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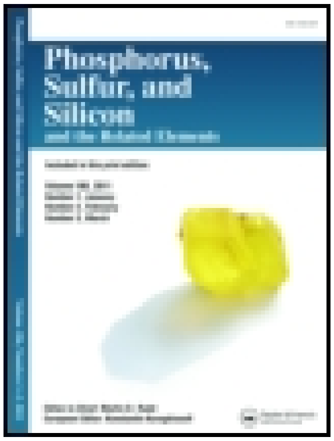

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Fluorinated Heterobutadienes/Trimethylphosphine: A Reactivity Study

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FLUORINATED HETEROBUTADIENES/TRIMETHYLPHOSPHINE: A REACTIVITY STUDY

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The reactions of fluorinated heterobutadienes $F_2C{=}X{-}C(R){=}Y$ (X = N, CH; Y = O, N-Mes; R = Ph, t-Bu), ***A–D****, with the PMe_3 were studied. In any case, a different reaction pathway was observed, depending on the specific nature of* ***A–D****. These reactions lead to some novel organophosphorus species, including P-ylides and λ^5-azaphosphinines. λ^5-phospholenes, as observed with phosphites, for example, were not observed, but with phosphinidine (P–Ph), the heterobutadienes* ***B*** *and* ***C*** *form λ^3-oxazaphospholenes. Therein the complex $(Me_3P)_3Ni[cyclo\text{-}P(Ph)OC(Ph)NC(CF_3)_2]$ was obtained and structurally characterized.*

Keywords: Fluororganics; heterobutadienes; phosphines; phosphinidenes; phospholenes; ylides

INTRODUCTION

Fluorinated heterobutadienes are valuable synthons in organic synthesis, in particular for pharmaceuticals, due to their high electrophilicity. To further exploit their synthetic potential, the heterobutadienes **A–D** (Figure 1) were introduced into organometallic systems with the aim of an "umpolung" of the heterobutadiene skeleton. Indeed, various metal complexes could be obtained with **A–D** as ligands (Ni, Ti, Zr, Fe, Rh[1]). In some cases, trimethylphosphine complexes of these metals were used. Since reactions of phosphites and phosphines with the heterobutadienes were known,[2] it was not surprising that reaction products with PMe_3 were observed in these cases. These reactions apparently took a different course as in the known cases, however. In particular, no

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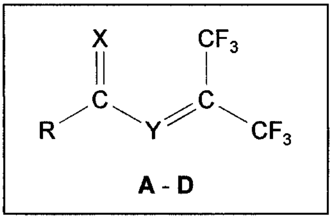


A - D

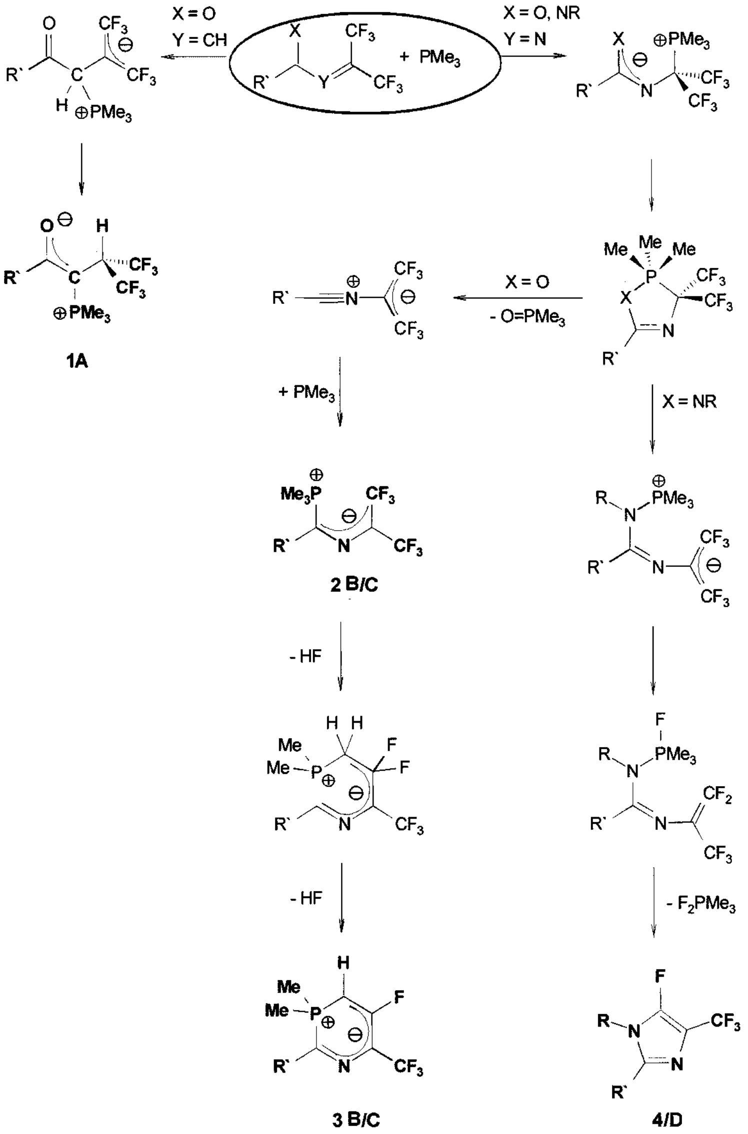
A: X = O, Y = CH, R = Ph
B: X = O, Y = N, R = Ph
C: X = O, Y = N, R = *t*-Bu
D: X = N-Mes, Y = N, R = Ph

FIGURE 1

λ^5-phospholenes were formed. We therefore investigated systematically the reactions of compounds **A–D** with PMe_3 and, in addition, with *in situ* generated phosphinidene P—Ph.

