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Transition metal complexes and cycloaddition products of pentafluorophenyl isocyanide

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Abstract

Reactions of pentafluorophenyl isocyanide with pentacarbonyl(η^2-*cis*-cyclooctene)chromium, tricarbonyl(η^6-cycloheptatriene)tungsten, and tetracarbonylnickel yield pentacarbonyl(pentafluorophenyl isocyanide)chromium I, *mer*-tricarbonyl-tris(pentafluorophenyl isocyanide)tungsten II, and tetrakis(pentafluorophenyl isocyanide)nickel III, respectively. The meridial structure of tricarbonyl-tris(pentafluorophenyl isocyanide)tungsten was elucidated by X-ray crystallography. The [2 + 1] cycloaddition reaction of pentafluorophenyl isocyanide with the diphosphene R=P=P=R [R = C(SiMe$_3$)$_3$] yields the three membered heterocyclic diphosphirane imine IV. The photolysis of pentafluorophenyl isocyanide in the presence of [bis(diisopropylamino)phophino]-(trimethylsilyl)diazomethane yields 1-pentafluorophenyl-2,4-bis(diisopropylamino)-3-trimethylsilyl-1,2-azaphosphetine V according to the results of an X-ray structure analysis at −158°C.

Keywords: Transition metal complexes; Cycloaddition products; Pentafluorophenyl isocyanide

1. Introduction

The chemistry of trifluoromethyl isocyanide has been explored in details during recent years, demonstrating strong fluorine substitution effects. In contrast to the good σ donor and poor π acceptor ligand, methyl isocyanide, trifluoromethyl isocyanide is one of the strongest π acceptor ligands known [1,2]. In comparison, the chemistry of pentafluorophenyl isocyanide is much less explored. Pentafluorophenyl isocyanide was first mentioned in the literature in 1975 [3]. However, the material obtained from *N*-pentafluorophenylformamide under very drastic conditions was impure. An analytically pure sample was prepared for the first time in 1988 [4] and its structure was elucidated recently by X-ray crystallography at −158°C [5]. Cp*Mn(CO)$_2$(CN–C$_6$F$_5$) [4] is the only transition metal complex of C_6F_5NC known thus far. In continuation of our work on fluorinated isocyanides, we report on further transition metal complexes and cycloaddition products of the only known fluorinated aromatic isocyanide.

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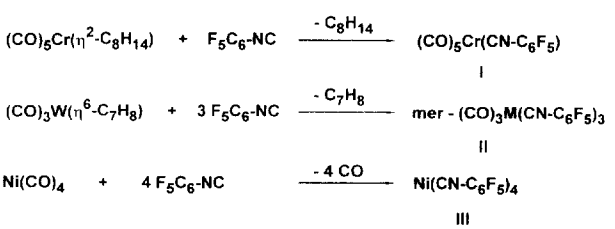
2. Results and discussion

Pentafluorophenyl isocyanide complexes are obtained according to Scheme 1. Due to the instability of pentafluorophenyl isocyanide in neat substance or concentrated solutions, all reactions require starting materials with labile ligands which react under mild reaction conditions. The alkene ligand of pentacarbonyl(*cis*-cyclooctene)chromium can be easily replaced by stronger ligands like C_6F_5NC yielding pentacarbonyl(pentafluorophenyl isocyanide)chromium as colourless crystals. The IR spectrum in *n*-pentane solution exhibits three absorptions between 1900 and 2200 cm^{-1} for the CO and CN stretching modes, respectively. An unambiguous assignment can be made for the E mode (C_{4v} local



Scheme 1.

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Table 1
Crystal data and structure refinement for *mer*-$(CO)_3W(CN\text{–}C_6F_5)_3$ II

Empirical formula	$C_{24}F_{15}N_3O_3$
W	
Formula weight	847.12
Temperature	20(2)°C
Wavelength	71.069 pm
Crystal system	Monoclinic
Space group	$A2/n$
Unit cell dimensions	$a = 862.3(2)$ pm
	$b = 1501.9(3)$ pm
	$c = 1950.1(3)$ pm
	$\beta = 94.48(1)°$
Volume	$2.5178(9)*10^6$ pm^3
Z	4
Density (calculated)	2.235 Mg/m^3
Absorption coefficient (mm^{-1})	4.735
Crystal size	0.3×0.3×0.3 mm
Theta range for data collection	2 to 25°
Index ranges	$-10 \le h \le 10$, $-17 \le k \le 17$, $-23 \le l \le 23$
Reflections collected	5202
Independent reflections	2218 [R(int) = 0.0532]
Absorption correction	PSI scan
Max. and min. transmission	0.999 and 0.748
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2218/0/212
Goodness-of-fit on F^2	1.028
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0356$, $wR_2 = 0.0619$
R indices (all data)	$R_1 = 0.0689$, $wR_2 = 0.0724$
Largest diff. peak and hole	$0.871*10^{-6}$ and $-0.566*10^{-6}$ epm^{-3}

symmetry) at 1968 cm^{-1} which is expected to be the strongest infrared active CO vibration. From the position of this absorption, one can conclude that pentafluorophenyl isocyanide can be compared to fluoromethyl isocyanide, FH_2C–NC, in its σ donor/π acceptor ratio. These results are in good agreement with the ^{13}C spectrum showing the normal chemical shift distribution of $\delta(CO_{trans}) = 214.6 > \delta(CO_{cis}) = 213.3$ ppm in $(CO)_5CrL$ complexes in contrast to very strong π acceptor ligands like trifluoromethyl isocyanide or thiocarbonyl which show the opposite effect.

