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C–C Activation of Phosphaalkynes by Bare Iron(I) Cations in the Gas Phase

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Abstract: The gas-phase ion chemistry of RCP/Fe^+ complexes ($R = C(CH_3)_3$, $C_2H_5C(CH_3)_2$) is very different from that of the analogous RCN/Fe^+ and RNC/Fe^+ systems. While from the latter, both spontaneously and collision induced, HCN (or HNC) and $Fe(H,C,N)^+$ are formed in competition, the chemistry of the RCP/Fe^+ complexes is dominated by the generation of neutral CH_4, C_2H_4, and C_3H_8 fragments. The study of $CH_3CH_2C(CD_3)_2CP/Fe^+$ ions proves that C_3H_8 generated from $C_2H_5C(CH_3)_2CP/Fe^+$ is not formed as intact "propane" but is rather due to the consecutive losses of ethylene and methane. The second step, i.e., methane generation, follows a multistep reaction path, involving highly specific hydrogen migration from and to the metal-ion center. In addition, the study of this complex provides detailed insight into the feasibility of several elementary steps of organometallic chemistry in the gas phase. Noteworthy are (i) the absence of any hydrogen scrambling processes, (ii) the nonoperation of α- and/or β-methyl migrations, and (iii) the preference of hydrogen transfer from a methylene rather than a methyl group.

The reaction of aliphatic unbranched nitriles, RCN, with bare transition-metal ions, e.g., Fe^+, is unique, in that selective C–H activation occurs only at positions *remote* from the cyanide functionality;[1] Fe^+ complexes of *tert*-butyl-substituted, aliphatic nitriles are characterized by *remote* functionalization of C–C bonds.[2] These unprecedented behaviors contrast with that of other unsaturated systems, such as alkynes,[3] where often activation of propargylic C–C and/or C–H bonds are reported to be the major mode of reaction, which are caused by an initial "side-on" complexation of the CC triple bond. The primary reason for the behavior of nitriles is due to the specific interaction of the cyanide group with the transition-metal ion Fe^+. The preferred coordination leads to an "end-on" complex characterized by a "linear"[4] $-CH_2-C-N-M^+$ entity (M = transition-metal atom). The linear fragment in turn constrains the remainder of the molecule such that Fe^+ inserts in remote C–H and C–C bonds while trying to minimize the strain. Interestingly, isonitriles, RNC, demonstrate a distinct behavior in their reactions with bare Fe^+; recently, circumstantial evidence for *both* "end-on" and "side-on" complexation was obtained.[5] While the former resulted in functionalization of C–H bonds remote from the functional group, the latter caused activation of C–H and C–C bonds in the vicinity of the isonitrile group.[5] This dichotomy of a functional group is without precedence in the reactivity of organometallic complexes in the gas phase.

No doubt that a study of the gas-phase chemistry of Fe^+ complexes of phosphaalkynes, $RC\equiv P$, is of particular interest, mainly for the following reasons. First, this functional group can potentially be complexed in a side-on or end-on fashion. Second, in the condensed phase many reactions of phosphaalkynes $RC\equiv P$ are very much like that of their carbon analogues, i.e., alkynes $RC\equiv CH$.[6] For example, addition of hydrogen halides[7] or halides[8] are known, and cycloadditions with 1,3-dipolar compounds[9] or dienes[10] were also reported. Moreover, several organometallic complexes exhibit similar types of bonding for both $RC\equiv P$ and $RC\equiv CH$; this is, for example, evidenced by the side-on coordination of platinum complexes to $(CH_3)_3CC\equiv P$ (**1**)[11] or the structurally related cobalt complexes formed with phosphaalkynes as well as alkynes.[11] Finally, the transition-metal-mediated cyclotrimerization, well-known for alkynes, is also operative for $RC\equiv P$, thus yielding 1,3,5-triphosphabenzene[12a] or Dewar-isomer derivatives.[12b] All these examples point to a close similarity of the chemistry of $RC\equiv P$ and $RC\equiv CH$ systems. Does this similarity also hold true for the reactions of these compounds with bare Fe^+ ions, or has the gas-phase chemistry of the $RC\equiv P/Fe^+$ complexes more in common with the $RC\equiv N/Fe^+$ or $RN\equiv C/Fe^+$ systems? An answer to this problem will be given in the following.

