1406 *Organometallics* 1983, *2*, 1406-1410

Mesityl–Phosphorus Compounds. Synthesis of a New Iminomethylenephosphorane and Its Dimers[1]

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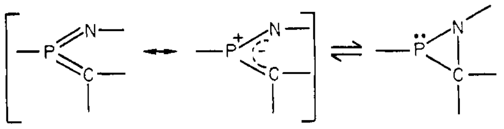
Received March 16, 1983

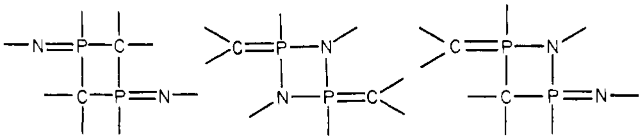
The reaction of CCl_4 with the sterically congested (silylamino)phosphine $(Me_3Si)_2NP(R)CH_2SiMe_3$ (1, R = 2,4,6-$Me_3C_6H_2$) unexpectedly yields the four-membered P_2N_2 ring system $[Me_3SiCH{=}P(R){-}NSiMe_3]_2$ (2). Heating of dimer 2 under a dynamic vacuum results in distillation of the monomeric, three-coordinate iminomethylenephosphorane $R{-}P({=}CHSiMe_3)({=}NSiMe_3)$ (3). Compound 3 exhibits reasonable stability at room temperature but reverts to dimer 2 on standing for a few days. Treatment of 3 with methanol affords the stable addition product $Me_3SiN{=}P(R)(OMe)CH_2SiMe_3$ (4). Direct bromination of the phosphine 1 occurs to give the expected *P*-bromophosphinimine 5 which, by reaction with $LiOCH_2CF_3$, is converted to $Me_3SiN{=}P(R)(OCH_2CF_3)CH_2SiMe_3$ (6). When either dimer 2 or monomer 3 is heated in a sealed tube, an isomeric, four-membered PCPN dimer, 7, is obtained quantitatively. Proton, ^{13}C, and ^{31}P NMR data are reported for the new compounds and the CCl_4 reaction of 1 is contrasted to that observed for related systems.

Introduction

Several recent studies have dealt with the synthesis, structure, and reactivity of a novel class of three-coordinate phosphorus(V) compounds known as iminomethylenephosphoranes (A). By variation of the steric and electronic properties of the substituent groups, such systems have been obtained as kinetically stabilized monomers A,[2-5] as dimers of two types C[3] and D[3,4] and, in one case, as the isomeric three-membered PNC ring B.[4] Unsymmetrical dimers of type E, however, have not been observed. Moreover, all of these compounds reported to date have contained bulky dialkyl or disilylamino substituents on phosphorus.

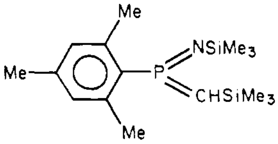


A B



C D E

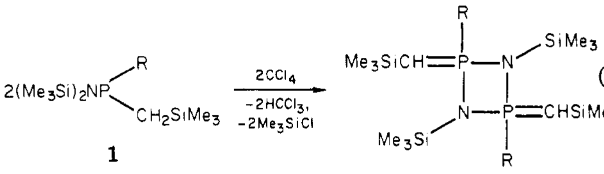
As part of our current investigation[6] of the chemistry of *P*-mesityl-substituted compounds, we report here the synthesis of a new iminomethylenephosphorane.



This compound exhibits limited thermal stability at room temperature as a monomer which, depending on temperature, forms either the P_2N_2 (D) or the novel PCPN (E) dimers.

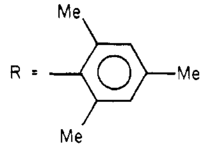
Results and Discussion

The new compounds described herein were obtained as derivatives of the recently prepared[6] *P*-mesityl-substituted (silylamino)phosphine 1. When phosphine 1 was treated with an excess of carbon tetrachloride (eq 1) at 0 °C in the absence of solvent, the novel four-membered P_2N_2 ring product 2 was isolated in about 70% yield. The characterization and possible formation pathway of compound 2 are discussed below.

