Mass Spectrometric Detection of Reactive Intermediates. Reaction Mechanism of Diazoalkanes with Platinum(0) and Gold(I) Complexes

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The reactions of [$Pt(CH_2{=}CH_2)(PPh_3)_2$] and [$Au(C_6F_5)(SC_4H_8)$] with diazoalkanes have been performed under FAB conditions. The formation of the carbene species [$Pt({=}CHCO_2Et)(PPh_3)_2$] and [$Au({=}CPh_2)(C_6F_5)$], respectively, which are the key reaction intermediates and which were not detected in solution using other analytical tools, has been revealed by modern mass spectrometric techniques. Since the reaction products obtained by FAB MS were the same as those obtained in solution, mass spectrometry, providing an entry to the detection of highly reactive intermediates, may give also mechanistic information otherwise not achievable.

Introduction

Mass spectrometry has been employed from its early days in the organometallic field, proving to be a valid analytical method to obtain information about the molecular weight and the structure of organometallic compounds. Until the 1970s electron impact (EI) was the only ionization method; it was, however, quite limited, since it failed with very low volatility and thermal lability of certain substrates.[1] The development of new ionization methods, alternative to EI, allowed the deposition/ionization of organometallic compounds under softer conditions, i.e. those not requiring the vaporization of the sample and realizing an internal energy deposition lower than under EI conditions. Thus, field desorption (FD)[2] and fast atom bombardment[3] (FAB) proved to be highly efficient techniques, which allowed systematic investigations on organometallic systems. More recently, new ionization methods such as electrospray (ESI)[4] and laser desorption/ionization (LD)[5] have also been successfully applied. However, mass spectrometry has been employed not only as a mere analytical tool but also as a powerful device to study the gas-phase reactivity of organometallic ions[6] as well as ion-molecule reactions, either for kinetic studies or for the characterization of elusive intermediates.[7]

The most efficient approach to gas-phase reactions studies is based on the use of ion trapping devices such

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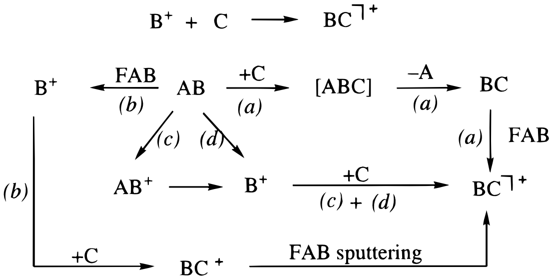
Scheme 1



as ion cyclotron resonance (ICR)[8] and quadrupole ion traps,[9] which allow the unambiguous selection of a reactant species. Conversely, with chemical ionization (CI) sources, the reactions take place as a highly complex mixture of ionic, neutral, and radical fragments, originating from the fragmentation of the reactant species.[10] Nevertheless, also in this latter case, relevant information can be achieved upon changing the stoichiometry of the reactants or by MS/MS experiments on selected ionic species.[10] As for FAB conditions, the reaction products could be generated either in the condensed phase or in the gas phase, since the ion−molecule reactions take place in the selvedge region close to the matrix surface.[3e] This latter aspect can be readily investigated by metastable ion studies or MS/MS experiments, which give an unambiguous indication of the presence of reactant ions also in the gas phase. This is exemplified by the gas-phase ion−molecule reaction occurring between B^+ ions, generated by a molecule AB, and neutral C molecules to give BC^+ cations, as illustrated in Scheme 1. Upon mixing AB and C in the FAB matrix, different reaction pathways can be, in principle, operative. For instance, neutral AB molecules can react in the condensed phase with neutral C molecules (route *a*), giving rise to the reaction intermediate [ABC], which, through loss of A, affords neutral BC. This latter species, once desorbed and ionized by FAB, eventually yields BC^+ cations. On the other hand, route *b* involves the FAB-induced formation within the matrix of B^+ ions, which then react with neutral C molecules to form BC^+ ions; upon sputtering by FAB, BC^+ ions in the gas phase are formed. Finally, two mechanisms operating only in the gas phase are shown by routes *c* and *d*. In the former case (route *c*) the AB^+ molecular ions readily decompose, generating B^+ ions, which then react in the gas phase with C to form BC^+ ions. In the case of route *d*, the initial direct FAB-induced formation of B^+ ions occurs, followed by the reaction with neutral C molecules to form BC^+ cations.

