Heteroatom Chemistry
Volume 2, Number 3, 1991

Trifluoromethyl Phosphaalkenes of the Type $F_3CP{=}C(OR)NR_2$: Synthesis, Spectroscopic Investigations, and Ligand Properties [1]

Joseph Grobe*, Duc Le Van, Ulrike Althoff, Bernt Krebs, and Mechtild Dartmann

Anorganisch-Chemisches Institut der Westfälischen Wilhelms-Universität Münster, Wilhelm-Klemm-Straße 8, D-4400 Münster, Germany

Rolf Gleiter

Organisch-Chemisches Institut der Universität Heidelberg, Im Neuenheimer Feld 270, D-6900 Heidelberg, Germany

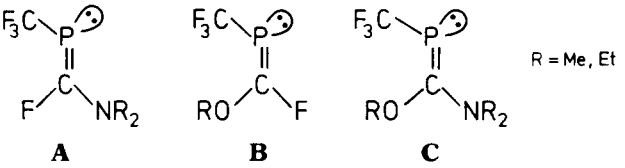
Received 11 January 1991.

ABSTRACT

The one-pot reaction of the alcohol adducts $F_3CP(H)CF_2OR$ of perfluoro-2-phosphapropene with secondary amines in a 1:3 molar ratio affords the stable phosphaalkenes $F_3CP{=}C(OR)NR_2$ (R = Me, Et) **1–4** *in yields of 58%. NMR and He(I) PE spectroscopic investigations show that the lone pair electrons on nitrogen and oxygen participate in n/π conjugation. In contrast to typical low-coordinated double bonds the new derivatives do not react with alcohols, amines, and 1,3-dienes. The derivatives are more closely related to the phosphaalkenes $F_3CP{=}C(F)NR_2$ than to perfluoro-2-phosphapropene. The reaction of $F_3CP{=}C(OEt)NMe_2$* (**3**) *with $Cr(CO)_5THF$ yields the $\eta^1(P)$ complex $Cr(CO)_5[F_3CP{=}C(OEt)NMe_2]$* (**7**) *with an unusually long sp^2 PC bond (1.809 Å).*

INTRODUCTION

During the last five years we have been able to synthesize several inert phosphaalkenes of type **A** and **B** and to study their properties [2, 3]. The following results are of particular interest: a) Compounds of type **A**, in contrast to **B**, are formed exclusively as *Z* isomers [4], b) they do not resemble fluoro olefines or alkyl, aryl, silyl, and perfluorophosphaalkenes [4], c) with trialkylphosphines they yield stable phosphorus ylides $R_3P{=}C(NR_2)P(F)CF_3$ [5], and d) they act as $(\eta^1\text{-}\mu_2)$ 4e donor ligands in $[Cr(CO)_5]_2P(CF_3)CFNR_2$ [6]. These results led us to investigate the hitherto unknown compounds of type **C** in order to study the changes in chemical behavior caused by R_2N substituents at the sp^2 carbon atom.



A **B** **C**

RESULTS AND DISCUSSION

Preparation of the Compounds $F_3CP{=}C(OR)NR_2$ (R=Me, Et)

The synthesis of the derivatives **1** to **4** is accomplished by the reaction of the precursors $F_3CP(H)CF_2OR$ with the corresponding secondary amines R_2NH in a 1:3 molar ratio (Equation 1).

Dedicated to Professor Marianne Baudler on the occasion of her seventieth birthday.

*To whom correspondence should be addressed.

1042-7163/91/$3.50 + .25

$$F_3CP{=}CF_2 \xrightarrow{ROH} F_3CP(H)CF_2OR \xrightarrow[-R_2NH\cdot HF]{R_2NH} F_3CP{=}C(F)OR \quad \mathbf{B} \quad (1)$$

$$\xrightarrow{R_2NH} [F_3CP(H)CF(OR)NR_2] \xrightarrow[-R_2NH\cdot HF]{R_2NH} F_3CP{=}C(OR)NR_2$$

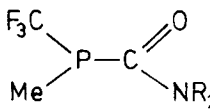
	1	2	3	4
OR	R: Me	Me	Et	Et
NR_2	R: Me	Et	Me	Et

The process can be carried out as a one-pot reaction without isolating the known intermediates **B** (R = Me, Et) [2], and it proceeds quantitatively even at −40°C. If perfluoro-2-phosphapropene is the starting material the overall yield of the derivatives **1** to **4** is reduced to about 58% by the isolation procedure. Attempts to detect the expected intermediates $F_3CP(H)CF(OR)NR_2$ by low temperature NMR measurements have so far proved unsuccessful.

Since the amino phosphaalkenes of type **A** are easily accessible by the reaction of $HP(CF_3)_2$ with secondary amines in a 1:3 molar ratio, an alternative route to compounds of type **C** could be the base-catalyzed addition of alcohols to **A** followed by HF elimination. In practice this route has failed because the aminophosphaalkenes do not react with alcohols.

Compounds **1** to **4** are oily substances that under vacuum or in an inert atmosphere are stable at room temperature. Composition and structure have been determined by elemental analysis (C, H, N) and spectroscopic measurements (MS, IR; ^1H, ^{19}F, ^{31}P, ^{13}C-NMR). Additional information was obtained for **1** by ^{15}N and ^{17}O NMR studies.

The synthesis of **1** and **2**, according to Equation 1, leads to small amounts (5 to 10%) of the constitutional isomers **5** and **6**, respectively, as byproducts.



5: R=Me
6: R=Et

Products **5** and **6** have been characterized by GC/MS, GC/IR, and NMR spectroscopic investigations. The mass spectrum of **5** shows a molecular ion M^+ (m/z = 187), but does not contain the peak m/z = 87 found for the isomer **1** and assigned to the characteristic fragment $[C(OMe)NMe_2]^+$. The presence of the carbamide group in **5** is suggested by the IR absorption band at 1653 cm^{-1} typical for urea derivatives. In accord with this result the ^{17}O resonance of **5** is observed at δ = 358 in the region of acid amides $\delta(^{17}O)$ = 320 to 380 [7]. The ^{19}F and ^{31}P NMR data confirm the structures suggested for the isomers **5** and **6**.

At present, the course of the reaction yielding the acylphosphines **5** and **6** can only be a matter of speculation, since their portion in the resulting product mixture is only slightly dependent on the ratio of $F_3CP(H)CF_2OMe$ to HNR_2 and on the reaction conditions (solvent, temperature). Thermal treatment of solutions of **1** or **2** with or without amines does not lead to a phosphaalkene/acylphosphine rearrangement.

NMR Spectra

The ^1H, ^{19}F, and ^{13}C resonances of **1** to **4** are detected at values characteristic for trifluoromethyl phosphaalkenes of the type $F_3CP{=}CX_2$ (X = F, NR_2, OR) [2, 3, 8]. The ^{13}C signal of the sp^2 carbon atom at δ = 205 shows large $^1J(PC)$ couplings of 77.3 to 81.6 Hz, which are typical for phosphaalkenes [9, 10]. It is interesting to note that the constants $^1J(P{-}sp^2C)$ and $^1J(P{-}sp^3C)$ of these compounds have similar values of about 80 Hz in contrast to the data of $F_3CP{=}CF_2$ [11] and $F_3CP{=}C(F)NR_2$ [3] for which $^1J(P{-}sp^3C)$ is about 20 Hz smaller than $^1J(P{-}sp^2C)$.