$RC(CH_3)_2CX$

	R	X
1	CH_3	P
2	C_2H_5	P
4	CH_3	CH
5	C_2H_5	CH
6	CH_3	N

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[1] (a) Lebrilla, C. B.; Schulze, C.; Schwarz, H. *J. Am. Chem. Soc.* **1987**, *109*, 98. (b) Drewello, T.; Eckart, K.; Lebrilla, C. B.; Schwarz, H. *Int. J. Mass Spectrom. Ion Processes* **1987**, *76*, R1. (c) Lebrilla, C. B.; Drewello, T.; Schwarz, H. *Ibid.* **1987**, *79*, 287. (d) Lebrilla, C. B.; Drewello, T.; Schwarz, H. *J. Am. Chem. Soc.* **1987**, *109*, 5639. (e) Prüsse, T.; Drewello, T.; Lebrilla, C. B.; Schwarz, H. *Ibid.*, in press. (f) Czekay, G.; Drewello, T.; Schwarz, H. *J. Am. Chem. Soc.*, in press. For a review see: (g) Czekay, G.; Drewello, T.; Eller, K.; Lebrilla, C. B.; Prüsse, T.; Schulze, C.; Steinrück, N.; Sülzle, D.; Weiske, T.; Schwarz, H. In *Organometallics in Organic Synthesis*; Werner, H., Erker, G., Eds.; Springer Verlag: Heidelberg, in press. (h) Schwarz, H. *Acc. Chem. Res.*, submitted.

[2] Prüsse, T.; Lebrilla, C. B.; Drewello, T.; Schwarz, H. *J. Am. Chem. Soc.* **1988**, *110*, 5986.

[3] (a) Peake, D. A.; Gross, M. L. *Organometallics* **1986**, *5*, 1236. (b) Schulze, C.; Schwarz, H.; Peake, D. A.; Gross, M. L. *J. Am. Chem. Soc.* **1987**, *109*, 2368. (c) Schulze, C.; Weiske, T.; Schwarz, H. *Chimia* **1986**, *40*, 362. See, however: (d) Schulze, C.; Schwarz, H. *Ibid.* **1987**, *41*, 29.

[4] In the present context we use the term "linear" very loosely, as we know little about the energetics and electronics of this complex. No doubt that depending on the nature of the transition-metal ion M^+ and on the internal energy of the $RCN-M^+$ complex, deviation from linearity of the $-CH_2-C-N-M^+$ unit must occur (see ref 1c for a comparison of Fe^+, Co^+, and Ni^+), which may even result in the formation of a "side-on" complex for $M^+ = Cu^+$; Lebrilla, C. B.; Drewello, T.; Schwarz, H. *Organometallics* **1987**, *6*, 2450. A quite interesting case has been reported recently[1e] for *unsatuated* aliphatic nitriles of the general structure $RCH{=}CH(CH_2)_mCN$ (R = alkyl). Data were reported that strongly suggest that depending on the length of the methylene chain $-(CH_2)_m-$, the bidentate Fe^+ complexes may contain an "end-on" or a "side-on" complexed nitrile function.

[5] Eller, K.; Lebrilla, C. B.; Drewello, T.; Schwarz, H. *J. Am. Chem. Soc.* **1988**, *110*, 3068.

[6] For a review on syntheses, reactions and coordination behavior of phosphaalkynes, see: Regitz, M.; Binger, P. *Angew. Chem.* **1988**, *100*, 1541.

[7] (a) Appel, R.; Maier, G.; Reisenauer, H. P.; Westerhaus, A. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 197. (b) Appel, R.; Westerhaus, A. *Tetrahedron Lett.* **1981**, 2159.

[8] Becker, G.; Becker, W.; Knebl, R.; Schmidt, H.; Weber, U.; Westerhausen, M. *Nova Acta Leopold.* **1985**, *59*, 55.

[9] (a) Rösch, W.; Regitz, M. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 900. (b) Yeung Lam Ko, Y. Y. C.; Carrié; Münch, A.; Becker, G. *J. Chem. Soc., Chem. Commun.* **1984**, 1634.

[10] Rösch, W.; Regitz, M. *Z. Naturforsch.* **1986**, *41B*, 931.