RESULTS

Every individual heterobutadiene **A–D** reacted in an individual manner, and thus four different types of products were obtained, as depicted in Scheme 1. The vinyl ketone **A** most likely is attacked at the central C_2 atom, yielding crystalline, orange **1A** [$\delta P\{^1H\} = 5.94$ s; $\delta F = 13.47$ d (9.9 Hz); δH: $CH(CF_3)_2 = 4.64$ dsept (9.9/28.6 Hz)]. The other three reactions of PMe_3 with heterobutadienes **B–D**, proceed via a common initial step, i.e., the phosphine attacks the heterobutadiene at the CF_3-substituted carbon atom. In the case of **B** and **C**, the respective intermediates can be identified by NMR spectroscopy: **B**: $\delta P\{^1H\} = 2.06$ s; $\delta F = 11.61$ s; $\delta C\{^1H\}$: $\underline{C}(CF_3)_2 = 74.1$ dsept (52.0/26.1 Hz); **C**: $\delta P\{^1H\} = -21.30$ s; $\delta F = 11.87$ s; $\delta C\{^1H\}$: $PMe_3 = 18.5$ d (91.4 Hz), $C(\underline{C}H_3)_3 = 27.6$ s, $\underline{C}(CH_3)_3 = 65.8$ Hz, $\underline{C}(CF_3)_3 = 72.60$ dsept (56.6/26.5 Hz), $CF_3 = 124.20$ dqq (7/3/287 Hz), $CO = 181.6$ d (9.5 Hz). Most likely via a cyclic intermedite or transition state (i.e., a phosphorane), Me_3PO is eliminated in the cases of **B** and **C**, and the residual nitril ylide adds another molecule of PMe_3 to give red crystals of **2B** [$\delta P\{^1H\} = 8.41$ s, br; $\delta F = 19.50$ dq (3.4/8.1 Hz), 22.29 dq (2.1/8.1 Hz); $\delta C\{^1H\}$: $C(CF_3)_2 = 131.66$ qq (1.2/3.3 Hz)] in the respective case. In the case of **C**, an analogous species **2C** [$\delta P\{^1H\} = 12.9$ s,br] can be identified spectroscopically as an intermediate, but above 0°C reacts further under a double HF elimination and cyclization to yield a yellow solid of the 1,3-λ^5-azaphosphinine **3C** [$\delta P\{^1H\} = -5.58$ dq (48.8/1.5 Hz); δF: $CF_3 = 12.49$ dd (19.8/1.5 Hz), $CF = -109.9$ ddq (9.1/48.8/19.8 Hz); δH: $CH = 4.08$ dd (14.3/9.1 Hz); $\delta C\{^1H\}$: $CH = 65.10$ dd (7.2/96.0 Hz), $C\text{-}^tBu = 179.39$ d (39.0 Hz), $CF = 123.63$ dd ($^2J_{CP} = 125.7/^1J_{CF} = 258.4$ Hz)]. Besides the signals of **3C**, the signals of Me_3PO and F_2PMe_3 [$\delta P\{^1H\} = -15.60$ t (543 Hz); $\delta F = 72.12$ ddec (543/12.2 Hz)] are



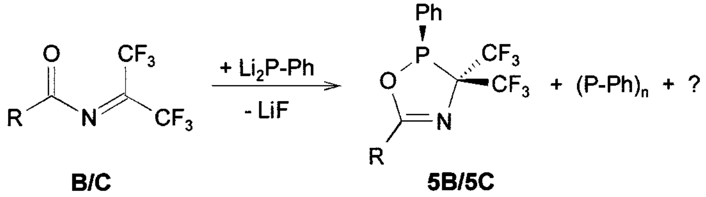
SCHEME 1 Reactions of Heterobutadienes **A–D** with PMe$_3$.

detected in the toluene extract from the solid obtained, whereas the pentane extract is essentially free of these impurities. An acid-base adduct of PMe$_3$ with HF was tentatively assigned [δP{^{1}H} = 1.20] but is obviously too volatile to survive the work-up and/or reacts further to F$_2$PMe$_3$. In contrast to **2C**, which with excess PMe$_3$

obviously acting as a base, gives **3C** spontaneously, **2B** gives the corresponding **3B** only in traces under the same conditions. On heating a solution of **2B** with excess PMe_3 (toluene/80°C) or by addition of a more powerful base than PMe_3 (i.e., DABCO or pyridine in THF), **3B** may be isolated as a yellow solid [$\delta P\{^1H\}$ = −4.75 d (51.9 Hz); δF: CF_3 = 12.74 d (20.1 Hz), CF = −106.7 ddq (20.1/51.9/9.1 Hz); δH: PMe_2 = 0.76 d (13.5 Hz), CH = 4.49 dd (13.5/9.1 Hz)].

