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Time-Resolved Infrared Observation of a Long-Lived Transient in the Photo-Decarbonylation of Mn(CO)₅C(O)CH₃: Potential Relevance to the CO Migratory Insertion Mechanism

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Summary: Flash photolysis experiments have been carried out at ambient temperature to probe potential reaction intermediates in the carbynylation of the metal-manganese complex CH₃Mn(CO)₅ (M) to give the acyl product CH₃C(O)Mn(CO)₅ (A). Photo-decarbonylation of A gives a long-lived transient C, whose time-resolved infrared spectrum shows that the reaction proceeds via the migratory insertion mechanism. The nature of C has been the subject of discussion and there are various experimental and theoretical studies, but the spectrum and kinetics of C have been elusive, except in very strongly coordinating media such as dimethyl sulfoxide. Recent experiments have demonstrated that the putative intermediate is surprisingly stable and suggests that it may have an α-carbonyl structure in weakly coordinating solvents such as alkanes and perfluorocarbons.

Fig. 1. TRIR spectrum of C in cyclohexane formed by 308-nm flash excitation of CH₃C(O)Mn(CO)₅ (eq 1). Data points represent the absorbance change measured 100 μs after the laser flash at individual monitoring frequencies. Conditions: [A] = 1 x 10⁻³ M; P_CO = 1.0 atm; T = 22 °C. Inset: spectral changes in acyl stretching region from analogous experiment with [A] = 3 x 10⁻³ M.

N.B. The same result was seen when the reaction is investigated in a methylcyclohexane solution containing a CO-independent state A manifesting itself as a CO-independent component in the formation of M. A similar result was observed when the photolysis was carried out in a solid inert-gas matrix; see ref 6.


(8) Axe, F. U.; Marynick, D. S. Organometallics 1987, 6, 572.
(11) Marynick, D. S.; unpublished results; personal communication to P.C.F.
Table I. Carbonyl Bands (υCO Values in cm⁻¹) for Intermediate C Formed by 308-nm Excitation of A* in Various Solvents at Ambient Temperature and at -78 °C As Measured by TRIR and FTIR, Respectively

<table>
<thead>
<tr>
<th>solvent</th>
<th>υCO data at room temp</th>
<th>υCO data at -78 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>cyclohexane</td>
<td>1990, 1952, 1607 (w)</td>
<td>2080 (w), 1988, 1941, 1607 (w)</td>
</tr>
<tr>
<td>methylcyclohexane</td>
<td>1990, 1952</td>
<td>2077 (w), 1977, 1928, 1602 (w)</td>
</tr>
<tr>
<td>dichloromethane</td>
<td>1987 (br), 1940 (br)</td>
<td>2077 (w), 1977, 1928, 1600 (w)</td>
</tr>
<tr>
<td>tetrahydrofuran</td>
<td>1981 (br), 1931 (br)</td>
<td>2077 (w), 1979, 1931, 1603 (w)</td>
</tr>
<tr>
<td>2-methyltetrahydrofuran</td>
<td>1979 (br), 1932 (br)</td>
<td>2077 (w), 1979, 1931, 1603 (w)</td>
</tr>
<tr>
<td>2,5-dimethyl-THF</td>
<td>1982 (br), 1932 (br)</td>
<td>2077 (w), 1979, 1931, 1603 (w)</td>
</tr>
</tbody>
</table>

* The CO stretching frequencies for A are 2110, 2051, 2012, and 1661 cm⁻¹ and are independent of solvent. * All solvents were dried and redistilled before use. * Room-temperature data taken from TRIR spectra 100 μs after 308-nm flash excitation. * Low-T data recorded on a Bio-Rad FTS-60 FTIR spectrometer immediately after 308-nm excitation with one pulse from an XeCl excimer laser.

Figure 2. Prospective structures for C.

The relative unreactive nature of C made it convenient to carry out photolyses at a lower temperature (200 K), where the transient spectra were recorded on a FTIR spectrometer. At this T, 308-nm irradiation (XeCl laser pulses) of A gave transient C with a lifetime of hours in each solvent. In methylcyclohexane, the FTIR spectrum recorded within a few minutes displayed υCO bands (2080 (w), 1988 (s), 1941 (s), 1607 (w, br) cm⁻¹), similar to the TRIR spectra in cyclohexane and methylcyclohexane. Furthermore, the spectra of C under these conditions are similar to that reported previously for the species generated by photolysis of A in frozen methanes (12 K) (υCO = 2084 (w), 1992 (s), 1948 (s), 1610 (vw) cm⁻¹). Thus, it is likely that the species formed in the varied alkane media are structurally analogous.