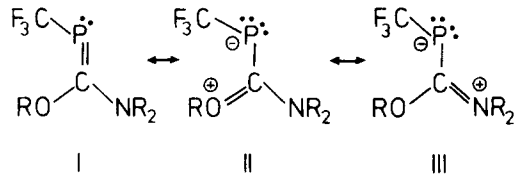
The ^{31}P shift of trifluoromethyl phosphaalkenes is very sensitive to the nature of the substituents on the sp^2 carbon atom. Thus, a low field shift of the ^{31}P signal of 130 to 150 is observed on replacement of a +M substituent X (F, OR, NR_2; δ = −4 to +19) in compounds of the type $F_3CP{=}C(F)X$ [12] by a hydrogen atom (δ = +150) or a CF_3 group (δ = +135) [8].

The NMR data prove that only one of the possible isomers (*E* or *Z*) is formed in reaction (1), but the absolute configurations of **1** to **4** cannot be deduced. A tentative structural assignment for the derivatives of type **C** has been put forward by comparing the data with those of the known structures of **A** (100% *Z*) and **B** (isomer mixture *E*:*Z* = 95:5) [2, 3]: We place the OR group in the cis and the NR_2 group in the trans position to the CF_3 substituent. This assignment was confirmed for **2** by an X-ray diffraction study of the corresponding complex $(CO)_5Cr[F_3CP{=}C(OEt)NMe_2]$ (**7**).

The $^{17}O\{^1H\}$NMR spectrum of **1** shows a singlet at δ = 80.3, a value between the ^{17}O resonances of ethers and carbonic acid esters. The high field shift of ca 40 relative to RCOOR′ absorption is due to the *p*-donor effect of the Me_2N substituent. It is known that an increasing *n*-donor strength of R in such compounds cuts down the lone pair participation of the OR′ group in the resonance stabilization and results in a high field shift of the ^{17}O NMR signal of the OR′ fragment [7, 13]. The preferred participation of the lone pair of the Me_2N substituent in the p/π conjugation of **1** is confirmed by the ^{15}N NMR spectrum with a signal at δ = 95.8 ($^2J(PN)$ = 16.3 Hz), indicating a bonding situation similar to that of nitrogen in amides or enamino ketones [14]. The interesting correlation of chemical shifts δ_N/δ_P of analogous compounds with bicoordinated N and P [15] at present cannot be verified for corresponding $F_3CE{=}C$ systems (E = N, P) because δ values

of such derivatives, e.g. $F_3CN{=}C(OR)NR'_2$ or $F_3CP{=}C(OR)PR'_2$, are not yet available.

The observed NMR parameters suggest an extensive π(PC), p(N), and p(O) delocalization in compounds of type **C**. Thus, the mesomeric forms I to III contribute to the ground state of the system.



I II III

As indicated by the NMR data, the main contribution to the electronic structure is reflected by formula III. As a consequence a considerable rotational barrier is expected for the C–NMe_2 fragment of **1**. This assumption has been confirmed by low temperature NMR measurements giving two signals for the methyl protons of the Me_2N group at −90°C (Figure 1).

Due to the participation of the mesomeric form II the coalescence temperature of **1** (−78°C) for the Me_2N rotation is considerably lower than for derivatives of the type $RP{=}C(H)NMe_2$ (R = ^{t}Bu, T_c = −46°C; R = Ph, T_c = −28°C; R = Mes, T_c = −15°C) [10].

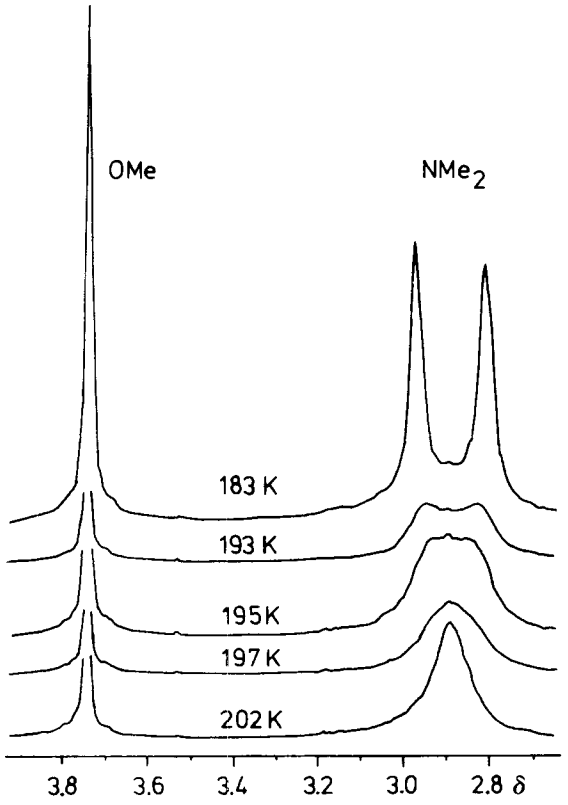


FIGURE 1 Temperature Dependent ^{1}H NMR Spectrum for **1**

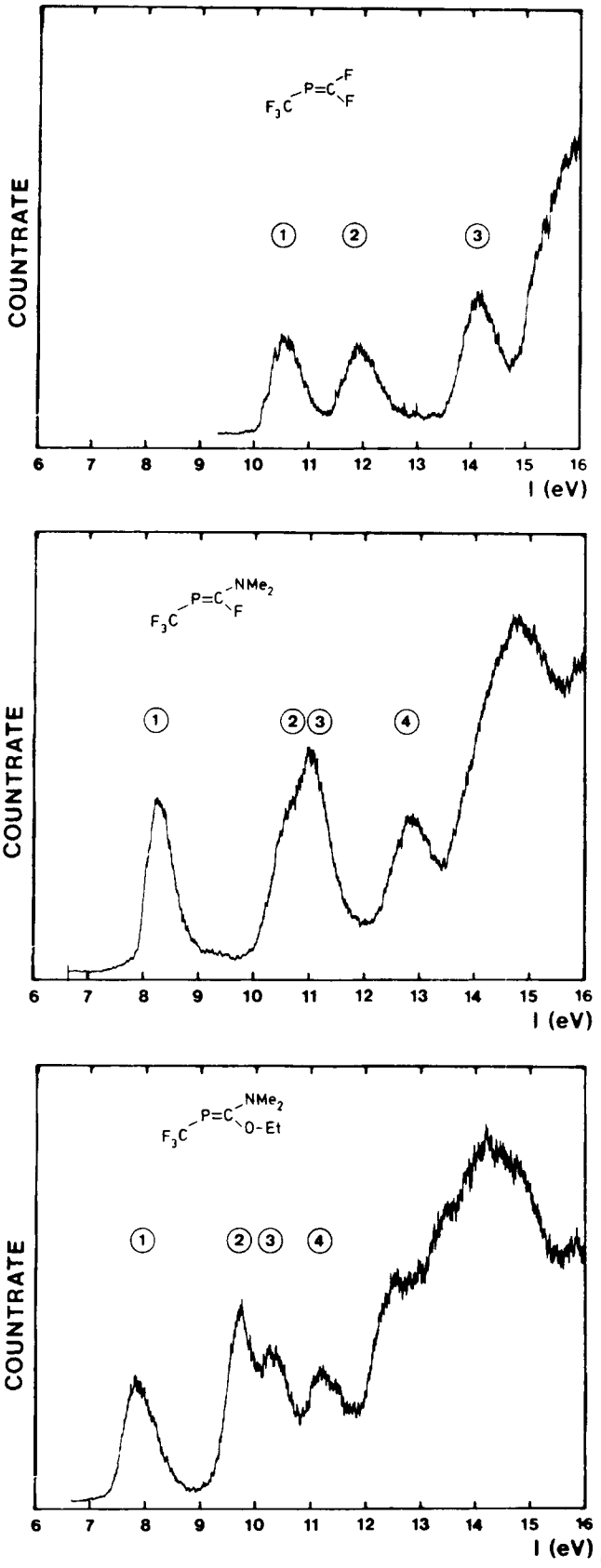


FIGURE 2 He(I)PE Spectra of $F_3CP{=}CF_2$, $F_3CP{=}C(F)NMe_2$, and $F_3CP{=}C(OEt)NMe_2$