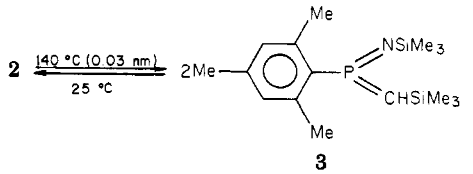


(1)

1 2



The crystalline solid 2 (mp 145 °C) was recognized as being one possible dimeric form of the three-coordinate phosphorus(V) compound mesityl((trimethylsilyl)imino)(trimethylsilyl)methylene)phosphorane (3). Indeed, we initially assumed that 2 was formed via the intermediacy of the thermally unstable monomer 3. This hypothesis was subsequently rejected upon finding that the thermolysis of 2 (eq 2) gave monomer 3 as an isolable, reasonably stable compound. Thus, when dimer 2 was heated slightly below



(2)

3

its melting point in a vacuum distillation apparatus, a colorless liquid distillate (bp 91–93 °C (0.03 mm)) was

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[1] Presented in part: Wisian-Neilson, P.; Roy, A. K.; Xie, Z.-M.; Neilson, R. H. "Abstracts of Papers", 184th National Meeting of the American Chemical Society, Kansas City, MO, September 1982; American Chemical Society: Washington, DC, 1982; INORG 141.

[2] Niecke, E.; Wildbredt, D.-A. *Angew. Chem., Int. Ed. Engl.* 1978, *17*, 199.

[3] Niecke, E.; Wildbredt, D.-A. *Chem. Ber.* 1980, *113*, 1549.

[4] Niecke, E.; Seyer, A.; Wildbredt, D.-A. *Angew. Chem., Int. Ed. Engl.* 1981, *20*, 675.

[5] Neilson, R. H. *Inorg. Chem.* 1981, *20*, 1679.

[6] Xie, Z.-M.; Neilson, R. H. *Organometallics* 1983, *2*, 921.

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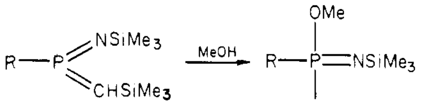
collected in high yield. The liquid was shown by NMR spectroscopy to be a mixture consisting largely of monomer **3** with lesser amounts of dimer **2**. On standing overnight, crystallization of the dimer occurred, leaving **3** as the spectroscopically pure supernatant liquid. After several days at room temperature, complete conversion of **3** to the crystalline dimer was observed.

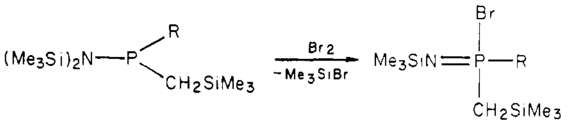
Due to its limited thermal stability, the three-coordinate phosphorane **3** was not submitted for standard elemental analysis. Satisfactory analytical data were obtained, however, for dimer **2**, an isomeric PCPN compound (see below), and the MeOH addition product **4** (eq 3). In addition to the formation of these stable derivatives, the identity of **3** is confirmed by NMR spectroscopy (Table I). The ^{31}P chemical shift of +122 ppm and the chemical shifts (^{1}H and ^{13}C) and ^{31}P coupling constants of the P=CH moiety are in good agreement with data reported on other imino methylenephosphoranes.[2-5] Like the related compound (Me$_3$Si)$_2$N—P(=CHSiMe$_3$)(=NSiMe$_3$)[5], the reaction of **3** with 1 equiv of MeOH (eq 3) occurs smoothly to afford the *P*-methoxyphosphinimine **4** as a distillable, fully characterized derivative.



3 **4** (3)

R = mesityl

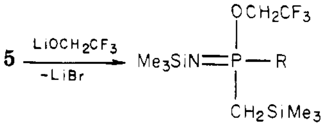
A compound analogous to **4**, containing the trifluoroethoxy group instead of methoxy, was prepared by a different procedure as part of this study. Direct bromination (eq 4) of the starting phosphine **1** proceeds as expected with elimination of Me$_3$SiBr to yield the *P*-bromophosphinimine **5**. Subsequent reaction with lithium trifluoroethoxide (eq 5) affords the more thermally stable product **6**. Phosphinimines **5** and **6** are of interest as possible precursors to cyclic[7] or polymeric[8] phosphazenes that can result from loss of Me$_3$SiX (X = Br, OCH$_2$CF$_3$). More to the point of this paper is the finding that the bromo compound **5** decomposes to some extent via elimination of HBr. When a freshly prepared and spectroscopically pure sample of **5** is distilled, the distillate is shown by NMR to contain substantial amounts of the HBr elimination product **3** and its dimer **2**. Unfortunately, more vigorous heating (sealed tube, 160 °C, 2 h) gives a complex mixture resulting from loss of Me$_3$SiBr as well as HBr. The possiblity of base-assisted dehydrohalogenation of halophosphinimines such as **5** is under curent investigation.