Replacement of the cycloheptatriene ligand in $(CO)_3W(\eta^6\text{-}C_7H_8)$ results in the formation of *mer*-tricarbonyltris(pentafluorophenyl isocyanide)tungsten II, which can be isolated as yellow crystals. Like tricarbonyltris(trifluoromethyl isocyanide)tungsten the ^{19}F NMR spectrum of tricarbonyltris(pentafluorophenyl isocyanide)-tungsten exhibits two sets of signals for the pentafluorophenyl groups. Assuming an octahedral coordination of the tungsten atom the complex exists as the meridial isomer. The meridial structure of $(CO)_3W(CNC_6F_5)_3$ is confirmed by a X-ray crystal structure analysis (Tables 1, 2 and 3, Fig. 1). *mer*-Tricarbonyltris(pentafluorophenyl isocyanide)tungsten crystallizes in the monoclinic space group $A2/n$ with half a molecule in the asymmetric unit. The tungsten atom, one carbonyl ligand and some atoms of one isocyanide ligand are on special positions, the two-fold crystallographic symmetry axis converts one part of the molecule into the other. All C–W–C angles are close to 90 or 180°, respectively. The W–C distances to the carbonyl ligand are slightly shorter in comparison to that to the isocyanide ligands indicating that the carbonyl ligand is the better π accepting ligand. All C–N–C bond angles are close to 180°. However, larger anisotropic thermal displacement parameters are found for the nitrogen atoms in the plane perpendicular to the C–N vectors indicating that the isocyanide nitrogen atoms may be on at least two disordered positions to the sides of the C–C vector.

Most previously prepared $(CO)_3W(CNR)_3$ complexes [7–9] including $(CO)_3W(CN\text{–}CH_2\text{–}CF_3)_3$ which exhibits a single set of resonances in the ^1H, ^{19}F and ^{13}C NMR spectra [10], were reported to adopt the facial structure based on spectroscopic data. Exceptions are *mer*-$(CO)_3W(CNCF_3)_3$ [11] and *mer*- and *fac*-$(CO)_3W(CN\text{–}t\text{-}Bu)_3$ [12]. All $(CO)_3W(CNR)_3$ complexes which have been characterized crystallographically exist as the facial isomer, however, this geometry might be forced by the tripodal nature of these isocyanide ligands [13–15].

Due to the instability of pentafluorophenyl isocyanide, it is difficult to synthesize homoleptic complexes. In contrast to hexacarbonylchromium or pentacarbonyliron, where a replacement of carbonyl ligands usually requires elevated temperature, ligand replacement in tetracarbonyl nickel occurs easily at ambient temperature. Using aryl isocyanides a complete substitution has been observed [16] forming $Ni(CN\text{–}Aryl)_4$, whereas only partial substitution occurs with

Table 2
Atomic coordinates ($*10^4$) and equivalent isotropic displacement parameters ($Å^{2}*10^{3}$) for *mer*-$(CO)_3W(CN-C_6F_5)_3$ II. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor

	x	y	z	U_{eq}
W(1)	2500	6033(1)	2500	50(1)
C(11)	646(8)	6026(4)	1782(3)	61(2)
C(12)	2500	7381(8)	2500	66(3)
C(13)	2500	4668(8)	2500	83(4)
C(14)	981(8)	6038(6)	3267(4)	74(2)
C(131)	2500	2996(8)	2500	78(3)
C(132)	1717(9)	2521(6)	2962(4)	77(2)
C(133)	1705(9)	1619(6)	2957(4)	75(2)
C(134)	2500	1174(8)	2500	79(3)
C(141)	−882(8)	5953(6)	4195(3)	68(2)
C(142)	−1445(8)	5135(6)	4396(4)	67(2)
C(143)	−2438(9)	5075(6)	4895(4)	75(2)
C(144)	−2894(9)	5823(7)	5199(4)	82(3)
C(145)	−2421(11)	6626(6)	5014(5)	81(2)
C(146)	−1435(10)	6701(5)	4514(4)	77(2)
F(132)	895(6)	2952(4)	3406(3)	142(2)
F(133)	908(7)	1169(4)	3400(3)	140(2)
F(134)	2500	287(5)	2500	142(3)
F(142)	−926(6)	4404(4)	4101(3)	115(2)
F(143)	−2889(7)	4282(4)	5091(3)	132(2)
F(144)	−3857(7)	5731(5)	5695(3)	151(3)
F(145)	−2966(8)	7345(4)	5319(3)	145(3)
F(146)	−961(8)	7504(4)	4329(3)	144(2)
N(13)	2500	3901(7)	2500	142(6)
N(14)	130(8)	6014(6)	3692(3)	118(3)
O(11)	−394(6)	6004(4)	1389(3)	89(2)
O(12)	2500	8141(6)	2500	119(3)

Table 3
Selected bond lengths [pm] and angles [°] for *mer*-$(CO)_3W(CN-C_6F_5)_3$ II

W(1)–C(12)	202.5(12)
W(1)–C(11)	204.2(8)
W(1)–C(13)	205.0(12)
W(1)–C(14)	206.4(7)
C(13)–N(13)	115.1(13)
C(14)–N(14)	114.9(9)
C(131)–N(13)	136.0(14)
C(141)–N(14)	136.6(9)
N(13)–C(13)–W(1)	180.0
N(14)–C(14)–W(1)	178.0(9)
C(13)–N(13)–C(131)	180.0
C(14)–N(14)–C(141)	177.9(11)

Symmetry transformations used to generate equivalent atoms: $1-x+0.5, y, -z+0.5$.