The conjugative effects explain the observed stability and reactivity of the compounds **1** to **4**, which differ in their chemical behavior from $F_3CP{=}CF_2$ and other perfluorophosphaalkenes [2, 8]. Thus, compound **3** reacts neither with HX partners like methanol or dialkylamines nor with 1,3-dienes. In addition, they do not undergo [2 + 2]cycloaddition to give 1,3-diphosphetanes, a reaction typical for phosphaalkenes. In conclusion, derivatives of type **C** resemble compounds of type **A** more closely than the perfluorophosphaalkenes.

He(I) Photoelectron Spectra

The changes in the electronic structure with the formal step by step replacement of the fluorine atoms at the sp^2 carbon center of $F_3CP{=}CF_2$, first by NMe_2 to give **A**, then by OEt to yield **C**, are anticipated to show up in the He(I) photoelectron (PE) spectra of these compounds. We expect large effects on the energies of the π-MO's and a smaller effect on the energy level of the lone pair on P. The PE spectra are displayed in Figure 2 and the first vertical ionization energies, $I_{v,j}$, of $F_3CP{=}CF_2$, $F_3CP{=}C(F)NMe_2$, and $F_3CP{=}C(OEt)NMe_2$ are collected in Table 1.

To demonstrate the effect of the substituents and to assign the first two PE bands, we have correlated the first vertical ionization energies of the three compounds with those of $H_3CP{=}CH_2$ [16]. In the PE spectrum of the latter compound the first two bands have been assigned to ionizations from the π-MO and the lone pair on P, respectively. From our earlier investigations of the effect of CF_3 groups in phosphorus compounds [17] and from studies of π systems in which H atoms are replaced by F [18], we expect for the comparison $H_3CP{=}CH_2/F_3CP{=}CF_2$ a strong shift (ca 1.0–1.5 eV) toward higher energy for the band that stems from the lone pair on P and a slightly smaller effect for the π band. This is in accord with the experimental result (Figure 3). A correlation between the first PE bands of $F_3CP{=}CF_2$, $F_3CP{=}C(F)NMe_2$, and $F_3CP{=}C(OEt)NMe_2$ allows us to draw the following conclusions (Figure 3): 1. The replacement of F by an amino group on the sp^2 carbon atom yielding trifluoromethylphosphaalkenes of type **A** or **C** causes a large decrease of the ionization energy of the first band. 2. The replacement of the second F atom on the sp^2 carbon center in $F_3CP{=}C(F)NMe_2$ by an alkoxy group leads only to a small change in the first ionization energy.

In this paper we have refrained from comparing calculated orbital energies with measured vertical

TABLE 1 Recorded Vertical Ionization Energies, $I_{v,j}$, of the Phosphaalkenes $F_3CP{=}CF_2$, $F_3CP{=}C(F)NMe_2$, $F_3CP{=}C(OEt)NMe_2$ (Values in eV).

Band	$F_3CP{=}CF_2$	$F_3CP{=}C(F)NMe_2$	$F_3CP{=}C(OEt)NMe_2$
①	10.5	8.2	7.8
②	11.9	10.55	9.7
③	14.1	10.9	10.2
④		12.7	11.1

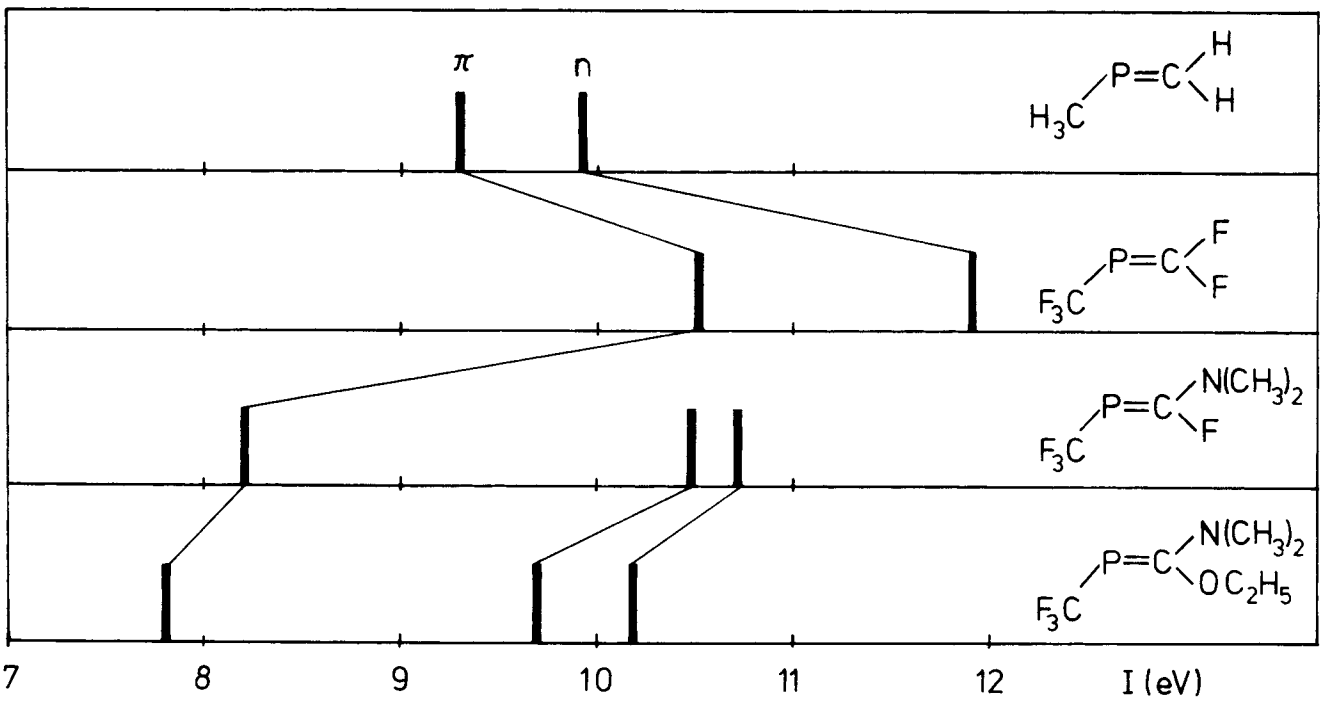


FIGURE 3 Comparison of the First Ionization Energies of $F_3CP{=}CF_2$, $F_3CP{=}C(F)NMe_2$, and $F_3CP{=}C(OEt)NMe_2$

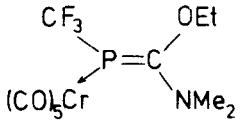
ionization potentials (Koopmans' theorem [19]). The main reason is that the calculated energy differences and orbital energies differ considerably from the experimental values both for semiempirical (MNDO) and ab initio (3-21G) calculations. Such discrepancies are usually found if CF_3 groups are present. A detailed investigation using more sophisticated calculations will be published elsewhere.

