Gas-Phase Reactions of Chromium and Chromium Fluoride Cations CrF_n^+ ($n = 0-4$) with Phosphane

Ulf Mazurek and Helmut Schwarz*

Institut für Organische Chemie, Technische Universität Berlin, Strasse des 17. Juni 135,
D-10623 Berlin, Germany

Received March 22, 2000

The reactions of chromium and chromium fluoride monocations CrF_n^+ ($n = 0-4$) with phosphane are investigated by Fourier-transform ion cyclotron resonance mass spectrometry. Besides condensing slowly with phosphane, Cr^+ is unreactive. The ionic products of the chromium fluoride cations are as follows: (i) CrF^+ yields $CrPH_2^+$ and subsequently $CrPH_3^+$; (ii) from CrF_2^+, the ions PH_3^+, Cr^+, and CrF_2H^+ are generated; and (iii) both CrF_3^+ and CrF_4^+ yield PH_3^+. The structure and formation of $[Cr,P,H_3]^+$ are investigated by collision-induced dissociation and isotopic labeling experiments. For the neutral species $[P,H_3,F_2]$ formed by reaction of CrF_2^+ with phosphane, the structures are interrogated by quantum-mechanical calculations at the MP2/6-31++G** level of theory.

Introduction

Besides a widespread use of phosphane in semiconductor and integrated-circuit production and a general interest in interstellar and planetary occurrences of PH_3, few gas-phase reactions of phosphane have been investigated, e.g., for H,[1] $Si^{\bullet+}$,[2] P^+,[3,4] Pt^+,[5] and FeO^+.[6] $PH_{1-3}^{+/0}$ species have been investigated by ab initio calculations.[7] On the other hand, methylated phosphanes and phosphoranes have attracted much interest from Wanczek and co-workers,[8−10] and the reaction of CH_3PH_2 with Ti^+ was investigated both experimentally[11] and theoretically.[12] The generation of both anionic and cationic transition metal−phosphorus clusters from mixtures of red phosphorus and metal powders[13] should be mentioned as well.

In a previous study, we investigated the formation of chromium and chromium fluoride monocations CrF_n^+ ($n = 0-4$) and their reactions with alkanes C_1 through C_4.[14] The present study addresses the reactivity of CrF_n^+ toward phosphane. Following the methodology used in our previous study, we chose the most electronegative element, fluorine, to serve as the partner of chromium. This choice allows for controlling the formal oxidation state of chromium easily by the number of fluorine atoms added to the metal center.

Experimental and Computational Details

Nitrogen trifluoride (Praxair, 99.99%), phosphane (Praxair, electronic grade (99.995%)), argon (AGA Gas, 99.996%), and solid chromium (Balzers, >99.9%) were obtained commercially and used without further purification. Deuterated phosphane is not available commercially. It was prepared from calcium phosphide (Strem Chemicals, Inc., 97%) and concentrated deuterated sulfuric acid (Merck Sharp & Dohme Canada Ltd., ≥99 atom% D) in a half-micro test tube directly connected to the spectrometer's gas-inlet system and used without further purification.

All experiments were performed with a Bruker Spectrospin CMS-47X Fourier-transform ion-cyclotron resonance (FT-ICR) mass spectrometer whose setup and operation have been described previously.[15,16] In brief, chromium monocations were generated from targets of pure chromium by laser desorption/laser ionization[17,18] in the external ion source of the spectrometer using a Nd:YAG laser (Spectron Systems, $\lambda_{max} = 1064$ nm). The chromium ions were extracted from the source and transferred to the analyzer cell via a system of electrostatic potentials. Next, the most abundant isotope chromium-52 (relative abundance 83.8%[19]) was mass-selected using FERETS,[20] a computer-controlled ion-ejection protocol that combines frequency sweeps and single-frequency pulses to optimize resonant excitation and ejection of all unwanted ions. After mass selection, $^{52}Cr^+$ was allowed to react with pulsed-in nitrogen trifluoride/argon mixtures. Both the composition of the gas mixture and the lengths of the gas pulses were adjusted to maximize the yield of the desired chromium fluoride cation, CrF_n^+ ($n = 1-4$). Subsequently, the ion of interest was mass-selected using FERETS again. Phosphane was admitted to the cell via a leak valve at a constant pressure measured by a calibrated[21] Balzers IMG 070 ion gauge. Unless otherwise noted, the phosphane pressure was $(1-1.5) \times 10^{-8}$ mbar (1 mbar = 10^2 Pa) whereas the background pressure was in the range $(1-5) \times 10^{-9}$ mbar.

---

* Corresponding author. Tel: ++49-30-314-23483. Fax: ++49-30-314-21102. E-mail: schw0531@www.chem.tu-berlin.de.