(4)

5

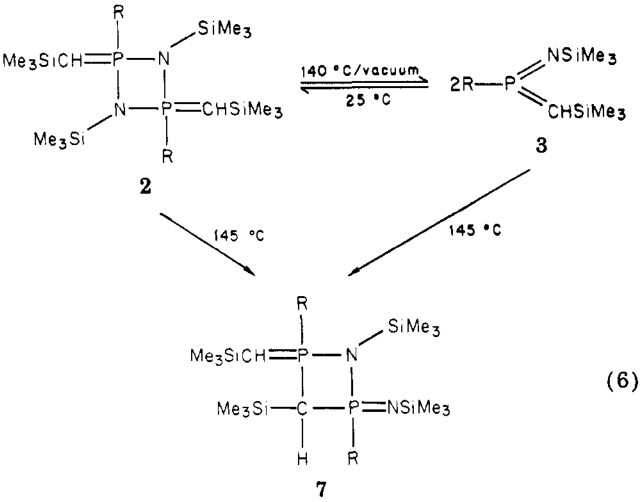
R = mesityl



$$\mathbf{5} \xrightarrow[-\mathrm{LiBr}]{\mathrm{LiOCH_2CF_3}} \mathrm{Me_3SiN{=}P(OCH_2CF_3)(R)(CH_2SiMe_3)} \qquad (5)$$

6

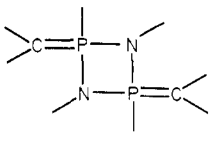
As mentioned above, the three-coordinate phosphorane **3** dimerizes across the P=N bond to yield **2** (eq 2) at room temperature. Other experiments, however, show that **2** is not the thermodynamically most stable dimer of **3**. Thus, if neat samples of either **2** or **3** are heated *in a sealed, evacuated tube* at 145 °C (i.e., just above the melting point of **2**) for several hours, then rearrangement (eq 6) to the novel PCPN four-membered ring system **7** occurs quantitatively. The unsymmetrical dimer **7** (mp 158–160 °C) simply sublimes when it is heated under a dynamic vacuum. Monomer **3**, therefore, is not produced by the thermal cracking of **7** as it is from the symmetrical dimer **2**.



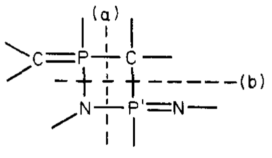
(6)

R = mesityl

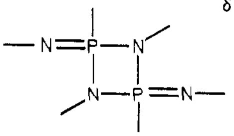
In addition to satisfactory elemental analyses and molecular weight determinations (by mass spectroscopy and cryoscopically in benzene), the ^{31}P NMR spectra provide good structural evidence for dimers **2** and **7**. Most importantly, the ^{31}P spectrum of the unsymmetrical dimer **7** consists of two doublets at +10.9 and −10.6 ppm with $^2J_{pp}$ = 15.5 Hz, consistent with two nonequivalent phosphorus atoms within the same molecule. Moreover, there is a smooth and internally consistent trend in the ^{31}P shifts of compounds **2**, **7**, and the bis(imino)phosphorane dimer **8** that we have recently reported.[6] For example, the average of the two ^{31}P shifts of **7** is almost exactly equal to the average of the values for the symmetrical model compounds **2** and **8**.



2, δ_P +22.3



7, δ_P +10.9
$\delta_{P'}$ −10.6



8, δ_P −19.7 (cis)
−24.7 (trans)

The mass spectral fragmentation patterns of dimers **2** and **7** are also in accord with the proposed structures. For example, the spectrum of **2** contains significant peaks for the dimer and monomer at *m/e* 646 and 323, respectively. Of more significance is the fact that **7** gives both a parent ion peak of *m/e* 646 and a set of three peaks (*m/e* 324, 323, 322) corresponding to the three possible monomer fragments that could result from symmetrical (a) or unsym-

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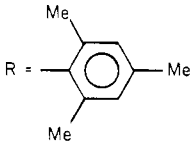
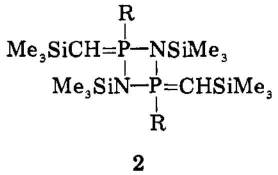
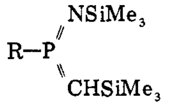
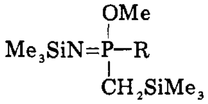
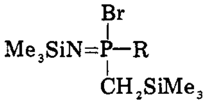
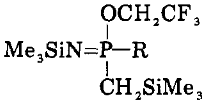
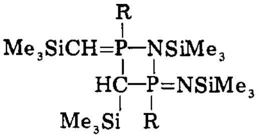
(7) Wisian-Neilson, P.; Neilson, R. H. *Inorg. Chem* **1980**, *19*, 1875.

