Atom Transfer Reactions Involving the Metal-centred Radical [(η^5-C$_5$H$_5$)Cr(CO)$_3$]·

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The metal-centred radical [(η^5-C$_5$H$_5$)Cr(CO)$_3$]· abstracts the halogen atoms from a number of alkyl, allyl and benzyl halides to form the halochromium compounds [(η^5-C$_5$H$_5$)Cr(CO)$_3$X] (X = Br, I) and the corresponding carbon-centred radicals; the latter subsequently undergo a wide variety of coupling, atom abstraction and atom donation reactions.

The interplay between carbon and metal-centred radicals has received considerable attention of late, and has led to numerous synthetically useful reactions.[1] We have previously shown that the chromium-centred radical [(η^5-C$_5$H$_5$)Cr(CO)$_3$]·, formed *via* the spontaneous thermal dissociation of the 18-electron dimer [η^5-C$_5$H$_5$Cr(CO)$_3$]$_2$, reacts with methyl iodide as in eqns. (1) and (2).[2]

$$[\{(\eta^5\text{-}C_5H_5)Cr(CO)_3\}_2] \rightleftharpoons 2[(\eta^5\text{-}C_5H_5)Cr(CO)_3]· \quad (1)$$

$$2[(\eta^5\text{-}C_5H_5)Cr(CO)_3]· + MeI \rightarrow$$
$$[(\eta^5\text{-}C_5H_5)Cr(CO)_3I] + [(\eta^5\text{-}C_5H_5)Cr(CO)_3Me] \quad (2)$$
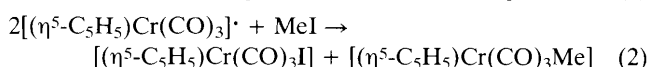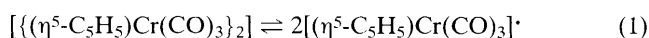
It was postulated that the reaction of eqn. (2) involves initial iodine abstraction by [(η^5-C$_5$H$_5$)Cr(CO)$_3$]· followed by coupling of the resulting methyl radical with a second [(η^5-C$_5$H$_5$)Cr(CO)$_3$]· to form the methylchromium by-product.[2] We now report a complementary investigation of analogous reactions of [(η^5-C$_5$H$_5$)Cr(CO)$_3$]· with a variety of other alkyl, allyl and benzyl halides; a series of product distributions very different from that of eqn. (2) is obtained, although the results ultimately tend to confirm the validity of the mechanism proposed for eqn. (2).

For instance, while benzyl bromide and allyl bromide (or iodide) react very readily with [{(η^5-C$_5$H$_5$)Cr(CO)$_3$}$_2$] to form [(η^5-C$_5$H$_5$)Cr(CO)$_3$X] (X = Br, I) and the corresponding benzyl and η^1-allyl compounds, [(η^5-C$_5$H$_5$)Cr(CO)$_3$CH$_2$Ph] and [(η^5-C$_5$H$_5$)Cr(CO)$_3$(η^1-C$_3$H$_5$)], the latter two new compounds are much less thermally stable than is [(η^5-C$_5$H$_5$)Cr(CO)$_3$Me], which is stable in solution for several hours at room temperature. Thus, the allyl and benzyl compounds both undergo spontaneous homolysis within minutes at room temperature to regenerate [(η^5-C$_5$H$_5$)Cr(CO)$_3$]· and to form the coupling products, bibenzyl and hexa-1,5-diene, respectively. Thus, as may be anticipated, the chromium–carbon σ bonds of these two compounds must be considerably weaker than either that of [(η^5-C$_5$H$_5$)-

Cr(CO)$_3$Me] or the chromium–hydrogen bond of [(η^5-C$_5$H$_5$)-Cr(CO)$_3$H], the latter estimated as about 260 kJ mol^{-1}.[3]

In contrast, other alkyl halides undergo a more complex variety of atom abstraction processes. Thus, reaction of a benzene solution of [(η^5-C$_5$H$_5$)Cr(CO)$_3$]· with a slight excess of ethyl iodide at room temperature results in essentially complete conversion of the radical to [(η^5-C$_5$H$_5$)Cr(CO)$_3$I] and [(η^5-C$_5$H$_5$)Cr(CO)$_3$H], no evidence for the ethyl compound [(η^5-C$_5$H$_5$)Cr(CO)$_3$Et][4] being detected although both ethylene and ethane were present in the reaction mixture. Indeed, reactions of [(η^5-C$_5$H$_5$)Cr(CO)$_3$]· under these conditions with a series of alkyl iodides containing β-hydrogen atoms (2-iodopropane, 2-iodo-2-methylpropane, 2-iodobutane, 1-iodobutane, 1-iodo-2-methylpropane, 1-bromoethylbenzene, methyl or ethyl 2-bromopropionate, methyl or ethyl 2-bromobutyrate) all produced mixtures of [(η^5-C$_5$H$_5$)Cr(CO)$_3$X], [(η^5-C$_5$H$_5$)Cr(CO)$_3$H], alkane and alkene, but not of the corresponding alkyl chromium compounds. Where yields of the products were obtained, the ratios [(η^5-C$_5$H$_5$)Cr(CO)$_3$I]:[(η^5-C$_5$H$_5$)Cr(CO)$_3$H] and alkene:alkane were always ⩾1, the proportions of alkane increasing as the amounts of hydride decreased. A reasonable mechanism is shown in eqns. (3)–(5).