(1) Arthur, N. L.; Cooper, I. A. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 521.
(2) Hrušak, J.; Schröder, D.; Schwarz, H.; Iwata, S. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 777.
(3) Antoniotti, P.; Operti, L.; Rabezzana, R.; Splendore, M.; Tonachini, G.; Vaglio, G. A. *J. Chem. Phys.* **1997**, *107*, 1491.
(4) Antoniotti, P.; Operti, L.; Rabezzana, R.; Tonachini, G.; Vaglio, G. A. *J. Chem. Phys.* **1998**, *109*, 10853.
(5) Brönstrup, M.; Schröder, D.; Schwarz, H. *Chem.*−*Eur. J.* **1999**, *5*, 1176.
(6) Brönstrup, M.; Schröder, D.; Schwarz, H. *Organometallics* **1999**, *18*, 1939.
(7) Gang, Z.; Su, K.; Wang, Y.; Wen, Z. *Chem. Phys.* **1998**, *228*, 31.
(8) Wanczek, K. P. *Z. Naturforsch., A* **1975**, *30*, 329.
(9) Wanczek, K. P. *Z. Naturforsch., A* **1976**, *31*, 414.
(10) Hartmann, O. R.; Wanczek, K. P.; Hartmann, H. *Dyn. Mass Spectrom.* **1978**, *5*, 146.
(11) Bjarnason, A.; Arnason, I. *Inorg. Chem*. **1996**, *35*, 3455.
(12) Irigoras, A.; Fowler, J. E.; Ugalde, J. E. *J. Am. Chem. Soc.* **2000**, *122*, 1411.
(13) Greenwood, P. F.; Dance, I. G.; Fisher, K. J.; Willett, G. D. *Inorg. Chem.* **1998**, *37*, 6288.
(14) Mazurek, U.; Schröder, D.; Schwarz, H. *Collect. Czech. Chem. Commun.* **1998**, *63*, 1498.
(15) Eller, K.; Schwarz, H. *Int. J. Mass Spectrom. Ion Processes* **1989**, *93*, 243.
(16) Eller, K.; Zummack, W.; Schwarz, H. *J. Am. Chem. Soc.* **1990**, *112*, 621.
(17) Freiser, B. S. *Talanta* **1985**, *32*, 697.
(18) Freiser, B. S. *Anal. Chim. Acta* **1985**, *178*, 137.
(19) Rosman, K. J. R.; Taylor, P. D. P. *Pure Appl. Chem.* **1997**, *70*, 217.
(20) Forbes, R. A.; Laukien, F. H.; Wronka, J. *Int. J. Mass Spectrom. Ion Processes* **1988**, *83*, 23.
(21) Schröder, D.; Schwarz, H.; Clemmer, D. E.; Chen, Y.; Armentrout, P. B.; Baranov, V. I.; Böhme, D. K. *Int. J. Mass Spectrom. Ion Processes* **1997**, *161*, 175.

10.1021/ic000318s CCC: $19.00

Electronically excited Cr^+ ions, which are known to be efficiently thermalized by collision with methane[22] rather than argon,[14] were allowed to multiply collide with pulsed-in methane. For reactions of Cr^+, the constant phosphane pressure in the cell was in the range $(1-4) \times 10^{-8}$ mbar. CrF^+ ions, which are known to require thermalization,[14] were allowed to undergo multiple collisions with phosphane and reisolated using FERETS. The other ions, CrF_n^+ ($n = 2-4$), did not need to be thermalized by collisions with reactant-gas molecules, according to the purely exponential decay of their intensities during the reactions investigated.

Reaction kinetics were analyzed by using a computer program that determines rate constants and branching ratios on the basis of the experimentally observed temporal evolution of ion intensities and a flexible kinetic model.[23] The reported rate constants are given as fractions of the measured bimolecular rate constants and the gas-kinetic collision rates according to the capture theory.[24] The parameters used for phosphane were as follows: dipole moment, 0.574 D;[25] polarizability 4.84×10^{-24} cm^3;[25] relative ion gauge sensitivity, 1.8 (estimated according to ref 26). The absolute error of the experimentally determined rate constants is in the range ±30%, while the ratios of the rate constants are more precise (±10%).[21] Reaction mechanisms were derived from kinetic arguments and complementary double-resonance experiments.[27] In a double-resonance experiment, a particular ion is ejected from the cell by resonant excitation for a certain amount of time. The resulting spectrum is compared to a reference spectrum obtained by "ejecting" a hypothetical ion (e.g., *m*/*z* 200) for the same amount of time. Disappearance of an ion indicates that it is formed from the ejected one. To elucidate the connectivity of the ionic species, collision-induced-dissociation (CID) experiments[28] were undertaken. In a CID experiment, the ion of interest is subjected to a pressure of typically $(1-4) \times 10^{-8}$ mbar of a nonreacting gas (typically argon) after having been kinetically activated by a low-energy radio-frequency pulse. Eventually, the ion will decompose into its fragments, thus revealing information about the connectivity of its atoms and, to a certain extent, the respective bond strengths.

Quantum-chemical calculations were carried out with the Gaussian 94 program executed on standard Intel PCs running either Microsoft Windows NT 4.0 and Gaussian 94W, Revision D.5,[29] or S.u.S.E. Linux 6.0 and Gaussian 94, Revision E.1.[30] Both geometry optimizations and energy calculations were undertaken at the MP2/6-31++G** level of theory; minima in energy and transition structures were confirmed by frequency calculations. Energies are given as electronic energies (MP2), electronic energies with zero-point vibrational energy corrections (MP2-(ZPVE)), and Gibbs free energies at 298 K. The intrinsic error of the ab initio calculations was estimated on the basis of known experimental data[31] for breaking H-H, H-F, F-F, P-H, and P-F bonds (Table 1).