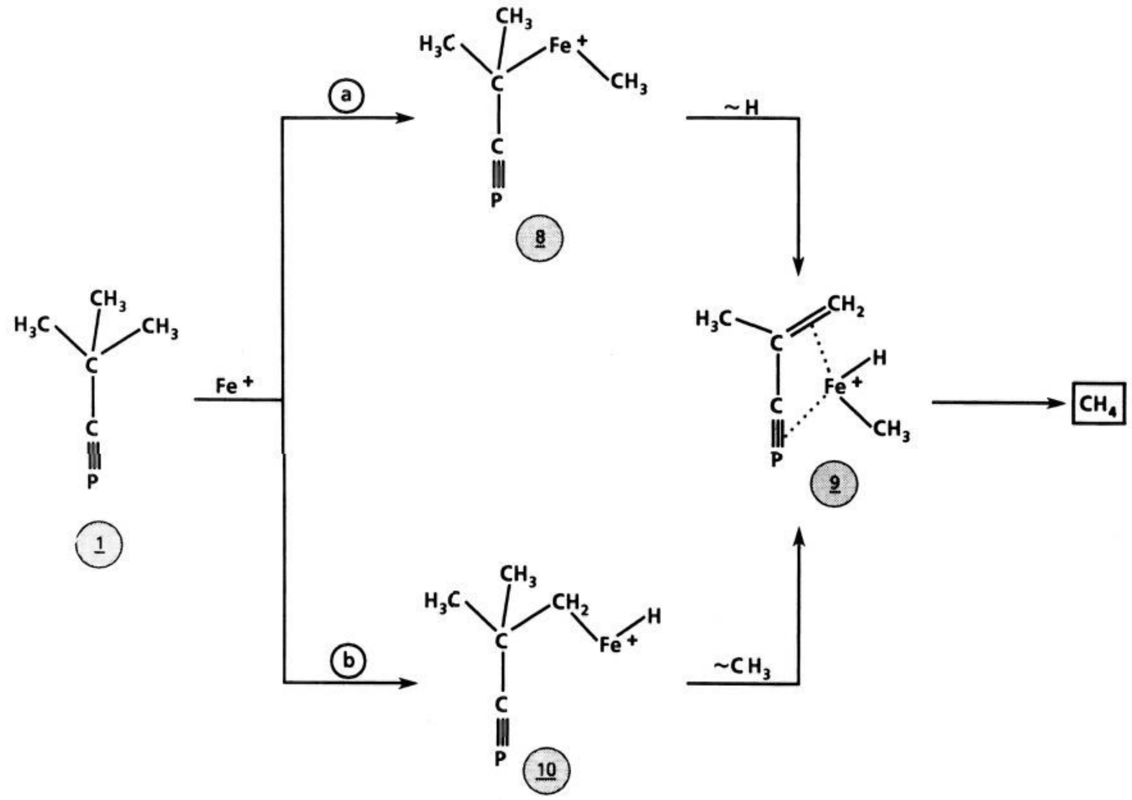
[11] Burkett-St.-Laurent, J. C. T. R.; Hitchcock, P. B.; Kroto, H. W.; Nixon, J. F. *J. Chem. Soc., Chem. Commun.* **1981**, 1141.

[12] (a) Barron, A. R.; Cowley, A. H. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 907. (b) Milczarek, R.; Rüsseler, W.; Binger, P.; Jonas, K.; Angermund, K.; Krüger, C.; Regitz, M. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 908.

[†] Technische Universität Berlin.
[‡] Universität Kaiserslautern.

0002-7863/89/1511-4228$01.50/0

Scheme I



As stable phosphaalkynes with one or two hydrogens at the α-carbon atom are unknown, preliminary experiments were performed with the α,α-dimethyl-substituted phosphaalkynes **1**, **2**, and **3** (**3** = $CH_3CH_2C(CD_3)_2CP$). The results were compared with those obtained for the corresponding alkynes **4** and **5**, the nitrile **6**, and the isonitrile $(CH_3)_3CNC$ (**7**), respectively.

The first experiments performed made it already obvious that the chemistry of the RCP/Fe^+ complexes is distinctly different from that of **6**–Fe^+ and **7**–Fe^+.[13] For the nitrile and isonitrile Fe^+ complexes, the major reactions (both unimolecular and collision induced) are due to the formation of $HCN–Fe^+$ (from **6**) and $HNC–Fe^+$ (from **7**) and the elimination of a neutral molecule with 27 amu (possibly HCN or, less likely on energetic grounds, HNC).[13] The analogous processes, i.e., formation of $Fe(H,C,P)^+$ and/or the elimination of neutral HCP[14] from the phosphaalkyne/Fe^+ complexes, are not observed at all. Rather, processes occur that seem to be more typical for the alkyne/Fe^+ systems. However, a closer inspection reveals that some of the similarities of the RCP/Fe^+ and $RCCH/Fe^+$ systems are deceptive. In addition, a quite remarkable process is characteristic for **2**–Fe^+, whose mechanistic details were uncovered by the study of the labeled analogue **3**.

In this contribution we focus on this particular aspect which not only may be of general importance for the understanding of ionic organometallic systems in the gas phase but also has some bearing on elementary processes in organometallic chemistry in general.

Experimental Section

The experimental setup and the machine and its operation have been described in detail in earlier papers.[1,15] Briefly, a VG Instruments ZAB-HF-3F triple-sector mass spectrometer with B(1)EB(2) configuration was used (B stands for magnetic and E for electrostatic sector). In a typical experiment, $Fe(CO)_5$ and the organic substrate were introduced into the ion source via the gas-inlet system and bombarded with an electron beam of 100-eV kinetic energy. Organometallic ions corresponding to a 1:1 adduct[16] of Fe^+ and the organic substrate were accelerated to 8-keV kinetic energy, mass selected by using B(1)E, and collided in a collision cell with He (pressure ca. 10^{-5} Torr); ionic fragments are analyzed by scanning B(2). In the collision experiment the intensity of the primary ion beam is attenuated to ca. 80–85%; this corresponds on average to 1.1 collisions.[17] Unimolecular reactions of metastable ions (MI) occurring in the field-free region between E and B(2) were monitored by scanning B(2) without admitting collision gas in the collision cell. As the results of the MI and CA spectra are, by and large, quite similar, only the latter will be discussed. To improve the signal-to-noise ratio and the reproducibility, spectra were averaged by using the VG 11/250 data system. Compounds **4–7** were synthesized by

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[13] Eller, K.; Schwarz, H. *Organometallics*, in press.

