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[(α-Imino)enamino]phosphonium Salts from Propyne Iminium Salts and a Phosphorane Imine

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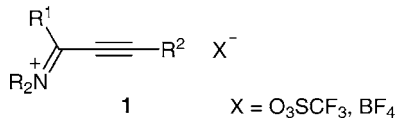
ABSTRACT: *Propyne iminium triflates* $R^1C(=N^+R^3R^4)C{\equiv}CR^2\ CF_3SO_3^-$ *readily react with* $Ph_3P{=}NPh$ *to form 1:1 adducts which formally result from a metathetical addition of the phosphorane imine across the triple bond of the alkyne. These adducts are best described as enamino-phosphonium salts or iminio-substituted phosphorus ylides. The configuration of these salts has been determined from NMR data and an X-ray crystal structure analysis of salt* **3h**. *The base-induced elimination of the* PPh_3 *substituent from enamino-phosphonium salt* **3a** *was studied.* © 2005 Wiley Periodicals, Inc. Heteroatom Chem 16:437–446, 2005; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20131

INTRODUCTION

Propyne iminium salts of the general structure **1** are readily prepared from enaminoketones and triflic anhydride [1,2] or from propyne imines by N-alkylation [3].



1 X = O_3SCF_3, BF_4

Their chemistry has two major aspects: (a) The ambient propyne iminium system reacts with a wide range of nucleophiles, including organolithium, organomagnesium, and organocuprate compounds [4,5] and heteronucleophiles such as phosphides and phosphanes [6], to yield either propargylamines or aminoallenes. (b) The presence of the iminium function renders the C,C triple bond more electron deficient than in the related acetylenic ketones, and therefore, propyne iminium salts are suitable dienophiles in Diels–Alder reactions [7]. The observation of a metathetical addition of *N*-phenyl benzaldimine across the C,C triple bond [8] led us to investigate whether an analogous reaction was possible with phosphorane imines. It is well known that acetylenedicarboxylic acid esters react readily with phosphorane imines to yield phosphorus ylides which may formally be considered as insertion products of the alkyne into the P—N bond of the phosphorane imine [9].

We report here that triphenylphosphorane phenylimine reacts with a variety of propyne iminium salts by analogy with the mentioned transformations to yield novel [(β-amino-α-imino)vinyl]phosphonium salts [10]. Several different approaches to (β-aminovinyl)phosphonium salts have been reported in the literature [11–15], but none of them

Dedicated to Professor Dr. Alfred Schmidpeter on the occasion of his 75th birthday.

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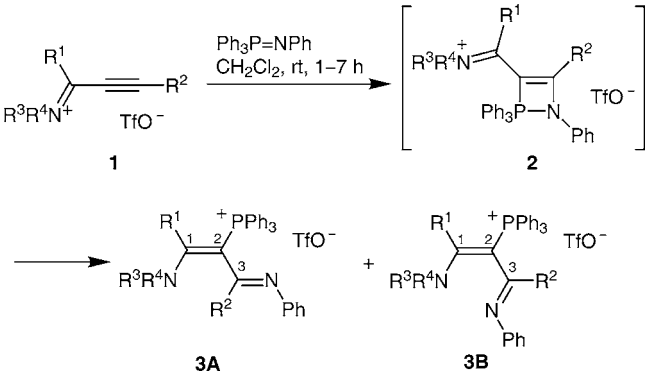
provided α-imino-substituted enaminophosphonium salts.

RESULTS AND DISCUSSION

Propyne iminium triflates **1a–h** (for the preparation of salt **1h**, see Experimental section) reacted smoothly with equimolar amounts of triphenylphosphorane phenylimine in dichloromethane to provide 1:1 adducts which were isolated as yellow solids and were identified as enaminophosphonium triflates **3a–h** (Scheme 1) based on their analytical and spectroscopic data. It is reasonable to assume that a [2 + 2] cycloaddition of the electron-deficient alkyne and the nucleophilic phosphorane imine generates a 1,2-dihydro-1,2-azaphosphete **2** as a reaction intermediate which then undergoes electrocyclic ring-opening to form products **3**.

It appears that the scope of this transformation cannot be extended to propyne iminium salts that bear a methyl group at the iminium carbon atom (e.g., **1**: R^1 = Me, R^2 = Me, NR^3R^4 = piperidino; R^1 = Me, R^2 = Ph, NR^3R^4 = morpholino): although these salts also reacted rapidly with the phosphorane imine, the reaction was not clean and no product could be isolated. This is unfortunate because the resulting propenylphosphonium salts (**3**, R^1 = Me) would have been precursors for novel alkylidene phosphoranes [11b].



1–3	R^1	R^2	R^3	R^4	Yield of **3** (%)	**3A**:**3B**[a]
a	H	Ph	CH_3	CH_3	63	3.7:1
b	H	Ph		$-(CH_2)_4-$	54	2.5:1
c	H	Ph		$-(CH_2)_5-$	51	3.6:1
d	H	Ph		$-(CH_2)_2O(CH_2)_2-$	81	4.2:1
e	Ph	Ph		$-(CH_2)_2O(CH_2)_2-$	53	**A** only
f	Ph	*c*-C_3H_5	CH_3	CH_3	68	**A** only
g	Ph	*t*-Bu	CH_3	CH_3	72	**A** only
h	Ph	Ph	CH_2Ph	CH_2Ph	45	**A** only

[a]At 300 K (**3d,f,g,h**) or 309 K (**3a,b,c,e**).

SCHEME 1 Note that the numbering for **3A,B** does not correspond to the systematic nomenclature of these compounds.