Table 1. Estimation of the Intrinsic Errors in the ab Initio Calculations[a]

reaction	$\Delta_r H_0$			$\Delta_r H_{298}$		
	exptl[b,c]	calcd[d]	deviation	exptl[b,c]	calcd[d]	deviation
$H_2 \rightarrow H + H$	103.3	94.2	−9.1 (−9%)	104.2	94.8	−9.4 (−9%)
$F_2 \rightarrow F + F$	37.0	33.7	−3.3 (−9%)	38.0	34.3	−3.7 (−10%)
$HF \rightarrow H + F$	135.2	131.4	−3.8 (−3%)	136.2	132.0	−4.2 (−3%)
$PH_3 \rightarrow PH_2 + H$	82.5	73.4	−9.6 (−11%)	84.1	74.0	−10.1 (−12%)
$PF_3 \rightarrow PF_2 + F$	132.1	125.1	−7.0 (−5%)	133.0	125.7	−7.3 (−5%)

[a] All energies are given in kcal mol^{-1}. [b] Ref 31. [c] Errors are within 0.6 kcal mol^{-1}, except those for for the decomposition of PF_3 (1.2 kcal mol^{-1}). [d] This work: MP2/6-31++G** level of theory including ZPVE corrections for both 0 and 298 K data.

It turns out that the strengths of chemical bonds are constantly underestimated by an average of about 7 kcal mol^{-1}, with bonds of hydrogen being more error-prone than bonds of fluorine; errors for 298 K data are about 0.4 kcal mol^{-1} larger than those for 0 K data. Frequency and energy scalings[32] were not undertaken because their effect would be small compared to the much larger intrinsic errors in the calculations.

Results and Discussion

Cr^+. Besides condensing slowly with phosphane, similar to the situation observed by Buckner et al. for Cr^+ and NH_3,[33] ground-state (^6S) bare chromium cations ($3d^5$) are unreactive. This absence of bond activation is expected on the basis of previous experimental findings.[14,33,34] Most probably, the condensation of Cr^+ and PH_3 involves termolecular processes. Not having analyzed these processes, we report the apparent bimolecular rate constants observed at a pressure of 4×10^{-8} mbar.

A summary of the reactions observed for the CrF_n^+/PH_3 couples is given in Table 2.

CrF^+. The only initial product of the reaction of CrF^+ with PH_3 is $CrPH_2^+$, corresponding to the loss of neutral HF, whose thermochemical stability may be considered as the driving force of the reaction. Subsequently, $CrPH_2^+$ reacts with PH_3 to yield $CrPH_3^+$ and neutral $PH_2^\bullet$ only. This second reaction poses two questions: (i) How is $CrPH_3^+$ formed from $CrPH_2^+$ and neutral PH_3 (ligand exchange vs hydrogen atom transfer)? (ii) What is the connectivity of the $[Cr,P,H_3]^+$ ion (Cr^+-PH_3 vs $H-Cr^+-PH_2$ vs $(H_2)-Cr^+-PH$ vs $(H)_2Cr^+-PH$)?

To answer the second question, we subjected $[Cr,P,H_3]^+$ to a collision-induced-dissociation experiment.[28] The only product species obtained in this experiment was Cr^+, thus supporting a Cr^+-PH_3 connectivity for the species in question. In an additional experiment, we allowed $[Cr,P,H_3]^+$ to react with leaked-in [D$_4$]ethene (D = deuterium). For a large variety of hydride species $H-M^+-L_n$, [D$_4$]ethene is known to yield $D-M^+-L_n$ easily[35] via β-H transfer.[35-37] However, we could not detect any deuterated species $[Cr,P,H_n,D_{3-n}]^+$ that should have been expected if a hydrido ligand was present. On the basis of these experimental results, we conclude that the

---

[22] Reents, W. D., Jr.; Strobel, F.; Freas, R. B., III; Wronka, J.; Ridge, D. P. *J. Phys. Chem.* **1985**, *89*, 5666.

[23] Mazurek, U.; Schwarz, H. *ICR Kinetics*, Version 3.0.1; TU Berlin: Berlin, 1998.

[24] Su, T.; Chesnavich, W. J. *J. Chem. Phys.* **1982**, *76*, 5183.

[25] Lide, D. R., Ed. *CRC Handbook of Chemistry and Physics*, 79th ed.; CRC Press: Boca Raton, FL, 1998.

[26] Bartmess, J. E.; Georgiadis, R. M. *Vacuum* **1983**, *33*, 149.

[27] Comisarow, M. B.; Grassi, V.; Parisod, G. *Chem. Phys. Lett.* **1978**, *57*, 413.

[28] Kretzschmar, I.; Schröder, D.; Schwarz, H.; Rue, C.; Armentrout, P. B. *J. Phys. Chem. A* **1998**, *102*, 10060.

[29] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*, Revision D.5; Gaussian, Inc.: Pittsburgh, PA, 1995.

[30] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*, Revision E.1; Gaussian, Inc.: Pittsburgh, PA, 1995.

[31] Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17* (Suppl. 1), 1.

[32] Foresman, J. B.; Frisch, Æ. *Exploring Chemistry with Electronic Structure Methods*, 2nd ed.; Gaussian, Inc.: Pittsburgh, PA, 1996.