$$[(\eta^5\text{-}C_5H_5)Cr(CO)_3]· + R_2CHCH_2I \rightarrow$$
$$[(\eta^5\text{-}C_5H_5)Cr(CO)_3I] + R_2CHCH_2· \quad (3)$$

$$R_2CHCH_2· + [(\eta^5\text{-}C_5H_5)Cr(CO)_3]· \rightarrow$$
$$[(\eta^5\text{-}C_5H_5)Cr(CO)_3H] + alkene \quad (4)$$

$$R_2CHCH_2· + [(\eta^5\text{-}C_5H_5)Cr(CO)_3H] \rightarrow$$
$$[(\eta^5\text{-}C_5H_5)Cr(CO)_3] + alkane \quad (5)$$
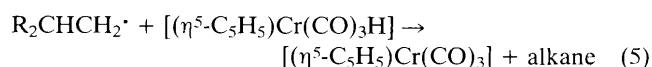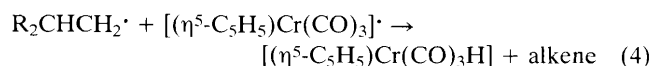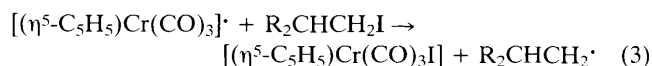
Thus, the organic radical R$_2$CHCH$_2$·, formed in eqn. (3), apparently undergoes hydrogen atom abstraction by a second [(η^5-C$_5$H$_5$)Cr(CO)$_3$]· to form alkene and the hydride [(η^5-C$_5$H$_5$)Cr(CO)$_3$H], an exothermic process. However, as the

concentration of the hydride increases, abstraction of the hydridic hydrogen atom by $R_2CHCH_2^\cdot$ to give alkane, also an exothermic process, becomes competitive. Congruent with this proposal, we find that reaction of $[(\eta^5\text{-}C_5H_5)Cr(CO)_3]^\cdot$ with 2-iodo[1,1,1,3,3,3-$^2H_6$]propane yields $[(\eta^5\text{-}C_5H_5Cr(CO)_3D]$ and both propene and propane labelled appropriately. Furthermore, in the reaction of $[(\eta^5\text{-}C_5H_5)Cr(CO)_3]^\cdot$ with 2-iodo-2-methylpropane, the ratio of isobutene : isobutane decreases with time from ca. 15:1 to ca. 1:1, while the amount of hydride decreases proportionately. On the other hand, addition to a reaction mixture of the hydride scavenger isoprene[2] results in almost complete conversion of the hydrocarbon moiety to isobutene.

We may rule out alternative routes to the processes of eqns. (4) and (5), for instance those involving either direct β-hydrogen elimination from $[(\eta^5\text{-}C_5H_5)Cr(CO)_3R]$, or coupling of the radical species formed in eqn. (3) to give alkylchromium compounds $[(\eta^5\text{-}C_5H_5)Cr(CO)_3R]$, followed by β-hydrogen abstraction by $[(\eta^5\text{-}C_5H_5)Cr(CO)_3]^\cdot$. Although both processes would yield alkene and hydride, there seems to be little reason to expect $[(\eta^5\text{-}C_5H_5)\text{-}Cr(CO)_3Et]$, at least, to be thermally unstable under the reaction conditions. Furthermore, we have found that mono-alkenes are not hydrogenated by $[(\eta^5\text{-}C_5H_5)Cr(CO)_3H]$. We also note that the possibility that the postulated free radicals undergo disproportionation is ruled out by the fact that no coupling products are obtained. If disproportionation of free radicals were a factor, the proportion of coupled species to alkenes would be much greater than is observed.[5]

Although accurate kinetics data for the reactions are not yet available, monitoring of a series of reactions run under the conditions described above indicates that the rates increase in the orders chlorides < bromides < iodides, MeI < EtI < Me_2CHI < MeEtCHI < Me_3CI ≈ CH_2=$CHCH_2Br$ ≈ $PhCH_2Br$ and $PhCH_2Br$ < PhCHMeBr. These trends correlate well with relative carbon–halogen bond strengths, and thus are entirely compatible with the postulated halogen abstraction step of eqn. (3). The observed trends are also very similar to those reported previously for reactions of alkyl halides with phenyl and tributyltin radicals,[6] as well as with $[Co(CN)_5]^{2-}$, which is a 17-electron cobalt(II) complex.[7] Interestingly, and in contrast to the chromium system repor-

ted here, this cobalt-centred radical couples readily with several of the alkyl radicals to give the corresponding alkylcobalt(III) compounds.

These and similar reactions are being studied further, as the present report is the first to deal extensively with the fates of the organic radicals generated when a 17-electron organometallic compound abstracts halogen atoms from alkyl halides. Although many such metal-centred radicals have been generated via photolysis of 18-electron metal–metal bonded dimers and do indeed behave as halogen atom abstractors, the nature of the organic products has only rarely been established.[8]

References

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