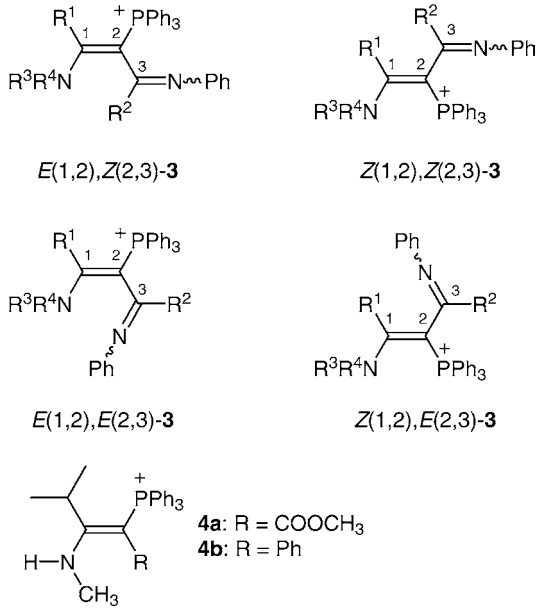
The NMR spectra (^{1}H: Experimental section; ^{13}C, ^{31}P: Table 1) of salts **3a–d** (R^1 = H) indicated the presence of two isomers (major isomer **A** and minor isomer **B**), whereas only one set of signals was found for salts **3e–h** (R^1 = Ph) which are disubstituted at the iminium carbon atom. The inspection of the NMR data suggests that the salts **3e–h** have the same structure as the major isomer of **3a–d**. The following significant differences between the major and the minor isomer of **3a–d** are observed: (a) The ^{31}P resonance of the major isomer is shifted to lower field by 4–5 ppm. (b) The chemical shift of the amino-substituted carbon atom C-1 appears at slightly lower field in the major isomer (δ = 156.0–157.9 vs. 153.3–155.4 ppm), and the $^2J_{P,C}$ coupling constants are somewhat larger (26.3–27.6 vs. 18.3–24.1 Hz). (c) The signal of the imino carbon atom C-3 is shifted to lower field by ca. 3 ppm in the major isomer; the $^2J_{P,C}$ coupling constant is very small in all cases (0–6.6 Hz). (d) In contrast to the rather small chemical shift differences for C-1 and C-3, the resonances of the PPh_3-substituted carbon atom C-2 differ by ca. 10 ppm for the two isomers, in addition, the P,C coupling constant is smaller by 10 Hz in the minor isomer (isomer **A**: δ = 78.8–82.4 ppm, $^1J_{P,C}$ = 112.7–114.3 Hz; isomer **B**: δ = 69.0–71.5 ppm, $^1J_{P,C}$ = 102.2–104.3 Hz). (e) In the ^{1}H NMR spectrum, a two-proton signal is observed at higher field than the rest of the aromatic proton signals. This signal, which is attributed to the ortho protons of the C=N-phenyl ring, appears at δ = 5.76–5.80 for the major isomer, and at δ = 6.18–6.27 for the minor isomer of **3a–d**. Notably, this signal is observed in the range δ = 5.53–5.87 for the single isomer of salts **3e–h**.

With respect to the bonding situation of **3a–h** (vide infra), configurational isomerism around the C-1—C-2, C-2—C-3 (restricted rotation) and C-3—N bonds can be expected (Scheme 2). For **3a–d**, it was expected that the configuration at the C-1—C-2 bond of isomers **A** and **B** could be derived from the magnitude of the $^3J_{P,H}$ coupling constant, because values of 13–25 Hz for $^3J_{P,H}$(cis) and of 33–50 Hz for $^3J_{P,H}$(trans) are considered typical for similar vinylphosphonium ions [12,15]. Although the signals of proton 1-H in both isomers appear in the aromatic region, we were able to locate it with the help of 2D experiments (^nJ(P,H) and ^1J(C,H) correlation) and to determine $^3J_{P,H}$ for the two isomers (**3b**: major isomer **A**: δ_{1-H} = 6.91 ppm, $^3J_{P,H}$ = 14.1 Hz; minor isomer **B**: δ = 7.13 ppm, $^3J_{P,H}$ = 16.2 Hz (T = 300 K); **3d**, isomer **A**: δ = 6.85 ppm, $^3J_{P,H}$ = 14.0 Hz; isomer **B**: δ = 7.06 ppm, $^3J_{P,H}$ = 17.1 Hz (T = 258 K)). The

TABLE 1 ^{13}C and ^{31}P NMR Data of Salts **3a–h**

		^{13}C (100.62 MHz, δ(ppm), J (Hz))[a,b,c]				
Compound	*Isomer*	*C-1, δ ($J_{P,C}$)*	*C-2, δ ($J_{P,C}$)*	*C-3, δ ($J_{P,C}$)*	*Other Signals*	*^{31}P[a] δ (ppm)*
3a	**A**	157.9 (27.6)	81.5 (112.7)	163.4	42.0/46.8 (NMe_2), 148.4 (i-C of NPh); common signals, **A** and **B**: 118.7–139.5 (C_{Ph}), 120.9 (q, $^1J_{C,F}$ = 328.5, $CF_3SO_3^-$)	28.8
	B	155.4 (19.1)	71.0 (102.2)	160.3	42.0/47.5 (NMe_2), 149.9 (i-C of NPh)	24.6
3b	**A**	156.0 (26.9)	82.4 (113.4)	164.7	23.8/26.1 (NCH_2CH_2), 52.9/55.8 (NCH_2), 150.2 (i-C of NPh); common signals, **A** and **B**: 120.6–136.2 (C_{Ph}), 141.6 (C_{Ph}), 121.6 (q, $^1J_{C,F} = 325.7$, $CF_3SO_3^-$)	33.6
	B	153.3 (18.3)	71.5 (103.9)	162.1	24.8/26.6 (NCH_2CH_2), 48.6/55.8 (NCH_2), 151.3 (i-C of NPh)	28.4
3c	**A**	157.6 (26.3)	78.8 (114.3)	164.3	25.9/26.6 (NCH_2CH_2), 51.8/56.7 (NCH_2), 149.9 (i-C of NPh); common signals, **A** and **B**: 22.8 ($N(CH_2)_2CH_2$), 120.1–139.6 (C_{Ph}), 123.4 (q, $^1J_{C,F} = 327.4$, $CF_3SO_3^-$)	33.6
	B	154.7 (24.1)	69.0 (104.3)	161.5	23.6/26.6 (NCH_2CH_2), 48.3/56.7 (NCH_2), 150.5 (i-C of NPh)	29.6
3d	**A**	156.6 (26.4)	81.3 (113.3)	163.4 (2.9)	50.3/54.3 (NCH_2), 64.7/66.0 (OCH_2), 148.4 (i-C of NPh); common signals, **A** and **B**: 119.0–138.2 (C_{Ph}), 121.6 (q, $^1J_{C,F} = 326.2$, $CF_3SO_3^-$)	33.9
	B	154.7 (21.9)	72.8 (103.5)	161.0 (6.6)	47.4/54.5 (NCH_2), 65.6/66.8 (OCH_2), 149.4 (i-C of NPh)	29.6
3e	**A**	173.8 (19.1)	86.0 (115.1)	164.4	50.8/55.9 (NCH_2), 66.5/67.0 (OCH_2); 119.6, 122.6, 128.0–134.2 (all C_{Ph}); 120.5 (q, $^1J_{C,F} = 320.4$, $CF_3SO_3^-$), 147.4 (i-C of NPh)	22.7
3f	**A**	174.1 (17.6)	80.9 (112.7)	169.5 (5.1)	7.2 (broad, C-2,3$_{cyclopropyl}$), 16.0 (d, $^3J_{C,P} = 6.6$, C-1$_{cyclopropyl}$), 45.1 (broad, NMe_2), 121.0 (q, $^1J_{C,F} = 321.3$ Hz, $CF_3SO_3^-$), 118.9, 125.0 (d, $J_{C,P} = 93.7$), 128.4, 128.8 (d, $J_{C,P} = 13.2$), 128.9, 131.5, 132.4 (d, $J_{C,P} = 2.2$), 132.5, 133.8 (d, $J_{C,P} = 10.3$), 149.2 (i-C of NPh)	22. 7
3g	**A**	174.0 (broadened)	82.5 (coalescing)	173.8 (coalescing)	29.8 (s, CMe_3), 43.8 (CMe_3), 43.9 (broad, NMe), 44.9 (broad, NMe), 117.2, 121.0 (q, $^1J_{C,F} = 320.8$, $CF_3SO_3^-$), 121.7, 124.8 (broad), 125.5 (broad), 127.8, 128.5, 128.8 (d, $J_{C,P} = 11.9$), 132.0 (d, $J_{C,P} = 25.7$), 132.5 (d, $J_{C,P} = 2.8$), 134.1 (d, $J_{C,P} = 9.2$), 148.1 (i-C of NPh)	22.9
3h	**A**	173.7 (20.2)	85.7 (110.9)	167.5 (4.6)	55.8/56.9 (NCH_2), 119.3–135.4 (C_{Ph}), 147.8 (i-C of NPh)	25.2