Although, as shown in Scheme 1, an FAB-based reaction study involves different pathways, the occurrence of gas-phase routes can be monitored by metastable ions or MS/MS experiments.[11] For instance, coming back to Scheme 1, the occurrence of route *c* can be evidenced by recording the daughter spectra of AB^+ ions as well as recording the parent spectra of B^+ ions.

In this frame work, we have previously studied, by detecting the reactive intermediates involved, the mechanism of the reaction of cyclic dithiocarbene hydrido complexes of Pt(II) of the type *trans*-$[PtH(\overline{CSCH_2CH_2S})(PPh_3)_2][BF_4]$ with NaCl[12a] and the ion−molecule interaction of *trans*-$[PtHCl(PPh_3)_2]$ with $SnCl_2$.[12b] More recently, we have obtained direct evidence of the formation of an unstable carbene species formed by reaction of $[Pt(CH_2{=}CH_2)(PPh_3)_2]$ with ethyl diazoacetate.[7a]

In spite of the promising results obtained by FAB/MS with a double-focusing instrument equipped with metastable ion and high collision energy facilities, the use of a triple-quadrupole instrument was thought to be more attractive, since it allows highly efficient, low collision energy MS/MS experiments. Therefore, we thought it of interest to reinvestigate the reaction of $[Pt(CH_2{=}CH_2)(PPh_3)_2]$ with ethyl diazoacetate and also to extend the mass spectrometric study to the reactions of $[(C_6F_5)Au(SC_4H_8)]$ with diazofluorene ($N_2CC_{12}H_8$) and diphenyldiazomethane (N_2CPh_2) using both double-focusing and triple-quadrupole instruments.

Experimental Section

$[Pt(CH_2{=}CH_2)(PPh_3)_2]$ (**1**)[13] and $[(C_6F_5)Au(tht)]$ (**2**)[14] were prepared by published methods. The diazo derivative N_2CHCO_2Et was used as purchased from Aldrich, while N_2CPh_2[15] and $N_2CC_{12}H_8$[16] have been prepared according to literature procedures.

The mass spectrometric measurements were performed on triple-quadrupole (VG Quattro, VG Fisons, Altrinchan, U.K.) and ZAB 2F (VG, Altrinchan, U.K.) instruments[17] equipped with FAB sources, bombarding 3-nitrobenzyl alcohol (Aldrich, 98%) solutions of the samples.[3f] The FAB cesium gun in the VG Quattro mass spectrometer operated from 2 to 10 kV. Positive ion mass spectra were obtained with MS-1 scanning over m/z 50−1500 at 9.6 s/decade. Product ion spectra were acquired by selecting the desired precursor ion with MS-1 and colliding it with argon at translational energy in the range 2−10 eV, in a collision cell located in the second field-free region (thickness of 2.30×10^{15} mol/cm^2; source pressure 2×10^{-6} mbar). The resulting fragment ions were detected by linked scanning of MS-2. The collision cell efficiency was tested using tetraethylsilane at 250 V. Repetitive scan spectra were recorded by a VG LAB BASE data system, mass-calibrated with the cluster ion spectrum of a 1:1 molar mixture of CsI and NaI between m/z 23 and 3500.

