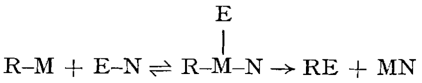
Competition between Cleavage of Alkyl– or Aryl–Transition Metal Bonds by Electrophiles

By Jaáfar K. Jawad and Richard J. Puddephatt*
(*Donnan Laboratories, The University of Liverpool, Liverpool* L69 3BX)

Summary Reactions of methyl(4-tolyl)metal derivatives with various electrophilic reagents give preferential cleavage of the methyl–metal bond in *cis*-[PtMe(4-MeC_6H_4)(PMe_2Ph)$_2$] but the 4-tolyl–metal bond in [PtMe(4-MeC_6H_4)(cyclo-octa-1,5-diene)] and in *cis*-[$AuMe_2$(4-MeC_6H_4)(PPh_3)].

Cleavage of metal–carbon σ-bonds by electrophiles is a process of fundamental importance in organometallic chemistry. It has been suggested that cleavage of alkyl– and aryl–platinum(II) bonds by electrophiles $E^{\delta+}$–$N^{\delta-}$ occurs by the general oxidative addition–reductive elimination mechanism shown in the Scheme, rather than by direct electrophilic attack at carbon (S_E2 mechanism) which is the established mechanism for reactions with alkyl and aryl derivatives of the main group elements. However, it has proved difficult to find direct evidence to distinguish between these mechanisms.[1]



$$\text{R–M} + \text{E–N} \rightleftharpoons \text{R–}\overset{\text{E}}{\overset{|}{\text{M}}}\text{–N} \rightarrow \text{RE} + \text{MN}$$

Scheme

In the search for a chemical test to distinguish between these mechanisms, we have studied the competition between cleavage by electrophiles of methyl–metal or 4-tolyl–metal bonds in some mixed methyl(4-tolyl) derivatives of platinum(II) and gold(III). The results are given in the Table; all the reactions occurred with high selectivity (>90%) as determined by the absence of signals due to other possible products in the n.m.r. spectra of reaction mixtures. The products were identified by comparison of the characteristic n.m.r. spectra with those of authentic samples; in reactions with HCl and $HgCl_2$, the products were subsequently isolated. The data show that electrophiles react with *cis*-[PtMe(4-MeC_6H_4)(PMe_2Ph)$_2$] to cleave the methyl group preferentially but with [PtMe(4-MeC_6H_4)(cod)] (cod = *cis-cis*-cyclo-octa-1,5-diene) and with *cis*-[$AuMe_2$(4-MeC_6H_4)(PPh_3)] to cleave the 4-tolyl group preferentially. The complex *cis*-[PtMe(4-MeC_6H_4)(PMe_2Ph)$_2$] appears to be the first example of an organometallic complex which undergoes preferential cleavage of an alkyl rather than an aryl group in such reactions.

In general, electrophilic cleavage of a metal–aryl bond from a mixed alkyl(aryl)metal derivative, R–M–Ar, is expected if the S_E2 mechanism operates, and this pattern

Table
Products of reaction of methyl(4-tolyl)metal derivatives with electrophiles[a]

Reagent	Electrophile	Product
cis-[PtMe(4-MeC_6H_4)(PMe_2Ph)$_2$]	HCl	*cis*-[PtCl(4-MeC_6H_4)(PMe_2Ph)$_2$] + CH_4
"	$HgCl_2$	*cis*-[PtCl(4-MeC_6H_4)(PMe_2Ph)$_2$] + MeHgCl
"	[PtI_2(cod)]	*trans*-[PtI(4-MeC_6H_4)(PMe_2Ph)$_2$] + [PtIMe(cod)]
"	[PtI_2($PMePh_2$)$_2$]	*trans*-[PtI(4-MeC_6H_4)(PMe_2Ph)$_2$] + *trans*-[PtIMe($PMePh_2$)$_2$]
[PtMe(4-MeC_6H_4)(cod)]	HCl	[PtClMe(cod)] + PhMe
"	$HgCl_2$	[PtClMe(cod)] + 4-MeC_6H_4HgCl
"	[PtI_2(PMe_2Ph)$_2$]	[PtIMe(cod)] + *trans*-[PtI(4-MeC_6H_4)(PMe_2Ph)$_2$]
cis-[$AuMe_2$(4-MeC_6H_4)(PPh_3)]	HCl	*cis*-[$AuClMe_2$(PPh_3)] + PhMe
"	$HgCl_2$	*cis*-[$AuClMe_2$(PPh_3)] + 4-MeC_6H_4HgCl
"	[PtI_2(PMe_2Ph)$_2$]	*cis*-[$AuIMe_2$(PPh_3)] + *trans*-[PtI(4-MeC_6H_4)(PMe_2Ph)$_2$]
"	[$PtCl_2$(cod)]	*cis*-[$AuClMe_2$(PPh_3)] + [PtCl(4-MeC_6H_4)(cod)]

[a] Solvent CH_2Cl_2.

of behaviour is always found in organometallic derivatives of the group IIB and group IVB elements.[2] This mechanism is expected in cleavage of gold(III)–carbon bonds [since gold(III) complexes cannot undergo oxidative addition] and the observed preferential cleavage of the aryl–gold bond in *cis*-[$AuMe_2(4\text{-}MeC_6H_4)(PPh_3)$] is therefore expected. On the other hand, if the oxidative addition–reductive elimination mechanism operates, the alkyl group should be cleaved preferentially since, in reductive elimination from platinum(IV), it has been shown that alkyl groups are lost more readily than aryl groups.[3] Thus we interpret the preferential cleavage of a methyl–platinum bond from *cis*-[$PtMe(4\text{-}MeC_6H_4)(PMe_2Ph)_2$] as evidence for the oxidative addition–reductive elimination mechamism in this case. Some support is obtained from the reaction with methyl iodide in which the intermediate Pt^{IV} species, [$PtIMe_2(4\text{-}MeC_6H_4)(PMe_2Ph)_2$], can be isolated and then shown to decompose on heating to give ethane and *trans*-[$PtI(4\text{-}MeC_6H_4)(PMe_2Ph)_2$].

If the selectivity between alkyl- or aryl–metal bond cleavage by electrophiles can be taken as a test of the reaction mechanism, then the preferred cleavage of an arylplatinum group from [$PtMe(4\text{-}MeC_6H_4)(cod)$] may indicate that this complex reacts by the S_E2 mechanism. This can be rationalised in terms of the expected lower rate of oxidative addition of the cod complex compared with the phosphine complex; thus oxidative addition of methyl iodide with *cis*-[$PtMe_2(PMe_2Ph)_2$] is rapid at room temperature[4,5] but with [$PtMe_2(cod)$] it is necessary to heat under reflux with neat methyl iodide for 48 h to complete the oxidative addition.[5,6] However, the mechanistic conclusion here is tentative and further studies with the cod complex are in progress.

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