[a] In $CDCl_3$ (**3a,e,f,g,h**) or CD_3CN (**3b,c,d**).
[b] $T = 309$ K (**3a,b**), 300 K (**3f**), 273 (**3g**), 263 K (**3d**), 253 K (**3c**), 233 K (**3e,h**).
[c] For numbering of C-1, C-2, and C-3, see Scheme 1.



SCHEME 2 Configurational isomerism in enaminophosphonium salts **3**.

magnitude and similarity of the coupling constants suggest that both isomers exist in the *E*(1,2) configuration. The similar values of the $^2J_{P,C\text{-}1}$ coupling constant in both isomers (see above) also indicate the same configuration at the C-1—C-2 bond, because much smaller values (0–6 Hz) are expected for the *Z* configuration [14b].

Unfortunately, due to the presence of mostly aromatic proton signals in the ^{1}H NMR spectra and of dynamic processes, additional neighboring relationships in the cations could not be firmly established by nOe experiments. However, the full geometrical information for salt **3h** could be obtained from an X-ray crystal structure determination (Fig. 1). This salt was found to crystallize with one $CHCl_3$ molecule per formula unit, the latter maintaining a weak coordination with the triflate counterion ($H_{CHCl3} - O_{triflate} = 2.28$ Å). It can be seen that **3h** exists in the *E*(1,2),*Z*(2,3),*E*(C3,N) configuration (**3hA**, Scheme 1). The *E* configuration at the enamine double bond agrees with the preferred configuration of the related enaminophosphonium salts **4a,b** [14b].

The torsion angles in **3h** (Fig. 1) indicate strong deviations of the vinamidine backbone N1—C1—C2—C3—N2 from planarity which are certainly caused by severe steric crowding. Nevertheless, the geometries around the individual bonds still allow some overlap of the π systems. Concerning the bond lengths in **3h**, it can be seen that the enamine bonds and C1—C2 represent partial double bonds, the P—C2 bond is shorter by 0.03—0.04 Å than the P—C_{Ph} bonds, while the C2—C3 distance corresponds

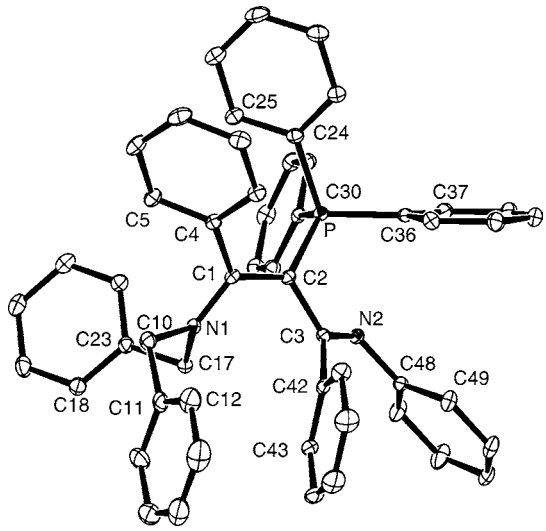
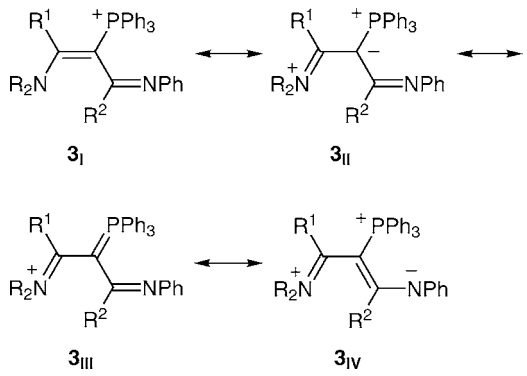


FIGURE 1 Molecular structure of the cationic part of **3h** in the solid state. Ellipsoids of thermal vibration are shown at 20% probability level. The triflate anion, the $CHCl_3$ solvate molecule, and the hydrogen atoms are not shown. Selected bond lengths (Å) and angles (°): N1—C1 1.349(2), C1—C2 1.406(3), C2—P 1.779(2), C2—C3 1.475(3), C3—N2 1.288(2); C4—C1—C2 122.3(2), C1—C2—P 126.5(1), C1—C2—C3 122.5(2), N1—C1—C2 120.3 (2). Torsion angles (°): C10—N1—C1—C2 156.2(2), C17—N1—C1—C2 −35.0(3), N1—C1—C2—C3 −30.5(3), N1—C1—C2—P 140.0(2), C1—C2—C3—N2 152.3(2), C2—C3—N2—C48 169.4(2).

to a C_{sp2}—C_{sp2} single bond and the C3—N2 distance to an undisturbed imine double bond. Thus, the bond structure of salts **3a–h** is best represented by the resonance structures of an enaminophoshonium ion $\mathbf{3_I}$ and an α-iminio-phosphorus ylide $\mathbf{3_{II}}$ or α-iminiophosphorane $\mathbf{3_{III}}$ while charge delocalization into the imine function ($\mathbf{3_{IV}}$) does not make a significant contribution (Scheme 3). In other words, the presence of the imino group does not significantly affect the bond structure that appears to be typical for enaminophosphonium ions in general [12,14b]. It is in-



SCHEME 3

teresting to note that almost identical values of the N1—C1 and C1—C2 bond lengths have been found in **4b**, while the corresponding values for the ester-substituted enaminophosphonium salt **4a** do in fact suggest a higher contribution of a resonance structure corresponding to $\mathbf{3_{IV}}$ [14b].

