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Journal of Organometallic Chemistry 572 (1999) 135–139

Journal of Organo metallic Chemistry

Preliminary communication

Penta(cyclopentadienyl)-η^5-cyclopentadienylmanganesetricarbonyl: structure and laser-induced conversion to fullerenes

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Received 3 July 1998; received in revised form 28 August 1998

Abstract

The title compound [$Cp_5CpMn(CO)_3$], **1**, has been characterized by X-ray crystallography and shown by laser-induced desorption/ionization (LDI) to undergo dissociative coalescence to fullerene C_{60} and other carbon clusters. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Oligocyclopentadienylmetals; Manganese; Fullerenes; Laser-induced desorption/ionization

Laser desorption/ionization experiments represent a powerful tool to obtain insight into the formation, structure and reactivity of carbon clusters. The historic approach, using laser vaporisation of graphite to produce fullerenes [1], has prompted numerous new developments and applications of this method. Replacing the graphite target with fullerenes, such as C_{60}, C_{70} or C_{84}, led to the observation of gas-phase coalescence reactions in which higher fullerenes could be formed as multiples of the initial precursor [2,3]. The reactivity with regards to coalescence shows a strong dependence on modifications of the fullerene surface. Oxygenated carbon spheres, for instance, were found to undergo fusion reactions at lower laser powers than pure fullerenes [4] and laser-ablated organic ligand-bearing derivatives resulted in products with an uneven number of carbon atoms [5]. The laser-induced fullerene formation from non-fullerene precursors is also of intense current research interest [6]. Illustrative examples include the production of metallofullerenes by laser ablation of pyrolysed dried algae residues [7] and the fullerene formation in coalescence reactions of cyclo[n]carbons [8] or dodecahedrane derivatives [9]. These investigations clearly show that the precursor material must not only provide a sufficient amount of carbon to drive the coalescence reaction, but that certain structural features seem to facilitate the laser-induced formation of fullerenes.

In this connection, the title compound [$Cp_5CpMn(CO)_3$], **1** [10], seemed an intriguing substrate as its π-ligand provides a C_{30} unit with a topography similar to semi-buckminsterfullerene, $C_{30}H_{10}$ [11], in which the arrangement of six pre-formed five-membered carbon moieties ideally satisfies the isolated pentagon rule [12]. Upon laser-induced desorption/ionization (LDI) intramolecular fusion might be envisaged to lead to the generation of this elusive species perhaps in metal-complexed form [13], or to coalescence via a dimer to (potentially metallated)

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PII: S0022-328X(98)00940-1

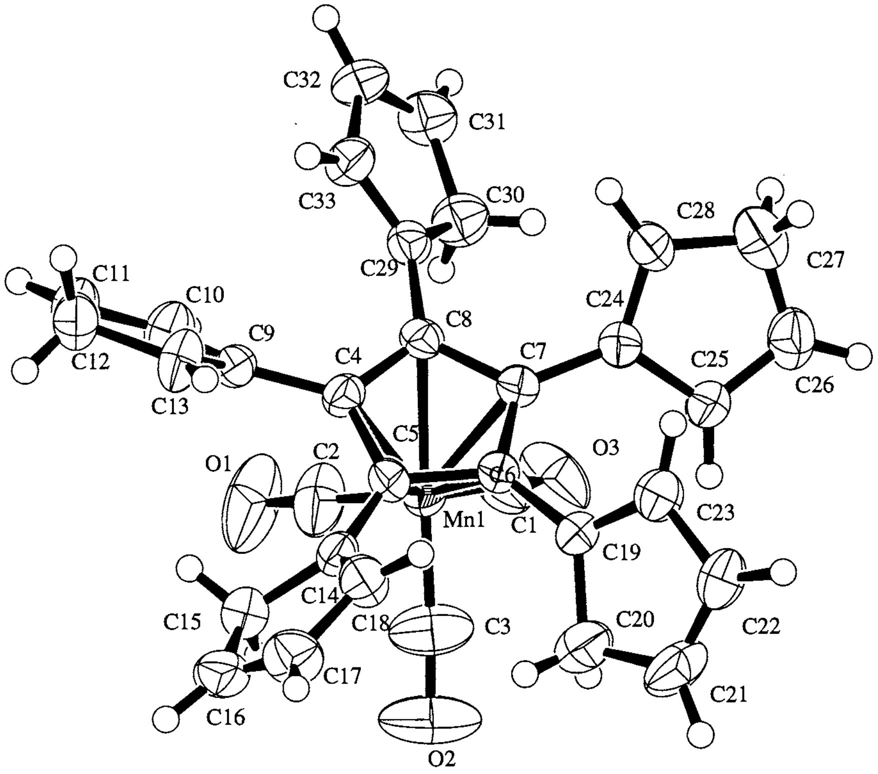

Fig. 1. Molecular structure of **1** in the crystal. Selected bond distances (Å): C(4)–C(9) 1.475(6), C(9)–C(10) 1.459(6), C(10)–C(11) 1.378(7), C(11)–C(12) 1.410(8), C(12)–C(13) 1.489(6), C(9)–C(13) 1.357(7), C(8)–C(29) 1.478(6), C(29)–C(30) 1.480(7), C(30)–C(31) 1.446(7), C(31)–C(32) 1.371(7), C(32)–(33) 1.469(7), C(29)–C(33) 1.354(6).