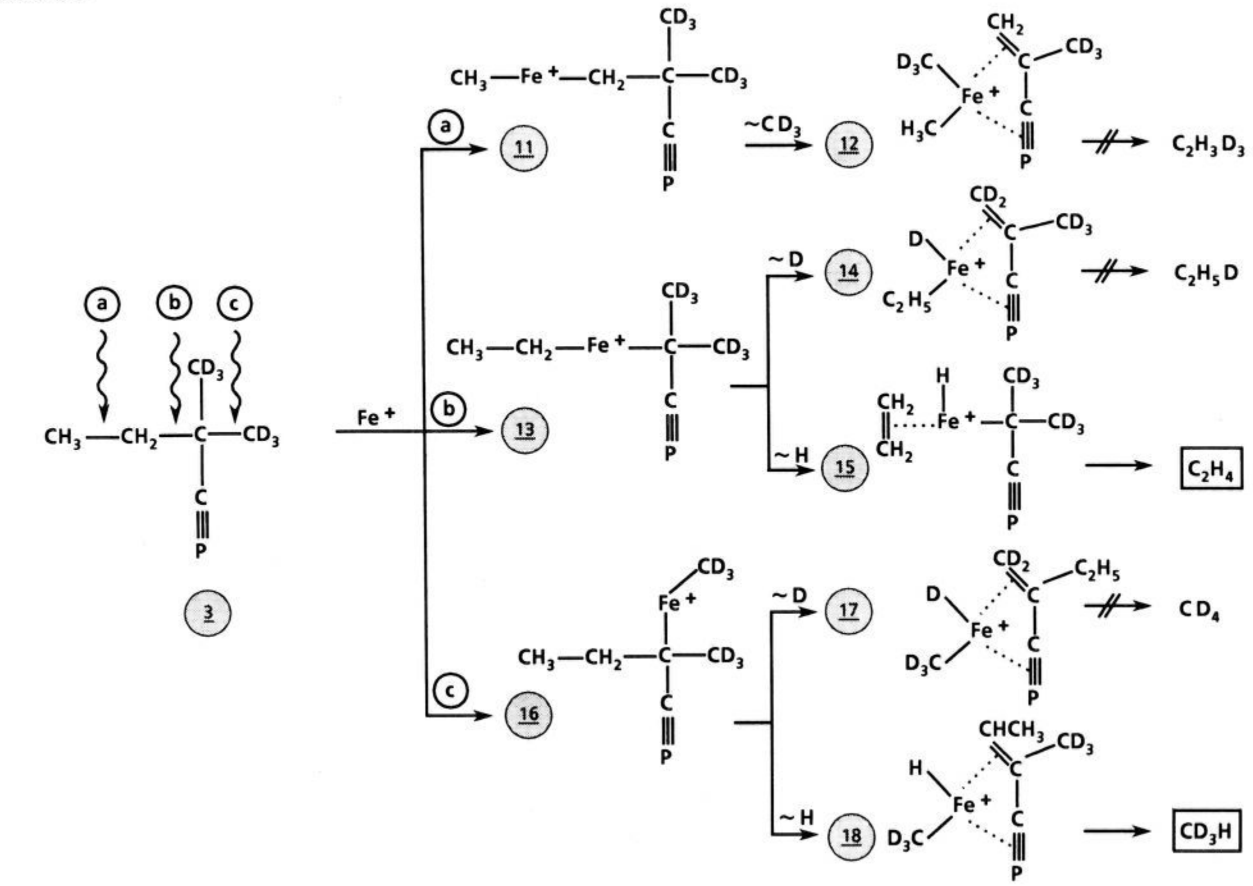
[14] For studies on the HCP molecule, see: (a) Gier, T. E. *J. Am. Chem. Soc.* **1961**, *83*, 1769. (b) Lavigne, J.; Pepin, C.; Cabana, A. *J. Mol. Spectrosc.* **1984**, *104*, 49, and references therein. (c) Kroto, H. W. *Chem. Soc. Rev.* **1982**, *11*, 435. Studies on $HCP^{\bullet+}$ are described by: (d) King, D. A.; Klapstein, D.; Kroto, H. W.; Maier, J. P.; Marthaler, O.; Nixon, J. F. *Chem. Phys. Lett.* **1981**, *82*, 543. (e) King, M. A.; Kuhn, R.; Maier, J. P. *Mol. Phys.* **1987**, *60*, 867.