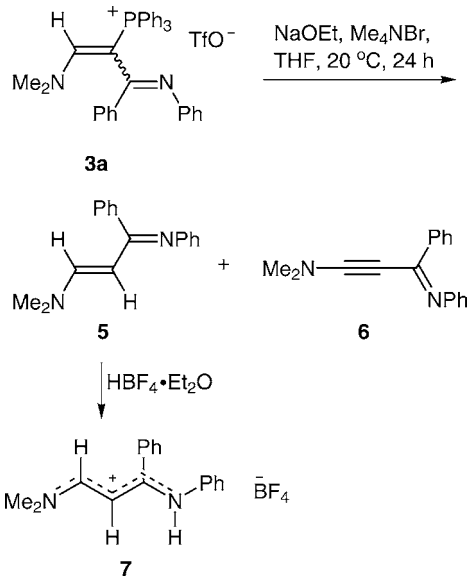
In agreement with the partial double bond character of the enaminic N1—C1 bond, rotation around this bond is slow on the NMR time scale but significant broadening of the ^{1}H and ^{13}C signals of the NCH_2 or NCH_3 groups is observed at 300 K (see Table 1 and Experimental section). In the case of the dibenzylamino-substituted salt **3h**, the proton signals of the two NCH_2 groups are in coalescence at 300 K (400.13 MHz spectrum). Below 233 K, a separate signal for each NCH proton is observed, i.e., not only has the rotation about the enaminic N—C bond become very slow, but the protons of each NCH_2 group have also become diastereotopic. The chemical shifts at 218 K are found at $\delta = 3.61$ (1H), 3.88 (2H), and 5.98 (1H). A comparison with propyne iminium salt **1h** ($\delta(NCH_2Ph) = 5.27$ and 5.58 ppm) shows that that three of the four NCH_2 protons have suffered an extreme upfield shift, indicating that they are situated over the π system of adjacent phenyl rings.

As discussed above, the NMR comparison suggests that the configuration found for **3hA** can also be assigned to salts **3e–g** and to the major isomer **A** of salts **3a–d** which are monosubstituted at C-1. Furthermore, it is likely that isomers **A** and **B** both have the *Z* configuration at the enaminic bond C-1—C-2. Therefore, the difference between **A** and **B** must reside in the geometry around the C-2—C-3 or the C-3—N bond. The ^{1}H NMR spectra indicate that the **A**:**B** ratio is temperature dependent (e.g., **3d**: **A:B** = 3.6 (325 K), 4.2 (300 K), 5.3 (258 K)), i.e. isomers **A** and **B** are equilibrating under these conditions. This observation provides strong evidence against syn/anti-isomerism around the imine bond because the C3—N bond length in **3hA** was found to correspond to a bond order of 2. Therefore, it is likely that isomers **A** and **B** are distinguished by restricted rotation around the sterically overloaded C-2—C-3 bond, i.e. the configuration is *Z*(2,3) for **A** and *E*(2,3) for **B** (see Scheme 2). The configuration at the imine bond in **B** could not be assigned firmly, but the *E* configuration as in isomer **A** is very likely for steric reasons.

The adduct **3g**, which carries the sterically most demanding substituent in the series ($R^2 = t$-Bu), was found not to be very stable thermally due to gradual reversal of their mode of formation shown in Scheme 1. This decomposition already takes place, both in solution and in the solid state, on storing at ambient temperature. For example, when a $CDCl_3$ solution of **3g** was heated at 50°C for 1 h, the ^{1}H and ^{13}C NMR spectra showed the presence of **3g** and propyne iminium salt **1g** in a 76:24 ratio. NMR monitoring indicated subsequent reactions taking place at 20°C. The details of these transformations could not be clarified.

Base-assisted elimination reactions of enaminophosphonium ions of the type $(Me_2N)CH{=}C(Ph)\text{-}P^+Ph_3$ have been investigated by Bredereck et al. [16]. Treatment of (β-ethoxyvinyl)triphenylphosphonium salts with NaOEt resulted in the conversion of the $^+PPh_3$ into a $P(O)Ph_2$ group [17]. Along these lines, we have studied exemplarily analogous reactions of salt **3a** (Scheme 4). When **3a** was treated with NaOEt in the presence of bromide ions or with sodium bis(trimethylsilyl)amide, an oil could be isolated which consisted mainly of vinamidine **5** (two isomers) and ynamine **6** in a 4.4:0.83:1 ratio. The two isomers of **5** both have the *E* configuration at the olefinic bond ($^3J_{H,H} = 13.3$ and 13.4 Hz), and the ^{1}H chemical shifts of the major isomer closely agree with those reported for the (*p*-anisyl)imine analogue [18]. The presence of ynamine **6** is indicated by a strong IR absorption at 2165 cm^{-1} for $\nu(C{\equiv}C)$ which agrees well with the values for other (β-imidoyl)ynamines [19]; furthermore, the large chemical shift differences of the acetylenic carbon atoms ($\delta = 64.9$ and 121.4 ppm) are typical for push–pull substituted alkynes [20].

The mixture of imines **5** and **6** could not be separated. However, after addition of tetrafluoroboric acid, vinamidinium salt **7** was isolated as a crystalline solid in modest yield. An X-ray diffraction



SCHEME 4

analysis confirmed the constitution and established the *E,E* configuration around the C1—C2 and C2—C3 bonds (Fig. 2). As expected, effective charge dispersal over the vinamidinium moiety is indicated by almost complete bond length equalization for the C—C and C—N bonds, respectively, of the backbone [21]. However, a small preference for the Me_2N^+=CH—CH=C(Ph)NHPh resonance structure can be concluded from the bond lengths.