The VG ZAB 2F instrument was equipped with an FAB source (8 keV of Xe atoms), and metastable transitions were detected by MIKE[11a] (mass-analyzed ion kinetic energy) and CID MIKE (collision-induced dissociation mass analyzed ion

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kinetic energy) spectrometry.[11b] Precursor ion scans were obtained by B^2/E = constant linked scans.[11b]

The pressure in the collision cell was such to reduce the main beam intensity to 60% of its usual value. The reactions were performed directly in 1.5 mL of the FAB matrix by initially mixing **1** (37.3 mg, 0.05 mol) with $\mathrm{N_2CHCO_2Et}$ (119 μl, 0.100 mol) or **2** (42.2 mg, 0.09 mmol) with $\mathrm{N_2CPh_2}$ (3.6 mg, 0.018 mmol) and $\mathrm{N_2CC_{12}H_8}$ (3.5 mg, 0.018 mmol), respectively, and placing the reaction mixture on the probe tip, which was then immediately introduced into the source.

Results and Discussion

It has been previously reported[18] that the reaction of $[\mathrm{Pt(CH_2{=}CH_2)(PPh_3)_2}]$ (**1**) with 2 equiv of $\mathrm{N_2CHCO_2Et}$ in $\mathrm{CH_2Cl_2}$ gives the fumarato complex **3** according to eq 1. A preliminary mass spectrometric study of reaction 1 performed under FAB conditions showed that it proceeds by initial replacement of ethylene by $\mathrm{N_2CHCO_2Et}$ with the subsequent formation of the reactive Pt(0) carbene species $[\mathrm{Pt(CHCO_2Et)(PPh_3)_2}]$. The FAB mass spectrum of $[\mathrm{Pt(CH_2{=}CH_2)(PPh_3)_2}]$ showed the molecular ion at *m/z* 746 (^{194}Pt) and the formation of $[\mathrm{Pt(PPh_3)_2}]^{\bullet+}$ at *m/z* 718 (^{194}Pt) as the base peak. According to the discussion reported in the Introduction, metastable ion studies were performed in order to confirm the formation of $[\mathrm{Pt(PPh_3)_2}]^{\bullet+}$ ions in the gas phase. This was evidenced by the MIKE spectra of the ions at *m/z* 746, which showed the loss of $\mathrm{C_2H_4}$ as the most favored decomposition pathway; furthermore, B^2/E linked scans performed on the ionic species $[\mathrm{Pt(PPh_3)_2}]^{\bullet+}$ indicated $[\mathrm{Pt(CH_2{=}CH_2)(PPh_3)_2}]^{\bullet+}$ as the only precursor. The whole study showed the formation of the diazoalkane adduct $[\mathrm{Pt(N_2CHCO_2Et)(PPh_3)_2}]^{\bullet+}$ (**A**, *m/z* 832; ^{194}Pt), together with the Pt(0) carbene species $[\mathrm{Pt(CHCO_2Et)(PPh_3)_2}]^{\bullet+}$ (**B**, *m/z* 804; ^{194}Pt), according to Scheme 2.

$$\underset{\mathbf{1}}{[\mathrm{Pt(CH_2{=}CH_2)(PPh_3)_2}]} + 2\mathrm{N_2CHCO_2Et} \rightarrow \underset{\mathbf{3}}{[\mathrm{Pt(}\textit{trans}\mathrm{-EtOOCCH{=}CHCOOEt)(PPh_2)_2}]} + 2\mathrm{N_2} + \mathrm{C_2H_4} \quad (1)$$

Scheme 2

$$\begin{array}{l}
2[\mathrm{Pt(CH_2{=}CH_2)(PPh_3)_2}] \xrightarrow{\mathrm{FAB}} \\
\underset{m/z\ 746}{2[\mathrm{Pt(CH_2{=}CH_2)(PPh_3)_2}]^{\bullet+}} \xrightarrow{-2\mathrm{C_2H_4}} \\
\underset{m/z\ 718}{2[\mathrm{Pt(PPh_3)_2}]^{\bullet+}} \xrightarrow{+2\mathrm{N_2CHR}} \\
\underset{m/z\ 832}{2[\mathrm{Pt(N_2CHR)(PPh_3)_2}]^{\bullet+}} \xrightarrow{-2\mathrm{N_2}} \\
\underset{m/z\ 804}{2[\mathrm{Pt(CHR)(PPh_3)_2}]^{\bullet+}} \rightarrow \underset{m/z\ 1608}{[\mathrm{Pt(CHR)(PPh_3)_2}]_2^{\bullet+}} \rightarrow \\
\underset{m/z\ 890}{[\mathrm{Pt(}\textit{trans}\mathrm{\text{-}CHR{=}CHR)(PPh_3)_2}]^{\bullet+}} + [\mathrm{Pt(PPh_3)_2}]^{\bullet+} \\
\mathrm{R} = \mathrm{CO_2Et}
\end{array}$$

