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Mass Spectrometric Behavior of Complexes with Metal–Carbon σ-Bonds Part II. Mass Spectrometric Synthesis: the Gas Phase, Ion–Molecule Reaction of Tetracyanoethylene with η^1-Allyl Complexes

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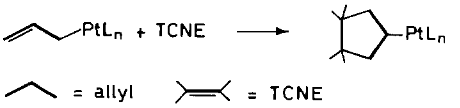
Abstract

Reactions between tetracyanoethylene and three different η^1-allyl complexes, performed within the ion source of a mass spectrometer, were studied. The time scale of the experiment allows the structural characterization of intermediates by collisional spectroscopy.

Introduction

The complexity of organometallic reactions involving transition metal ions makes almost any system a single case which, in terms of reaction mechanisms, cannot immediately be related to reference models [1, 2]. Moreover, these reactions often occur via different intermediates since ancillary ligands are able to adjust their bonding mode as a function of the reaction mechanism. A further problem is the difficulty of finding analytical methods with time scales and reliability suitable for structural characterization of these intermediates. An example of these arguments concerns the [2 + 3] cycloaddition of tetracyanoethylene (TCNE) to the allyl group of η^1-allyl Pt(II) complexes (eqn. 1) [3]



(1)

Depending on the nature of L ligands, TCNE attack may involve either the metallic center or the double bond of the allylic group. Some reaction intermediates have been detected in solution by low temperature NMR experiments, while others have been suggested only by analogy with the general mechanism of similar reactions in the case of 18-electron η^1-allyl complexes [4, 5].

The availability of a mass spectrometer suitable both for the study of gas phase reactions and for the characterization of reaction products and of intermediates [6, 7] prompted us to study the cycloaddition of TCNE and allyl group for 16- and 18-electron systems, with the aim of structurally identifying the primary reaction intermediates.

The approach employed here will take the two following steps: (i) exact mass measurements and isotopic cluster analysis in order to obtain the elemental formula of the product ions; (ii) B/E linked scans and CAD MIKE (Collisionally Activated Decomposition Mass Analyzed Ion Kinetic Energy) analysis [6, 7] in order to obtain structural information and assignments.

Experimental

The starting η^1-allyl complexes and the corresponding cycloaddition products of type **2** were prepared and characterized as described in Part I [8]. All these species have already been analyzed by EI (Electron Impact) mass spectrometric analysis [8].

Mass Spectrometric Procedures

All mass spectrometric measurements were performed on a VG ZAB2F instrument [9] operating in chemical ionization (CI) mode (100 eV, 2 mA). Compounds $[PtCl(\eta^1\text{-}C_3H_5)(PPh_3)_2]$ (**1a**), $[PtCl(\eta^1\text{-}C_3H_5)(Ph_2P{-}C_2H_2{-}PPh_2)]$ (**1b**), $[Mn(\eta^1\text{-}C_3H_5)(CO)_5]$ (**1c**), and $\{PtCl[\overline{CHCH_2C(CN)_2C(CN)_2CH_2}](PPh_3)_2\}$ (**2a**), $\{PtCl[\overline{CHCH_2C(CN)_2C(CN)_2CH_2}](\overline{PPh_2{-}C_2H_2{-}Ph_2P})\}$ (**2b**), $\{Mn[\overline{CHCH_2C(CN)_2C(CN)_2CH_2}](CO)_5\}$ (**2c**), were introduced under direct electron impact (DEI) [10] conditions, with a source temperature of 200 °C. For ion–molecule reactions, the reacting species were admitted to the source through different introduction ports, in order to guarantee the reaction occurrence in the gas phase;

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TCNE was introduced via septum inlet heated to 180 °C. Sample vapour pressures were monitored by means of a Pirani head directly mounted on one of the insertion ports of the ion source [11]. The typical pressure range for ion–molecule reaction occurrence was 0.1–1 torr. CAD MIKE spectra [6] were obtained by 8 keV ions colliding with air in the second field-free region. The pressure in the collisional chamber was such as to reduce the main beam intensity to 40% of its value. Metastable transitions were detected by B/E linked scan experiments [7] which are indicated in the Schemes by asterisks. Exact mass measurements were performed by the peak matching technique at 20000 resolving power (10% valley definition).