In conclusion, we have shown that propyne iminium triflates **1** react smoothly with Ph_3P=NPh to yield [(α-imino)enamino]phosphonium triflates in a metathetical addition of the phosphorane imine across the C≡C triple bond. However, these products cannot be obtained when the iminium carbon atom of **1** bears a methyl rather than a H or Ph substituent. Furthermore, the metathetical addition is reversible when the adduct is sterically overloaded (**3**, R^2 = *t*-Bu).

EXPERIMENTAL

General Comments

The following spectroscopic and analytical instruments were used. NMR: Bruker AM 400 (^{1}H: 400.13 MHz, ^{13}C: 100.62 MHz), Bruker DRX 400 (^{1}H: 400.13 MHz; ^{13}C: 100.62 MHz; ^{31}P: 161.98 MHz), Bruker AMX 500 (^{1}H: 500.14 MHz; ^{13}C: 125.77 MHz). For ^{1}H spectra, TMS was used as internal standard. For ^{13}C NMR spectra, the solvent signal was used as internal standard [$\delta(CHCl_3) = 77.0$, $\delta(CH_3CN) = 118.2$]. Signal assignments for ^{13}C spectra are based on DEPT 135, gs-HMBC, gs-HSQC, and gs-HMQC experiments. IR: Perkin-Elmer 1310, Bruker Vector 22 FT-IR spectrophotometer. Mass spectrometry: Finnigan MAT SSQ 7000 (EI spectra), Finnigan TSQ 7000 (FAB spectra, positive and negative modes; matrix: 3-nitrobenzylalcohol (*m*-NBA)), Bruker Daltonics Reflex III (MALDI-TOF). X-ray diffraction: STOE IPDS and Enraf Nonius CAD4. Elemental analyses: Perkin-Elmer EA 2400 and Elementar Vario EL.

All reactions were performed in oven-dried glassware, in anhydrous solvents, and under an argon atmosphere. Propyne iminium triflates **1a–e** [2], **1f** [22], and **1g** [23] were prepared as reported.

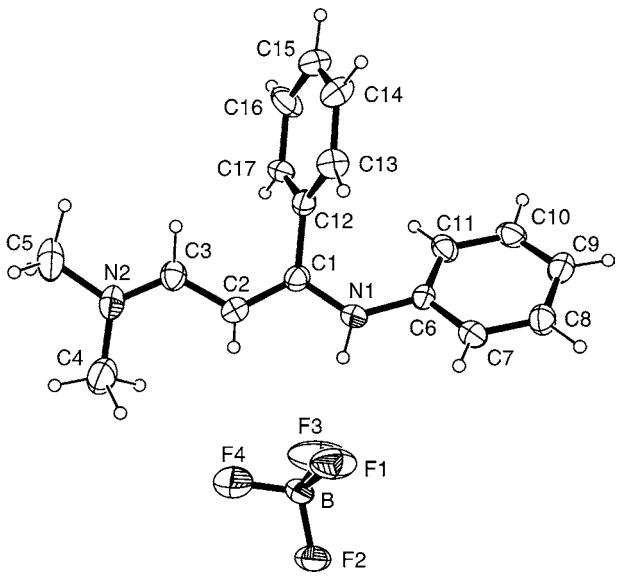


FIGURE 2 Structure of salt **7** in the solid state. Ellipsoids of thermal vibration are shown at 30% probability level. Bond lengths (Å) and torsion angles (°): N1–C1 1.327(6), N1–C6 1.412(7), C1–C2 1.352(7), C2–C3 1.370(8), C3–N2 1.310(7); C6–N1–C1–C2 173.4(4), N1–C1–C2–C3 172.2(4), C1–C2–C3–N2 175.6(5), C2–C3–N2–C5 176.6(5). Hydrogen bond: H(N1)···F1 2.10(6), N1–H(N1)···F1 168(6).

(E/Z)-3-Dibenzylamino-1,3-diphenyl-2-propen-1-one

A solution of 1,3-diphenylpropyn-1-one (0.50 g, 2.40 mmol) and dibenzylamine (0.47 mL, 2.40 mmol) in anhydrous ether (5 mL) was stirred overnight and then set aside for 2 days. The crystalline precipitate was separated from the mother liquor by pipetting off the latter. The solid was washed with anhydrous ether and dried at 20°C/0.001 mbar, yielding off-white crystals (0.86 g, 90% yield) of (*E*)- and (*Z*)-isomers (*E*:*Z* = 8:1 according to ^{1}H NMR), mp 132–133°C. IR (KBr): ν 1627 (s), 1538 (s), 1494 (m), 1453 (m), 1357 (s), 1209 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$, 400.13 MHz): *E*-isomer: δ 4.36 (s, 4 H, NCH_2), 6.05 (s, 1 H, 2-H), 7.12–7.39 (m, 18 H_{Ph}), 7.56 (d, 2 H, ortho-H_{Ph}). *Z*-isomer: δ 3.77 (s, 2 H, NCH_2), 4.33 (s, 2 H, NCH_2), 5.80 (s, 1 H, 2-H), 7.12–7.45 (m, 18 H_{Ph}), 7.82 (d, 2 H, ortho-H_{Ph}). ^{13}C NMR ($CDCl_3$, 100.62 MHz): *E*-isomer: δ 53.04 (2 N*C*H_2), 96.41 (C-2), 127.53–141.44 (24 C_{Ph}, *E* and *Z* isomer), 163.61 (C-3), 187.80 (C-1). *Z*-isomer: δ 48.54 (N*C*H_2), 55.91 (N*C*H_2), 99.28 (C-2), C-1 and C-3 not found. MS (GC-EI): *m/z* 404 ([M + H]$^+$). Anal. Calcd for $C_{29}H_{25}NO$ (403.51): C, 86.32; H, 6.24; N, 3.47; found: C, 86.23; H, 6.24; N, 3.42.