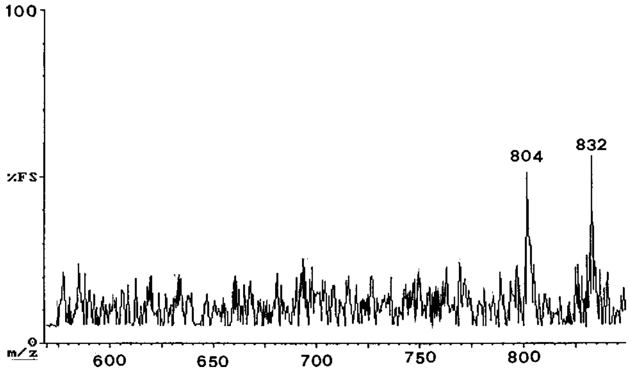

Figure 1. Neutral loss spectrum of the ion at *m/z* 832, showing the loss of a species of 28 mass units.

The formation of a carbene species from a metal-coordinated diazoalkane[19] is a known process,[20] but only a few examples of this conversion have been clearly demonstrated using, for instance, spectroscopic methods.[20] The conversion of the ionic diazoalkane species **A** to the carbene species **B** (eq 2) has been confirmed by reinvestigating reaction 1 using the triple-quadrupole mass spectrometer, which also allows us to detect unambiguously neutral losses. The results obtained when the reactant mixture is bombarded with Cs$^+$ ions at either 4 or 2 keV closely match those previously obtained on the VG ZAB 2F instrument using Xe atoms at 8 keV, thus confirming the proposed reaction mechanism (Scheme 2). Furthermore, the conversion of the diazoalkane **A** to the carbene species **B**, where the $\mathrm{N_2}$ loss of 28 mass units occurs, has been clearly detected by neutral loss scans from ions at *m/z* 832 of **A** to form ions at *m/z* 804 of **B**, as shown in Figure 1. Although the observed loss of 28 mass units could be attributed to a CO molecule instead of $\mathrm{N_2}$, the proposed $\mathrm{N_2}$ loss from the diazo ester seems to be more reasonable, since organic esters RCO−OR′ are known to give readily and preferentially loss of the OR′ fragment to form RCO$^+$ ions.[21]

$$\underset{\mathbf{A}\ (m/z\ 832)}{[\mathrm{Pt(N_2CHCO_2Et)(PPh_3)_2}]^{\bullet+}} \xrightarrow{-\mathrm{N_2}} \underset{\mathbf{B}\ (m/z\ 804)}{[\mathrm{Pt(CHCO_2Et)(PPh_3)_2}]^{\bullet+}} \quad (2)$$

It is noteworthy that no evidence of the formation of the carbene species $[\mathrm{Pt({=}CHCO_2Et)(PPh_3)_2}]$ (**B**) was obtained following reaction 1 by NMR spectroscopy even at low temperature, probably due to its extremely low concentration in solution. On the other hand, the formation of such a carbene intermediate was substantiated chemically by observing the formation of cyclopropanes from styrene and $\mathrm{N_2CHCOOEt}$ in the presence