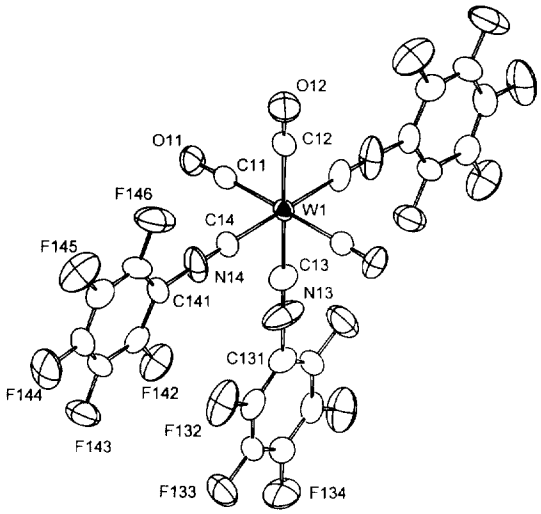


Fig. 1. Molecular structure (ORTEP [6], 30% ellipsoids) of *mer*-$(CO)_3W(CN-C_6F_5)_3$ II.

alkyl isocyanides except trifluoromethyl isocyanide [17]. Tetrakis(pentafluorophenyl isocyanide)nickel forms air stable yellow crystals of high chemical stability. No decomposition occurs even in concentrated sodium hydroxide solution. No reaction was observed with bis(cyclopentadienyl)nickel although $Ni(CNCF_3)_4$ reacts forming the dinuclear complex $[(\eta^5\text{-}C_5H_5)Ni(CNCF_3)]_2$ [17]. The vibrational spectra exhibit a single broad absorption at 2033 cm^{-1} (IR) and 2046 cm^{-1} in the CN stretching region demonstrating local tetrahedral symmetry in agreement with the ^{13}C NMR data exhibiting multiplets for the aromatic carbon atoms between 107.3 and 149.0 ppm and a single resonance for the isocyanide carbon at 182.6 ppm.

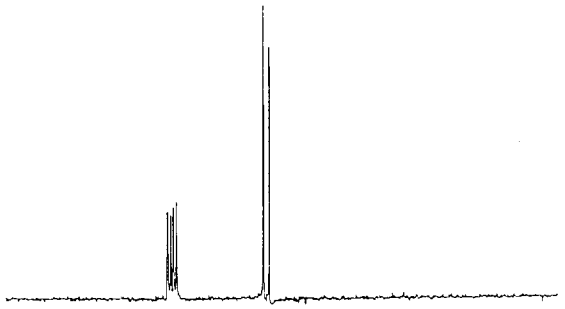


Fig. 2. Variable temperature ^{19}F NMR Spectra of *N*-pentafluorophenyldiphosphiranimine IV.

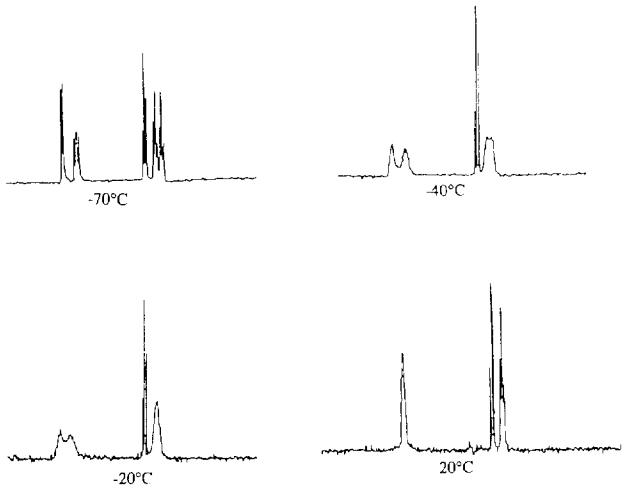
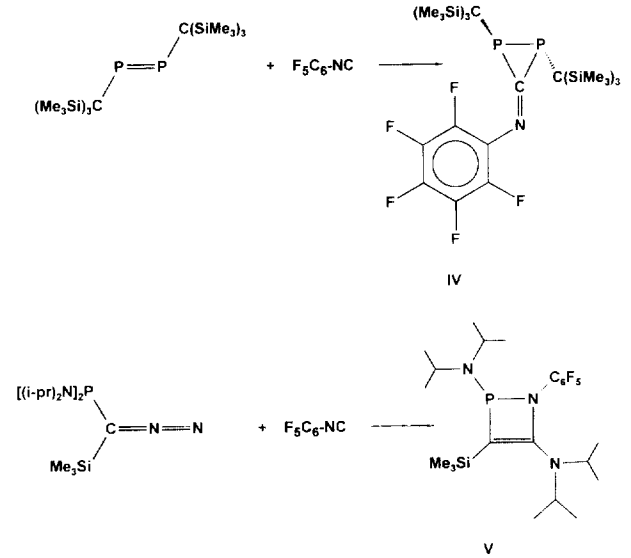


Fig. 3. $^{31}P\{^1H\}$ NMR spectrum of *N*-pentafluorophenyldiphosphiranimine IV at −70°C.