Results and Discussion

In the [2 + 3] cycloaddition of TCNE to the $-C_3H_5$ group in η^1-allyl complexes, eqn. 2, the original coordination environment at the metal ion is maintained, the other ligands not being directly involved in the electrophilic attack of TCNE. The structural characterization of *in situ* generated '1 + TCNE' adducts requires a preliminary mass spectrometric study of species **1** and **2**. In fact, the study of reaction (2) in gas phase must be performed with reacting species that are stable under the operating conditions. Thus, $[Fe(\eta^5\text{-}C_5H_5)(\eta^1\text{-}C_3H_5)(CO)_2]$ undergoes pyrolysis processes related to its evaporation, so that it is not suitable as a reagent for reaction (2). On the other hand, **1a**, **1b** and **1c** give rise to molecular ions and represent significant examples, displaying different coordination and metal electron availability *versus* TCNE attack; furthermore, the cyclopentyl products **2a**, **2b** and **2c** are thermally stable and under EI conditions lead to well detectable molecular ions.

1 **2**

(2)

In Part I we described the mass spectrometric behavior of **1** and **2** [8] and showed that:

(i) η^1-Allyl complexes may undergo preferential fragmentation via η^3-allyl species by loss of one of the neutral ligands present in the coordination sphere of **1**.

(ii) Loss of the allyl moiety is the most favoured fragmentation process in chelated phosphine compounds (such as, for example, **1b**).

(iii) The mass spectrometric behavior of the cyclopentyl compounds (**2**) turns out to be similar to that of ordinary metal–C σ complexes, showing preferential loss of the entire '$C_3H_5 \cdot$TCNE' moiety owing to the easy metal–C σ bond breaking. Significantly, no retrocycloaddition reactions (reverse of reaction (1)) were observed. The fragmentation pattern of **2c** indicates a complex skeletal rearrangement of the cyclopentyl group with loss of $C_3H_5^{\bullet}$, while $C(CN)_2\text{-}C(CN)_2$ remains coordinated.

Ion–Molecule Reactions

When compounds (**1**) are introduced into the ion source through the direct inlet port in an atmosphere of TCNE (previously introduced via septum inlet at a pressure of 0.1–1 torr), genuine ion–molecule reaction products become detectable, arising from the pathway

$$M_{(1)} + M_{(\mathrm{TCNE})}\urcorner^{+\bullet} \longrightarrow [M_{(1)} + M_{(\mathrm{TCNE})}]^{+\bullet} \tag{3}$$

This behavior is further confirmed by the linear dependence of product ion abundance on TCNE pressure in the range 0.1–1 torr.

In the condensed phase the analogous reaction involves neutral TCNE. Hence the gas phase ion–molecule reaction (3) involves a TCNE moiety with more pronounced electrophilic character, ultimately enhancing its reactivity *versus* the free olefinic end of the η^1-allyl ligand or, if available, the metallic center. Thus, electrophilic attack in the gas phase can be compared with that in the condensed phase.

In the reaction of neutral **1a** molecules reacting with $\mathrm{TCNE}\urcorner^{+\bullet}$, ionic species at m/z 923 are easily detected, they show the elemental composition $C_{45}H_{35}N_4ClP_2Pt$ as indicated by both exact mass measurement and isotopic clusters: these ions at m/z 923 are attributed to $M\urcorner^{+\bullet}$ of the one to one adduct formed by **1a** and TCNE. B/E linked scans performed on these ionic species (Fig. 1) led to a fragmentation pattern according to Scheme 1. Single bond cleavages lead to the ions at m/z 882 and 661, due to loss of the allyl radical and PPh_3, respectively. Other ions at m/z 821, 601 and 524 result from bond breakings with CN rearrangements.

However, the CAD MIKE spectrum of ionic species at m/z 923 obtained by the ion–molecule reaction in the ion source is not identical to that of $M\urcorner^{+\bullet}$ of **2a** [8]. This structural difference might, in principle, be due either to a different reactivity of $\mathrm{TCNE}\urcorner^{+\bullet}$ in comparison with neutral TCNE or to the presence (due to the very narrow time window of the mass spectrometer, about 10^{-7} s) of a real, always proposed but never heretofore confirmed, reaction (2) intermediate. For the higher electrophilic properties of $\mathrm{TCNE}\urcorner^{+\bullet}$, we are inclined to the latter hypothesis. The primary loss of the allyl group, observed either by B/E or by collisional spectroscopy (CAD) from $M\urcorner^{+\bullet}$ of the [**1a** + TCNE] adduct suggests that the allyl and TCNE groups are single ligands. The TCNE group in this adduct is not yet involved in allylic carbon bonding, but is firmly coordinated to the metal center: consistently, no