Preparation and Molecular Structure of the Complex $(CO)_5Cr[F_3CP{=}C(OEt)NMe_2]$ [7]

In order to gain some information on the ligand properties of compounds of type **C** and to confirm their structure, **3** was combined with a solution of photochemically prepared $Cr(CO)_5THF$ in a 1 : 1 molar ratio. The reaction according to Equation 2 gives the mononuclear complex **7** in 82% yield.

$$F_3CP{=}C(OEt)NMe_2 + Cr(CO)_5THF \xrightarrow{-THF}$$

3



(2)

7

The low coordination shifts $\Delta\delta = \delta(\text{complex}) - \delta(\text{ligand})$ ($\Delta\delta_F = -1.4$, $\Delta\delta_p = -4.8$, $\Delta\delta_C(sp^2C) = 3.9$) suggest a η^1(P) coordination of **3** [3, 20] in accord with the results of an X-ray diffraction study on single crystals (Figure 4). The Me_2N and CF_3 substituents occupy trans positions. As in the case of $Cr(CO)_5[F_3CP{=}C(F)NMe_2]$ the CrP bond (2.469 Å) is longer than in other η^1 phosphaalkene chromium pentacarbonyl complexes (e.g., $(CO)_5Cr[MesP{=}CPh_2]$, d(CrP)2.356 Å [21]) and trifluoromethylphosphine derivatives [22]. The build-

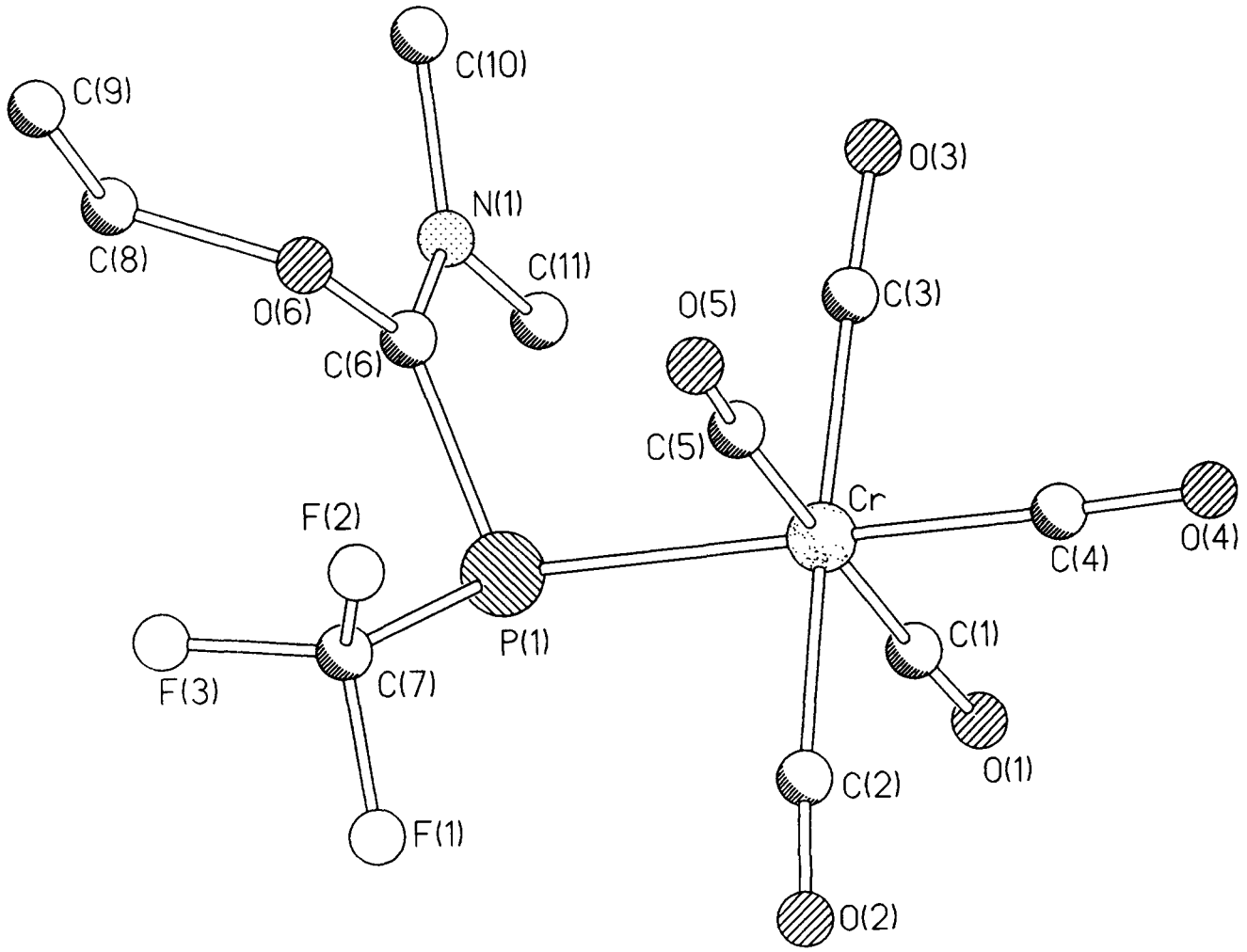
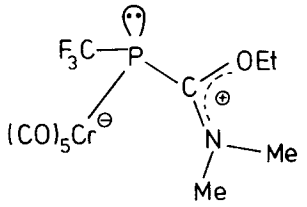


FIGURE 4 Molecular Structure of **7**

ing units CPON and NC_3 of the ligand are planar (sp^2 hybridization). The PC(sp^2) bond distance of 1.809 Å is close to the single bond value (covalent radii: P(sp^3) 1.10, C(sp^3) 0.72 Å [23]). While the C(6)O(6) bond of 1.325 Å is only slightly shorter than a CO single bond, a considerable shortening is observed for the C(6)N bond (1.308 Å) (Table 2).

In analogy to the complex $(CO)_5Cr[F_3CP{=}C(F)NMe_2]$ the geometrical arrangement of the P-substituents of **7** completes a trigonal pyramid indicating the presence of a lone pair on the phosphorus. The structural data of **7**, therefore, suggest zwitterionic formula IV as a reasonable representation of the bonding.