Scheme 2.

As compounds with formally divalent carbon, isocyanides are, in general, very reactive species which exhibit a great potential in preparative organic chemistry. Fluorine substitution increases the reactivity of the compounds, thus trifluoromethyl isocyanide decomposes even below −80°C in the condensed phase. Nevertheless, its reactivity has been studied and it turned out that it easily reacts with carbon–carbon [18] and carbon–sulfur triple-bonds [19], diphosphenes [20], cyclotrisilanes [21] and hexafluoroacetone [22,23] forming various cycloaddition products. Pentafluorophenyl isocyanide which has been included in two of these studies [19,21] possesses a high reactivity, too.

Reaction of pentafluorophenyl isocyanide with bis[tris(trimethylsilyl)methyl]diphosphene yields the expected diphosphiranimine IV as yellow orange air stable crystals which melt at 148°C without decomposition. The high stability resembles that of the trifluoromethyl-substituted compound and is in contrast to the methyl substituted [20] and to similar compounds isolated by Baudler and Simon [24]. The structure of the compound is easily proved by spectroscopic data. The mass spectrum exhibits $m/e = 702$ as largest fragment ion which corresponds to the molecular ion minus a methyl group and smaller fragment ions which can be fully assigned. At ambient temperature the $^{31}P\{^1H\}$ NMR spectrum exhibits an AB pattern for the chemically non-equivalent phosphorus atoms showing additional fine structure due to coupling with fluorine atoms of the aromatic ring. The phosphorus–phosphorus coupling constant of $^1J(^{31}P_A–^{31}P_B) = 78.8$ Hz is slightly larger than that observed for similar ring systems [20,24]. Again, the barrier of inversion at the nitrogen atom is large enough to make the phosphorus atoms chemically inequivalent at ambient temperature in contrast to a similar disilacyclopropane imine which exhibits a single resonance in the ^{29}Si NMR spectrum indicating a low activation barrier for the inversion at the nitrogen atom [25]. Both the $^{31}P\{^1H\}$ and ^{19}F NMR spectrum (Fig. 3) show interesting effects on cooling to −70°C which can be explained by a hindered rotation of the fluorinated aromatic ring around the carbon–nitrogen single bond. At −70°C, all five fluorine atoms are chemically and magnetically inequivalent giving rise to five signals in the ^{19}F NMR spectrum at −148.6, −150.9 (F_o), −161.1 (F_p) and −162.7, −163.6 (F_m) ppm. The $^{31}P\{^1H\}$ NMR spectrum (Fig. 2) consists of a doublet of doublets and a doublet at −78.0 and −111.9 ppm, respectively. Only the low field signal exhibits a through space 36.6 Hz coupling to one of the ortho fluorine atoms and thus, can be assigned to the phosphorus at the same side as the aromatic ring. On warming, the signals of the ortho and meta fluorine atoms broaden, whereas that of the para fluorine remains virtually unchanged. At ambient temperature, an AA′BB′CX type spectrum can be observed indicating free rotation around the carbon–nitrogen single bond.

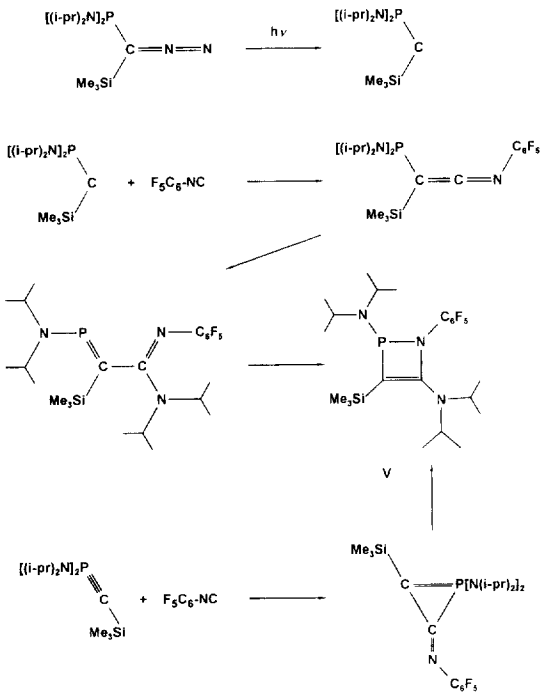
The reactions of trifluoromethyl isocyanide and pentafluorophenyl isocyanide with alkylidynesulfur trifluoride, $F_3C–C\equiv SF_3$ and $F_5S–C\equiv SF_3$, most likely occur via a carbene type exited state, $R_f–C–SF_3$ and a ketene imine intermediate

which stabilizes itself by 1,3 fluorine shift to the final product, $R-N=C(F)-C(R_f)=SF_2$ [19]. Similar silaketene imine species are believed to be the primary products in the photochemical reaction of fluorinated isocyanides and cyclotrisilanes [21] (Scheme 2).