[15] (a) Weiske, T. Ph.D. Thesis, Technical University Berlin, D 83, 1985. (b) Terlouw, J. K.; Weiske, T.; Schwarz, H.; Holmes, J. L. *Org. Mass Spectrom.* **1986**, *27*, 665.

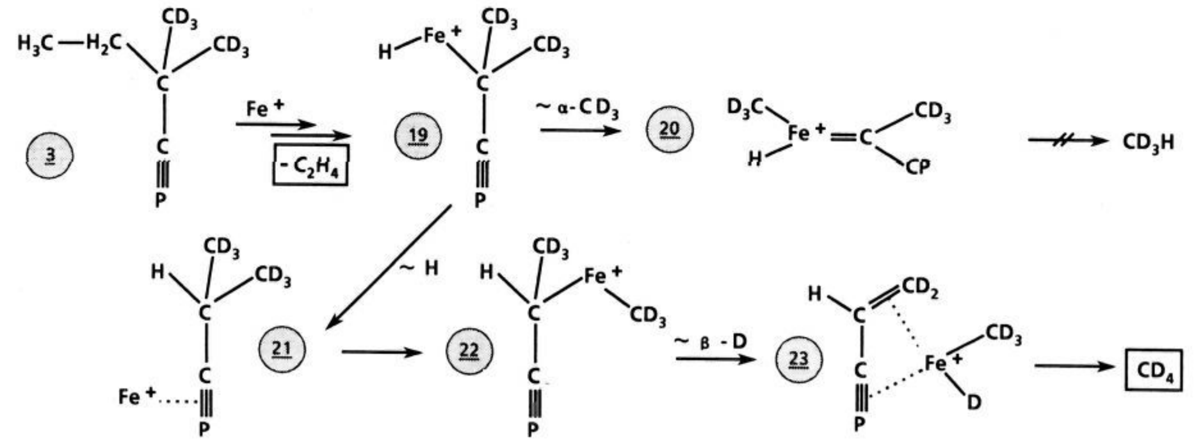
[16] With regard to the detailed mechanism of the generation of the 1:1 adduct, very little is known. According to FTICR studies ((a) Nibbering, N. M. M.; Schwarz, H.; et al., unpublished results. (b) Stepnowski, R. M.; Allison, J. *Organometallics* **1988**, *7*, 2097) $Fe(CO)_x^+$ ions ($x = 1, 2$) serve as major precursor species. Similarly, ligand displacement processes were reported as a major source for the generation of alkyne/Fe^+ complexes (Peake, D. A.; Gross, M. L. *Anal. Chem.* **1985**, *57*, 115). It should be emphasized that double-resonance experiments performed at $p < 10^{-7}$ Torr give results that may not strictly apply at the high pressure ($p > 10^{-3}$ Torr) used under chemical ionization conditions. With regard to the detailed structure(s) of the species formed we should like to stress that proposed structures are very often hypothetical in mass spectrometric studies. Similarly, the neutrals formed from the organometallic complexes are not structurally characterized but inferred indirectly from the mass differences between mass-selected precursor and observed daughter ions. On energetic grounds there cannot exist any doubt that mass differences of 2, 16, 26, and 28 must correspond to intact H_2, CH_4, C_2H_2, and C_2H_4 molecules. The generation of, for example, CH_3CH or H_2CC would be too costly energetically.

[17] For leading references on collisional activation (CA) mass spectrometry, see: (a) Levsen, K.; Schwarz, H. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 509. (b) *Collision Spectroscopy*; Cooks, R. G., Ed.; Plenum: New York, 1978. (c) *Tandem Mass Spectrometry*; McLafferty, F. W., Ed.; Wiley: New York, *1983*. (d) Levsen, K.; Schwarz, H. *Mass Spectrom. Rev.* **1983**, *2*, 77. (e) Holmes, J. L. *Org. Mass Spectrom.* **1985**, *20*, 169.

Scheme II



Scheme III



standard laboratory procedures, and the phosphaalkynes **1**–**3** by using the methods described in ref 18; all compounds were purified by GC and/or careful distillation and fully characterized by spectroscopic means.