(8) Neilson, R. H.; Wisian-Neilson, P. *J. Macromol. Sci., Chem.* **1981**, *A16*, 425.

Table I. NMR Spectroscopic Data[a] for Mesityl (R)-Phosphorus Compounds



compd	signal	¹H NMR δ	¹H NMR J_{PH}	¹³C NMR δ	¹³C NMR J_{PC}	³¹P NMR δ
 2	Me_3SiN	−0.23	···	2.23	4.9[b]	22.3
	Me_3SiC	0.60	···	5.59	4.2[b]	
	CH	0.63	19.8	23.25	110.5	
	o-Me	2.48	···	24.42	3.0	
				24.61	2.4	
	p-Me	2.07	···	20.71	···	
	C_6H_2	6.40	3.3	126-142[c]		
 3	Me_3SiN	−0.07	···	2.27	3.6	122.7
	Me_3SiC	0.24	···	0.94	6.1	
	CH	3.15	2.7	73.80	119.0	
	o-Me	2.60	1.7	22.68	6.5	
	p-Me	2.29	···	21.30	0.6	
	C_6H_2	6.67	4.2			
	C_1			134.52	83.6	
	$C_{2,6}$			138.21	9.2	
	$C_{3,5}$			128.06	11.6	
	C_4			140.05	2.4	
 $Me_3SiN{=}P(OMe)(R)CH_2SiMe_3$ 4	Me_3SiN	0.12	···	3.45	3.7	22.9
	Me_3SiC	0.12	···	−0.14	3.1	
	PCH_2	1.48	17.6	23.83	90.3	
	OMe	3.50	12.4	48.85	6.1	
	o-Me	2.69	1.3	22.63	3.7	
	p-Me	2.30	···	20.83	···	
	C_6H_2	6.88	3.8			
	C_1			130.15	123.3	
	$C_{2,6}$			141.32	11.0	
	$C_{3,5}$			130.92	12.2	
	C_4			139.61	2.4	
 $Me_3SiN{=}P(Br)(R)CH_2SiMe_3$ 5	Me_3SiN	0.05	···	0.14	4.2	0.8
	Me_3SiC	0.34	···	2.99	5.5	
	PCH_2	2.4[d]	···	36.57	60.4	
	o-Me	2.82	2.2	24.36	3.7	
	p-Me	2.32	···	21.20	···	
	C_6H_2	6.87	4.1			
	C_1			130.56	116.0	
	$C_{2,6}$			141.99	11.6	
	$C_{3,5}$			132.23	14.6	
	C_4			141.66	5.5	
 $Me_3SiN{=}P(OCH_2CF_3)(R)CH_2SiMe_3$ 6	Me_3SiN	0.07	···	−0.28	3.7	23.4
	Me_3SiC	0.13	···	3.39	3.7	
	PCH_2	1.57	18.6	24.31	84.9	
	OCH_2	4.2[c]	···	59.02	4.3[e]	
	CF_3	···	···	123.32	11.6[f]	
	o-Me	2.65	1.3	23.70	3.1	
	p-Me	2.28	···	20.87	···	
	C_6H_2	6.87	4.1			
	C_1			128.60	128.2	
	$C_{2,6}$			141.62	11.6	
	$C_{3,5}$			131.27	12.8	
	C_4			140.56	3.1	
 7	Me_3SiN	−0.28	···	1.8-6.1[c]		10.9[g]
		−0.16	···			−10.6[g]
	Me_3SiC	0.55	···			
		0.60	···			
	CH	0.6[h]	···	24.2[c]		
	PCHP	3.40	10.5[b]	52.52	34.2, 40.2	
	o-Me	2.5[c]	···	24.2[c]		
	p-Me	2.10	···	20.59	···	
	C_6H_2	6.43	4.2	126-141[c]		