IV

This description is supported by the fact that **7** in organic solvents ($CDCl_3$, [D_8]-toluene), similar to $(CO)_5Cr[F_3CP{=}C(F)NMe_2]$, is transformed to the binuclear complex **8** and the free ligand **3** (Equation 3).

$$2\ (CO)_5Cr[F_3CP{=}C(OEt)NMe_2] \longrightarrow \underset{\mathbf{7}}{} \quad F_3CP{=}C(OEt)NMe_2 \quad (3)$$

$$\mathbf{3}$$

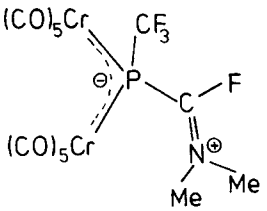
$$+ \quad [(CO)_5Cr]_2[F_3CP{=}C(OEt)NMe_2]$$

$$\mathbf{8}$$

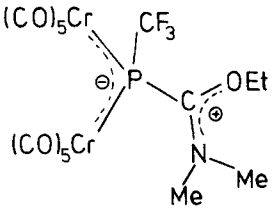
This transformation goes along with characteristic coordination shifts $\Delta\delta$ = δ(complex **8**) − δ(complex **7**): $\Delta\delta_F = -13.2$, $\Delta\delta_P = 76.5$, indicative of the combination of the second $Cr(CO)_5$ fragment with the P atom of **3**. So far, it has been impossible to grow single crystals of **8** suited for an X-ray diffraction study. However, since the chemical properties of **3** are very similar to those of $F_3CP{=}C(F)NMe_2$ and the molecular structure of the binuclear system $[(CO)_5Cr]_2[F_3CP{=}C(F)NMe_2]$ corresponds to formula V [6] there is no question that the bonding situation in **8** can be well represented by the zwitterionic description of formula VI.

EXPERIMENTAL

All reactions were carried out in closed vessels or under an argon atmosphere using a standard high vacuum line. All solvents were purified, dried, and degassed.



V



VI

Spectroscopic Investigations

MS: Model CH5, MAT Finnigan; electron energy: 70 eV; GC/MS: Combination of Varian-MAT 111, gas chromatograph Varian 2700 (column: FS-SE 50/52 m CB) and computer Varian 1400. IR: Spectrometer 683, Perkin-Elmer, liquid sample cells with KBr windows; solvents: pentane or chloroform; GC/IR: Combination of Bruker IFS 48 FT-IR spec-

TABLE 2 Selected Structural Parameters (bond distances [Å], bond angles [deg]) for the Complex **7**

Cr–P	2.469(2)	P–Cr–C(1)	89.1(2)
Cr–C(1)	1.896(6)	P–Cr–C(2)	89.5(2)
Cr–C(2)	1.890(6)	P–Cr–C(3)	93.0(2)
Cr–C(3)	1.887(6)	P–Cr–C(4)	179.4(2)
Cr–C(4)	1.834(6)	P–Cr–C(5)	92.5(2)
Cr–C(5)	1.885(6)	C(1)–Cr–C(2)	88.8(3)
		C(1)–Cr–C(3)	91.0(3)
C(1)–O(1)	1.136(8)	C(1)–Cr–C(4)	90.3(3)
C(2)–O(2)	1.136(8)	C(1)–Cr–C(5)	177.9(3)
C(3)–O(3)	1.144(8)	C(2)–Cr–C(3)	177.9(2)
C(4)–O(4)	1.162(7)	C(2)–Cr–C(4)	90.5(3)
C(5)–O(5)	1.153(8)	C(2)–Cr–C(5)	89.9(3)
		C(3)–Cr–C(4)	87.0(3)
		C(3)–Cr–C(5)	90.0(3)
		C(4)–Cr–C(6)	88.1(3)
		Cr–C(1)–O(1)	175.6(6)
		Cr–C(2)–O(2)	175.7(5)
		Cr–C(3)–O(3)	177.4(5)
		Cr–C(4)–O(4)	178.3(3)
		Cr–C(5)–O(5)	175.6(5)
P–C(6)	1.809(5)	Cr–P–C(6)	106.9(2)
P–C(7)	1.876(7)	Cr–P–C(7)	109.1(2)
		C(6)–P–C(7)	97.7(3)
C(6)–N	1.308(7)	P–C(6)–N	121.2(4)
C(6)–O(6)	1.325(7)	P–C(6)–O(6)	119.5(4)
		N–C(6)–O(6)	119.2(5)
C(7)–F(1)	1.359(9)	P–C(7)–F(1)	106.8(5)
C(7)–F(2)	1.323(8)	P–C(7)–F(2)	120.0(5)
C(7)–F(3)	1.352(8)	P–C(7)–F(3)	112.5(4)
		F(1)–C(7)–F(2)	106.4(6)
		F(1)–C(7)–F(3)	104.8(6)
		F(2)–C(7)–F(3)	105.3(5)
C(8)–C(9)	1.463(10)	C(9)–C(8)–O(6)	107.8(5)
C(8)–O(6)	1.484(7)	C(6)–C(6)–C(8)	119.5(4)
		C(6)–N–C(10)	123.5(5)
N–C(10)	1.457(7)	C(6)–N–C(11)	121.4(5)
N–C(11)	1.454(7)	C(10)–N–C(11)	114.7(5)

trometer with a gas chromatograph (Shimadzu) and an Aspect 1000 computer (Bruker). NMR: 84.66 (^{19}F) and 36.44 (^{31}P) MHz, WH 90 spectrometer (Bruker); standard (extern): CCl_3F (^{19}F) and 85% H_3PO_4 (^{31}P). 360.0 (^1H), 75.43 (^{31}C), 48.81 (^{17}O), 36.48 (^{15}N) MHz; AM 300 (^{13}C) and AM 360 spectrometer (Bruker) with external standards TMS(^1H, ^{13}C), H_2O(^{17}O), liquid NH_3(^{15}N). PE-spectra: PS 18 spectrometer, Perkin-Elmer, He(I) source, calibration using Ar and Xe; resolution 20 meV for the $^2P_{3/2}$ argon line.

Starting Compounds

Perfluoro-2-phosphapropene [24], its alcohol adducts $F_3CP(H)CF_2OR$ [2], and the complex $Cr(CO)_5THF$ [25] have been prepared according to literature prescriptions.

Preparation of $F_3CP{=}C(OR)NR_2$, Compounds **1–4**

To a solution of 5 mmol of the corresponding alcohol adduct $F_3CP(H)CF_2OR$ (R = Me, Et) in 5 mL CH_2Cl_2 kept in a Schlenk vessel, 15.5 mmol of the secondary amine ($HNMe_2$ or $HNEt_2$) was added by low temperature vacuum condensation (−196°C). The vessel was then transferred into a −78°C bath, and, with stirring, the reaction mixture was slowly warmed to room temperature. At −40°C the precipitation of ammonium salts indicated the start of the reaction. In order to complete the reaction the mixture was stirred at room temperature for an additional 30 minutes. Then all volatile compounds (CH_2Cl_2,R_2NH) were pumped off under vacuum, and the remaining oily residue was taken up in 5 mL of pentane yielding a precipitate of ammonium salt. The pentane solution of the product was transferred under an inert gas into a short path distillation apparatus by means of a pipette. After removal of the solvent by vacuum condensation the raw material was purified by distillation in vacuo (temperature of the heating bath: 25°C, temperature of the cooling finger: −35°C). Yield: 58%.