TRIR (295 K) and FTIR (200 K) spectra in various solvents ranging from perfluoromethylcyclohexane (PFMC) to the differently methylated tetrahydrofurans are summarized in Table I. These are qualitatively similar to those described above for the alkanes and are consistent with labilization of a CO adjacent to the acetyl ligand to give a tetracarbonyl intermediate such as proposed in thermal carbonylation. The bands shift modestly to lower frequency on going from poorly coordinating perfluoroalkane solutions to the bulkier THF and 2,5-dimethyl-THF each gave identical υCO band frequencies for C despite differences in the coordinating abilities of these solvents. If C were the solvento complex CH3C(O)Mn(CO)4(S = solvent), υCO would be expected to shift to higher energy on going from THF to the bulkier 2,5-dimethyl-THF.

Prospective structures for C are illustrated in Figure 2. The solvento species 1 and the coordinatively unsaturated pentacarbonyl species CH3C(O)Mn(CO)4 proposed in the matrix studies can also be excluded given the sluggishness of the reactions of C. As noted above, C did not undergo measurable reaction with CO in cyclohexane at υCO = 1 atm within the 1-ms time window of the TRIR detection device. If one conservatively assumes a 10% loss of signal would have been detected, upper limits of k2 < 2 × 10⁴ M⁻¹ s⁻¹ for trapping C by CO and of k1 < 2 × 10⁴ s⁻¹ for unimolecular methyl migration to M can be calculated for eq 2. Notably, C proved to be surprisingly unreactive in each of the solvents investigated, including PFMC. More accurate rate constant values were determined in cyclohexane by carrying out kinetic flash photolysis studies of A using optical detection (which allowed for observing longer lived species). These gave the respective rate constants k1 = 10 s⁻¹ and k2 = 3.8 × 10⁴ M⁻¹ s⁻¹ under the same conditions.

The relatively low reactivity of C in alkane and perfluoroalkane solutions is remarkable when compared to reactivities of other unsaturated metal carbonyls. For example, earlier studies demonstrated that the intermediate cis-Mn(CO)4(CH3)S (generated by flash photolysis of M) reacts with CO with a k2 of 2.0 × 10⁴ M⁻¹ s⁻¹.
s\(^{-1}\) in alkane solution but is 4 orders of magnitude slower (1.4 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}) in THF. Similarly, flash photolysis of Cr(CO)\(_6\) leads to formation of the solvato complex Cr-(CO)\(_5\)S, which reacts with CO at \(k_2\) values of 3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1} and \sim 3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1} in cyclohexane and perfluorokanes, respectively.\(^{17}\) The acyl intermediate C is orders of magnitude less reactive than are the above solvato complexes in the latter solvents, thus, C's extraordinary stability must be due to some type of intramolecular stabilization such as chelation by the acyl ligand as shown in structures 2 and 3. Of these, agostic coordination of the methyl group as in 3 has the appeal of appearing to be closer to the transition state expected for the methyl migration pathway. However, \textit{ab initio} calculations\(^{5b}\) have concluded that isomer 2 should be the much more stable of these two. Thus, the unusual longevity of C appears to be the result of its stabilization by \(\eta^2\)-coordination of the acyl.\(^{18}\)

The acyl \(\nu_{\text{CO}}\) band (1607 cm\(^{-1}\)) recorded for C in cyclohexane is significantly shifted to lower frequency from A and falls within the range (1470–1625 cm\(^{-1}\)) observed for stable \(\eta^2\)-(C=O) coordinated acyl complexes.\(^{18}\) However, this is not as convincing evidence for such coordination as is the kinetic properties, since parameters such as ligand substitution can have comparable effects on the acyl \(\nu_{\text{CO}}\) band. The relatively high frequency would be consistent with the "lightly stabilized" nature of this reactive intermediate.

In summary, the surprisingly slow reactivity of C even in weakly donor solvents suggests \(\eta^2\)-coordination of the acyl ligand under such conditions in accord with theoretical analyses which indicate the probable stability of such a species. One might ask whether C, which is generated as the result of photolabilization of CO from A, and I, which is the purported intermediate in the thermal transformation of M, are indeed the same, since the principles of microscopic reversibility do not apply given the independent pathways involved. Nonetheless, the two species have the same stoichiometry, and the reported thermal reaction kinetics\(^3\) are consistent with the intermediacy of a species I which undergoes back-reaction to re-form M competitive with trapping by CO to give A when \(P_{\text{CO}}\) is 1 atm. The kinetic flash photolysis experiments reported here indicate that this is also the case for C. Further studies are in progress to determine quantitative solvent and temperature effects on the kinetics of C and of other transients formed in reactions of related manganese complexes.

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\(^{18}\) For other examples of \(\eta^2\)-acyl complexes, see: Durfee, L. D.; Rothwell, I. P. Chem. Rev. 1988, 88, 1059.