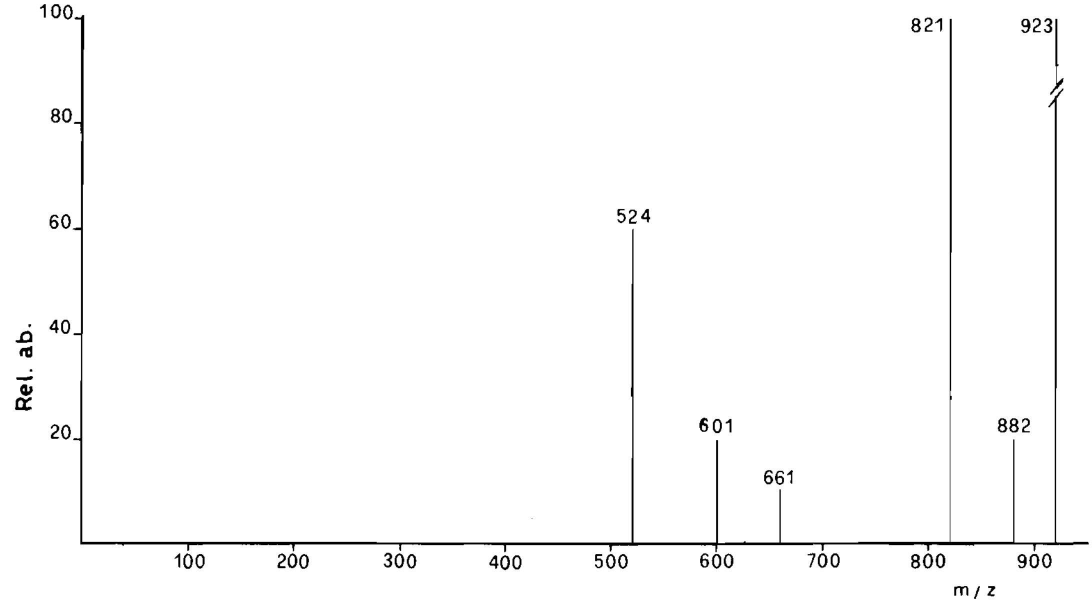
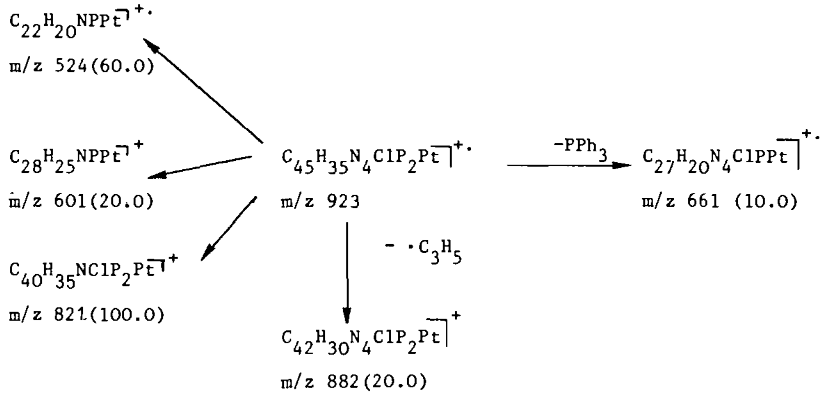
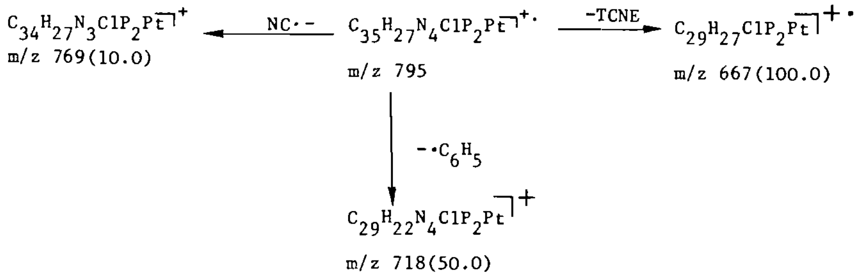


Fig. 1. B/E linked scan of ionic species at *m/z* 923 arising from ion–molecule reaction between **1a** and $\text{TCNE}\rceil^{+\cdot}$.



Scheme 1.



Scheme 2.

TCNE release was observed. Therefore, the primary intermediate of $\text{TCNE}\rceil^{+\cdot}$ attack on **1a** must be a 5-coordinated species retaining the original ligands in the coordination sphere.