(E)-(1-Dimethylamino-1-methoxy)-3,3,3-trifluoro-2-phospha-1-propene (**1**)

^1H NMR (CD_2Cl_2): δ = 2.9 (d, $^4J_{PH}$ 3.0 Hz, 6H, NMe_2), 3.8 (s, 3H, OMe); ^{19}F NMR (CD_2Cl_2): δ = −38.5 (d, $^2J_{PF}$ 59.0 Hz); ^{31}P NMR (CD_2Cl_2): δ = 17.3 (q); ^{13}C NMR ($CDCl_3$): δ = 38.8 (d, $^3J_{PC}$ 13.4 Hz, NMe_2), 63.2 (d, $^3J_{PC}$ 5.1 Hz, OMe), 135.6 (dq, $^1J_{FC}$ 316.7 Hz, $^1J_{PC}$ 76.2 Hz, CF_3), 205.8 (dq, $^1J_{PC}$ 77.3 Hz, $^3J_{FC}$ 7.6 Hz, sp^2C); ^{17}O NMR (CD_2Cl_2): δ = 80.3 (s); ^{15}N NMR (CD_2Cl_2): δ = 95.8 (d, $^2J_{PN}$ 16.3 Hz); mass spectrum: *m/z* 187 (M^+, 38%), 118 ($M^+ - CF_3$, 59%), 87 ($M^+ - PCF_3$, 10%), 72 ($CONMe_2^+$, 75%), 44 (NMe_2^+, 100%); IR spectrum: 730 (vw), 950 (w), 983 (m), 1084 (vs), 1114 (vs), 1172 (m), 1182 (m), 1214 (m), 1297 (s), 1378 (s), 1380 (s), 1382 (s), 1501 (s), 2947 (w), 3010 (w) cm^{-1}. Anal. Calcd. for $C_5H_9F_3NOP$: C, 32.09, H, 4.81; N, 7.49. Found: C, 31.68; H, 4.97; N, 7.66.

(E)-(1-Diethylamino-1-methoxy)-3,3,3-trifluoro-2-phospha-1-propene (**2**)

^1H NMR (CD_2Cl_2): δ = 0.7 (t, $^3J_{HH}$ 7.2 Hz, 6H, NCH_3), 2.9(q, $^3J_{HH}$ 7.2Hz, 4H, NCH_2), 3.5 (s, 3H, OMe); ^{19}F NMR (CD_2Cl_2): δ = −37.8 (d, $^2J_{PF}$ 59.0); ^{31}P NMR (CD_2Cl_2): δ = 16.0 (q); ^{13}C NMR ($CDCl_3$): δ = 11.2 (d, $^4J_{PC}$ 4.2 Hz, CH_2CH_3), 43.6 (d, $^3J_{PC}$ 12.5 Hz, NCH_2), 64.0 (s, OCH_3), 135.9 (dq, $^1J_{FC}$ 317 Hz, $^1J_{PC}$ 80.6 Hz, CF_3), 205.0 (dq, $^1J_{PC}$ 81.3 Hz, $^3J_{FC}$ 7.6 Hz, sp^2C); mass spectrum: *m/z* 215 (M^+, 48%); 146 ($M^+ - CF_3$, 36%), 100 (PCF_3^+, 96%), 86 ($PCNEt^+$, 27%), 74 ($PCOMe^+$, 16%), 72 (NEt_2^+, 100%); IR spectrum: 737 (w), 783 (vw), 854 (vw), 909 (vw), 983 (w), 1086 (vs), 1112 (vs), 1158 (m), 1265 (m), 1313 (m), 1361 (m), 1381 (w), 1412 (m), 1425 (m), 1452 (m), 1488 (m), 2889 (w), 2947 (m), 2984 (m) cm^{-1}. Anal. Calcd. for $C_7H_{13}F_3NOP$: C, 39.07; H, 6.05; N, 6.51. Found: C, 39.99; H, 6.82; N, 7.18.

(E)-(1-Dimethylamino-1-ethoxy)-3,3,3-trifluoro-2-phospha-1-propene (**3**)

^1H NMR (CD_2Cl_2): δ = 1.2 (t, $^3J_{HH}$ 7.0 Hz, 3H, OCH_2CH_3), 2.8 (d, $^4J_{HH}$ 3.2 Hz, 6H, NMe_2), 3.9 (q, 2H, OCH_2); ^{19}F NMR (CD_2Cl_2): −38.3 (d, $^2J_{PF}$ 59.0 Hz); ^{31}P NMR (CD_2Cl_2): δ = 18.2 (q); ^{13}C NMR ($CDCl_3$): δ = 14.2 (s, CH_2CH_3), 38.7 (d, $^3J_{PC}$ 13.8 Hz, NMe_2), 72.5 (d, $^3J_{PC}$ 5.0 Hz, OCH_2), 135.6 (dq, $^1J_{FC}$ 316.3 Hz, $^1J_{PC}$ 77.6 Hz, CF_3), 204.7 (dq, $^1J_{PC}$ 77.4 Hz, $^3J_{FC}$ 7.6 Hz, sp^2C); mass spectrum: *m/z* 201 (M^+, 1%), 126 (F_3CPN^+, 100%), 101 (M^+F_3CP, 23%), 72 ($CONMe_2^+$, 30%); IR spectrum: 717 (vw), 861 (w), 1014 (m), 1071 (vs), 1109 (vs), 1201 (m), 1293 (s), 1369 (m), 1384 (m), 1396 (w), 1496 (m), 2941 (w) cm^{-1}. Anal. Calcd. for $C_6H_{11}F_3NOP$: C, 35.82; H, 5.47; N. 6.97. Found: C, 35.55; H, 5.56; N, 7.27.

(E)-(1-Diethylamino-1-ethoxy)-3,3,3-trifluoro-2-phospha-1-propene (**4**)

^1H NMR (CD_2Cl_2): δ = 1.0 (t, $^3J_{HH}$ 7.2 Hz, 6H, NCH_2CH_3), 1.3 (t, $^3J_{HH}$, 7.0 Hz, 3H, OCH_2CH_3), 1.3 (t, $^3J_{HH}$ 7.0 Hz, 3H, OCH_2CH_3), 3.2 (q, $^3J_{HH}$ 7.2 Hz, 4H, NCH_2), 4.0 (q, $^3J_{HH}$ 7.0 Hz, 2H, OCH_2); ^{19}F NMR (CD_2Cl_2): δ = −37.8 (d, $^2J_{PF}$ 59.0 Hz); ^{31}P NMR (CD_2Cl_2): δ = 16.2 (q); ^{13}C NMR ($CDCl_3$); δ = 11.5 (d, $^4J_{PC}$ 3.9 Hz, NCH_2CH_3), 14.4 (s, OCH_2CH_3), 43.6 (d, $^3J_{PC}$ 12.5 Hz, NCH_2), 73.6 (d, $^3J_{PC}$ 2.2 Hz, OCH_3), 136.1 (dq, $^1J_{PC}$ 317.0 Hz, $^1J_{PC}$ 80.7 Hz, CF_3), 203.9 (dq, $^1J_{PC}$ 81.6 Hz, $^3J_{FC}$ 7.8 Hz, sp^2C); mass spectrum: *m/z* 229 (M^+, 100%); IR spectrum: 713 (m) 738 (w), 787 (w), 848 (w), 890 (w), 941 (w), 1021 (s), 1082 (vs), 1114 (vs), 1141 (m), 1180 (s), 1259 (s), 1312 (s), 1348 (m), 1361 (m), 1370 (m), 1383 (m), 1396 (m), 1426 (s), 1463 (m), 1492 (s), 2877 (m), 2937 (m), 2982 (m) cm^{-1}. Anal. Calcd. for $C_8H_{15}F_3NOP$:

C, 41.92; H, 6.55; N, 6.11. Found: C, 41.80; H, 6.88; N, 6.92.