Results and Discussion

Data for the collision-induced dissociation of the Fe^+ complexes of **1**, **2**, **4**, and **5** are given in Table I. As already mentioned in the introduction, the *tert*-butyl nitrile and isonitrile, **6** and **7**, will not be included in the present discussion as their Fe^+ complexes have nothing in common with the analogous RCP/Fe^+ species.[13]

For the Fe^+ complex of *tert*-butylphosphaalkyne, **1**-Fe^+, in addition to the ligand detachment reaction to generate Fe^+, the only C–H/C–C bond activation process corresponds to the generation of CH_4. For the formation of this product two pathways are conceivable (Scheme I): (a) The reaction commences with oxidative addition of a CC bond to Fe^+, followed by β-hydrogen transfer (**1** → **8** → **9**), or (b) with an initial addition of a C–H bond to the metal ion, **1** → **10**, which is completed by a β-methyl

Table I. Collisional Activation Mass Spectra of Fe^+ Complexes[a]

precursor substrate	fragment					
	H_2	CH_4	C_2H_4	CH_4/C_2H_2[b]	C_2H_4/CH_4	Fe^+
1		93				7
2		6	77		17	5
4	6	33		54		7
5[c]	2	6	82	4		5

[a] Data are given in %∑fragment = 100%. Errors are ±2%. Signals with <2% relative intensity were omitted. [b] See text for a discussion. [c] Additional metal-ion-containing signals (<2%) are observed at m/z 96 ($FeC_3H_4^+$) and m/z 82 ($FeC_2H_2^+$).

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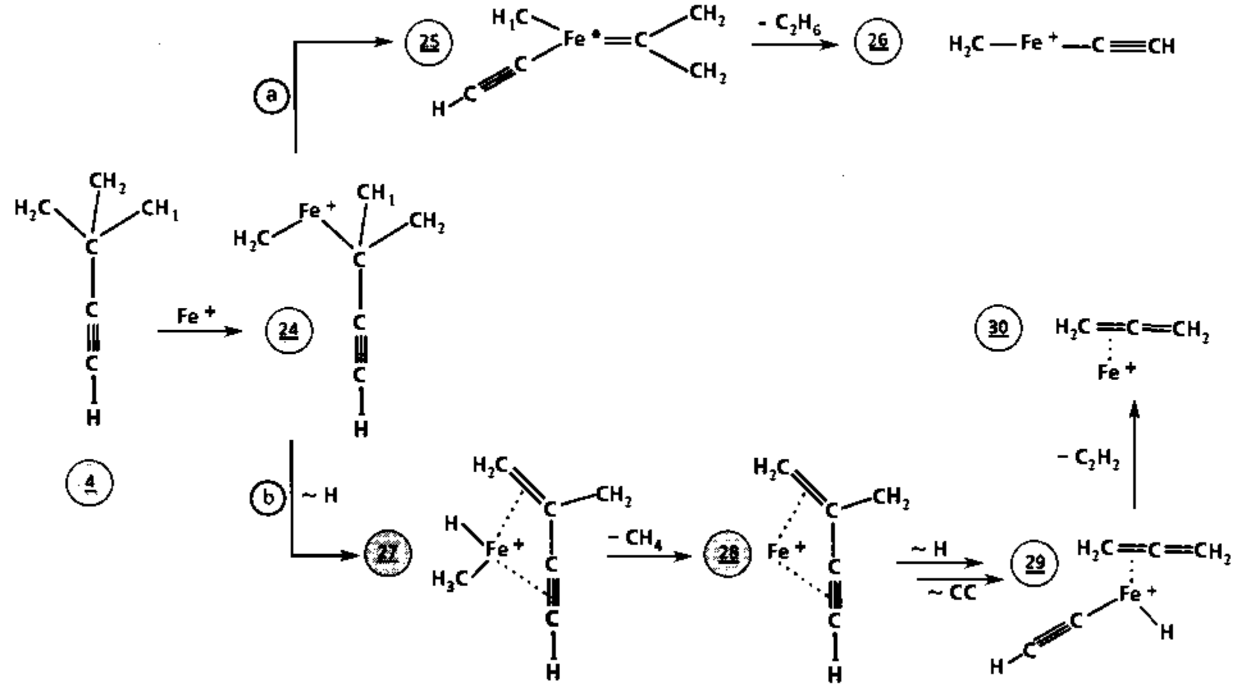
(18) Allspach, T. Ph.D. Thesis, Universität Kaiserslautern, 1986.

Scheme IV



migration to generate the same intermediate **9**; from the latter, CH_4 is formed via reductive elimination. While β-alkyl migrations are reported to exist in a few organometallic systems in solution,[19] they are extremely rare in the gas phase,[20] if they exist at all. In fact, in a recent study[2] of Fe^+ complexes of *tert*-butyl-substituted nitriles evidence was presented that CH_4 is generated in a process analogous to sequence (a) and not (b). While in the present case no definitive conclusion can be drawn, in view of these results we tentatively prefer pathway (a) for the generation of CH_4 from **1**–Fe^+.