Thermal or photolytical decomposition of (diaminophosphino)(trimethylsilyl)diazomethane yields compounds which can be described both as λ^3-phosphino carbenes or λ^5-phosphaalkynes [26–32]. According to the NMR data, a formulation with a P–C triple bond plays an important role. Depending on the reagent, formal products of a P–C triple bond or carbene have been obtained. With *t*-butyl isocyanide, a ketene imine has been isolated and characterized spectroscopically [27,28].

The isolated product in the photolysis reaction of [bis(diisopropylamino)phosphino](trimethylsilyl)diazomethane with pentafluorophenyl isocyanide is neither a ketene imine nor a simple cycloaddition product. The formation of the 1,2-azaphosphetine can be explained by two different mechanism (Scheme 3). Reaction of the carbene formed by photolytic nitrogen elimination results in a ketene imine species. 1,3 Diisopropylamino migration gives a product comparable to $F_5C_6-N=C(F)-C(R_f)=SF_2$, the final product of the analogous reaction with $R_f-C\equiv SF_3$ [19]. Ring closure yields the final product. In the alternative pathway, the [2+1] cycloaddition product, a phosphacyclopropene imine, undergoes a ring expansion reaction forming the isolated product.

1-Pentafluorophenyl-2,4-bis(diisopropylamino)-3-trimethylsilyl-1,2-azaphosphetine forms a colourless crystalline solid. The ^{19}F NMR spectrum exhibits the three expected signals of an AA′BB′CX spin system. The ^{31}P resonance is



Scheme 3.

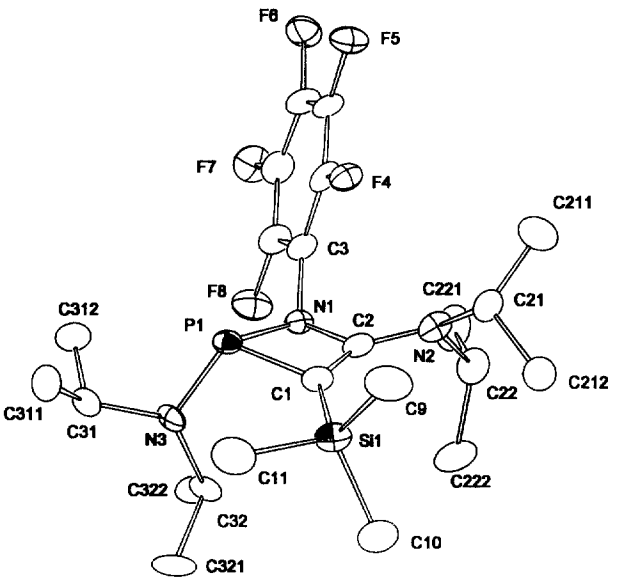


Fig. 4. Molecular structure (ORTEP [6], 50% ellipsoids) of 1-pentafluorphenyl-2,4-bis(diisopropylamino)-3-trimethylsilyl-1,2-azaphosphetine V.

split into a triplet [$J(^{31}P-^{19}F)=12$ Hz] due to coupling with the two chemically equivalent ortho fluorine atoms. According to the low symmetry of the molecule, four chemically inequivalent isopropyl groups are expected. The ^1H NMR spectrum shows a single line at 0.30 ppm for the trimethylsilyl substituent. The isopropyl groups give signals between 0.7 and 1.3 ppm for six chemically inequivalent methyl groups in a ratio of 6:3:6:3:3:3 exhibiting doublet splitting of 6.5 to 6.9 Hz. Three different signals can be observed at 3.16 [^1H, $^3J^{31}P-^1H)=15$ Hz, $^3J(^1H-^1H)=6.7$ Hz], 3.51 [2H, $^3J(^1H-^1H)=6.9$ Hz] and 4.07 [^1H, $^3J(^{31}P-^1H)$, $^3J(^1H-^1H)=6.7$ Hz] for the isopropyl protons. The two signals exhibiting phosphorus proton couplings can be easily assigned to the phosphorus bond diisopropylamino group.

1-Pentafluorophenyl-2,4-bis(diisopropylamino)-3-trimethylsilyl-1,2-azaphosphetine crystallizes in the acentric orthorhombic space group $P2_12_12_1$ with four molecules in the unit cell. The molecular structure and the atomic numbering scheme are depicted in Fig. 4. The main structural motif is the non-planar four-membered heterocyclic ring [the plans C1, C2, N1 and C1, N1, P1 form an angle of 15.4(4)°] with two planar configurated carbon atoms (sum of the bond angles at C1 and C2 360.0 and 360.0°). The nitrogen atom and the phosphorus atom are pyramidal (sum of the bond angle 293.3 P1 and 328.8 N1). The bond angles within the ring differ strongly from 90°. The smallest angle is observed as expected at the phosphorus atom (C1–P1–N1 75.5(3)°). The distance C1–C2 corresponds to a C–C double bond. Large differences are observed for the exoclic and endocyclic C–N bond distances due to steric crowding. The phosphorus–nitrogen distance to N1 is unexpectedly long.

