Reactions of *O*-Alkyl and *O*-Cycloalkyl *S*-Methyl Xanthates with $MCl(PPh_3)_3$ (M = Rh, Ir) and $M(PPh_3)_4$ (M = Pd, Pt). Easy 1,2-Bond Shifts in Alkyl and Cycloalkyl–Metal Intermediates

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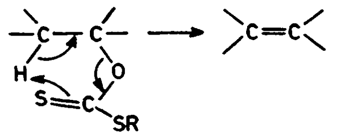
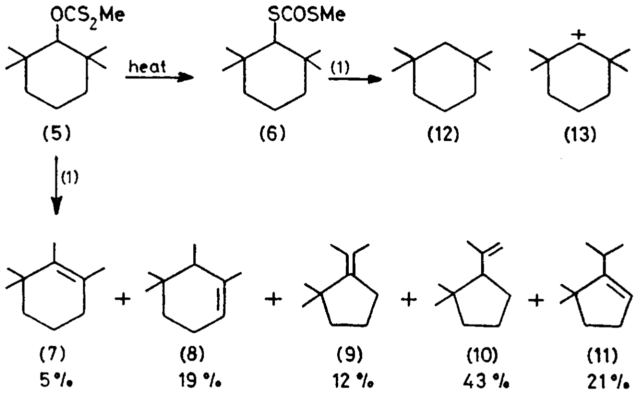
Summary Reactions of *O*-alkyl and *O*-cycloalkyl *S*-methyl xanthates with $RhCl(PPh_3)_3$ (**1**), $IrCl(PPh_3)_3$ (**2**), $Pd(PPh_3)_4$ (**3**), or $Pt(PPh_3)_4$ (**4**) at temperatures from 373 to 423 K give olefinic products whose structures clearly reveal 1,2-bond shift skeletal rearrangements in alkyl–metal intermediates; these rearrangements are exactly analogous to several of those occurring in hydroisomerisation of cycloalkanes and alkanes at elevated temperatures on transition metal surfaces.

Pyrolysis of *O*-alkyl *S*-methyl xanthates which contain a β-hydrogen *cis* to the xanthate group produces olefins in the well-known Chugaev elimination which is believed to occur by a cyclic mechanism (reaction 1). Xanthates without a β-hydrogen obviously cannot react in this fashion although γ-hydrogen abstraction from some 2-norbornyl xanthates to give nortricyclenes has been reported.[1] The xanthate derivative (**5**) from 2,2,6,6-tetramethylcyclohexanol thus gives only the corresponding dithiocarbonate (**6**) on heating to 523 K.[2]



(1)

We now report that when (**5**) is mixed with an equimolar amount of (**1**) and heated under nitrogen to 373 K at least five olefins [(**7**)—(**11**)] are formed.† When (**6**) is heated with (**1**) the only hydrocarbon product formed is (**12**). The same products were obtained in similar proportions when (**1**) was replaced by (**2**), (**3**), or (**4**).



The possibility that the olefins are formed by rearrangement of the carbonium ion (**13**) with subsequent proton loss must be considered. Hydrolysis of 2,2,6,6-tetramethylcyclohexanol in trifluoroacetic acid at room temperature, where (**13**) is the initial intermediate, leads to formation of (**7**) (30%), (**8**) (50%), and (**9**) (20%) only. In addition, the high yield of the terminal olefin (**10**), the least stable isomeric product, from the metal initiated xanthate decomposition is not indicative of a carbonium ion process, and shows that subsequent double bond shift cannot be rapid.

The *S*-methyl xanthate of 3,3-dimethylbutan-2-ol which does have a β-hydrogen gives only the normal product, 3,3-dimethylbut-1-ene on pyrolysis,[3] but when heated in the presence of (**1**) gives not only 3,3-dimethylbut-1-ene (40%) but also the rearranged products 2,3-dimethylbut-1-ene (20%) and 2,3-dimethylbut-2-ene (40%).

Heating the xanthates formed from primary alcohols with (**1**) affords the corresponding alkyl chlorides irrespective of whether or not there is a β-hydrogen. Thus *O*-n-hexyl *S*-methyl xanthate gives n-hexyl chloride, but *O*-neopentyl *S*-methyl xanthate‡ gives both neopentyl chloride and some 1-chloro-3-methylbutane under these conditions. In marked contrast when the latter xanthate is warmed with (**3**) or (**4**) at only 373 K, some 2-methylbut-1-ene and a little 2-methylbutane are released. The absence of the thermodynamically more stable isomer 2-methylbut-2-ene and the high reactivity with the electron-rich M^0 complexes again show that carbonium ions are not involved.

Even though we do not know the exact nature of the organometallic intermediates involved, all of these olefinic product distributions clearly indicate a novel organometallic reaction, namely, the formation and rearrangement of a metal alkyl. In this respect the reactions may well be exactly analogous skeletal rearrangements to those of paraffins which occur in excess of hydrogen at elevated temperatures on transition metal surfaces,[4] and thus provide a further important link between heterogeneous catalysis and the chemistry of metal complexes. The heterogeneously catalysed rearrangements have been of great mechanistic interest during the last decade and several theories[5] concerning the nature of the rearrangement processes have been proposed. One of these, for which there is good evidence, is that an alkyl group which is attached to a transition metal atom or ion, even though the bonding is essentially covalent, may rearrange in a manner akin to that of a carbonium ion.[6] The major reason cited is that the half-reaction state, *e.g.* (**15**) from (**14**), is relatively lowered in energy, in comparison to a free

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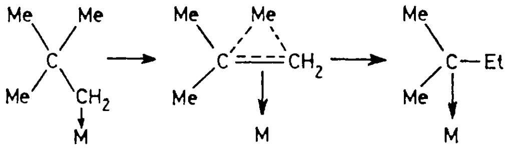
† The products were separated by preparative g.l.c. and characterised by mass spectrometry and ^1H and ^{13}C n.m.r. spectroscopy.

‡ Simple pyrolysis of this xanthate gives the corresponding dithiocarbonate (see ref. 2).

radical process, by virtue of π-bonding to the metal. A detailed molecular orbital description of (**15**) has already been published.[7]



(14) (15) (16)

As yet we have not thoroughly explored the fate of the xanthate group or fully analysed the residual products, but we have identified the formation of $RhCl(CO)(PPh_3)_2$ from (**1**) and $(Ph_3P)_2Pt(S_2CO)$[8] from (**4**) as well as some methanethiol.

The above results show that there is a distinct possibility that certain vicinal interchange rearrangements involving catalysis by coenzyme B-12 may occur by a parallel 1,2-bond shift mechanism rather than one[9] involving cobalt–carbene complexes.

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