Reactions of Two- and Three-Coordinate (Silylamino)phosphines with Propargyl Halides[1]

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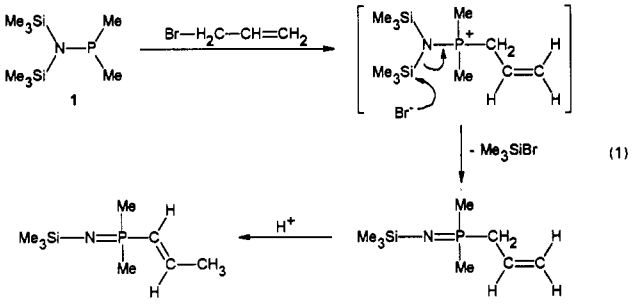
Reaction of the 3-coordinate (silylamino)phosphine, $(Me_3Si)_2NPMe_2$ (**1**), with propargyl chloride, $HC{\equiv}CCH_2Cl$, proceeded via elimination of Me_3SiCl to the intermediate acetylene-substituted phosphoranimine, $Me_3SiN{=}PMe_2CH_2C{\equiv}CH$ (**3**). In situ reaction of **3** with Me_3SiCl led to the (silylpropynyl)phosphoranimine, $Me_3SiN{=}PMe_2CH_2C{\equiv}CSiMe_3$ (**4**), while HCl-catalyzed rearrangements of **3** gave the allene species $Me_3SiN{=}PMe_2CH{=}C{=}CH_2$ (**5**) and the acetylenic phosphoranimine, $Me_3SiN{=}PMe_2C{\equiv}CCH_3$ (**6**). In contrast, the 2-coordinate (silylamino)phosphine, $(Me_3Si)_2NP{=}N\text{-}SiMe_3$ (**2**) reacted with $HC{\equiv}CCH_2Cl$ via electrophilic addition of the acetylenic C—H bond to afford an acetylene-substituted P(III) derivative, $[(Me_3Si)_2N](Me_3SiNH)PC{\equiv}CCH_2Cl$ (**7**). Subsequent reaction of **7** with the 3-coordinate phosphine **1** occurred at the terminal $-CH_2Cl$ site to give the novel 1,3-diphosphapropyne system, $[(Me_3Si)_2N](Me_3SiNH)PC{\equiv}CCH_2PMe_2{=}NSiMe_3$ (**8**). The structural characterization of these new compounds (**4**–**8**) by NMR spectroscopy (^1H, ^{13}C, and ^{31}P) is described.

Introduction

The chemistry of 3-coordinate (silylamino)phosphines such as $(Me_3Si)_2NPMe_2$ (**1**) is dominated by their *nucleophilic* character. Most reactions of these reagents also involve Si–N bond cleavage that leads either to an intramolecular silyl migration or to the elimination of a silane byproduct.[3] In some cases, further rearrangement (usually acid-catalyzed by atmospheric moisture) of unsaturated organic side groups also occurs. Several of these features are illustrated by the interaction of (silylamino)phosphine **1** with allyl bromide (eq 1).[4]



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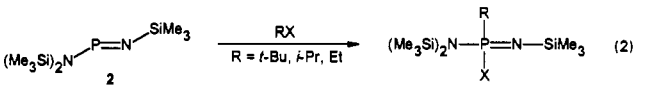
In contrast, 2-coordinate phosphines, such as the (silylamino)*imino*phosphine **2** are *electrophilic* reagents with a rich derivative chemistry[5] that generally involves addition or cycloaddition to the low-coordinate phosphorus center. With alkyl halides, for example, they undergo oxidative addition to yield 4-coordinate phosphoranimines (eq 2)[6] rather than phosphonium salts as do the (silylamino)phosphines (e.g., **1**, eq 1).