Our findings have clearly demonstrated that pentafluorophenyl isocyanide is a good ligand in transition metal chem-

istry and versatile reagent for cycloaddition reactions, although its use is hindered by the fact that it is unstable at ambient temperature and has to be synthesized in two steps, starting with commercially available pentafluoroaniline.

3. Experimental

3.1. Spectra

Infrared spectra, Perkin Elmer 883; Raman spectra, Ramalog Spex, Argon laser excitation; mass spectra, Varian 711, 80 eV, EI; and NMR spectra JEOL FX 90Q (90 MHz), JEOL LAMBDA (400 MHz) and BRUKER (270 MHz). Chemical shifts are given in ppm according to IUPAC convention using TMS (^{1}H, ^{13}C), $CFCl_3$ (^{19}F) and H_3PO_4 85% (^{31}P) as reference standards.

3.2. Reagents

Pentafluorophenyl isocyanide [4], pentacarbonyl(η^2-*cis*-cyclooctene)chromium [33], tricarbonyl(η^6-cycloheptatriene)tungsten [34], bis[tris(trimethylsilyl)methyl]-diphosphene [35–37] and [bis(diisopropylamino)phosphino](trimethylsilyl)diazomethane [26] were prepared according to literature methods. Tetracarbonylnickel was bought from Alfa and used as received. All solvents were dried and stored under argon.

4. Pentacarbonyl(pentafluorophenyl isocyanide) chromium I

Pentacarbonyl(*cis*-cyclooctene)chromium (500 mg, 1.65 mmol) were dissolved in 50 ml of dichloromethane at −30°C. Pentafluorophenyl isocyanide (450 mg, 2.33 mmol) dissolved in 10 ml of *n*-pentane were added through a rubber septum using a syringe. The reaction mixture was allowed to warm to ambient temperature under stirring using a magnetic stirring bar. After 16, h the solution was filtered through a layer of silica and the solvent was removed under vacuum. Crystallization from *n*-pentane yielded I, 410 mg (34%), as colourless crystals, m.p. 130°C.

^{19}F NMR ($CDCl_3$): $\delta = -142.4$ (F_o), -150.6 (F_p), -158.4 (F_m) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 214.6$ (CO_{trans}), 213.3 (CO_{cis}), 193.8 (CN), 128–158 (m, C_6F_5) ppm; IR (*n*-pentane): $\upsilon = 2125$ (w), 2041 (m), 1968 (s) cm^{-1}; MS: $m/e = 385$ (M^+), 329 (M^+–2CO), 301 (M^+–3CO), 273 (M^+–4CO), 245 (M^+–5CO), 193 ($C_6F_5NC^+$).

Table 4
Crystal data and structure refinement for 1-pentafluorophenyl-2,4-bis(diisopropylamino)-3-trimethylsilyl-1,2-azaphosphetine V

Empirical formula	$C_{23}H_{37}F_5N_3PSi$
Formula weight	509.62
Temperature	−158°C
Wavelength	71.069 pm
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Unit cell dimensions	$a = 751.4(4)$ pm
	$b = 1347.9(6)$ pm
	$c = 2646.3(6)$ pm
Volume	$2.680(2)*10^9$ pm^3
Z	4
Density (calculated)	1.263 Mg/m^3
Absorption coefficient	0.198 mm^{-1}
Crystal size	0.3*0.3*0.1 mm
Theta range for data collection	2 to 25°
Index ranges	$0 \le h \le 8$, $0 \le k \le 16$, $0 \le l \le 31$
Reflections collected	2720
Independent reflections	2690 [R(int) = 0.0000]
Absorption correction	no
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2690/0/332
Goodness-of-fit on F^2	1.142
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0516$, $wR_2 = 0.1183$
R indices (all data)	$R_1 = 0.0820$, $wR_2 = 0.1527$
Absolute structure parameter	0.2(3)
Extinction coefficient	0.0024(5)
Largest diff. peak and hole	$0.865*10^{-6}$ and $-0.821*10^{-6}$ epm^{-3}

5. *mer*-Tricarbonyltris(pentafluorophenylisocyanide)tungsten II

Pentafluorophenyl isocyanide (240 mg, 1.24 mmol) was dissolved in 50 ml of diethylether. Tricarbonyl(η^6-cycloheptatriene)tungsten (150 mg, 0.38 mmol) were added in small portions to the stirred solution at ambient temperature. The product immediately deposits as fine yellow crystals. After 1 h, the solvent was removed with a pipette and the crystals were dried under vacuum. Recrystallization from toluene/pentane yielded 250 mg (78%), yellow crystals, m.p. 181–182°C. ^{19}F NMR ($CDCl_3$): $\delta = -142.8$ (F_o, 2F), -143.0 (F_o, 4F), -151.0 (F_p, 1F), -153.0 (F_p, 2F), -158.9 (F_m, 2F), -159.2 (F_m, 2F) ppm. MS: $m/z = 847$ (M^+), 819 (M^+–CO), 791 (M^+–2CO), 763 (M^+–3CO), 570 (M^+–3CO–CNC_6F_5) and smaller fragment ions. The isotopic pattern of the molecular ion is in good agreement with the calculated. IR(CH_2Cl_2): 2127 (w), 2003 (m), 1940 (s) cm^{-1}.