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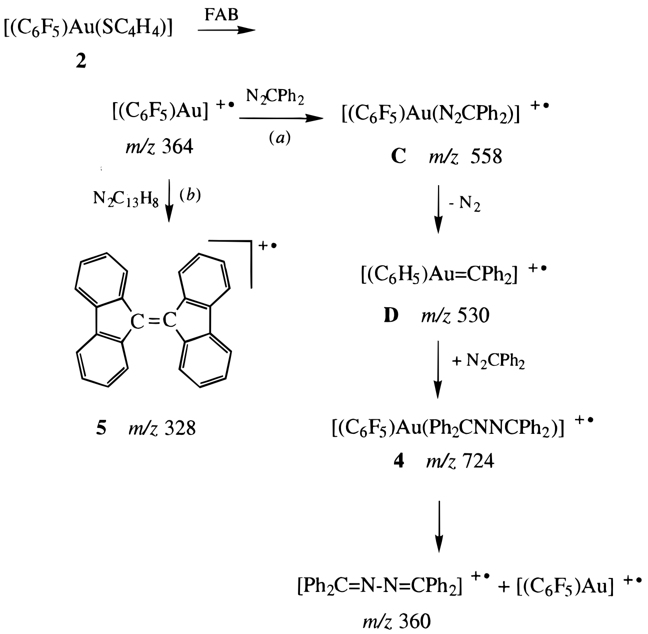
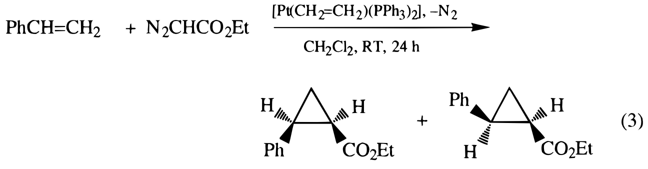
Scheme 3

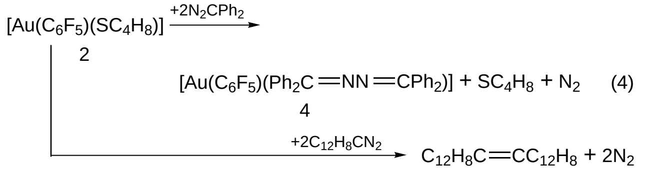


of $[Pt(C_2H_4)(PPh_3)_2]$ (eq 3), which is believed to involve coupling of the carbene with the olefin[20a,22]



(3)

The analysis by the above-described mass spectrometric techniques has been extended to the reaction of $[Au(C_6F_5)(SC_4H_8)]$ (**2**) with diazoalkanes. It has been previously reported[23] that the reaction of **2** with 2 equiv of N_2CPh_2 in diethyl ether yields the ketazine complex **4** (eq 4), while a similar reaction with $N_2CC_{12}H_8$ leads to the formation of the corresponding olefin $C_{12}H_8C{=}C{-}C_{12}H_8$ (**5**). The condensed-phase mechanism for both



$$\underset{2}{[Au(C_6F_5)(SC_4H_8)]} \xrightarrow{+2N_2CPh_2} \underset{4}{[Au(C_6F_5)(Ph_2C{=}NN{=}CPh_2)]} + SC_4H_8 + N_2 \qquad (4)$$

$$\xrightarrow{+2C_{12}H_8CN_2} C_{12}H_8C{=}CC_{12}H_8 + 2N_2$$

reactions has been tentatively discussed in terms of the formation of an unstable gold(I) carbene species of the type $[(C_6F_5)Au{=}CR_2]$, which undergoes diazoalkane N-addition at the carbene carbon atom to give **4** or, after N_2 loss, the free olefin **5** and the complex **2**.

The results of the mass spectrometric study of reaction 4 are reported in Scheme 3. Both reactions *a* and *b* of Scheme 3 involving N_2CPh_2 and $N_2CC_{12}H_8$, respectively, were run under FAB conditions either in the double-focusing or in the triple-quadrupole instruments. As for reaction *a*, the spectra of the reaction mixture show the presence of easily detectable ionic species at *m/z* 724 (^{197}Au) attributed to the molecular ion of species **4**, together with ions at *m/z* 558, 530, and 360, the last being the most abundant. The mass spectrum of the reaction mixture performed in the VG Quattro instrument is reported in Figure 2.