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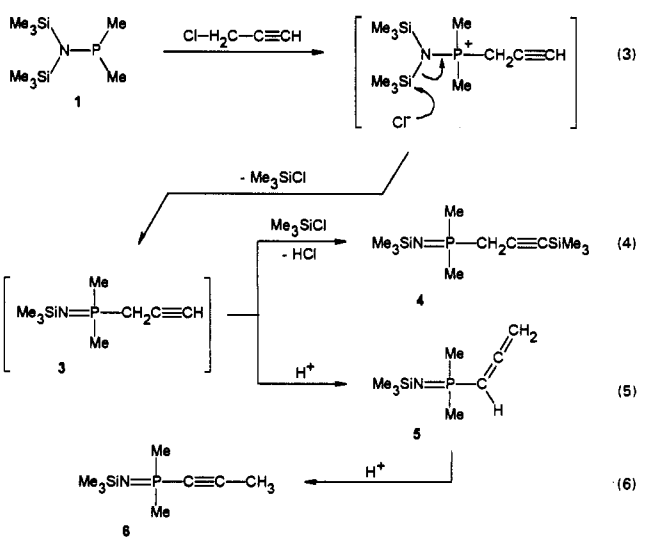
In addition to its relationship to these prior results, this paper comprises part of our broader study of the reactivity of low-coordinate phosphines [e.g., **2** and the P=C analog, $(Me_3Si)_2NP{=}CHSiMe_3$] toward unsaturated organic substrates. We have recently reported, for example, the novel *ene* reactions of acetylenes[7] and allenes[8] with these 2-coordinate phosphines. In this context, we report here some reactions of the 2- and 3-coordinate (silylamino)phosphines (**2** and **1**) with propargyl halides, $HC{\equiv}CCH_2X$. By combining two functional groups (i.e., $-CH_2X$ and $-C{\equiv}CH$) within one molecule, these reagents offer unique possibilities for comparing and contrasting the reactivity of these two different types of Si–N–P compounds.

Results and Discussion

Reactions of $(Me_3Si)_2NPMe_2$. The interaction of the 3-coordinate phosphine **1** with propargyl chloride in CH_2Cl_2 solution was a relatively complicated process that involved a series of reactions (eqs 3–6). Ultimately, the acetylene derivatives **4** and **6** were isolated separately and the allene **5** was clearly identified as a mixture with **6**.



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(1) Presented in part at the 202nd National Meeting of the American Chemical Society, New York, NY, 1991. For a brief summary, see: Neilson, R. H.; Angelov, C. M. *ACS Symp. Ser.* **1992**, *486*, 76.
(2) Permanent address: Department of Chemistry, University of Shoumen, 9700 Shoumen, Bulgaria.
(3) See, for example, the following and references cited therein: (a) Morton, D. W.; Neilson, R. H. *Organometallics* **1982**, *1*, 289. (b) Wisian-Neilson, P.; Ford, R. R.; Goodman, M. A.; Li, B.-L.; Roy, A. K.; Wettermark, U. G.; Neilson, R. H. *Inorg. Chem.* **1984**, *23*, 2063. (c) Neilson, R. H.; Wisian-Neilson, P.; Wilburn, J. C. *Inorg. Chem.* **1980**, *19*, 413. (d) Wilburn, J. C.; Neilson, R. H. *Inorg. Chem.* **1979**, *18*, 347.
(4) Morton, D. W.; Neilson, R. H. *Organometallics* **1982**, *1*, 623.
(5) For some general reviews of the field of low-coordinate phosphorus compounds, see for example: (a) Niecke, E.; Gudat, D. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 217. (b) Appel, R.; Knoll, F. *Adv. Inorg. Chem.* **1989**, *33*, 259. (c) Regitz, M. *Chem. Rev.* **1990**, *90*, 191. (d) Cowley, A. H. *Polyhedron* **1984**, *3*, 389. (e) Markovski, L. N.; Romanenko, V. D. *Tetrahedron* **1989**, *45*, 6019.
(6) Neilson, R. H.; Engenito, J. S. *Organometallics* **1982**, *1*, 1270 and references cited therein.