*N,N-Dibenzyl-(1,3-diphenylprop-2-yn-1-ylidene)-ammonium Trifluoromethanesulfonate (***1h***)*

A solution of triflic anhydride (1.30 mL, 7.88 mmol) in dichloromethane (50 mL) was cooled at −78°C, and solid (*E/Z*)-3-dibenzylamino-1,3-diphenyl-2-propen-1-one (3.00 g, 7.43 mmol) was added in several portions. The mixture was brought to 20°C during 2 h, and the solvent was evaporated at

20°C/0.001 mbar. The oily residue, consisting mostly of *N*,*N*-dibenzyl[1,3-diphenyl-3-(trifluoromethylsulfonyl)oxy)-prop-2-en-1-ylidene]ammonium trifluoromethanesulfonate, was washed with 3×15 mL of ether, then dried at 20°C/0.001 mbar to leave a fine yellow powder. This solid (4.08 g) was heated in a Kugelrohr apparatus in a vacuum (0.001 mbar). Melting occurred at 80°C, and at 170°C elimination of triflic acid took place. After 10 min at this temperature and cooling at 20°C, the residue was dissolved in anhydrous acetonitrile (5 mL). On addition of anhydrous ether, a light-brown solid separated which was recrystallized from acetonitrile/ether until the mp remained constant. Yield: 1.30 g (41%); mp 149–151°C. IR (KBr): ν 2199 (s, C≡C), 1602 (m), 1580 (m), 1447 (m), 1268 (s), 1143 (m), 1031 (s) cm^{-1}. ^1H NMR ($CDCl_3$, 400.13 MHz): δ 5.27 (s, 2 H, NCH_2), 5.58 (s, 2 H, NCH_2), 6.93–7.82 (20 H_{Ph}). ^{13}C NMR ($CDCl_3$, 100.62 MHz): δ 59.20 (NCH_2), 61.94 (NCH_2), 85.93 (C-2), 117.84 (C-3), 123.29 (ipso-C_{Ph}), 128.31–133.90 (23 C_{Ph}), 165.52 (C-1). MS (FAB, 8 keV): *m/z* 386 (M^+ of cation). Anal. Calcd for $C_{30}H_{24}F_3NO_3S$ (535.58): C, 67.28; H, 4.52; N, 2.62; found: C, 67.02, H, 4.53, N, 2.50.

Reactions of Propyne Iminium Triflates **1** *with* Ph_3P=*NPh*

Variation A: Salt **1** (ca. 1–6 mmol) was dissolved in dichloromethane (20 mL), and an equimolar solution of triphenylphosphorane phenylimine [24] in dichloromethane (10 mL) was added gradually. The mixture was then stirred for 1 h to complete the reaction (the consumption of **1** was monitored by IR), concentrated to 5 mL, and ethyl acetate (15 mL) was added. Crystallization was induced by scratching the flask wall to obtain a powdery solid which was collected and rinsed with ethyl acetate.

Variation B: A solution of salt **1** (0.25 mmol) and triphenylphosphorane phenylimine [24] (0.09 g, 0.25 mmol) in dichloromethane (2.5 mL) was stirred until **1** had disappeared (2 h, IR control). Ether (5 mL) was added to precipitate the product, which was isolated by filtration and rinsed with ether.

*[(2-Dimethylamino-1-phenyl-1-(α-(phenylimino)-benzyl)vinyl] triphenylphosphonium Trifluoromethanesulfonate (***3a***)*

From **1a** by variation A, bright yellow powder; yield: 63%. Mixture of isomers, **A:B** = 3.7:1 (309 K). mp 184–186°C. IR (KBr): ν 1600 (s, C=N), 1565 (s), 1250 (vs), 1130 (s), 1090 (s), 1015 (vs) cm^{-1}. ^1H NMR ($CDCl_3$, 400.13 MHz, 309 K): δ 2.39 and 2.90 (2 s, broad, NMe_2, **A**), 3.10 and 3.23 (2 s, NMe_2, **B**), 5.77 (d, $^3J_{H,H}$ = 6.6 Hz, 2 ortho-H of NPh, **A**), 6.18 (d, $^3J_{H,H}$ = 6.7 Hz, 2 ortho-H of NPh, **B**), 6.70–7.98 (m, CH=N^+, H_{Ph}, both isomers). Anal. Calcd for $C_{26}H_{32}F_3N_2O_3PS$ (660.69): C, 65.45; H, 4.88; N, 4.24; found: C, 65.4; H, 4.9; N, 4.3.

3b: From **1b** (0.38 g, 1.14 mmol) by variation A, bright yellow powder; yield: 0.42 g (54%). Mixture of isomers, **A:B** = 2.5:1 (309 K). mp 172–174°C. IR (KBr): ν 1600 (s, C=N), 1580 (s, C=N), 1560 (s), 1280 (vs), 1265 (vs), 1145 (s), 1030 (s) cm^{-1}. ^1H NMR ($CDCl_3$, 400.13 MHz, 300 K): δ 1.69 (broadened s, 4H of **A**, $NCH_2(CH_2)_2$), 1.79–2.16 (2 m, 4H of **B**, $NCH_2(CH_2)_2$), 2.40 (broadened s, 2H of **A**, NCH_2), 3.41 (broadened s, 2H of **A**, NCH_2), 3.24/3.50/3.62/3.94 (4 m, 4H of **B**, H_2C–N–CH_2), 5.75 (d, $^3J_{H,H}$ = 7.1 Hz, 2 ortho-H of NPh, **A**), 6.08 (d, $^3J_{H,H}$ = 7.3 Hz, 2 ortho-H of NPh, **B**), 6.73–8.00 (m, 24H, 1-H, H_{Ph}). Anal. Calcd for $C_{38}H_{34}F_3N_2O_3PS$ (686.72): C, 66.46; H, 4.99; N, 4.08; found: C, 66.3; H, 5.2; N, 4.0.

3c: From **1c** (1.45 g, 4.17 mmol) by variation A, bright yellow powder; yield: 1.49 g (51%). Mixture of isomers, **A:B** = 3.6:1 (309 K). mp 176–178°C. IR (KBr): ν 1600 (s), 1575 (vs, br), 1260 (vs, br, s), 1220 (s), 1150 (s, br), 1025 (vs) cm^{-1}. ^1H NMR (CD_3CN, 400.13 MHz, 263 K): δ 0.84 (broadened s, 2H, $NCH_2CH_2CH_2$, **A**+**B**), 1.23 (broad s, 2H of **A**, NCH_2CH_2), 1.33 (broad s, 2H of **A**, NCH_2CH_2), ~1.30–1.78 (coalescing signals, 4H of **B**, NCH_2CH_2), 2.90 (broadened s, 2H of **A**, NCH_2), 3.04 (broadened s, 2H of **A**, NCH_2), 3.30–3.72 (coalescing signals, 2H of **B**, NCH_2), 5.76 (d, $^3J_{H,H}$ = 7.6 Hz, 2 ortho-H of NPh, **A**), 6.25 (d, $^3J_{H,H}$ = 7.6 Hz, 2 ortho-H of NPh, **B**), 6.61–7.99 (m, 24H, 1-H, H_{Ph}). Anal. Calcd for $C_{39}H_{36}F_3N_2O_3PS$ (700.75): C, 66.85; H, 5.18; N, 4.00; found: C, 66.4; H, 5.4; N, 3.9.