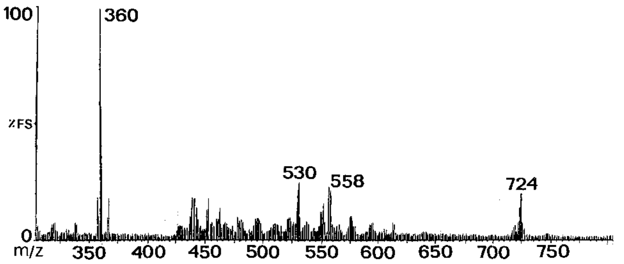


Figure 2. FAB mass spectrum of the reaction mixture of reaction 4 measured on the VG Quattro instrument.

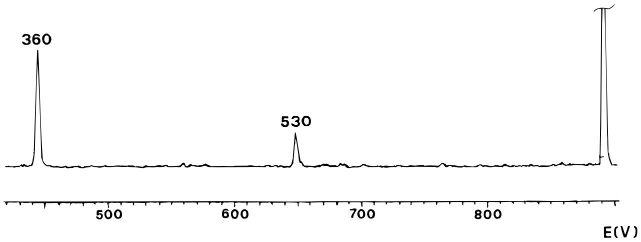


Figure 3. MIKE spectrum of ions at *m/z* 724.

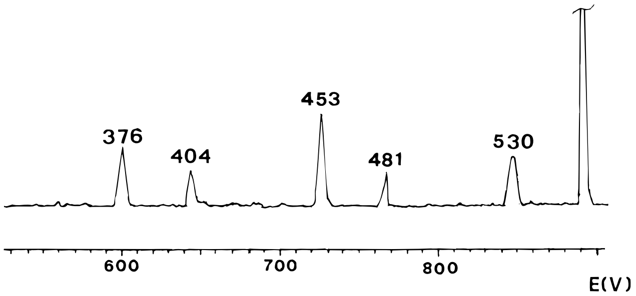


Figure 4. MIKE spectrum of ions at *m/z* 558.

The MIKE spectrum of ions at *m/z* 724 (Figure 3) shows the formation of ions at *m/z* 360 corresponding to the species $Ph_2C{=}NN{=}CPh_2$, together with a weaker signal due to the formation of ions at *m/z* 530. Although the ions at *m/z* 360 could originate from different species (e.g. free N_2CPh_2), precursor ion scan experiments show that ions at *m/z* 724 are the only sources of the azine species.

The ions at *m/z* 558 may be attributed to the species **C** formed by replacement of the labile SC_4H_8 tetrahydrothiophene ligand with N_2CPh_2. Species **C** upon loss of N_2 forms the carbene intermediate **D** at *m/z* 530 (^{197}Au). These latter ions then add to a second molecule of N_2CPh_2 to form the molecular ions of **4** at *m/z* 724. The MIKE spectrum of ions **C** at *m/z* 558, performed in the ZAB 2F instrument (Figure 4), shows the unambiguous formation of ions at *m/z* 530 corresponding to the carbene species **D**, generated by loss of N_2, together with the species originated by sequential losses of two phenyl radicals from the ions at *m/z* 558 (leading to ions at *m/z* 481 and 404) and from ions at *m/z* 530 (leading to species at *m/z* 453 and 376). The formation in the gas phase of the key intermediate carbene species **D** from the adduct **C** was confirmed by the daughter spectrum of ions at *m/z* 558, performed in the triple-quadrupole instrument (Figure 5), which shows a

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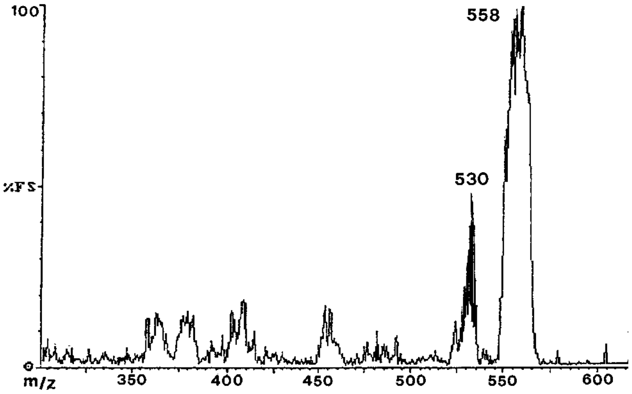

Figure 5. Daughter ion spectrum of ions at *m/z* 558.