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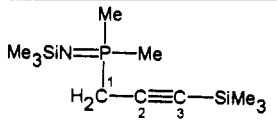
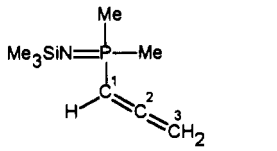
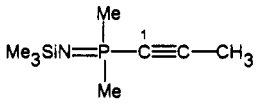
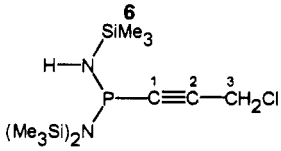
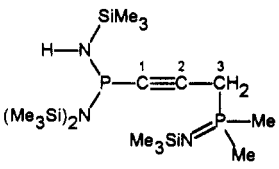
Table I. NMR Spectroscopic Data[a] for New Acetylenic and Allenic Phosphorus Compounds

compound	signal	^{1}H NMR δ	^{1}H NMR J_{PH} (Hz)	^{13}C NMR δ	^{13}C NMR J_{PC} (Hz)	^{31}P NMR δ
 **4**	Me_3Si	0.17		3.84	4.1	6.6
	Me_3SiC	0.30		−0.29		
	Me_2P	1.20	12.6	17.19	71.4	
	$^1CH_2$	2.33	16.2	26.94	59.9	
	^2C			99.29	9.0	
	^3C			88.40	6.7	
 **5**	Me_3SiN	−0.36		3.65	4.4	−2.9
	Me_2P	1.14	12.9	19.61	75.4	
	^1CH	5.03	2.9 (6.8)[b]	87.61	88.2	
	^2C			210.16		
	$^3CH_2$	4.50	10.8 (6.8)[b]	74.90	12.0	
 **6**	Me_3SiN	−0.26		3.15	5.2	−18.0
	Me_2P	1.28	14.0	22.50	84.8	
	$^3CH_3$	1.65	3.6	4.23	3.2	
	^2C			98.20	26.1	
	^1C			77.51	138.2	
 **7**	$(Me_3Si)_2N$	0.18		4.18	8.2	40.3
	Me_3SiN	0.05		1.46	6.5	
	NH	2.57				
	$^3CH_2Cl$	4.13		31.32		
	^2C			97.30	3.2	
	^1C			93.92	37.7	
 **8**	$(Me_3Si)_2NP$	0.14	1.2	4.16	7.8	41.8
	Me_3SiNH	0.01		1.45	6.4	J_{PP} = 8.8 Hz
	$Me_3SiN{=}P$	−0.09		4.17		7.4
	Me_2P	1.42	12.6	17.80	70.6	
	NH	2.47				
	$^3CH_2$	2.65	16.6, 3.6	27.42	58.3	
	^2C			96.79	9.9, 4.1	
	^1C			90.50	25.0	

[a] Proton and ^{13}C chemical shifts downfield from Me_4Si; ^{31}P shifts downfield from H_3PO_4; $CDCl_4$ solvent. [b] J_{HH} values in parentheses.

As in the reaction of **1** with allyl bromide (eq 1), this process most likely involves an initial *nucleophilic* attack of **1** on the $-CH_2Cl$ functional group, followed by rapid elimination of Me_3SiCl (eq 3), to give the propynyl-substituted phosphoranimine **3**. Although this intermediate (**3**) was not isolated, it is reasonably assigned to a transient signal observed at δ 4.0 when the reaction was monitored by ^{31}P NMR spectroscopy. Upon solvent removal, NMR analysis (Table I) revealed the presence of three different products, **4**–**6**.

Distillation of this product mixture under reduced pressure gave two clear fractions, both colorless liquids. The minor, high-boiling component (ca. 10–15% yield based on **1**) was readily identified as the (3-silylpropynyl)phosphoranimine **4**. In addition to the distinct signals for two Me_3Si groups and one Me_2P group in both the ^{1}H and the ^{13}C NMR spectra, peaks assignable to the $-CH_2C{\equiv}C-$ linkage were readily apparent. The PCH_2 moiety gave rise to doublets with large coupling constants[9] ($^1J_{PC}$ = 59.9 Hz; $^2J_{PH}$ = 16.2 Hz), indicative of the adjacent P(V) center. Moreover, two doublets in the ^{13}C NMR spectrum (δ 88.4 and 99.3) were found within the chemical shift range[10] expected for acetylenic carbons. The relatively small coupling constants (ca. 6–9 Hz) of these signals further confirmed that the $-C{\equiv}C-$ group is not directly bonded to phosphorus in this compound.