[14] fullerene C_{60}. This paper reports the X-ray structure of **1** and LDI experiments that reveal the occurrence of such coalescence processes.

Although **1** is obtained as a mixture of equilibrating 1,3- and 1,4-cyclopentadiene tautomers [10], slow crystallisation of one isomer occurred at −20°C in hexanes as yellow crystals amenable to (routine) X-ray analysis (Fig. 1) [15]. The molecule shows an alternating tautomeric pattern of the five appended Cp rings with C(14), C(19) and C(29) constituting carbons marking the terminus of the diene unit, C(9) and C(24) constituting their internal analogs [16]. Most notable is the lack of coplanarity of the Cp substituents, with dihedral angles ranging from 42.2° to 46.4° and bending angles [of the carbons of attachment from the least-squares plane of C(4)–C(8)] averaging 10° (away from the metal). While the average distance of the α-carbons in neighbouring Cp substituents is ca. 3.3 Å, Spartan modelling of the all-coplanar conformer narrows it to ca. 2.2 Å.

A nitrogen laser was used for LDI, operating at $\lambda = 337$ nm with a pulse length of 3 ns. Cations generated as the result of the LDI process were accelerated by a potential difference of 20 kV and analysed by reflectron time-of-flight mass spectrometry (ref-TOF). The mass spectrometer, which has been described in more detail elsewhere [17], has been successfully applied to induce coalescence reactions of fullerenes and fullerene derivatives, such as highly fluorinated fullerenes [17]. The mass spectra shown here represent the accumulation of 200 single-laser-shot data. Since it was found that the precursor material degraded over a period of several days at r.t., the target compound was either freshly prepared for the investigation or stored at low temperatures. For the experiments, the complex was deposited onto a stainless steel target slide in the form of a dichloromethane solution and dried before the introduction into the ion source.

Fig. 2 shows the positive ion LDI mass spectrum, obtained for **1** with laser power adjusted just above the threshold for ion formation. The spectrum is characterised by four major signal groups, each consisting of several peaks spaced by one mass unit, indicating the loss of hydrogen and with the most intense signals observed at m/z 317 ($C_{25}H_{17}$), m/z 385 (Cp_5Cp), m/z 440 (Cp_5CpMn) and m/z 493 ($[Cp_5CpMn(CO)_2{-}H_2]$). The assignment of these signals was further supported by investigating fully deuterated $C_{30}D_{25}Mn(CO)_3$, which showed the expected mass shifts due to the presence of deuterium. For both precursors, the molecular ion could not be detected and the only abundantly observed CO-containing fragment ion resulted from the loss of one CO unit. This fragment ion forms the only species of moderate intensity, together with Cp_5CpMn,