3d: From **1d** (1.95 g, 5.59 mmol) by variation A, deeply yellow powder; yield: 3.17 g (81%). Mixture of isomers, **A:B** = 4.2 (300 K). mp 140–142°C. IR (KBr): ν 1600 (s), 1580 (vs, br), 1260 (vs), 1145 (s), 1100 (s), 1025 (vs) cm^{-1}. ^1H NMR ($CDCl_3$, 400.13 MHz), T = 300 K: δ 2.8–4.0 (coalescing broad signals, NCH_2CH_2O, **A**+**B**), 5.72 (d, $^3J_{H,H}$ = 7.5 Hz, 2 o-H of NPh, **A**), 6.16 (d, $^3J_{H,H}$ = 7.6 Hz, 2 ortho-H of NPh, **B**), 6.73 (t, p-H of NPh, **A**), 6.82 (t, 2 m-H of NPh, **A**), 6.89 (d, $^3J_{P,H}$ = 14.0 Hz, 1-H, **A**), 7.05–7.98 (several m, 1-H of **B** and H_{Ph}); T = 258 K: 2.92 (broadened s, 4H of **A**, NCH_2 and OCH_2), 3.28 (broadened s, 2H of **A**, OCH_2), 3.55 (broadened s, 2H of **A**, NCH_2), 3.45–3.60 (m, 2H of **B**, NCH_2), 3.72–3.78 (m, 2H of **B**, NCH_2), 3.80–3.85 (m, 2H of **B**, OCH_2), 3.95–4.05 (m, 2H of **B**, OCH_2). Anal. Calcd for $C_{38}H_{34}F_3N_2O_4PS$ (702.72): C, 64.95; H, 4.88; N, 3.99; found: C, 64.9; H, 5.0; N, 3.9.

3e: A solution of salt **1e** (1.00 g, 2.82 mmol) and triphenylphosphorane phenylimine [24] (1.20 g,

2.82 mmol) in dichloromethane (30 mL) was stirred until **1** had disappeared (7 h, IR control). The solution was cooled at −78°C and ether (60 mL) was added to precipitate the orange-colored product, which was isolated by filtration and rinsed with ether; yield: 1.17 g (53%); mp 210°C. IR (KBr): ν 1575 (m), 1265 (vs), 1220 (s), 1140 (s), 1110 (s), 1025 (s) cm^{-1}. ^1H NMR ($CDCl_3$, 400.13 MHz, 309 K): δ 3.07 (broad, unstructured, 4H, NCH_2), 3.69 (pseudo-t, OCH_2), 5.80 (d, $^3J = 7.1$ Hz, 2H, ortho-H of NPh), 6.75–7.84 (m, 28H, H_{Ph}). Anal. Calcd for $C_{44}H_{38}F_3N_2O_4PS$ (778.83): C, 67.86; H, 4.92; N, 3.60; found: C, 67.5; H, 4.9; N, 3.6.

3f: From **1f** (0.087 g, 0.25 mmol) by variation B, yellow powder; yield: 0.12 g (68%). mp 193–194°C. IR (KBr): ν 1589 (s), 1529 (s), 1423 (s), 1398 (s), 1272 (vs), 1223 (m), 1149 (s), 1030 (s) cm^{-1}. ^1H NMR ($CDCl_3$, 400.13 MHz, 300 K): δ 0.45–0.65 (coalescing signal, 4H, cyclopropyl), 1.47 (coalescing signal, 1H, cyclopropyl), 2.65–4.10 (coalescing signal, 6H, NMe_2), 5.87 (d, $^3J_{H,H} = 7.6$ Hz, 2 H, ortho-H of NPh), 6.86–7.57 (m, 23H, H_{Ph}). MS (MALDI): *m/z* 551.4 (M^+ of cation). Anal. Calcd for $C_{39}H_{36}F_3N_2O_3PS$ (700.75): C, 66.85; H, 5.18; N, 4.00; found: C, 66.79; H, 5.21; N, 3.93.

3g: From salt **1g** (0.091 g, 0.25 mmol) by variation B, bright yellow powder; yield: 0.12 g (72%). mp 130–131°C. The product partly decomposed within several hours at ambient temperature both as a solid and in chloroform solution, but could be stored at −18°C under argon for several days. IR (KBr): ν 1603 (m), 1536 (s), 1399 (s), 1265 (s), 1221 (m), 1146 (s), 1032 (s) cm^{-1}. ^1H NMR ($CDCl_3$, 400.13 MHz, 300 K): δ 1.05 (s, 9H, CMe_3), 3.32 (s, broadened, 6H, NMe_2), 5.68 (s, broadened, 2H, ortho-H of NPh), 6.81–7.56 (m, 23 H, H_{Ph}). MS (MALDI): *m/z* = 567.2 (M^+ of cation).

3h: From salt **1h** (0.13 g, 0.25 mmol) by variation B, orange-yellow powder; yield: 0.10 g (45%). mp 181–182°C (chloroform/ether). IR (KBr): ν 1585 (m), 1573 (m), 1474 (s), 1426 (s), 1266 (s), 1222 (m), 1148 (m), 1101 (m), 1031 (s) cm^{-1}. ^1H NMR ($CDCl_3$, 500.14 MHz, 218 K): δ 3.61 (d, $^2J_{H,H} = 13.2$ Hz, 1H, NCH^a), 3.86–3.89 (2 overlapping d, 2H, NCH^a, and NCH^b), 5.53 (broad, 2H, o-H of NPh), 5.83 (broadened s, 2H, H_{Ph}), 5.99 (d, $^2J = 12.6$ Hz, 1H, NCH^b), 6.73–8.35 (several m, H_{Ph}). MS (MALDI): *m/z* 739.5 (M^+ of cation). Anal. Calcd for $C_{54}H_{44}F_3N_2O_3PS \times CHCl_3$ (1008.31): C, 65.51; H, 4.46; N, 2.78; found: C, 65.33; H, 4.53; N, 2.72.