In the case of the 1,3-Diaza-1,3-butadiene **D**, the assumed cyclic phosphorane intermediate obviously undergoes a rapid degradation reaction, where the PMe_3 removes two fluorines from a CF_3 group under formation of F_2PMe_3. The remaining imidazole ring **4D** [δF: CF_3 = 16.64 d (12.2 Hz), CF = −63.54 q (12.2 Hz)] is known and was also obtained on thermal decomposition of the cyclic reactions products from **D** with $SnCl_2$, with $GeCl_2$ or with $SiCl_2$.[3]

Unlike phosphines, *in situ* generated phosphinidene P—Ph (from **B** or **C** and Li_2PPh via LiF abstraction) reacts with **B** and **C** under formation of cyclic phospholenes **5B** [$\delta P\{^1H\}$ = 111.4 qq (27/2 Hz); δF = 6.74 dq (2/9.5 Hz) and 14.40 dq (27/9.5 Hz)] and **5C** [$\delta P\{^1H\}$ = 110.1 q (29 Hz); δF = 5.93 dq (29/9.5 Hz) and 13.90 q (9.5 Hz); δC: $\underline{C}(CF_3)_2$ = 88.6 dsept (48/24 Hz)] (Scheme 2).

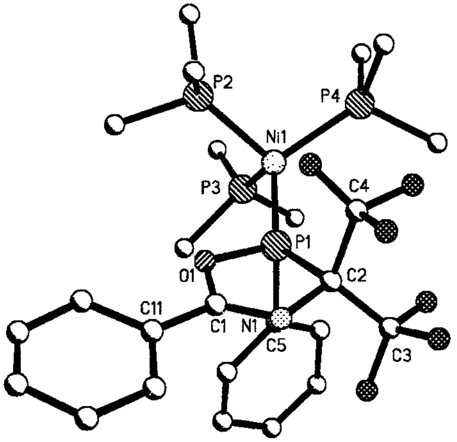


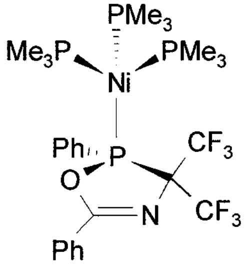
SCHEME 2

Red crystals of the oxazaphospholene nickel complex **6B** [$\delta P\{^1H\}$: PMe_3 = −19.40 dq (43.1/5.0 Hz), PPh = 125.79 qq (43.1/19 Hz); δF = 10.27 dqq (19/5.0/10 Hz) and 15.68 q (10 Hz)] are isolated from the reaction of **5B** with $(Me_3P)_2Ni(COD)$. An X-ray structure determination of the crystals ($P2_1/C$; a = 31.552(6), b = 11.754(2), c = 27.345(6) Å; Z 12) confirmed the presence of the phospholene ring as a ligand to a tetrahedrally coordinated nickel(0) centre with three additional PMe_3 ligands (Figure 2). The structural parameters of the 12 molecules in the unit cell differ to some extent, however, and large standard deviations result in some uncertainty for the mean values for distances and angles (Table I).

TABLE I Some Mean Distances [Å] and Angles [°] of **6B**

P(1)—O(1):	1.72(3)	P(1)—O(1)—C(1):	114(2)
O(1)—C(1):	1.38(8)	O(1)—C(1)—C(11):	115(2)
C(1)—N(1):	1.28(2)	N(1)—C(1)—C(11):	125(3)
N(1)—C(2):	1.45(2)	O(1)—C(1)—N(1):	120(3)
C(2)—P(1):	1.98(7)	C(1)—N(1)—C(2):	111(3)
Ni(1)—P(1):	2.04(2)	O(1)—P(1)—C(2):	85(1)
Ni(1)—P(2,3,4):	2.18(3)	C(2)—P(1)—C(5):	98(3)
P(1)—C(2)—N(1):	106(2)	O(1)—P(1)—C(5):	97(1)
C(3)—C(2)—C(4):	110(3)	Ni(1)—P(1)—C(2):	134(2)
P(1)—C(2)—C(3):	115(2)	Ni(1)—P(1)—C(5):	117(1)
P(1)—C(2)—C(4):	109(4)	Ni(1)—P(1)—O(1):	115(1)
N(1)—C(2)—C(3):	109(2)	P(2-4)—Ni(1)—P′(2-4):	Ø 106.3
N(1)—C(2)—C(4):	107(2)	P(2-4)—Ni(1)—P(1):	Ø 112.3





6B

FIGURE 2 Molecular Structure of **6B**.

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