[33] Buckner, S. W.; Gord, J. R.; Freiser, B. S. *J. Am. Chem. Soc.* **1988**, *110*, 6606.

[34] Schilling, J. B.; Beauchamp, J. L. *Organometallics* **1988**, *7*, 194.

[35] Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1985**, *107*, 72.

[36] Reger, D. L.; Culbertson, E. C. *J. Am. Chem. Soc.* **1976**, *98*, 2789.

[37] Pardy, R. B. A.; Taylor, M. J.; Constable, E. C.; Mersh, J. D.; Sanders, J. K. M. *J. Organomet. Chem.* **1982**, *231*, C25.

Table 2. Reactions of Chromium and Chromium Fluoride Monocations CrF_n^+ ($n = 0-4$) with Phosphane[a,b]

Cr^+	+	PH_3	$\xrightarrow{1.1 \times 10^{-3}\%}$	$CrPH_3^+$		
CrF^+	+	PH_3	$\xrightarrow{10\%}$	$CrPH_2^+$	+	HF
$CrPH_2^+$	+	PH_3	$\xrightarrow{14\%}$	$CrPH_3^+$	+	PH_2
$CrPH_3^+$			$\xrightarrow{\text{CID}}$	Cr^+	+	PH_3
CrF_2^+	+	PH_3	$\xrightarrow{34\%}$	CrF_2	+	PH_3^+
			$\xrightarrow{25\%}$	Cr^+	+	$[P,H_3,F_2]$
			$\xrightarrow{17\%}$	CrF_2H^+	+	PH_2
CrF_3^+	+	PH_3	$\xrightarrow{160\%}$	CrF_3	+	PH_3^+
CrF_4^+	+	PH_3	$\xrightarrow{120\%}$	CrF_4	+	PH_3^+
			$\xrightarrow{30\%}$	Cr^+	+	$[P,H_3,F_4]$

[a] Reaction efficiencies ϕ are given as fractions of the experimentally observed rate constant and that calculated according to the capture theory:[24] $\phi = k_{exptl}/k_{cap}$. [b] For comments on efficiencies apparently greater than unity, see text.

Table 3. Bond Dissociation Energies (BDEs) of Ligated Chromium Cations[a]

species	BDE (kcal mol^{-1})	method	D	refs[c]
$Cr^+-C_2H_4$	$32^b \pm 5$	ion beam	D_0	38
	$\geq 30^b \pm 5$	ion beam	D_0	49 q 38; 50 q 38 and 49
	$30.0^b \pm 5.1$	ion beam	D_0	39 q 38
	22	theory	D_e	40
	26	theory	D_0	50 q 40
	23 ± 2.5	ion beam	D_0	39
Cr^+-H_2O	29.0 ± 3	CID	D	42
	29.0	CID	D	50 q 42
	$21.9 \pm <4$	CID	D	41
	21.9	CID	D	50 q 41
	31.8	theory	D_e	44
	30.1	theory	D_0	44; 50 q 44
	30.9 ± 2.1	ion beam	D_0	43; 49 q 43; 50 q 43
Cr^+-PH_3	≥ 18.7	thermochemistry[d]	D_{298}	31
	26.5 ± 3.5	ligand exchange	D_0	this work

[a] Very few values quoted by ref 50 needed to be corrected according to their original source. For the sake of completeness, we quote all original data in the table. [b] Value probably due to a misinterpretation of the underlying reaction.[39] [c] All numbers are reference numbers. q = quoting. [d] Endothermic reactions cannot be observed in an ion cyclotron resonance mass spectrometer. Consequently, for the reaction $CrF^+ + 2\ PH_3 \rightarrow Cr^+-PH_3 + HF + PH_2^\bullet$ to occur, $D_{298}(Cr^+-PH_3)$ must exceed the given value of 18.7 kcal mol^{-1}. Heats of formation ($\Delta_f H_{298}$) were taken from ref 31.

$[Cr,P,H_3]^+$ ion possesses the connectivity Cr^+-PH_3. Accordingly, we assume $[Cr,P,H_2]^+$ to possess the connectivity Cr^+-PH_2.

Control experiments with undeuterated ethene confirmed that there is no ligand exchange between $[Cr,P,H_3]^+$ and ethene. On the other hand, water present in the background led to ligand exchange. On the basis of these experimental findings and the known bond dissociation energies (Table 3), we estimated the Cr^+-PH_3 bond dissociation energy to be $D_0 = 26.5 \pm 3.5$ kcal mol^{-1}. We consider the BDE values for $Cr^+-C_2H_4$ and Cr^+-H_2O of 23 and 30 kcal mol^{-1}, respectively, to be the most reliable ones. The value of $D_0(Cr^+-C_2H_4) = 32 \pm 5$ kcal mol^{-1} (ref 38) is far too high and is probably due to a misinterpretation of the underlying chemical reaction.[39] The BDE value obtained by quantum-chemical calculations[40] is in good agreement with the corrected experimental value.[39] The value of $D_0(Cr^+-H_2O) = 21.9 \pm 4$ kcal mol^{-1} (ref 41) deviates largely from all other findings and was therefore not considered. The other values obtained experimentally by collision-induced-dissociation[42] and ion-beam experiments[43] as well as theoretically by quantum-chemical calculations[44] lead to a BDE of 30 kcal mol^{-1}.