The acylphosphines **5** and **6**, respectively, are formed as byproducts (5 to 10%) during the synthesis of **1** or **2**. So far, isolation from the product mixture has not been possible. Compounds **5** and **6** are characterized by the following spectroscopic data:

5: ^{19}F NMR: δ = −55.4 (d, $^2J_{PF}$ 54.0 Hz); ^{31}P NMR: δ = 15.3 (qq, $^2J_{PF}$ 54.0 Hz, $^2J_{PH}$ 5.0 Hz); ^{17}O NMR: δ = 385.0 (s); mass spectrum (GC-MS): 187 (M^+, 2%), 143 ($M^+ - NMe_2$, 0.2%), 118 ($M^+ - CF_3$, 0.6%), 72 ($CONMe_2^+$, 100%), 56 ($CNMe_2^+$, 4%); IR spectrum (GC-IR): 650 (w), 710 (w), 737 (vw), 785 (w), 856 (w), 891 (w), 943 (vw), 1123 (vs), 1159 (s), 1219 (m), 1254 (m), 1310 (m), 1410 (m), 1462 (w), 1653 (vs), 1697 (vw), 1703 (vw), 2889 (w), 2947 (m), 2983 (m), cm^{-1}.

6: ^{19}F NMR: δ = −54.3 (d, $^2J_{PF}$ 54.0 Hz); ^{31}P NMR: δ = 10.9 (qq, $^2J_{PF}$ 54.0 Hz, $^2J_{PH}$ 5.0 Hz).

Preparation of $(CO)_5Cr[F_3CP{=}C(OEt)NMe_2]$ (7)

A 300 mL sample of dry and stabilizer-free tetrahydrofuran (THF) together with 4 mmol (0.88 g) of $Cr(CO)_6$ were placed in a photoreactor (NORMAG) and irradiated with UV light at 10°C (TQ 718). The CO evolved during the irradiation was determined indirectly by measuring the volume of gas leaving the reactor. The UV lamp was switched off when 4 mmol CO had been replaced by THF.

The solution containing the complex $Cr(CO)_5$ THF was transferred to a Schlenk vessel and a solution of 4 mmol (0.8 g) $F_3CP{=}(OEt)NMe_2$ (**3**) in 20 mL THF was added slowly by use of a dropping funnel. After 12 hours of stirring at room temperature the solvent was removed under vacuum. The residue obtained consisted of the new complex **7** and some $Cr(CO)_6$, which could be separated by sublimation. Repeated crystallization from pentane gave the pure product, but the crystals obtained without exception were twinned and therefore not suited for X-ray diffraction measurements. Suitable crystals have been grown by a vapor phase transport in an evacuated ampoule along a temperature gradient from 65 to 20°C. Yield, referred to $F_3CP{=}C(OEt)NMe_2$: 82%.

Pentacarbonyl-[1-dimethylamino-1-ethoxy)-3,3,3-trifluoro-2-phospha-1-propene]chromium (7)

^1H NMR ($CDCl_3$): δ = 1.5 (t, $^3J_{HH}$ 6.8 Hz, 3H, OCH_2CH_3); 3.36 (s, 6H, NMe_2); 4.6 (q, $^3J_{HH}$ 6.8 Hz, 2H, OCH_2). ^{19}F NMR ($CDCl_3$): δ = −39.7 (d, $^2J_{PF}$ 69.0 Hz); ^{31}P NMR ($CDCl_3$): δ = 13.4 (q); ^{13}C NMR ($CDCl_3$): δ = 15.3 (s, OCH_2CH_3), 42.0 (br, NMe_2), 74.0 (d, $^2J_{PC}$ 9.4 Hz, OCH_2), 135.8 (dq, $^1J_{FC}$ 319.4 Hz, $^1J_{PC}$ 60.1 Hz, CF_3), 208.6 (dq, $^1J_{PC}$ 87.1 Hz, $^3J_{FC}$ 6.4 Hz, sp^2C), 217.7 (s, cis-CO), 224.3 (s, trans-CO); mass spectrum: 393 (M^+, 11%), 365 ($M^+ - CO$, 11%), 337 ($M^+ - 2CO$, 2%), 309 ($M^+ - 3CO$, 3%), 281 ($M^+ - 4CO$, 14%), 253 ($M^+ - 5CO$, 9%), 201 ($F_3CPC(OEt)NMe_2^+$, 5%), 182 ($F_2CPC(OEt)NMe_2^+$, 100%); IR spectrum (CO region): 1920 (s), 1930 (s),

TABLE 3 Crystallographic Data for Compound **7**

Crystal size [mm]	0.30 × 0.25 × 0.30
Molecular formula	$C_{11}H_{11}F_3NO_6PCr$
Molecular weight	393.18
Crystal system	Monoclinic
Space group	$P2_1$
Cell dimensions	
a, Å	6.672(4)
b, Å	12.080(7)
c, Å	10.126(6)
β, deg	91.46(5)
V, Å^3	815.9
Z	2
d_x, g/cm^{-3}	1.60
Diffractometer	Siemens R3
μ(Mo-Kα), cm^{-1}	8.3
T, C°	22
Scan mode/scan range	$2\Theta - \Theta$; $4° < 2\Theta < 54°$
No. of measured reflections	3892
No. of obsd. data with $I > 1.96\,\sigma(I)$	3224
No. of variables	207
$R = \Sigma(\|\|F_o\| - \|F_c\|\|)/\Sigma\|F_o\|$	0.058
$R_w = [\Sigma w(\|F_o\| - \|F_c\|)^2/\Sigma wF_o^2]^{1/2}$	0.064
Solution	Direct methods, SHELXTL PLUS
Weighting scheme	$w = [\sigma(F_o)^2 + 0.0001\|F_o\|^2]^{-1}$ $\sigma(F_o) = \sigma(I)/(2 \times \|F_o\| \times Lp)$

TABLE 4 Atomic Coordinates and Equivalent Isotropic Displacement Parameters for Compound **7**

	x	*y*	*z*	U_{eq}
Cr	0.8908(1)	0.7988(0)	0.3790(7)	0.0363(2)
P(19)	1.0180(2)	0.9153(1)	0.1992(1)	0.0452(5)
C(1)	1.0109(10)	0.8974(5)	0.5033(6)	0.0520(19)
C(2)	1.1326(9)	0.7173(5)	0.3798(5)	0.0474(19)
C(3)	0.6460(9)	0.8766(5)	0.3848(5)	0.0470(19)
C(4)	0.7977(9)	0.7131(5)	0.5139(5)	0.0472(18)
C(5)	0.7746(10)	0.6964(5)	0.2594(6)	0.0523(20)
C(6)	0.8013(8)	0.9691(4)	0.1093(5)	0.0389(16)
C(7)	1.1149(11)	0.8238(5)	0.0655(7)	0.0662(27)
C(8)	0.7255(11)	0.9780(5)	−0.1262(5)	0.0592(22)
C(9)	0.6241(14)	0.9067(7)	−0.2236(6)	0.0880(32)
C(10)	0.5334(9)	1.0859(5)	0.1056(6)	0.0584(22)
C(11)	0.7860(10)	1.1245(5)	0.2580(6)	0.0595(22)
N(1)	0.7055(7)	1.0564(4)	0.1509(4)	0.0400(14)
F(1)	1.2967(7)	0.7857(5)	0.1088(4)	0.0983(18)
F(2)	1.0108(8)	0.7360(3)	0.0264(4)	0.0892(19)
F(3)	1.1532(7)	0.8803(4)	−0.0463(4)	0.0801(16)
O(1)	1.0820(9)	0.9513(5)	0.5837(5)	0.0899(22)
O(2)	1.2730(8)	0.6641(4)	0.3863(5)	0.0758(19)
O(3)	0.4945(8)	0.9205(5)	0.3908(5)	0.0810(19)
O(4)	0.7338(8)	0.6595(5)	0.5983(4)	0.0716(18)
O(5)	0.7023(8)	0.6292(5)	0.1930(5)	0.0879(21)
O(6)	0.7350(6)	0.9175(3)	0.0014(3)	0.0497(12)

$U_{eq} = 1/3\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* a_i a_j$

1939 (vs), 1986 (w), 2062 (w). Anal. Calcd. for $C_{11}H_{11}CrF_3NO_6P$: C, 33.59; H, 2.80; N, 3.56. Found: C, 33.64; H, 2.78; N, 3.56.

