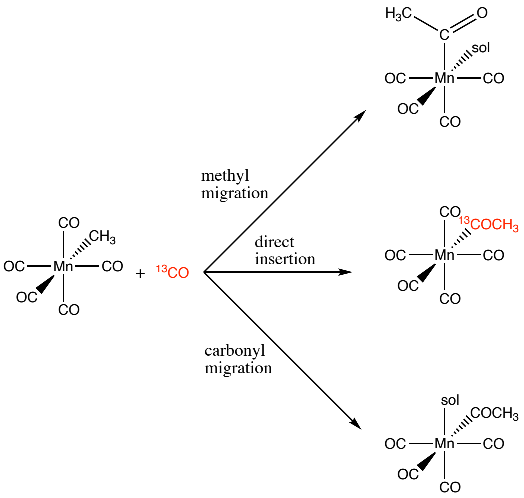
Guided inquiry problem on the 1,1-insertion mechanism

A classic example of an insertion reaction is the reaction that transforms $Mn(CH_3)(CO)_5$ into $Mn\{C(=O)CH_3\}(CO)_5$ under an atmosphere of CO. The methyl group on the manganese is transformed into an acyl group, and the original name for the reaction was the *carbonyl insertion* reaction, because in the product it appears that a CO ligand has inserted itself into the Mn–CH_3 bond. Since other substrates, such as NO, can do this reaction, it is more correctly referred to as the *migratory insertion* reaction. Both of these names appear to imply something about the mechanism of the reaction. There are three readily conceivable mechanisms for the formation of the acyl product: alkyl migration, where the alkyl group moves to a CO ligand *cis* to the alkyl, leaving an empty coordination site that is eventually filled by the incoming CO ligand, direct insertion, where the CO directly inserts into the M-alkyl bond never forming an empty coordination site, and carbonyl migration, or indirect insertion, where the CO moves to the alkyl group *cis* to its starting position, leaving an empty coordination site that is later filled by the incoming CO ligand. The transient intermediates $Mn\{C(=O)CH_3\}(CO)_4(sol)$ that is proposed for the methyl and carbonyl migration reactions is supported by the fact that a solvent adduct can sometimes be detected by IR. We now know that the mechanism of insertion is different with different metals and substrates, and all three mechanisms have been observed. The carbonyl insertion reaction was studied extensively in the late 1960s by Fausto Calderazzo in Italy, culminating in a paper that gave strong experimental evidence to support a single mechanism (*J. Organometal. Chem.,* **1967**, *10*, 101-104). Your job is to take the data from that paper and see if you can determine the mechanism of the reaction.



Experimental considerations and data

$CH_3Mn(CO)_5$ has the following CO stretching frequencies (cm^{-1}):

2112, 2110 (for the A_1 and E modes for the 4 equatorial COs)
1991 (the A_1 mode for the axial CO)

$CH_3(O{=})CMn(CO)_5$ has the following CO stretching frequencies (cm^{-1}):

2115, 2011 (for the A_1 and E modes)
2003 (for the axial CO)
1664 (much lower stretch for the organic carbonyl in the acyl group)

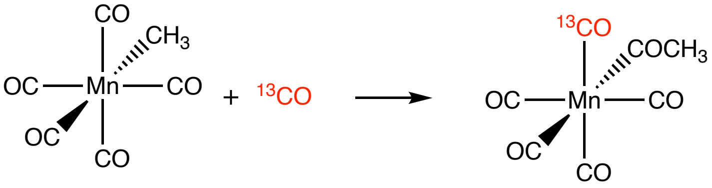
These features are well-resolved so the authors can tell what complex they have using IR.

Question 1: verify the number of IR active CO stretching modes for $CH_3Mn(CO)_5$ in C_{4v}.
see LOs:

Question 2: Predict the stretching vibration for a ^{13}C labeled acyl given that the ^{12}C acyl stretches at 1664 cm^{-1}. Repeat your calculation for the axial CO stretches. The authors report these at 1625 for the ^{13}CO acyl and 1949 and 1963 for the axial ^{13}CO stretches.

Experiment 1:

The reaction of Mn(CH$_3$)(CO)$_5$ with ^{13}CO gave only a single product, the *cis* isomer.

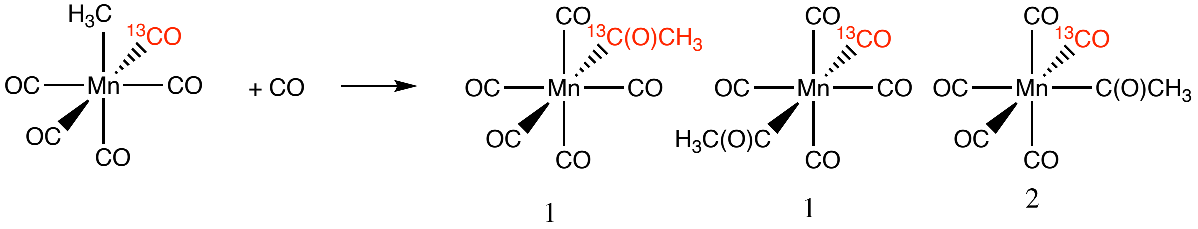


Experiment 2

No scrambling of the ^{13}C label (from the *cis* to the *trans* position) in the product of reaction 1 was observed under experimental conditions.

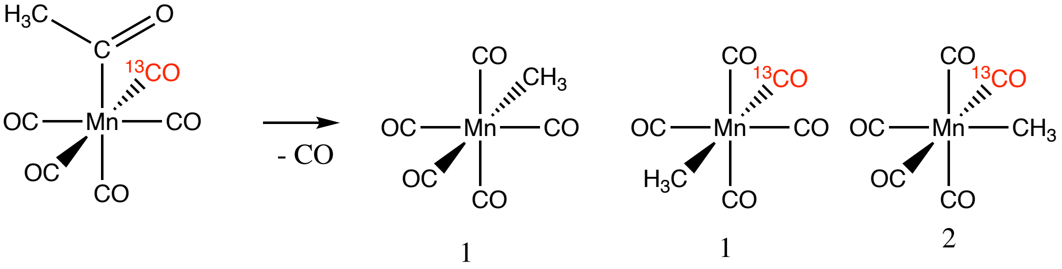
Experiment 3

Reaction of labeled starting material with unlabeled CO gave 3 products in a 1:1:2 ratio.



Experiment 4

Decarbonylation of acyl gave 3 products in a 1:1:2 ratio.



Question 3 (in parts): Use this data to propose the mechanism of the 1,1-insertion reaction for manganese carbonyl complexes.

1: predict the products of the reaction in experiment 1 for the three postulated mechanisms, direct insertion, alkyl migration, and carbonyl migration.

2: predict the products of the reaction in experiment 3 for the three postulated mechanisms, direct insertion, alkyl migration, and carbonyl migration.

3: briefly explain why looking at the decarbonylation reaction would give information about the insertion reaction.

4: predict the products of the reaction in experiment 4 for the three postulated mechanisms, direct insertion, alkyl migration, and carbonyl migration.

5: what information does experiment 2 provide? Why is it important?

6: based on your answers to the above, suggest the correct mechanism for this reaction.

7: is it *possible* that more than one mechanism is active? Why or why not?