Before addressing the first question posed above, we wish to comment on the mere occurrence of the reaction $Cr^+-PH_2 + PH_3 \rightarrow Cr^+-PH_3 + PH_2^\bullet$. Irrespective of its actual mechanism, this reaction must be exothermic or at least thermoneutral to be observed in an ion cyclotron resonance mass spectrometer. For a ligand exchange reaction, this simply means that the dissociation energy of the formally covalent Cr^+-PH_2 bond cannot exceed that of the coordinative Cr^+-PH_3 bond. For a hydrogen transfer reaction, we make the additional assumption that the P−H bond dissociation energies are independent of coordination of PH_3 to the metal center (which seems to be reasonable on the basis of the much smaller extent of sp^3 hybridization compared to that of NH_3) and arrive at the same conclusion regarding the dissociation energies of the Cr^+-PH_2 and Cr^+-PH_3 bonds.

To answer the question of the reaction mechanism, we isolated $CrPH_2^+$ and allowed it to react with leaked-in PD_3 while constantly ejecting one particular ion at a time from the reaction cell by double-resonance excitation.[27] This series of experiments, however, was adversely affected by its intrinsic conditions: (i) Generating the reactant ion $CrPH_2^+$ required two subsequent pulses of NF_3 and PH_3, respectively, thus demanding a daunting optimization of the reactant gas/argon mixtures and the respective pulse lengths. Consequently, the spectra obtained were rather noisy. (ii) The neutral reactant was not the leaked-in PD_3 but a mixture of PD_3, PHD_2, PH_2D, and PH_3, being formed by H/D exchange reactions between the leaked-in PD_3 and hydrogen atoms coating the reaction cell surface after pulsing in PH_3. (iii) Owing to the on-line preparation of PD_3, its concentration in the ICR cell changed during the series of double-resonance experiments. (iv) Double-resonance excitation could not, for the limits set by our FT-ICR mass spectrometer, resolve the isobaric doublets of $CrPHD^+$ (relative mass 85.936 20) and $CrPH_3^+$ (relative mass 85.937 75) and of $CrPD_2^+$ (relative mass 86.942 48) and $CrPH_2D^+$ (relative mass 86.944 03). (v) A distinction between the conversion of $[Cr,P,H_2,D]^+$ to $[Cr,P,H,D_2]^+$ by H/D exchange and the same conversion by PH_2D/PHD_2 ligand exchange was, for obvious reasons, impossible by our experiments.

For a strict approach, we decided to base our experiments and their interpretation on a formal reaction scheme including all conceivable pathways as shown in Figure 1. Three types of chemical reactions can occur and are depicted by different reaction-arrow styles. (i) Ligand exchange reactions are shown in Figure 1a and are represented by straight arrows throughout the entire figure. (ii) H/D exchange reactions are shown in Figure 1b and are represented by curved arrows throughout the entire figure. (iii) H and D transfer reactions are shown in Figure 1c and are represented by dashed curved arrows throughout the entire figure. (iv) A synopsis of all three kinds of possible reactions is given in Figure 1d.

---

(38) Georgiadis, R.; Armentrout, P. B. *Int. J. Mass Spectrom. Ion Processes* **1989**, *89*, 227.

(39) Sievers, M. R.; Jarvis, L. M.; Armentrout, P. B. *J. Am. Chem. Soc.* **1998**, *120*, 1891.

(40) Sodupe, M.; Bauschlicher, C. W., Jr.; Langhoff, S. R.; Partridge, H. *J. Phys. Chem.* **1992**, *96*, 2118.

(41) Marinelli, P. J.; Squires, R. R. *J. Am. Chem. Soc.* **1989**, *111*, 4101.

(42) Magnera, T. F.; David, D. E.; Michl, J. *J. Am. Chem. Soc.* **1989**, *111*, 4100.

(43) Dalleska, N. F.; Honma, K.; Sunderlin, L. S.; Armentrout, P. B. *J. Am. Chem. Soc.* **1994**, *116*, 3519.

(44) Rosi, M.; Bauschlicher, C. W., Jr. *J. Chem. Phys.* **1990**, *92*, 1876.

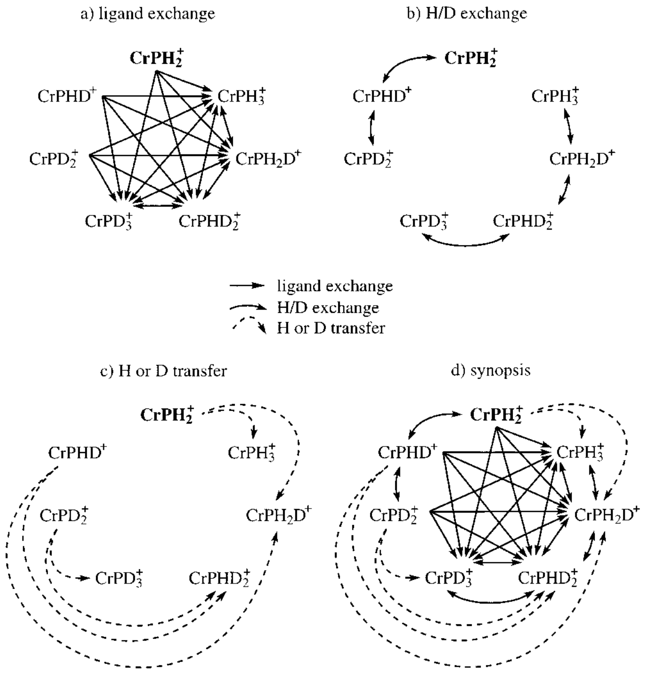

Figure 1. Possible reactions of $CrPH_2^+$ with PH_3, PH_2D, PHD_2, and PD_3.

