Labelling of Organometallic Groups for Study of Exchange Reactions

By S. C. Srinivasan and D. R. Wiles*

(*Chemistry Department, Carlton University, Ottawa, Canada*)

Summary A method is described for the labelling of $-{}^*Mn(CO)_5$ for use in exchange studies, and it is suggested that similar methods may be applied to the labelling of other large organometal groups; preliminary results are given for the exchange of $I^*Mn(CO)_5$ with $RMn(CO)_5$ (R = H, Me, or Ph).

Exchange-like processes often appear to be involved in the formation of radioactive molecules by neutron bombardment of metal atoms in organometallic compounds. Two simple examples are found in $Ni(CO)_4$ [1] and $Cr(CO)_6$.[2] To our knowledge, however, no study has been reported which involves exchange of larger groups, as in the general reaction (1) (L = any non-labile ligand, such as CO, PR_3, π-Cp, π-C_6H_6) where the difficulty of preparing the appropriately labelled reactants is a major barrier to such studies. Labelling a ligand in the group will only lead to ambiguity, in that it will not be possible to distinguish between migration of $[ML_x]$, as in equation (1), and migration of L, as in equation (2).

$$R^1\text{–}[ML_x] + R^2\text{–}{}^*[ML_x] \rightleftharpoons R^1\text{–}{}^*[ML_x] + R^2\text{–}[ML_x] \quad (1)$$

$$R^1ML_x + R^2ML_{x-1}{}^*L \rightleftharpoons R^1ML_{x-1}{}^*L + R^2ML_x \quad (2)$$

The preparation of $-{}^*Mn(CO)_5$ in a useful form is based on the following observations: (*i*) $IMn(CO)_5$ exchanges rapidly with $\cdot Mn(CO)_5$ in light petroleum;[3] (*ii*) the reaction of I_2 with $HMn(CO)_5$ gives $IMn(CO)_5$ rapidly and quantitatively;[4] (*iii*) the yield of $H^*Mn(CO)_5$ from direct thermal neutron activation of $HMn(CO)_5$ is fairly high.[5]

The method used initially was as follows: pure $IMn(CO)_5$ was irradiated with neutrons, preferably at low temperature (−78°) to give ^{56}Mn. The irradiated crystals were dissolved in light petroleum, the solution was passed through a silica-gel column, and the $IMn(CO)_5$ was eluted with light petroleum. [It is usually advantageous to add some $Mn_2(CO)_{10}$ as carrier to the initial solution, to make the separation of this radioactive contaminant visible.] After the light petroleum had been removed, the $I^*Mn(CO)_5$ was further purified by vacuum sublimation.

A better method was as follows. $HMn(CO)_5$ was prepared and purified by known methods,[6] and sealed *in vacuo* in quartz vials. (These vials may be stored in a refrigerator until use.) The $HMn(CO)_5$ was then irradiated with neutrons, preferably at low temperature. The irradiated vial was opened under nitrogen in subdued (incandescent) light, and treated with a solution of iodine and $Mn_2(CO)_{10}$ in light petroleum. The $I^*Mn(CO)_5$ was purified by column chromatography and by vacuum sublimation. The chemical recovery of $IMn(CO)_5$ was quite high, and the yield of ^{56}Mn in this form is *ca.* 20% of the total ^{56}Mn.

This second method has two advantages: (*i*) the radiochemical yield is much higher, and (*ii*) no ^{128}I is produced to interfere with the radioactivity measurements. An obvious disadvantage is the difficulty of handling $HMn(CO)_5$. By the use of the nitrogen glove[7] or similar technique the preparation and handling can be developed into a routine. For studying the exchange reaction (3) the two reactants

$$I^*Mn(CO)_5 + RMn(CO)_5 \rightleftharpoons IMn(CO)_5 + R^*Mn(CO)_5 \quad (3)$$

are dissolved in the chosen solvent under nitrogen in subdued light, and the solutions mixed thoroughly. The preferred method for stopping the reaction depends on the reaction rate. $HMn(CO)_5$ exchanges rapidly, so the $HMn(CO)_5$ must be removed quickly by vacuum transfer. After purification the $HMn(CO)_5$ can be converted into $IMn(CO)_5$ by addition of a slight excess of iodine. The $IMn(CO)_5$ can then be separated and purified by chromatography. In slower reactions, as with $MeMn(CO)_5$ and $PhMn(CO)_5$, the reactants can be separated by chromatography or by vacuum distillation at reduced temperature. We have not yet found it convenient to take aliquot portions of the solutions for study, but this is presumably possible.

Preliminary results have shown that $HMn(CO)_5$ exchanges with $IMn(CO)_5$ at room temperature more rapidly than the experiment can be done; that is, the exchange is complete in < 30 s. $Mn_2(CO)_{10}$, $MeMn(CO)_5$, and $PhMn(CO)_5$, on the other hand, exchange more slowly than can be detected in 10 min.

It is thus possible to study the exchanges given by equation (3) by the use of recoil-labelled $-^*Mn(CO)_5$. We have so far observed the rapid exchange of $^{\bullet}Mn(CO)_5$ and of $HMn(CO)_5$ with $IMn(CO)_5$, and have noted the relative inertness of $MeMn(CO)_5$ and $PhMn(CO)_5$ to the same exchange. We believe that exactly the same method can be applied to study of the many other $RMn(CO)_5$ compounds. It is possible that recoil labelling may be applied to exchange studies in numerous other systems involving, for for example, the groups $-Re(CO)_5$ and $-Fe(Cp)(CO)_2$.[8]

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