The same reaction with **1b** leads to ionic species of elemental composition $C_{35}H_{27}N_4ClP_2Pt$ (*m/z* 795). B/E linked scans (Fig. 2) show a fragmentation pattern (Scheme 2) involving a significant loss of TCNE but not of $C_3H_5^{\cdot}$ or $C_3H_5TCNE^{\cdot}$. The CAD MIKE spectrum (Fig. 3) of ionic species at *m/z* 795, obtained by ion–molecule reaction in the ion source, is different from that of $M\rceil^{+\cdot}$ of **2b**. This rules out the structural identity of $M\rceil^{+\cdot}$ of the [**1b** + TCNE] adduct with either **2b** or a 5-coordinated species still

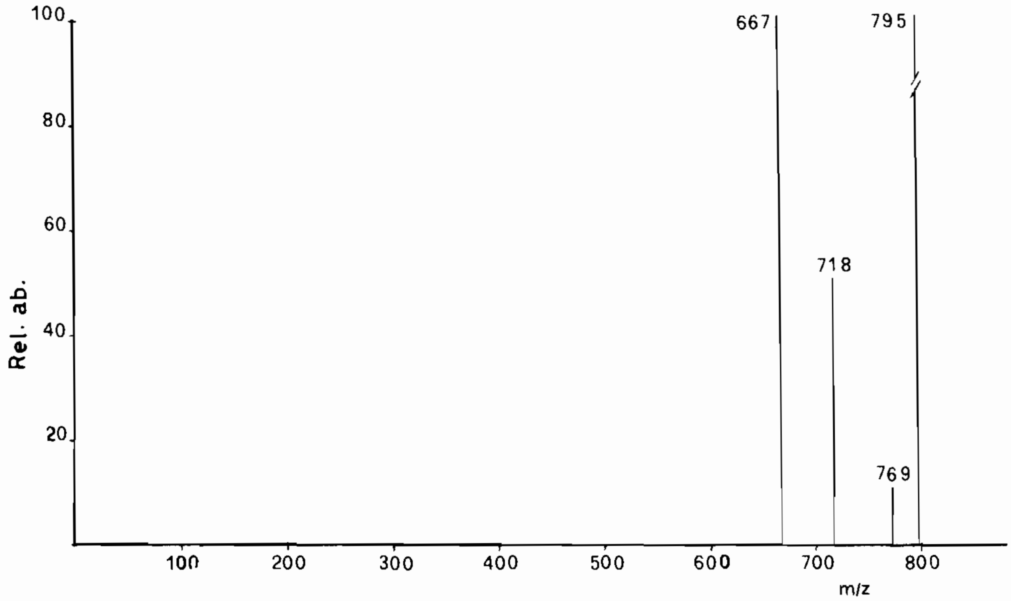


Fig. 2. B/E linked scan of ionic species at *m/z* 795 arising from ion–molecule reaction between **1b** and TCNE┐$^{+\bullet}$.