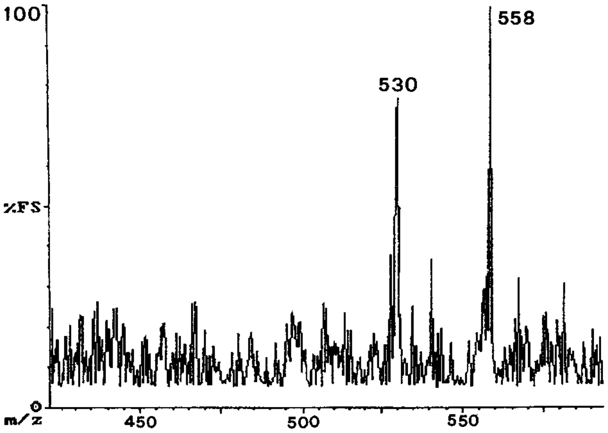

Figure 6. Neutral loss spectrum of the ion at *m/z* 558, showing the loss of a species of 28 mass units.

neutral loss of 28 (Figure 6), corresponding to N_2. The MIKE spectrum of the species at *m/z* 530 does not show spontaneous fragmentation processes, indicating that the M−C bond in the species **D** is relatively strong, as expected for a carbene system.[24]

In the FAB mass spectrum of the mixture of reaction *a* (Scheme 3), ions of low abundance at *m/z* 332 are also present, corresponding to the molecular ions of the olefin $Ph_2C{=}CPh_2$, which are likely formed by the coupling of two organic carbene moieties generated by decomposition of free diphenyldiazomethane rather than from **D**. This is confirmed by the FAB mass spectrum of free N_2CPh_2, which shows the formation of a large amount of ions at *m/z* 332 attributed to $[Ph_2C{=}CPh_2]^{\bullet+}$ together with a weak signal of ions at *m/z* 360 due to $[Ph_2C{=}NN{=}CPh_2]^{\bullet+}$.

In the case of route *b*, only the formation of the olefin derivative **5** (molecular ions at *m/z* 328) is observed, with no evidence of Au adducts. This behavior may be explained by the high stability of the organic product **5**, as also shown by its MIKE spectrum, which does not show unimolecular fragmentation processes, except for a loss of H_2. However, the presence in the mass spectrum of the reaction mixture of ions at *m/z* 364 might indicate that the formation of **5** is likely catalyzed by the metal, as also found in solution. It is noteworthy that free diazofluorene decomposes under strong reaction conditions (reflux in $EtOH/H_2SO_4$) to give the corresponding azine as the only product.[25]

In conclusion, FAB MS methods may provide a valuable aid in studying certain solution reactions, as shown here for the investigation of the reactions of diazoalkanes with d^{10} metal complexes, which closely parallel the results obtained in solution and the detection of reactive Pt(0) and Au(I) carbene species has been achieved.

The data discussed above demonstrate well the potential of metastable ion studies and MS/MS experiments in the detection and structural characterization of intermediates. All the steps of the reaction pattern reported in Scheme 3 have been confirmed to occur in the gas phase, even if their presence also in the FAB matrix cannot be, a priori, excluded.

The observation of the same product ions and of the same intermediates with both double-focusing and triple-quadrupole instruments, through the employment of their specific facilities, make us more confident of the results obtained and show the unique versatility of mass spectrometry as a technique for the detection of reactive species.

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