For the next higher homologue, i.e., **2**, CH_4 is also generated; the major reaction, however, is due to the formation of C_2H_4. This may reflect the fact that, as noted earlier by Radecki and Allison,[21] insertion of a metal ion in a CH_2CH_2–C bond is favored over that in a CH_2–C bond due to the different ionization energies of a $C_2H_5^{\bullet}$ versus a $CH_3^{\bullet}$ radical. Both neutrals CH_4 and C_2H_4 are formed in a highly specific manner with regard to the positions from which methane and ethylene originate. This is evidenced by the study of **3**. The deuterated complex **3**–Fe^+, upon collisional activation, undergoes exclusive losses of CD_3H and C_2H_4, respectively. No traces of other isotopomeric products are observed. This result is in keeping with the mechanism depicted in Scheme II. We note the following: (i) The absence of products arising from reductive elimination of C_2H_6 (from **2**–Fe^+) or any $C_2H_{6-x}D_x$ isotopomers from **3**–Fe^+ reflects that the insertion step (a) in Scheme II (**3** → **11**) and/or the β-methyl migration (**11** → **12**) cannot compete with other reactions of **3**-Fe^+. That the formation of **11** is unfavored energetically is not unexpected in view of the relationship between the ionization energies of radicals and the propensity of a given C–C bond to be oxidatively added to a metal ion.[21] In addition, the rearrangement **11** → **12** would require an unfavored β-methyl shift.[2]

(ii) The absence of a signal due to loss of C_2H_5D suggests that **13** prefers to rearrange to **15** rather than to **14**. This could be due to a significant activation barrier and/or a smaller frequency factor for the reductive elimination of ethane, but we should like to point out that it may also reflect the inherent propensity for β-hydrogen migration involving CH bonds of differently substituted carbon atoms. This presumption is evidenced by the "fate" of **16** from which, via **18**, exclusively CD_2H is reductively eliminated. The complete absence of CD_4 loss points to the fact that a $-CH_2-$ unit is more prone to undergo β-hydrogen transfer to a metal-ion center than a methyl group, although this result may in the present case, to some extent, be affected by a kinetic isotope effect.[22] This observation is in line with earlier results reported by Tsarbopoulos and Allison.[23] We note for the RCP/Fe^+ system the absence of any hydrogen migration different from β-transfer.[24]

Next, we will discuss the origin of the neutral corresponding to 44 amu generated from **2**–Fe^+. At first sight, one might conclude that the neutral fragment corresponds to the elusive HCP molecule,[14] generated from **2**-Fe^+ in analogy to HCN (or HNC) from **6**-Fe^+ and **7**-Fe^+.[12] If this were indeed the case, one should observe in the CA mass spectrum of **3**–Fe^+ no loss of deuterium-labeled neutrals, except for DCP (i.e., elimination of 44 and/or 45 amu). This is not the case. In contrast, the only signal observed in the appropriate *m*/*z* region corresponds to the loss of 48 amu! Obviously, four out of the six deuterium atoms of **3**–Fe^+ go with the neutral molecule(s). HC≡P formation, of course, cannot account for this experimental finding. A solution to the puzzle, being in keeping with all experimental data, is suggested in Scheme III. The major conclusions are as follows: (i) The neutral 44 amu from **2**–Fe^+ corresponds to C_3H_8 and not HCP. (ii) However, the hydrocarbon C_3H_8 is actually *not* propane but rather consists of two entities, i.e., ethylene and methane. (iii) The specific loss of 48 amu from **3**–Fe^+ requests a sequence of events that will commence with loss of C_2H_4 followed by elimination of CD_4. The reverse reaction, i.e., methane loss followed by the elimination

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(19) For example, see: Watson, P. L.; Roe, D. C. *J. Am. Chem. Soc.* **1982**, *104*, 6471.

(20) (a) Armentrout, P. B.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 784. (b) Halle, L. F.; Armentrout, P. B.; Beauchamp, J. L. *Organometallics* **1982**, *1*, 963. (c) Houriet, R.; Halle, L. F.; Beauchamp, J. L. *Ibid.* **1983**, *2*, 1818. (d) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1983**, *105*, 5197. (e) Tolbert, M. A.; Beauchamp, J. L. *Ibid.* **1984**, *106*, 8117. (f) Tonkyn, R.; Ronan, M.; Weisshaar, J. C. *J. Phys. Chem.* **1988**, *92*, 92.

(21) Radecki, B. D.; Allison, J. *Organometallics* **1986**, *5*, 411.

(22) Kinetic isotope effects 1.5 ≤ k_H/k_D ≤ 6 (depending on the excess energy) were reported for β-hydrogen transfer by: (a) Bomse, D. S.; Woodin, R. L.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1979**, *101*, 5503. (b) Reference 11h.

(23) Tsarbopoulos, A.; Allison, J. *J. Am. Chem. Soc.* **1985**, *107*, 5085.