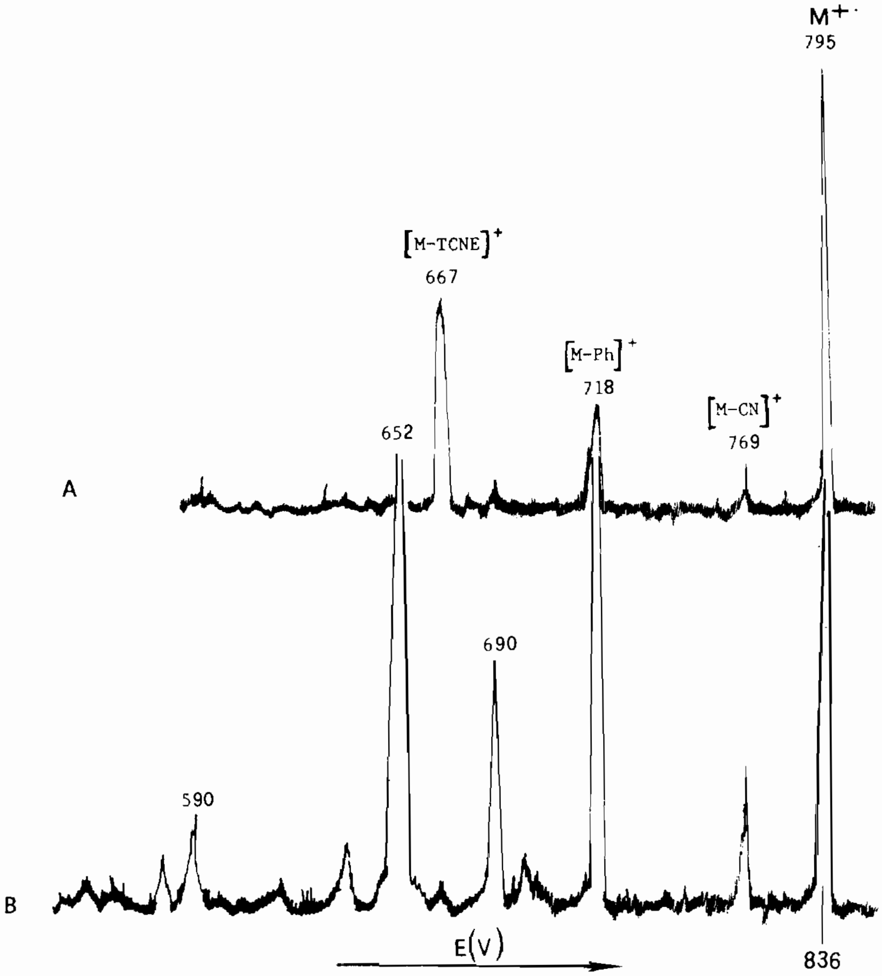


Fig. 3. (a) CAD MIKE spectrum of ionic species at *m/z* 795 arising from ion–molecule reaction between **1b** and TCNE┐$^{+\bullet}$; (b) CAD MIKE spectrum of M┐$^{+\bullet}$ of **2b**.

holding an η^1-allyl ligand. If we consider TCNE loss as a retro-reaction, the structural identification of the gas phase reaction product between **1b** and TCNE$\rceil^{+\bullet}$ reasonably leads to the zwitterionic species $\{Pt^+Cl\text{-}[\eta^2\text{-}CH_2{=}CHCH_2C(CN)_2C^-(CN)_2](Ph_2PC_2H_2PPh_2)\}^{+\bullet}$ where the allyl group is added to TCNE with one C–C bond but remains η^2-bonded to the metal ion. This result seems particularly interesting since zwitterionic species of the type proposed here have been frequently invoked to account for electrophilic attack on η^1-allyl complexes; they were not detected [4, 5] lacking further reactions suitable for carbanion trapping [12, 13].

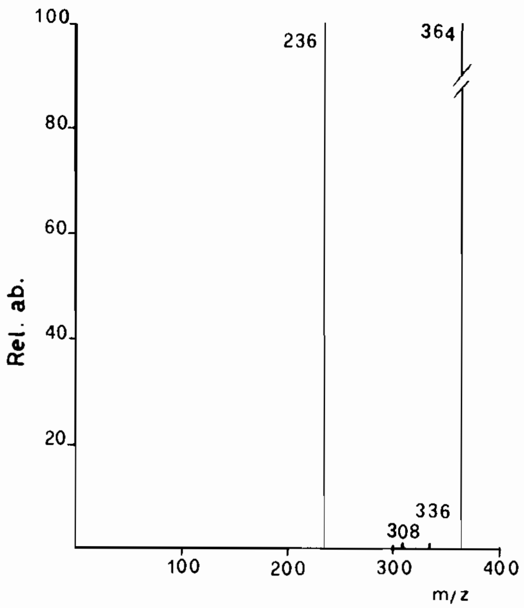
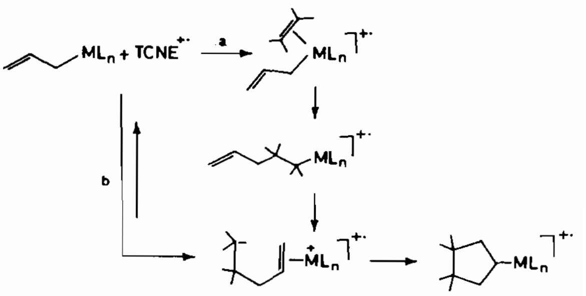


Fig. 4. B/E linked scan of ionic species at *m/z* 364 arising from ion–molecule reaction between 1c and TCNE$\rceil^{+\bullet}$.