Conversion of Salt **3a** *into* **5, 6**, *and* **7**

A solution of salt **3a** (6.750 g, 10.2 mmol) and tetramethylammonium bromide (1.695 g, 11.0 mmol) in dry THF (100 mL) was prepared, NaOEt (0.749 g, 11.0 mmol) in THF (20 mL) was gradually added, and the mixture was stirred for 20 h. The solvent was evaporated at 0.005 mbar, and the residue was triturated with hot pentane (3 × 100 mL). The pentane extracts were combined, the solvent was evaporated, and the residual oil was triturated again with hot pentane (3 × 100 mL). Evaporation of the solvent from the combined pentane extracts left a viscous orange-colored oil which consisted mainly of (3*E*)-4-dimethylamino-1,2-diphenyl-1-azabuta-1,3-diene (**5**, 5.3:1 mixture of isomers) and of (3-dimethylamino-1-phenylprop-2-ynylidene)phenylamine (**6**). Separation and purification of these components by usual procedures was not successful. Therefore, the oil was dissolved in dichloromethane (30 mL), the solution was cooled at 0°C, and HBF_4 etherate (ca. 54%, 1.5 mL) in ether (10 mL) was added dropwise. The mixture was then stirred for 20 min at 0°C, brought to 20°C and concentrated to a volume of 10 mL. A beige powder was precipitated by addition of ether (20 mL) and was recrystallized from CH_2Cl_2/ether. Yield of (2*E*)-3-dimethylamino-1-phenyl-1-phenylaminotrimethinium tetrafluoroborate (**7**): 0.449 g (13%), mp 134–136°C. An analogous procedure, where **3a** (4.960 g, 7.5 mmol) was treated with $NaN(SiMe_3)_2$ (1.467 g, 8.0 mmol), gave 0.274 g (11%) of **7**.

5: ^1H NMR (400.13 MHz, $CDCl_3$, 309 K), major isomer **A**, minor isomer **B**: δ 2.70 (s, NMe_2, **A**), 2.72 (s, NMe_2, **B**), 5.00 (d, $^3J = 13.4$ Hz, 3-H, **A**), 5.44 (d, $^3J = 13.3$ Hz, 3-H, **B**), 6.58 (d, $^3J = 13.4$ Hz, 4-H, **A**), 6.92–7.62 (m, H_{Ph}, **A** and **B**, and 4-H, **B**). ^{13}C NMR (100.62 MHz, $CDCl_3$, 253 K): δ 36.4/44.4 (NMe_2, **A**), 91.4 (C-3, **A**), 151.7 (C-4, **A**), 168.3 (C-2, **A**), signals of minor isomer **B** not detected.

6: NMR data (in admixture with **5**): ^1H: δ 2.85 (s, NMe_2). ^{13}C: 42.3 (NMe_2), 64.9 (C-2), 121.4 (C-1). IR: ν 2156 cm^{-1} (s, C≡C).

7: ^1H NMR (CD_3CN, 400.13 MHz): δ 2.99/3.17 (2 s, NMe_2), 5.71 (d, $^3J = 11.6$ Hz, 2-H), 7.44–7.87 (m, 3-H, H_{Ph}), 8.79 (s, br, NH). ^{13}C NMR (CD_3CN, 100.6 MHz): δ 39.0/47.3 (NMe_2), 91.7 (C-2, $J_{C,H} = 161.2$ Hz), 125.5, 128.6, 129.9, 130.6, 132.8, 133.6, 137.9 (ipso-C of NPh), 164.5 (C-3, $J_{C,H} = 170.8$ Hz), 170.2 (C-1). Anal. Calcd for $C_{17}H_{19}BF_4N$ (338.16): C, 60.38; H, 5.66; N, 8.29; found: 60.3; H, 5.7; N, 8.3.

X-Ray Crystal Structure Determination for **3h** *and* **7**

Single crystals of **3h** were grown from chloroform/ether by the diffusion method; they contained one $CHCl_3$ molecule per formula unit. Crystals of **7** were obtained from dichloromethane at −36°C.

TABLE 2 Crystallographic Data and Details for Salts **3h** and **7**

	3hA	**7**
Empirical formula	$C_{54}H_{44}F_3N_2O_3PS \times CHCl_3$	$C_{17}H_{19}BF_4N_2$
Formula weight	1008.31	338.2
Temperature (K)	193 (2)	295 (2)
Wavelength (Å)	0.71073	0.71073
Crystal size (mm)	0.38 × 0.31 × 0.15	0.60 × 0.60 × 0.45
Crystal system	Monoclinic	Monoclinic
Space group	$P\,2_1/c$	$P\,c$
a (Å)	11.159 (1)	7.951 (2)
b (Å)	22.941 (2)	6.143 (2)
c (Å)	19.527 (2)	17.492 (6)
α (°)	90	90
β (°)	95.02 (1)	97.97 (2)
γ (°)	90	90
Volume (Å^3)	4979.8 (7)	846.1 (7)
Z	4	2
ρ_{calc} (g · cm^{-3})	1.345	1.327
μ(MoK_α) (cm^{-1})	3.15	1.03
Diffractometer	Stoe IPDS	Enraf-Nonius CAD4
θ range (°)	2.04–25.96	4.00–48.00
Index ranges	$-13 \le h \le 13$ $-28 \le k \le 28$ $-24 \le l \le 23$	$-9 \le h \le 9$ $0 \le k \le 7$ $-19 \le l \le 19$
Reflections collected	38963	3486
Independent reflections (R_{int})	9681 (0.0619)	1414 (0.044)
Data/restraints/parameters	9681/0/613	1084/0/291
Goodness-of-fit on F^2	0.872	0.799
Final R indices [$I > 2\sigma(I)$]; $R1$, $wR2$	0.0391, 0.0856	0.0416, 0.0423
R indices (all data); $R1$, $wR2$	0.0770, 0.0947	
Largest diff. peak and hole [e · Å^{-3}]	0.48, −0.42	

The structures were solved with direct methods and refined by a full-matrix least-squares method (**3h**: SHELX-97 [25]; **7**: MolEN [26]). Hydrogen atoms of **3h** were calculated geometrically and treated as riding on their bond neighbors in the refinement procedure; H atoms of **7** were refined isotropically. Molecule plots: ORTEP-3 [27]. Crystallographic data and details of the refinement for the two structures are given in Table 2. CCDC-256239 (**3h**) and –256483 (**7**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk).

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