For the reaction scheme and its interpretation, the following simplifications were adopted: (i) Single-headed reaction arrows represent quasi-irreversible reactions whereas double-headed arrows indicate equilibria. (ii) For reasons of legibility, the species are shown by their chemical formulas instead of the usual square bracket notation. A particular connectivity between atoms shall not be implied by this notation. (iii) Possible isotope effects are neglected; e.g., if the reaction $Cr^+{-}PH_2 + PH_3 \rightarrow Cr^+{-}PH_3 + PH_2^\bullet$ was to be ruled out on experimental grounds, the reaction $Cr^+{-}PH_2 + PD_3 \rightarrow Cr^+{-}PH_2D + PD_2^\bullet$ would be ruled out as well. (iv) Ligand exchange equilibria were considered only for neutral PH_nD_{3-n} ($n = 0-3$) as the reactant gas. Neutral PH_nD_{2-n} ($n = 0-2$) being formed only from $CrPH_nD_{2-n}^+$ ($n = 0-2$) by ligand exchange reactions with neutral PH_nD_{3-n} ($n = 0-3$) was excluded from the scheme due to its low concentration in the reaction cell.

As already mentioned, we isolated $CrPH_2^+$ and subjected it to the above-mentioned mixture of PH_nD_{3-n} ($n = 0-3$) while continuously ejecting $CrPH_2D^+$ from the analyzer cell. Our argument is as follows: If $CrPHD_2^+$ was formed from $CrPH_2^+$ by ligand exchange exclusively, it would not disappear upon ejection of $CrPH_2D^+$ from the cell. If, in contrast, $CrPHD_2^+$ was formed from $CrPH_2D^+$ by H/D or ligand exchange, it should disappear upon elimination of $CrPH_2D^+$ from the cell.

The results of the double-resonance experiments are given in Table 4 and are interpreted as follows. (i) As already observed in the kinetic measurements, Cr^+ being formed originates from $CrPH_nD_{3-n}^+$ ($n = 1-3$), thus indicating a low activation barrier for breaking the $Cr^+{-}PH_3$ bond. (ii) The strong increase of the Cr^+ signal under double-resonance conditions is easily attributed to unintentional collision-induced dissociation of the ejected ion. (iii) The decrease in the reference signals of $CrPHD_2^+$ and the parallel increase in the Cr^+ signals are attributed to an unwanted increase in background water that originates from the on-line preparation of PD_3 during the series of double-resonance measurements. (iv) Ejecting $CrPHD_2^+$ from the cell leads to a significant decrease in the signal of $CrPH_2D^+$. This is consistent with fast ligand or H/D exchange between $CrPH_2D^+$ and $CrPHD_2^+$. (v) Ejecting $CrPHD^+$ and $CrPH_3^+$ from the cell causes all ions, except $CrPHD_2^+$ and Cr^+, to disappear. The increase of Cr^+ was discussed in item ii above. The disappearance of the other ions is attributed to fast H/D exchange (see Figure 1b) between $CrPH_2^+$ and $CrPHD^+$ and between $CrPH_3^+$ and $CrPH_2D^+$. The remaining $CrPHD_2^+$ signal is attributed to either ligand exchange between $CrPH_2D^+$ and PHD_2 (Figure 1a) or rapid D transfer to $CrPHD^+$ (Figure 1c). (vi) Ejection of $CrPH_2D^+$ does not affect the intensities of the Cr^+ and $CrPH_2^+$ signals significantly. The decrease in the intensity of the $CrPH_3^+$/$CrPHD^+$ signal is attributed to fast ligand or H/D exchange between $CrPH_3^+$ and $CrPH_2D^+$. The significant decrease in the intensity of the $CrPHD_2^+$ signal shows that a substantial amount of that ion is formed via the ejected $CrPH_2D^+$ ion, which, in turn, must be formed from the isolated $CrPH_2^+$ ion via direct or indirect H or D transfer (Figure 1b,c), since ligand exchange between $CrPH_2^+$ and $CrPH_2D^+$ is ruled out as is ligand exchange between $CrPH_2^+$ and $CrPH_2D^+$. The remaining signal intensity of $CrPH_2D^+$ is attributed to deuterium transfer to $CrPHD^+$ or to protium transfer to $CrPD_2^+$, respectively.