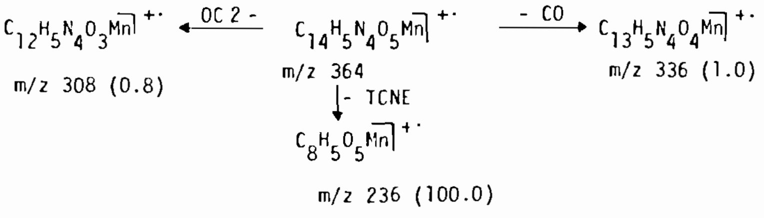
A similar behavior was observed for the gas phase reaction of **1c** and TCNE$\rceil^{+\bullet}$ affording the one to one adduct at *m/z* 364 corresponding to the elemental composition $C_{14}H_5N_4O_5Mn$. B/E linked scans (Fig. 4) led to the fragmentation pattern shown in Scheme 3. Apart from the quite usual loss of one and two CO molecules, the retro-synthetic TCNE loss with formation of $[C_8H_5O_5Mn]^{+\bullet}$ (*m/z* 236) is worth noting. On the other hand the absence of $^\bullet CHCH_2C(CN)_2\text{-}C(CN)_2CH_2$ and $C_3H_5^\bullet$ eliminations, which constitute strongly favoured paths of M$\rceil^{+\bullet}$ of **2c** electron induced fragmentation (see Scheme 6 in Part I) [8], again excludes that the observed *m/z* 364 ion corresponds to the final cycloaddition product. These results allow identification of the M$\rceil^{+\bullet}$ of [**1c** + TCNE] adduct as the zwitterionic ion $\{Mn^+[\eta^2\text{-}CH_2{=}CHCH_2C(CN)_2C^-(CN)_2](CO)_5\}^{+\bullet}$, analogous to the case of M$\rceil^{+\bullet}$ of [**1b** + TCNE] adduct.

In conclusion, our gas phase ion–molecule reactions and mass spectrometric identifications of primary reaction products confirm the difficulty of rationalizing organometallic reactions within a simple model case. On the other hand, the fundamental parameters ruling the [2 + 3] cycloaddition of TCNE to the η^1-allyl complexes in the condensed phase [3–5] also appear to operate in the gas phase ion–molecule reactions between TCNE$\rceil^{+\bullet}$ and the same complexes. Using Scheme 4 as a general simplified case for both gas and condensed phases, primary electrophilic attack on the metal center (path a) was observed only for starting species *trans*-$[PtCl(\eta^1\text{-}C_3H_5)(PPh_3)_2]$ (**1a**) both in the present mass spectrometric study and in the NMR investigation [3].

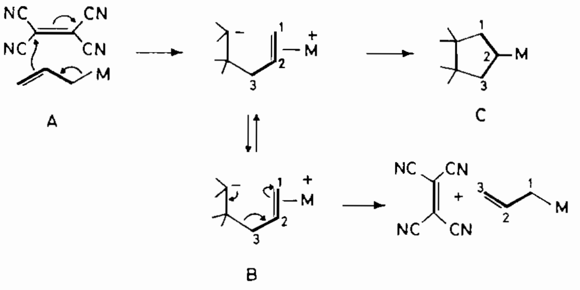


Scheme 4.

Moreover, direct electrophilic attack on the η^1-allyl olefinic end affording the zwitterionic intermediate (path b), Scheme 4, can be invoked for $[PtCl(\eta^1\text{-}C_3H_5)(Ph_2PC_2H_2PPh_2)]$ (**1b**) and $[Mn(\eta^1\text{-}C_3H_5)(CO)_5]$ (**1c**) complexes for both gas and condensed systems. The observed reversibility in path b (zwitterion formation) may be considered the crucial issue of the process. The occurrence of the zwitterion involves the A bond arrangement. Therefore, according to the microreversibility principle,



Scheme 3.



the retro-reaction implies B bond arrangement, which affords free TCNE and the original metal–carbon σ bond.

In the light of the coordinated double bond activation *versus* nucleophilic attack [14], the cycloaddition product, **C**, arises from nucleophilic attack of the carbanion to the partially electrophilic carbon C_1. Therefore, carbon C_1 can behave either as a nucleophile or an electrophile, leading to retro-reaction or to cycloaddition, respectively. In other words, the energy demands for reaction paths affording the zwitterionic species, its retro-reaction, and the [2 + 3] cycloaddition product fall within the narrow energy interval of the metal shuttle between terminal carbons of the $C_1{=}C_2$ double bond. At variance, the non-observed reversibility of path a in Scheme 4 suggests the zwitterionic occurrence via TCNE insertion on the metal–allyl σ bond which, in this case, may constitute the key step of the process.

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