The major, lower-boiling fraction (ca. 50% yield) was found (by NMR spectroscopy and elemental analysis) to be a mixture of structural isomers, the allene **5** and the methylacetylene **6**. The rearrangement of intermediate **3** into **5** and, finally, **6**, which is analogous to that observed for the allyl derivatives (eq 1),[4] is probably acid-catalyzed by the HCl produced in the formation of the Me_3Si derivative **4**. This proposed pathway is supported by two additional observations: (1) longer reaction times lead to the formation of the final product **6** in greater proportion; (2) the same reaction with propargyl bromide (in which the stronger acid, HBr, is generated) occurs much more rapidly and leads to the formation of **6** as the only isolated product.

Elemental analysis and NMR spectral data for **6** (prepared free of **5** from propargyl bromide) clearly confirmed it as one component of the isomeric mixture that was obtained in the reaction with propargyl chloride. The attachment of the acetylene unit, $-C{\equiv}CCH_3$ directly to phosphorus is indicated by the large, one-bond P–C coupling ($^1J_{PC}$ = 138.2 Hz) for this carbon (δ 77.5). While the allene isomer **5** was always the minor component (ca. 25% by NMR signal integration) of the mixture with **6**, its structure was still readily apparent from the ^{1}H and ^{13}C NMR spectral data. In this case, the most notable features were the low-field ^{13}C signal for the central allene carbon (δ 210)[10] and the very distinctive pattern of doubled doublet ($=CH_2$) and doubled triplet ($=CHP$) resonances for the protons of the $-CH{=}C{=}CH_2$ group.[11]

Interestingly, the P–H coupling constants in the allene **6** dramatically illustrate the influence of stereochemical relation-

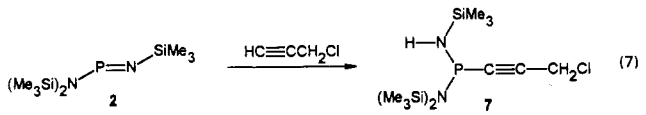
(7) Angelov, C. M.; Neilson, R. H. *Inorg. Chem.* **1993**, *32*, 334.
(8) Angelov, C. M.; Neilson, R. H. *Tetrahedron* **1992**, *48*, 10227.
(9) Verkade, J. G., Quin, L. D., Eds. *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis* VCH; Deerfield Beach, FL, 1987; Chapters 11 and 12.
(10) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectroscopic Characterization of Organic Compounds*, 4th ed.; Wiley; NY, 1981; p 289.
(11) Phosphorus(V) compounds containing allene functional groups are readily prepared by a variation of the Arbusov reaction. See, for example: Ignatiev, V. M.; Ionin, B. I.; Petrov, A. A. *J. Gen. Chem. USSR (Engl. Transl.)* **1967**, *37*, 1807. See also ref 7 and 8.

ships[9] between the coupled nuclei. Thus, the four-bond coupling ($^4J_{PH}$ = 10.8 Hz) to the terminal $=CH_2$ protons, where the dihedral angle is 90°, is much larger than the two-bond coupling ($^2J_{PH}$ = 2.9 Hz) to the adjacent CH proton, where the dihedral angle is 0°. The four-bond H–H coupling within the allene group is a typical value (6.8 Hz).[11]

Another noteworthy aspect of the NMR spectral data of these compounds is the clear trend in the one-bond P–C coupling constants for the series **4**, **5**, and **6**, in which the hybridization at the a carbon (^{1}C) changes from sp^3, to sp^2, to sp. With the other substituents on phosphorus held constant, the value of $^1J_{PC}$ increases markedly with increasing *s* character in the P–C bond.

compound	hybridization at ^{1}C	$^1J_{PC}$ (Hz)
4 (PCH_2—)	sp^3	59.9
5 (PCH=)	sp^2	88.2
6 (PC≡)	sp	138.2