(24) For examples of α-hydrogen migrations to metal centers in both the gas phase and solution, see: (a) Schulze, C.; Schwarz, H. *Chimia* **1987**, *41*, 245. (b) Schulze, C.; Weiske, T.; Schwarz, H. *Organometallics* **1988**, *7*, 898. (c) Burk, M. J.; McGrath, M. P.; Crabtree, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 620.

of ethylene, can be discounted on the grounds that this combination should result in an overall loss of 47 amu (note that according to Scheme II the only $CH_{4-x}D_x$ isotopomer generated from **3**-Fe^+ corresponds to CD_3H). (iv) If methane loss follows the elimination of C_2H_4 from **3**–Fe^+ (via **15**, Scheme II), one further has to conclude from the exclusive formation of CD_4 that **19** (Scheme III) is unable to serve as immediate precursor for the reductive elimination of methane. Otherwise, loss of CD_3H should occur, which together with the elimination of C_2H_4 would give rise to an overall loss of 47 amu; this is not observed. Obviously, α-methyl transfer (**19** → **20**) is too energy demanding. Rather, **19** rearranges to a species that is able to transfer a deuterium prior to the reductive elimination step. We suggest the sequence outlined in Scheme III (**19** → **21** → **22** → **23**) as a possible model. We also note the absence of α-hydrogen transfer[24] via **22** → **20** (Scheme III).

The generations of CH_4 and C_2H_4 from the Fe–alkyne complexes **4**–Fe^+ and **5**–Fe^+ (see Table I) are likely to follow the reactions depicted for the phosphaalkynes in Schemes I and II, respectively. Noteworthy and not yet fully understood is the origin of the signal due to the formal loss of a neutral fragment with 42 amu. There are several mechanistic variants conceivable to account for this reactions, as for example the following: (i) C_3H_6 is formed as an intact entity from the alkyne–Fe^+ complexes. This would require substantial skeleton rearrangements, some of which are indicated for **4**–Fe^+ in Scheme IV, path (a). (ii) The fragment C_3H_6 does not consist of an intact molecule but is rather two distinct molecules; for energetic reasons these can correspond only to CH_4 and C_2H_2. Path (b) in Scheme IV depicts a possible mechanism that is supported by the following experiments. First of all, structure **28** is a complex of Fe^+ with 2-methyl-1-buten-3-yne (**31**). This complex (**28**) can also be generated independently in the ion source from $Fe(CO)_5$ and **31**. The predominant reaction of the so-formed complex, both collision induced and for metastable ions, is the loss of acetylene. This unusual elimination can probably be attributed to the allylic nature of the methyl group, which facilitates the combined insertion of the metal ion in the C–H bond and the CC cleavage to generate **29**.

To determine the structure of the $(M-42)^+$ signal in the spectra of **4**–Fe^+, a CA experiment was conducted with this ion.[25] The following results were obtained: For the structure indicative[3a] losses of CH_3 (to generate m/z 81) versus C_2H_2 (to generate m/z 70) we obtain a ratio of 2.2. For the Fe^+ complexes generated from authentic allene, i.e., **30**, and 1-propyne (the latter may give rise to the insertion product **26**), Peake and Gross report[3a] ratios of 2.0 ± 0.1 for Fe^+/allene and 4.1 ± 0.2 for Fe^+/propyne. Thus the measured ratio suggests that we are dealing with **30** instead of **26**.

No doubt that further studies, including extensive labeling work and additional structure determination of the neutral(s) by CIDI (collisional induced dissociative ionization)[26] are necessary to get the final proofs for the suggested path (b).

In conclusion, the present results demonstrate for the first time that the gas-phase chemistry of Fe^+ complexes of phosphaalkynes, RCP, is very distinct from that of analogous nitriles, RCN, and isonitriles, RNC. Although the reactions of RCP/Fe^+ have some similarities with those of $RC{\equiv}CH/Fe^+$ complexes, there also exist pronounced differences. Moreover, the study of labeled phosphaalkynes not only reveals a remarkable reaction path for the successive losses of C_2H_4 and CH_4 (Scheme III) but provides detailed insight into the feasibility of several elementary reactions of organometallic species in the gas phase. Noteworthy are (i) the absence of any scrambling reactions, (ii) the nonoperation of α- and β-methyl migrations as well as α-hydrogen rearrangements, and (iii) the preference of β-hydrogen transfer from a CH_2 rather than a CH_3 group.

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(25) In this experiment the following strategy was applied: The complex **4**–Fe was mass selected by means of B(1), the product of unimolecular decomposition to generate $(M-42)^+$ occurring in the field-free region between B(1) and E was "isolated" by E, collisional activation of this species was then brought about in the field-free region between E and B(2), and the fragment ions were recorded by scanning B(2).

(26) For references, see: (a) Burgers, P. C.; Holmes, J. L.; Mommers, A. A.; Terlouw, J. K. *Chem. Phys. Lett.* **1983**, *102*, 1. (b) Wesdemiotis, C.; McLafferty, F. W. *Chem. Rev.* **1987**, *87*, 485. (c) Terlouw, J. K.; Schwarz, H. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 805.