Table 5
Atomic coordinates ($*10^4$) and equivalent isotropic displacement parameters (A^2*10^3) for 1-pentafluorophenyl-2,4-bis(diisopropylamino)-3-trimethylsilyl-1,2-azaphosphetine. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor

	x	y	z	U_{eq}
P(1)	7510(3)	1259(1)	8864(1)	21(1)
Si(1)	7506(3)	281(2)	7728(1)	28(1)
C(1)	7729(10)	250(5)	8426(2)	22(2)
C(2)	8006(8)	−401(6)	8811(3)	23(2)
C(3)	7511(12)	4(5)	9714(2)	24(1)
C(4)	5807(9)	−357(5)	9771(2)	23(2)
C(5)	5082(10)	−583(6)	10233(3)	26(2)
C(6)	6043(10)	−381(6)	10667(3)	30(2)
C(7)	7696(12)	8(5)	10626(2)	29(2)
C(8)	8427(10)	224(6)	10163(3)	27(2)
C(9)	5555(12)	−420(8)	7481(3)	45(2)
C(10)	9601(12)	−136(7)	7412(3)	39(2)
C(11)	7144(12)	1616(6)	7558(3)	40(2)
F(4)	4789(5)	−524(3)	9362(1)	26(1)
F(5)	3412(6)	−916(3)	10270(2)	34(1)
F(6)	5331(7)	−568(3)	11123(2)	36(1)
F(7)	8646(6)	217(3)	11051(1)	37(1)
F(8)	10084(6)	577(3)	10140(2)	34(1)
N(1)	8305(8)	224(4)	9246(2)	20(1)
N(2)	8012(7)	−1417(5)	8881(2)	24(1)
N(3)	9190(8)	2051(4)	8783(2)	24(1)
C(21)	6780(10)	−2018(6)	8566(2)	25(2)
C(211)	5889(10)	−2801(6)	8894(3)	33(2)
C(212)	7636(12)	−2492(6)	8108(3)	32(2)
C(22)	9696(10)	−1905(6)	9038(3)	30(2)
C(221)	10084(12)	−1829(6)	9599(3)	38(2)
C(222)	11283(11)	−1532(7)	8722(3)	42(2)
C(31)	8990(11)	3052(5)	9001(3)	29(2)
C(311)	7530(13)	3613(5)	8725(3)	40(2)
C(312)	8645(12)	3021(7)	9569(3)	40(2)
C(32)	11036(9)	1702(5)	8685(3)	26(2)
C(321)	11847(11)	2283(7)	8240(3)	37(2)
C(322)	12247(11)	1718(6)	9136(3)	33(2)

6. Tetrakis(pentafluorophenyl isocyanide)nickel III

Pentafluorophenyl isocyanide (900 mg, 4.7 mmol) were dissolved in 40 ml of dichloromethane in a 100-ml Schlenk flask. Tetracarbonylnickel (177 mg, 1 mmol) were condensed into the flask using a glass vacuum line. The flask was flushed with argon, and allowed to warm to ambient temperature. On stirring at ambient temperature, CO gas was formed rapidly. To complete the reaction the mixture was stirred for 12 h upon which the product crystallizes as yellow needle shaped crystals which were collected on a sintered glass fritt. The filtrate can be concentrated yielding a second fraction of the product. Recrystallization from dichloromethane gave 590 mg (71%) III, yellow crystals; m.p. 154°C dec.

^{19}F NMR ($CDCl_3$): $\delta = -144.0$ (F_o), -153.8 (F_p), -160.4 (F_m) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 182.6$ (CN), 143.4, 140.8, 138.0 ($^1J(^{19}F-^{13}C \approx 256$ Hz), 107.3 ppm; IR (*n*-pentane): $\nu = 2033$ (CN, vbr) cm^{-1}; Ra (solid): $\nu = 2046$ (m, vbr), 1656 (vs), 1513 (m), 1461 (m), 1326 (m), 1128 (w), 987 (w), 615 (s), 567 (s), 464 (s), 425 (m), 381 (m), 337 (w), 157 (w), 120 (m) cm^{-1}; MS: $m/e = 193$ ($C_6F_5NC^+$) and smaller fragment ions.

7. 1,2-Bis[tris(trimethylsilyl)methyl]-*N*-pentafluorophenyl-3-diphosphiranimine IV

Bis[tris(trimethylsilyl)methyl]diphosphene (95 mg, 0.2 mmol) were dissolved in 3 ml of *n*-pentane. Pentafluorophenyl isocyanide (200 mg, 1.04 mmol) were added. After 12 h at ambient temperature, the product was purified by preparative TLC. The yellow product fraction was eluted

Table 6
Selected bond lengths [pm] and angles [°] for 1-pentafluorophenyl-2,4-bis(diisopropylamino)-3-trimethylsilyl-1,2-azaphosphetine V

P(1)–N(3)	166.7(6)
P(1)–C(1)	179.4(7)
P(1)–N(1)	182.4(6)
Si(1)–C(1)	185.5(6)
C(1)–C(2)	136.0(9)
C(2)–N(2)	138.3(10)
C(2)–N(1)	144.5(8)
C(3)–N(1)	140.5(8)
N(3)–P(1)–C(1)	109.5(3)
N(3)–P(1)–N(1)	108.3(3)
C(1)–P(1)–N(1)	75.5(3)
C(2)–C(1)–P(1)	91.1(4)
C(2)–C(1)–Si(1)	140.7(6)
P(1)–C(1)–Si(1)	128.2(4)
C(1)–C(2)–N(2)	137.8(7)
C(1)–C(2)–N(1)	104.2(6)
N(2)–C(2)–N(1)	118.0(6)
C(3)–N(1)–C(2)	120.9(6)
C(3)–N(1)–P(1)	120.8(5)
C(2)–N(1)–P(1)	87.2(4)

using dichloromethane and recrystallized from pentane yielding IV, yellow orange crystals (30 mg, 24%; m.p. 148°C).

