The Stereochemistry of Formation and Cleavage of Alkyl-transition-metal Derivatives

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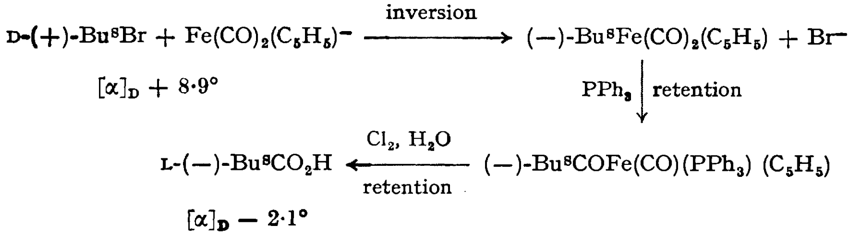
Summary Formation of alkyl–metal compounds by displacement of halide ion from alkyl halides by transition-metal nucleophiles occurs with inversion of configuration; cleavage of the carbon–metal bond with bromine occurs with retention of configuration.

WE report the results of stereochemical studies on the formation and cleavage of alkyl–transition-metal bonds. All of the organometallic derivatives prepared in this study are new compounds which have been characterized by i.r., n.m.r., and o.r.d. spectroscopy. The alkyl compounds are oils which slowly decompose at room temperature even under N_2. All purifications were done by chromatography on alumina or silica gel (elution with pentane and/or ether). I.r. data are reported in the Table.

I.r. data

Compound	ν(C≡O), cm^{-1}	ν(C=O),cm^{-1}
$Bu^sFe(CO)_2(C_5H_5)$	2005(s) 1954(s)	
$Bu^sCOFe(CO)(PPh_3)(C_5H_5)$	1920(s)	1610(m)
$PhMeCHCOMn(CO)_4(PPh_3)$	2057(m) 1985(s) 1957(vs)	1625(m,br) 1611(m,br)
$MeCH(CO_2Et)Mn(CO)_5$	2108(m) 2047(m) 2023(s) 1996(s)	1700(m)

Slow addition of D-(+)-2-bromobutane, $[\alpha]_D + 8{\cdot}9°$, to a tetrahydrofuran solution of $NaFe(CO)_2(C_5H_5)$ gave (−)-$Bu^sFe(CO)_2(C_5H_5)$, $[\alpha]_D - 14°$. This was converted into (−)-$Bu^sCOFe(CO)(PPh_3)(C_5H_5)$ on treatment with PPh_3 for 30 h. Reaction with Cl_2 and H_2O cleaved the acyl group from the metal to give L-(−)-2-methylbutanoic acid, $[\alpha]_D - 2{\cdot}1°$ (see Scheme 1).



SCHEME 1

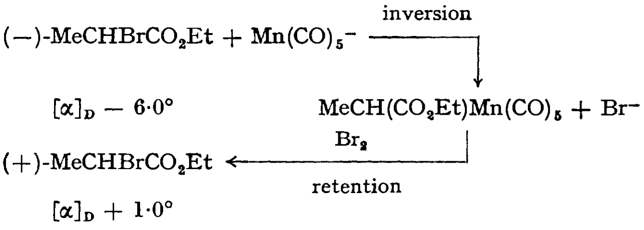
$Mn(CO)_5^-$, a much weaker nucleophile than $Fe(CO)_2$-$(C_5H_5)^-$, reacts very slowly with 2-bromobutane. Therefore D-(−)-α-phenethyl bromide was added slowly to $NaMn(CO)_5$ in tetrahydrofuran. I.r. and o.r.d. spectra showed the formation of (+)-$PhMeCHMn(CO)_5$, but it could not be isolated in a pure state due to its spontaneous decomposition to $PhMeCHCOMn(CO)_5$. In further experiments, (+)-$PhMeCHMn(CO)_5$ was prepared in the presence of PPh_3 to yield the more stable acyl derivative, $PhMeCHCOMn(CO)_4(PPh_3)$. Cleavage of the acyl group by Br_2 and H_2O gave D-(−)-$PhMeCHCO_2H$, $[\alpha]_D - 6{\cdot}7°$.

Our results confirm the findings of Whitesides and Boschetto[1] and Jensen *et al.*[2] Attack of a transition-metal nucleophile on an alkyl halide leading to displacement of halide ion occurs with inversion of configuration. Our results are shown in Scheme 1. Only two steps involve the asymmetric carbon atom. Since alkyl migration is known to proceed with retention of configuration,[1,3] the inversion must occur in the nucleophilic attack by $Fe(CO)_2(C_5H_5)^-$. Correlation of the magnitudes of the rotations shows a stereospecificity of >75%. Exactly the same arguments hold for the phenethyl–manganese system which demonstrated a stereospecificity of >80% in nucleophilic attack by $Mn(CO)_5^-$.

To investigate the stereochemistry of reactions involving cleavage of alkyl–metal bonds, (−)-$Bu^sFe(CO)_2(C_5H_5)$ was treated with bromine following the procedure used by Jensen and Gale[4] in the stereospecific cleavage of Bu^sHgBr. No bromobutane was isolated, presumably due to the elimination reaction:

$$Bu^sFe(CO)_2(C_5H_5) + Br_2 \xrightarrow{(py)} \text{butene} + HBr + BrFe(CO)_2(C_5H_5)$$

$PhMeCHMn(CO)_5$ was also unsuitable for this study since it could not be obtained pure. (−)-$MeCHBrCO_2Et$, $[\alpha]_D$ $-6{\cdot}0°$, reacted with $NaMn(CO)_5$ to form a more stable alkyl–manganese derivative which was cleaved with Br_2 in tetrahydrofuran at −78°. The reaction was easily monitored by the i.r. band of the ester group. Work-up of the products gave (+)-$MeCHBrCO_2Et$, $[\alpha]_D + 1{\cdot}0°$ (see Scheme 2).



SCHEME 2

We have shown that nucleophilic attack by $Mn(CO)_5^-$ occurs with inversion of configuration. Therefore, as shown in Scheme 2, cleavage of the alkyl–metal bond occurs with retention of configuration. This is the first report on the stereochemistry of cleavage of alkyl–transition-metal bonds. It is the result expected on the basis of work on organomercurials.[5] The stereospecificity is relatively low (net inversion in the two steps is only 60%). However, further experiments have shown that most of the racemization occurs during the formation and isolation of MeCH(CO_2Et)Mn(CO)$_5$. In the presence of an excess of $Mn(CO)_5^-$ an exchange reaction has been observed to cause racemization:

$$(-)\text{-MeCH}(\text{CO}_2\text{Et})\text{Mn(CO)}_5 + {}^*\text{Mn(CO)}_5^- \rightleftharpoons (+)\text{-MeCH}(\text{CO}_2\text{Et}){}^*\text{Mn(CO)}_5 + \text{Mn(CO)}_5^-$$

The stereospecificity of bromine cleavage is therefore substantially greater than 60%.

The above result has been used to investigate the stereochemistry of oxidative addition of $MeCHBrCO_2Et$ to IrCl(CO)$(PPh_3)_2$.[6] In contrast to the cases reported above, nucleophilic attack by this d^8-system involves formation of both metal–carbon and metal–halide bonds. In this case concerted addition results in retention of configuration at carbon.

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