Reactions of $(Me_3Si)_2NP{=}NSiMe_3$. The interaction of the 2-coordinate (silylamino)*imino*phosphine **2** with propargyl chloride took a more straightforward course than that described above. However, we did not find the anticipated oxidative addition of the $-CH_2Cl$ functional group to the 2-coordinate phosphorus center (as in eq 2). Instead, the reaction occurred via 1,2-addition of the terminal C—H bond of the acetylene to the P=N bond (eq 7) to give the acetylenic (silylamino)phosphine **7**. The same process has been recently observed in the reaction of **2** with simpler mono-substituted acetylenes, HC≡CR (R = Ph, $SiMe_3$).[7]



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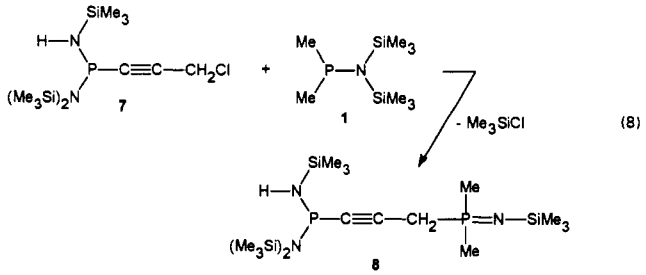
Compound **7** was obtained in 57% yield as a colorless, distillable liquid that was fully characterized by NMR spectroscopy (Table I) and elemental analysis. The 3-coordinate P(III) character of **7** is consistent with the downfield chemical shift (δ 40.3) in the ^{31}P NMR spectrum relative to the P(V) analogs (e.g., **4**–**6**). Moreover, as expected,[9] the one-bond PC≡ coupling in **7** ($^1J_{PC}$ = 37.7 Hz) is much smaller than that found for the 4-coordinate P(V) analog **6** ($^1J_{PC}$ = 138.2 Hz). A broad signal (δ 2.57) in the ^{1}H NMR spectrum was observed for the NH proton.

We were also able to combine the different modes of reactivity of the 2- and 3-coordinate phosphines toward propargyl chloride in a single reaction sequence. Thus, treatment of a solution of **7**, prepared as in eq 7, with an equimolar amount of the (silylamino)phosphine **1** (eq 8) afforded the novel 1,3-diphosphapropyne system **8**. Compound **8** was isolated in 50% yield as a colorless, high-boiling liquid. In this case, there was no acetylene–allene rearrangement as described above for the reaction of **1** with propargyl chloride (eqs 3–6). Even though such a rearrangement would lead to conjugation of the P=N bond with a C=C or a C≡C bond, it did not occur. This is probably due to the absence of the likely acid catalyst (i.e., HCl) in this reaction mixture.



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Several key features of the NMR spectra of compound **8** were structurally informative. First, two doublets [δ 41.8 for P(III) and δ 7.4 for P(V); $^4J_{PP}$ = 8.8 Hz] were found in the ^{31}P NMR spectrum. Second, both the protons and the carbon of the internal CH_2 group exhibited large couplings (similar to those in the close analog **4**) to the adjacent P(V) center. Third, the ^{13}C signals of the acetylenic carbons had chemical shifts and P(III)–C coupling constants that were very close to those of the similar acetylenic phosphine **7**. Fourth, three distinct signals for the different types of Me_3Si groups were observed in the ^{1}H and ^{13}C NMR spectra. Finally, the resonances of both the PCH_2 protons and the central ≡C carbon were doubled doublet patterns due to coupling with the two different phosphorus centers.

In summary, the reactions of 2- and 3-coordinate (silylamino)phosphines with propargyl halides provide simple, one-step synthetic routes to a variety of new acetylene derivatives (and, in one case, an allene) of Si—N—P(III) and/or Si—N=P(V) systems. Additional synthetic reactions as well as the derivative chemistry of some these novel products are under further study in this laboratory.

Experimental Section

Materials and General Procedures. Propargyl chloride (neat) and propargyl bromide (80% w/w in toluene) were obtained from commercial sources and used without further purification. The (silylamino)phosphines, $(Me_3Si)_2NPMe_2$ (**1**)[12] and $(Me_3Si)_2NP{=}NSiMe_3$ (**2**)[13] were prepared according to published procedures. Dichloromethane was distilled from CaH_2 and stored over molecular sieves prior to use. Proton and ^{13}C NMR spectra were recorded on a Varian XL-300 spectrometer. A JEOL FX-60 instrument was used for ^{31}P NMR spectra. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside NY. All reactions and other manipulations were carried out under an atmosphere of dry nitrogen or under vacuum. The following procedures are typical of those used for the preparation of the new compounds in this study.