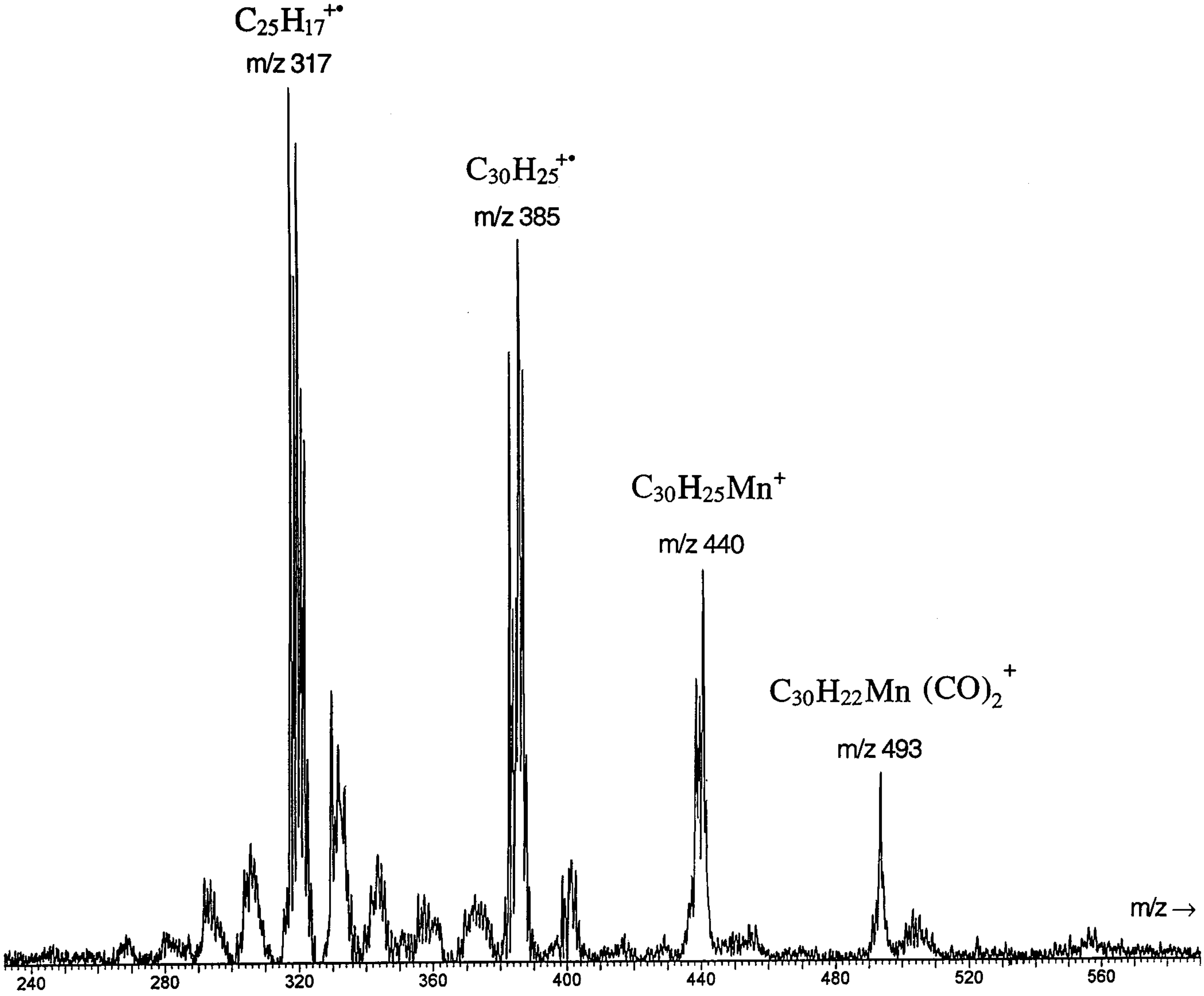

Fig. 2. Positive ion LDI mass spectrum of **1** with the laser power adjusted to just above the threshold for the ion formation.

which still contain the metal atom attached to the carbon framework of the Cp ligand. For comparison, under electron impact conditions (70 eV), the molecular ion is with 56% relative intensity perfectly detectable and the Cp_5CpMn fragment ion represents the base peak. Thus, LDI under the applied conditions leads to a more pronounced dissociation behaviour. This is further corroborated by increasing the laser power in order to promote coalescence reactions. Coalescence reactions of fullerene-based material were found to occur efficiently only if a sufficient amount of target material is ablated into the gas-phase [18] and if the dissociation leads to energised fragments, which act as the initialising particles for these reactions [19]. Upon increasing the laser power more fragmentation occurs, due to the dissociation of the Cp_5Cp ligand. Under these conditions, ions correlating to higher carbon clusters could not be detected; their abundance remained below the detection limit of the experimental set-up.

Only by applying an ion gate was it possible to obtain the spectrum in Fig. 3. The ion gate consists of two charged plates parallel to the ion flight path that allows the selection of one particular ion for further investigations (tandem mass spectrometry, post source decay) [20] and provides higher sensitivity for the detection of the gated ions, as saturation of the detector is prevented by decreasing the total number of ions reaching it. Fig. 3 clearly shows the formation of carbon clusters in the C_{60} region. However, semi-buckminsterfullerene and metallofullerenes could not be detected. The overall abundance of the fullerenes generated in this manner is at least two orders of magnitude lower than that observed in the laser-induced fusion of C_{60} under similar conditions. Repeated runs revealed C_{60}