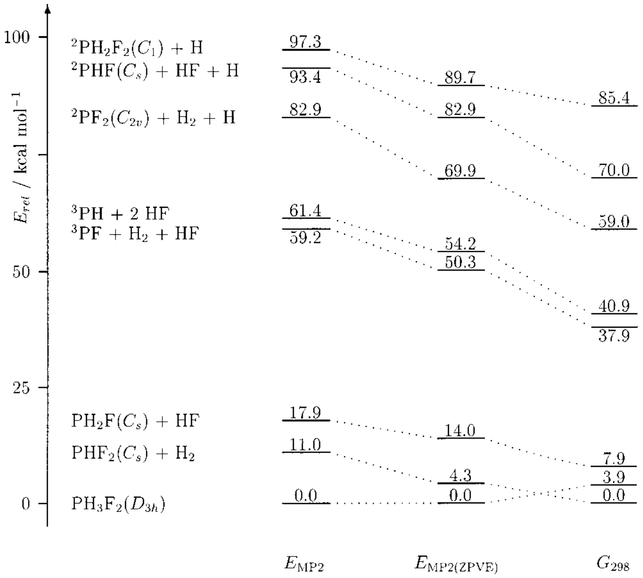

Figure 2. Relative energies of the species $[P,H_3,F_2]$ calculated at the MP2/6-31++G** level of theory.

From these results, we conclude that the reaction $Cr^+{-}PH_2 + PH_3 \rightarrow Cr^+{-}PH_3 + PH_2^\bullet$ proceeds predominantly, if not exclusively, via hydrogen transfer and not via ligand exchange. Note that H/D exchange reactions occur rapidly for both $CrPH_nD_{2-n}^+$ ($n = 1, 2$) and $CrPH_nD_{3-n}^+$ ($n = 1-3$), thus indicating that breaking of the P−H and P−D bonds in free PH_nD_{3-n} ($n = 1-3$) is favored over breaking of the $Cr^+{-}P$ bond in $CrPH_nD_{3-n}^+$ ($n = 1-3$).

CrF_2^+. Possessing as a neutral an only slightly smaller ionization energy than phosphane (Table 5), CrF_2^+ shows the most diverse reactivity toward PH_3. With a reaction efficiency of 76%, 45% of the reacting ions undergo charge transfer. Another 33% of these ions become completely defluorinated in what appears to be either a very facile single reaction or a sequence of very fast sequential reactions according to double-resonance experiments eliminating the ions $[Cr,P_{0,1},F_{0,2},H_{0-3}]^+$ from the reaction cell. The formations of the thermodynamically favored H-F and P-F bonds could be considered to be driving forces of this rapid reaction (see below). The remaining 22% of the reacting ions are converted to CrF_2H^+ via hydrogen radical abstraction from PH_3.

Because neutrals generated in ion/molecule reactions cannot be detected directly in an ICR mass spectrometer, we used

Table 4. Data for Elucidation of the Mechanism of the Reaction $CrPH_2^+ + PH_3 \rightarrow CrPH_3^+ + PH_2$ by Combined Isotopic Labeling and Double-Resonance Experiments at a Pressure of 4×10^{-8} mbar and a Reaction Time of 12 s[a−c]

obsd ion	reference intensity[d]			intensity upon continuous ejection of[e]				
				$CrPHD^+$ ($CrPH_3^+$)	$CrPH_3^+$ ($CrPHD^+$)		$CrPH_2D^+$ ($CrPD_2^+$)	$CrPHD_2^+$
Cr^+	60.2	72.9	87.1	195.2	208.9	195.7	73.2	70.7
$CrPH_2^+$	100.0	101.8	93.5				102.0	88.3
$\left.\begin{matrix}CrPH_3^+\\CrPHD^+\end{matrix}\right\}$	57.0	46.4	47.3				23.8	43.5
$CrPH_2D^+$ [f]	68.4	58.2	61.8					48.5
$CrPHD_2^+$	54.4	43.0	32.4	15.4	20.1	14.3	23.3	

[a] For a detailed discussion, see text; see also Figure 1. [b] Similar measurements were undertaken for pressures of 1×10^{-8} mbar ($t = 48$ s), 2×10^{-8} mbar ($t = 24$ s), and 6×10^{-8} mbar ($t = 6$ s). [c] All intensities are arbitrarily scaled to $I = 100$ for the base peak in column 2. [d] Reference spectra were obtained by "ejecting" the hypothetical ion at m/z 200. [e] Species given in parentheses were inevitably ejected as well. [f] The isobaric species $CrPD_2^+$ was not detected in high-resolution mass spectra.

Table 5. Ionization Energies of Chromium Fluorides and Phosphane

species	ionizn energy (eV)	ref	species	ionizn energy (eV)	ref
Cr	6.766	31	CrF_3	11.5 ± 0.4	14
CrF	8.4 ± 0.3	31	CrF_4	12.3 ± 0.3	14
CrF_2	10.1 ± 0.3	14	PH_3	9.869 ± 0.002	31

quantum-mechanical calculations to obtain information about the most probable structure(s) of neutral [P,H_3,F_2] species whose atoms were permutated in order to obtain data for the most conceivable structures. The relative energies of the possible product combinations are shown in Figure 2. While a complete scan for all possible electronic states and structures was undertaken, only ground-state species in their minimum-energy conformations possessing relative energies of ≤ 100 kcal mol^{-1} are shown. Three different relative energy scales are shown: (i) electronic energy only, (ii) electronic energy plus ZPVE corrections, and (iii) Gibbs free energy at 298 K.