On storing a chloroform solution of **7** at room temperature a very slow conversion to the binuclear complex $[(CO)_5Cr]_2$ $[F_3CP{=}C(OEt)\ NMe_2]$ (**8**) and the free ligand **3** was observed. The rate of conversion was so small that the amount of **8** formed within 6 weeks did not allow for a detailed investigation. Attempts to enhance rate and conversion of the reaction by heating the solution to 60°C led to the decomposition of the free ligand **3** and to formation of undesired byproducts, but not to an increase of the yield. The direct synthesis of **8** by the reaction of **7** with $Cr(CO)_5$ THF also failed. NMR data of **8** ($CDCl_3$ solution): ^{19}F NMR: $\delta = -52.9$ (d, $^2J_{PF}$ 50.6 Hz); ^{31}P NMR: $\delta = 89.9$ (q, $^2J_{PF}$ 50.6 Hz).

X-ray Diffraction Study of **7**

The data were collected on a Siemens R3 Four-Cycle-Diffractometer using Mo-Kα radiation, λ = 0.71069 Å. The structure was solved by direct methods (SHELXTL system). Details of the structure determination are given in Table 2. Atomic coordinates and selected bond lengths and angles are presented in Tables 3 and 4.

SUPPLEMENTARY MATERIAL AVAILABLE

Further details about this structural investigation are available from the Fachinformationszentrum Energie, Physik, Mathemathik GmbH, D-7514 Eggenstein-Leopoldshafen 2, referring to the depot number CSD 55130, the authors, and the literature reference.

ACKNOWLEDGMENT

This work was supported by the Deutsche Forschungsgemeinschaft, the Minister für Wissenschaft and Forschung Nordrhein-Westfalen, and the Fonds der Chemischen Industrie. We thank Mr. A. Flatow for recording the PE spectra.

REFERENCES AND NOTES

[1] Part 27 of the series "Reactive E=C(p–p)π-Systems" Part 26: J. Grobe, D. Le Van, B. Lüth, M. Hegemann, *Chem. Ber., 123,* 1990, 2317.

[2] J. Grobe, D. Le Van, J. Nientiedt, *Z. Naturforsch. B, Chem. Sci., 41,* 1986, 149.

[3] J. Grobe, D. Le Van, J. Nientiedt, B. Krebs, M. Dartmann, *Chem. Ber., 121,* 1988, 655.

[4] (a) R. Appel, F. Knoll, *Adv. Inorg. Chem. 33,* 1989, 259; L. N. Markowski, V. D. Romanenko, *Tetrahedron, 45,* 1989, 6019; (b) Fluorophosphaalkenes: J. Grobe, D. Le Van, J. Schulze, J. Szameitat, *Phosphorus Sulfur, 28,* 1986, 239.

[5] J. Grobe, D. Le Van, J. Nientiedt, *New J. Chem., 13,* 1989, 363.

[6] J. Grobe, D. Le Van, B. Krebs, R. Fröhlich, A. Schiemann, *J. Organomet. Chem., 389,* 1990, C29.

[7] W. G. Klemperer, *Angew. Chem., 90,* 1978, 258; *Angew. Chem. Int. Ed. Engl., 17,* 1978, 246.

[8] J. Grobe, M. Hegemann, D. Le Van, *Z. Naturforsch. B, Chem. Sci., 45,* 1990, 148.
[9] R. Appel, M. Immenkeppel, *Z. Anorg. Allg. Chem., 553,* 1987, 7; Z. M. Xie, P. Wisian-Neilson, R. H. Neilson, *Organometallics, 4,* 1985, 339; K. Issleib, H. Schmidt, E. Leissring, *Z. Chem. 26,* 1986, 406.
[10] G. Becker, W. Uhl, H. J. Wessely, *Z. Anorg. Allg. Chem., 479,* 1981, 41.
[11] J. Grobe, D. Le Van, unpublished results.
[12] J. Grobe, D. Le Van, J. Nientiedt, *Z. Naturforsch. B., Chem. Sci., 42,* 1987, 984.
[13] J. P. Kitzinger, in P. Diehl, E. Fluck, R. Kosfeld (eds): *NMR Basic Principles and Progress,* Springer Verlag, Berlin, Vol. 17, p. 64, (1981); D. W. Boykin, T. S. Subramanian, A. L. Baumstark, *Spectrochim. Acta, 45,* 1989, 335.
[14] W. von Philipsborn, R. Müller, *Angew Chem., 98,* 1986, 381; *Angew. Chem. Int. Ed. Engl., 25,* 1986, 383; J. Mason, *Chem. Rev., 81,* 1981, 205; W. Schwotzer, W. von Philipsborn, *Helv. Chim. Acta, 60,* 1977, 1501; G. J. Martin, M. L. Martin, J. P. Gouesnard, in P. Diehl, E. Fluck, R. Kosfeld (eds): *NMR Basic Principles and Progress,* Springer Verlag, Berlin, Vol. 18, pp. 135–41, (1981).
[15] A. Schmidpeter, B. Wrackmeyer, *Z. Naturforsch. B, Chem. Sci., 41,* 1986, 553.
[16] H. Bock, M. Bankmann, *Angew. Chem., 98,* 1986, 287; *Angew. Chem. Int. Ed. Engl., 25,* 1986, 265.
[17] R. Gleiter, W. D. Goodman, W. Schäfer, J. Grobe, J. Apel, *Chem. Ber., 116,* 1983, 3745.
[18] C. R. Brundle, N. A. Kuebler, M. B. Robin, H. Basch, *J. Am. Chem. Soc., 94,* 1972, 7.
[19] T. Koopmans, *Physica, 1,* 1934, 104.
[20] J. F. Nixon, *Chem. Rev., 88,* 1988, 1327.
[21] Th. C. Klebach, R. Lourens, F. Bickelhaupt, C. H. Stam, H. von Herk, *J. Organomet. Chem., 210,* 1981, 211.
[22] J. Grobe, T. Grosspietsch, D. Le Van, J. Schulze, B. Krebs, M. Dartmann, *J. Organomet. Chem., 385,* 1990, 255.
[23] L. Pauling: *Die Natur der chemischen Bindung,* Verlag Chemie, Weinheim/Bergstr., Germany, 1976.
[24] J. Grobe, D. Le Van, *Angew. Chem., 96,* 1984, 716; *Angew. Chem. Int. Ed. Engl., 23,* 1984, 710.
[25] W. Strohmeier, F. J. Müller, *Chem. Ber., 102,* 1969, 3608.