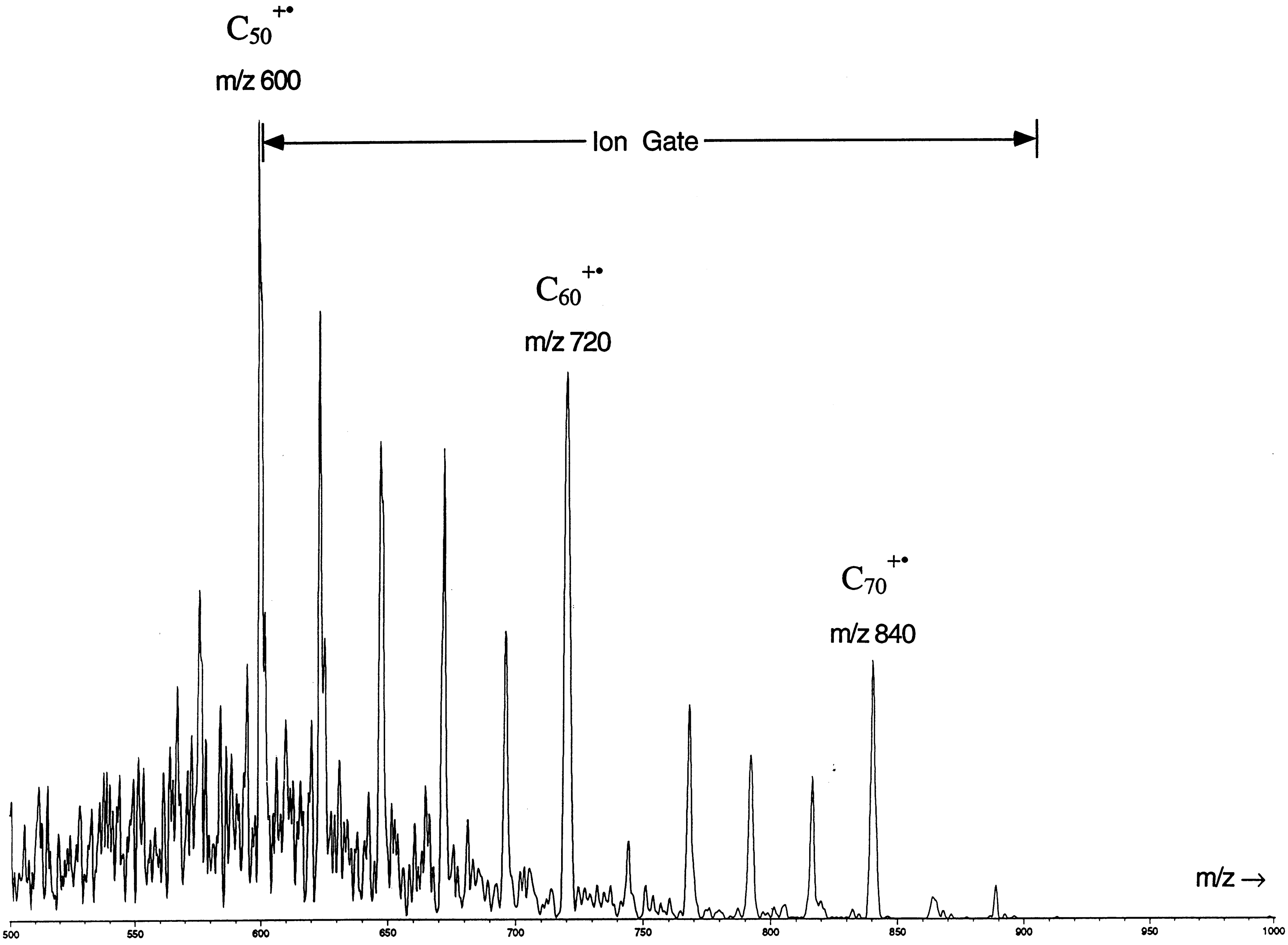

Fig. 3. Partial positive ion LDI mass spectrum of **1** under high laser power conditions, in conjunction with use of an ion gate for the indicated mass region to increase sensitivity.

always as the slightly dominant signal but also a plethora of higher carbon clusters. The overall cluster distribution varied for different experimental runs, which might indicate a moderate degree of fragmentation of the initially formed coalescence products. The instrumental resolution does not allow the exclusion of a possible contamination of the carbon clusters with hydrogen. The width of the particular peaks, however, suggests that the amount of hydrogen possibly still bonded to the fullerene ions is rather low.

In summary, it appears that LDI-induced coalescence of **1** occurs after the strategically positioned central metal atom has been removed from the ligand. The low fullerene yield may be due to the tendency of the ligand itself to undergo facile fragmentation by the loss of Cp, which makes a simple fusion of two intact ligands rather unlikely. The high degree of σ-bonded hydrogen atoms possibly plays a further unfavourable role, consistent with the distinctly attenuated tendency for $C_{60}H_{36}$ to undergo coalescence in comparison with that of pure C_{60} [21].

Acknowledgements

This work was supported by the EPSRC, the Leverhulme Trust and the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the US Department of Energy under Contract DE-AC03-76SF00098. The authors thank Erik Williams of Micromass Ltd. for obtaining the spectrum in Fig. 2 with the TofSpec-E. M.G. acknowledges a postdoctoral fellowship by the Deutsche Forschungsgemeinschaft.

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