Reaction of 1 with Propargyl Chloride. The (silylamino)phosphine **1** (11.1 g, 50 mmol) was added via syringe to a stirred solution of $HC{\equiv}CCH_2Cl$ (4.0 mL, 52 mmol) in CH_2Cl_2 (25 mL) at 0 °C. The mixture was stirred for 2 days at 0 °C. After solvent removal, distillation through a 10-cm column afforded two distinct fractions, both colorless liquids. Fraction **A** (4.7 g, 51% yield, bp 47–50 °C at 0.35 mmHg) was identified by NMR spectroscopy (Table I) as a mixture of structural isomers **5** and **6** (ca. 75% **6**). Anal. Calcd for $C_8H_{18}NPSi$: C, 51.30; H, 9.69. Found: C, 51.22; H, 9.70. Fraction **B** (1.0 g, 11% yield, bp 65–70 at 0.15 mmHg) was identified by NMR spectroscopy (Table I) as the silylpropynyl derivative **4**. Elemental analysis of **4** was not attempted due to its contamination with a small amount (ca. 5%) of the more volatile fraction **A**. When the same reaction mixture was stirred for 6 days at 0 °C, the acetylene isomer **6** was isolated in pure form (43% yield, bp 42–43 °C at 0.3 mmHg). Anal. Calcd for $C_8H_{18}NPSi$: C, 51.30; H, 9.69. Found: C, 51.17; H, 9.99.

Reaction of 1 with Propargyl Bromide. Phosphine **1** (11.1 g, 50 mmol) was added via syringe to a stirred solution of $HC{\equiv}CCH_2Br$ (7.7 mL of 80% w/w solution in toluene, 52 mmol) in CH_2Cl_2 (25 mL) at −30 °C. The mixture was stirred for 3 h at which point ^{31}P NMR spectroscopy indicated that the reaction was complete. After the mixture was warmed to room temperature, the solvent was removed under reduced pressure. Distillation afforded the acetylene derivative **6** in 40% yield.

Preparation of Acetylenic Phosphine 7. The 2-coordinate (silylamino)phosphine **2** (8.4 g, 30 mmol) was added via syringe to a stirred solution of $HC{\equiv}CCH_2Cl$ (2.4 mL, 30 mmol) in CH_2Cl_2 (15 mL) at 0 °C. The mixture was warmed to room temperature and stirred for 24 h. After solvent removal, distillation afforded **7** as a colorless liquid (6.0 g, 57% yield, bp 75–76 °C at 0.15 mmHg). Anal. Calcd for $C_{12}H_{30}ClN_2PSi_3$: C, 40.82; H, 8.56. Found: C, 40.53; H, 8.66.

Preparation of 1,3-Diphosphapropyne 8. Phosphine **2** (5.6 g, 22 mmol) was added via syringe to a stirred solution of $HC{\equiv}CCH_2Cl$ (1.6 mL, 22 mmol) in CH_2Cl_2 (15 mL) at 0 °C. The mixture was warmed to room temperature and stirred for 24 h. After the mixture was cooled to 0 °C, the (silylamino)phosphine **1** (2.5 g, 22 mmol) was added via syringe. The mixture was then warmed to room temperature and stirred for 6 h. After solvent removal, distillation afforded **8** as a colorless liquid (4.5 g, 50% yield, bp 118–119 °C at 0.2 mm). Anal. Calcd for $C_{17}H_{45}N_3P_2Si_4$: C, 43.83; H, 9.74. Found: C, 43.55; H, 9.22.

Acknowledgment. We thank the Robert A. Welch Foundation and the Texas Christian University Research Fund for financial support of this research.

(12) Neilson, R. H.; Wisian-Neilson, P. *Inorg. Chem.* **1982**, *21*, 3568.
(13) Niecke, E.; Flick, W. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 585.