The zero relative energy level was found to be represented by PH_3F_2 (D_{3h} symmetry) for both the MP2 and MP2(ZPVE) energies. For the relative Gibbs free energy at 298 K, however, the decomposition products PHF_2 (C_s symmetry) and H_2 are favored on entropic grounds. The numerical values of the energy levels obtained by the quantum-mechanical calculations cannot be assumed to represent the thermochemical differences in a quantitatively exact manner because of their intrinsic errors; nevertheless, they allow for a qualitative interpretation. In our case, the calculated levels of energy correspond to the decomposition of PH_3F_2 at higher temperatures observed by Seel and Velleman,[45] who reported PH_3F_2 to decompose, forming PH_2F_3, PH_3, and HF. However, these experimental results could not be supported by the quantum-mechanical calculations reported by Keil and Kutzelnigg[46] or be confirmed experimentally by Minkwitz and Liedtke.[47] For the sake of completeness, we undertook additional calculations on the decomposition of PH_3F_2 as well as on the relative energies of plausible decomposition products ($PH_2F_3/PH_3/HF$ and $PH_2F_3/PH_2F/H_2$). Our findings are as follows: (i) The relative energy of $^1/_2(PH_2F_3/PH_3/HF)$ is within the intrinsic error of the calculation (3.9 kcal mol^{-1} at the MP2 level, 1.6 kcal mol^{-1} at the MP2(ZPVE) level, and 0.9 kcal mol^{-1} at the 298 K Gibbs free energy level). (ii) The relative energy of $^1/_2(PH_2F_3/PH_2F/H_2)$ is close to or within the calculation's error as well (6.9 kcal mol^{-1} at the MP2 level, 3.5 kcal mol^{-1} at the MP2(ZPVE) level, and 3.1 kcal mol^{-1} at the 298 K Gibbs free energy level). (iii) The transition structure for the 1,1-H_2 elimination from PH_3F_2 is 82.6 kcal mol^{-1} (MP2), 78.3 kcal mol^{-1} (MP2(ZPVE)), and 77.1 kcal mol^{-1} (G_{298}) above the lowest energy species. Hence, even though unimolecular dissociation of PH_3F_2 into PHF_2 and H_2 is thermodynamically favored, it is hindered by a considerable barrier.

CrF_3^+ and CrF_4^+. As expected according to the ionization energies of the reactants (Table 5), both CrF_3^+ and CrF_4^+ undergo charge transfer with PH_3. Both charge transfer reactions were observed to proceed faster than the collision rates. While, for CrF_4^+, the uncertainty may be explained by a low signal-to-noise ratio, that reason cannot hold true for CrF_3^+. For this ion (and to a smaller extent for CrF_4^+ as well), we assume the capture theory[24] to expose some pitfalls[48] when describing the outer-sphere electron transfer. For CrF_4^+, the occurrence of an additional reaction, $CrF_4^+ + PH_3 \rightarrow Cr^+ + [P,H_3,F_4]$, is uncertain. The generation of bare Cr^+ ions may also be caused by unspecific background reactions.

Conclusions

In this study, we have investigated the reactions of chromium and chromium fluoride monocations CrF_n^+ ($n = 1-4$) with phosphane. Besides undergoing slow condensation with phosphane, Cr^+ is unreactive. Both CrF_3^+ and CrF_4^+ undergo facile charge transfer with phosphane. CrF_2^+ shows a broad reactivity, undergoing charge transfer, complete defluorination, and hydrogen addition via hydrogen atom transfer from phosphane. CrF^+ gives rise to $Cr^+{-}PH_2$ and subsequently, via hydrogen atom transfer, to $Cr^+{-}PH_3$. This reaction shows an exceptional feature: The formally covalent $Cr^+{-}PH_2$ bond is not stronger than the coordinative $Cr^+{-}PH_3$ bond.

Acknowledgment. This work was supported by the Fonds der Chemischen Industrie, the Volkswagen-Stiftung, and the Deutsche Forschungsgemeinschaft. We wish to thank Drs. Detlef Schröder, Mark Brönstrup, and Ilona Kretzschmar for helpful discussions.

Supporting Information Available: Gaussian output archive entries for frequency calculations on the system [P,H_3,F_2]. This material is available free of charge via the Internet at http://pubs.acs.org.

IC000318S

---

(45) Seel, F.; Velleman, K. *Z. Anorg. Allg. Chem.* **1971**, *385*, 123.

(46) Keil, F.; Kutzelnigg, W. *J. Am. Chem. Soc.* **1975**, *97*, 3623.

(47) Minkwitz, R.; Liedtke, A. *Inorg. Chem.* **1989**, *28*, 4238.

(48) Stöckigt, D.; Sen, S.; Schwarz, H. *Chem. Ber.* **1993**, *126*, 2553.

(49) Armentrout, P. B.; Kickel, B. L. In *Organometallic Ion Chemistry*; Freiser, B. S., Ed.; Kluwer: Dordrecht, The Netherlands, 1996; pp 1−46.

(50) Freiser, B. S.; Auberry, K.; Clinton, K. In *Organometallic Ion Chemistry*; Freiser, B. S., Ed.; Kluwer: Dordrecht, The Netherlands, 1996; pp 283−332.