MS (80 eV): m/e=702 (M^+–CH_3), 614 (M^+–Si–4CH_3), 524 (M^+–Si–10CH_3), 451 (M^+–2Si–12CH_3), 335 (M^+–4Si–19CH_3), 293 (M^+–5Si–17CH_3), 261 (M^+–5Si–17CH_3–P), 193 ($C_6F_5NC^+$), 77 [$Si(CH_3)_3^+$]; ^{31}P NMR (toluene-d_8, −78°C): δ= −111.9 (d), −78 (dd) ppm. $^1J(^{31}P–^{31}P)$=78.8 Hz, $^6J(^{31}P–^{19}F)$=36.6 Hz; ^{19}F NMR (toluene-d_8, −78°C): δ= −148.9, −150.9 (F_o), −161.1 (F_p), −162.7, 163.6 (F_m) ppm. ^{19}F NMR (toluene-d_8, 20°C): δ= −148.2 (F_o), −161.5 (F_p), −162.9 (F_m) ppm. ^{1}H NMR (toluene-d_8): δ=0.29, 0.60 ppm ($SiMe_3$) ppm.

8. 1-Pentafluorphenyl-2,4-bis(diisopropylamino)-3-trimethylsilyl-1,2-azaphosphetine

[Bis(diisopropylamino)phosphino](trimethylsilyl)diazomethane (440 mg, 0.88 mmol) were dissolved in 10 ml of *n*-pentane and cooled to 0°C. Pentafluorophenyl isocyanide (300 mg, 1.6 mmol) were added. The reaction mixture was irradiated by UV light at 0°C for 1 h. A colour change to orange and brown and a mild gas evolution was observed. An additional amount (200 mg, 1.05 mmol) of pentafluorophenyl isocyanide was added using a syringe and irradiation was continued for 30 min. After storage for 2 days at −20°C, colourless crystals were formed which could be isolated at −30°C, washed with cold pentane and dried in a stream of argon. Yield 25 mg, 4.5%, m.p. 75°C.

^{31}P{^{1}H} NMR (C_6D_6): δ=97.5, $J(^{19}F_o–^{31}P)$ = 12 Hz; ^{19}F NMR (C_6D_6): δ= −147.9 (2F, F_o), −159.1 (1F, F_p), −164.1 (2F, F_m); ^{1}H NMR (C_6D_6, 270 MHz): δ=0.30 (9H, $SiMe_3$), 0.74 [6H, $^3J(^1H–^1H)$=6.9 Hz, CH_3], 0.99 [3H, $^3J(^1H–^1H)$=6.8 Hz, CH_3], 1.09 [6H, $^3J(^1H–^1H)$=6.8 Hz, CH_3], 1.27 [3H, $^3J(^1H–^1H)$=6.8 Hz, CH_3], 1.28 [3H, $^3J(^1H–^1H)$=6.5 Hz, CH_3], 1.30 [3H, $^1J(^1H–^1H)$=6.5 Hz, CH_3], 3.16 [^{1}H, $^3J^{31}P–^1H)$=15 Hz, $^3J(^1H–^1H)$=6.7 Hz, CH], 3.51 [2H, $^3J(^1H–^1H)$=6.9 Hz, CH] and 4.07 [^{1}H, $^3J(^{31}P–^1H)$, $^3J(^1H–^1H)$=6.7 Hz, CH].

9. Crystal structure determinations

Suitable crystals of *mer*-$(CO)_3W(CN–C_6F_5)_3$ II (ambient temperature) and 1-pentafluorphenyl-2,4-bis(diisopropylamino)-3-trimethylsilyl-1,2-azaphosphetine V (at low temperature with a device described elsewhere [38,39]) were mounted at the end of glass fibres adjusted on a goniometer head. Unit cell data were obtained on a CAD 4 four-circle diffractometer which was used for data collection at ambient temperature and −158°C, respectively. The structures were solved by the program SHELXS86 [40] and SHELXL93 [41], respectively. Molecular drawings were performed using ORTEP [42] as modified by Zsolnai [6]. Important crystallographic details are summarized in Tables 1 and 4. Atomic coordinates, important bond length and angles are summarized in Tables 2, 3, 5 and 6. A Flack parameter of 0.2(3) indicates that the absolute structure of V cannot be determined reliably. Further details of the crystal structure analyses may be obtained from: The Director, CCDC, 12 Union Road, Cambridge CB 1EZ (Fax: Int. +1223/336-033; e-mail: deposit@chemcrys.cam.ac.uk), on quoting the supplementary publication number CCSD-101093.

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