 5 minutes in an infrared cell or an NMR tube with a Hanau TQ 150 lamp water-cooled in a Pyrex jacket and emitting above 300 nm. The course of the reaction was monitored by the appearance of characteristic infrared CO bands or proton NMR signals. Infrared measurements were made on a Perkin—Elmer 325 instrument and NMR measurements on a Varian T60 spectrometer. Control experiments were carried out to confirm that no thermal reaction occurred under the conditions used.

Acknowledgements. We are grateful to Mrs. J. Hénique for efficient technical assistance.

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