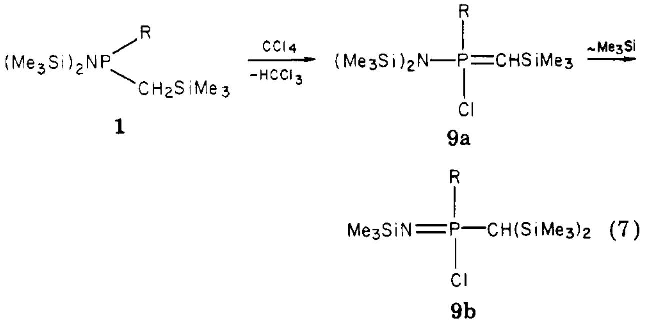
[a] Chemical shifts downfield from Me_4Si for ¹H and ¹³C and from H_3PO_4 for ³¹P spectra; coupling constants in Hz. Solvents: ¹H, CH_2Cl_2; ¹³C and ³¹P, $CDCl_3$. [b] Peaks are deceptively simple "triplets". [c] Complex multiplet with unresolved couplings and/or overlapping signals. [d] Partially hidden by *p*-Me signal. [e] J_{FC} = 36.6 Hz. [f] J_{FC} = 276.5 Hz. [g] J_{PP} = 15.5 Hz. [h] Partially hidden by a Me_3Si signal.

metrical (b) cleavage of the dimer **7**.

The proton and ^{13}C NMR spectral data (Table I) provide additional evidence for the structures of these dimers. Some relevant points include (1) the multiplicity of Me_3Si peaks in the ^{1}H NMR spectra (two signals for **2** and four signals for **7**), (2) the relatively high-field resonance[9] observed for the ylide proton (P=CH, δ 0.60 (J_{PH} = 19.8 Hz)) of **2** (the corresponding signal of **7** is partially obscurred by a Me_3Si peak), and (3) the coupling to *two* phosphorus atoms observed for the CH moiety (both ^{1}H and ^{13}C) in the PCPN ring of **7**.

The formation of dimer **2** in high yield from the CCl_4 reaction of phosphine **1** is, indeed, an unexpected result. Especially perplexing is the fact that monomer **3** is not observable when the reaction is monitored by ^{1}H and ^{31}P NMR spectroscopy. When prepared by thermal cracking of dimer **2**, however, compound **3** exhibits long-term stability in solution at room temperature. Therefore, the intermediacy of **3** in the CCl_4 reaction, which is rapid at 0 °C, seems to be precluded.

On the basis of other recent work,[10,11] the reaction of **1** with CCl_4 was expected to proceed with elimination of $HCCl_3$ and silyl migration from nitrogen to carbon to yield phosphinimine **9b** (eq 7), probably via the ylide intermediate **9a**. This pathway seemed quite reasonable since it has been observed for a large series of similar reactions involving (silylamino)phosphines containing the CH_2SiMe_3 group.[11] The 1,2 elimination of Me_3SiCl from either **9a** or **9b** could then yield the iminomethylenephosphorane **3**. However, since **3** is not observed in the reaction mixture, the formation of dimer **2** must occur by a more complicated, probably bimolecular, pathway. Efforts are underway to synthesize **9b** and related compounds by other preparative methods in order to further address this problem.



R = mesityl

Experimental Section

Materials and General Procedures. The following reagents were obtained from commercial sources and used without purification: Br_2, *n*-BuLi, CCl_4, CF_3CH_2OH, and MeOH. Benzene, CH_2Cl_2, Et_2O, and hexane were distilled form CaH_2 prior to use. The starting phosphine $(Me_3Si)_2NP(mesityl)CH_2SiMe_3$ (**1**) was prepared by a straightforward procedure as described elsewhere.[6] Proton NMR spectra were recorded on a Varian EM-390 spectrometer; ^{13}C and ^{31}P NMR, both with ^{1}H decoupling, were obtained in the FT mode on a JEOL FX-60 instrument. Mass spectral data were obtained on a Finnagin GC-MS system. 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 procedures described herein are typical of those used for the preparation of the new compounds in this study.

P_2N_2 Dimer 2. Carbon tetrachloride (20 mL, 0.20 mol) was added at 0 °C with stirring to a neat sample of phosphine **1**[6] (41.0 g, 0.103 mol). After being stirred for 6 h at 0 °C, the mixture was warmed to room temperature and the excess CCl_4 and other volatiles were removed under vacuum. Chloroform, Me_3SiCl, and a small amount of Me_3SiCCl_3 were identified in the volatile mixture by ^{1}H NMR. The remaining solid was dissolved with heating in hexane (~20 mL). Cooling to -15 °C afforded pale yellow crystals of dimer **2** (22.3 g, 69% yield; mp 145 °C): Major mass spectral peaks, *m/e* (relative intensity) 646 (8), 631 (14), 577 (11), 559 (20), 323 (12), 308 (54), 236 (18), 146 (11), 130 (27), 73 (100), 59 (22), 45 (32), 43 (16). Proton, ^{13}C, and ^{31}P NMR data are listed in Table I. Anal. Calcd: C, 59.39; H, 9.35; mol wt, 646. Found: C, 58.86; H, 9.26; mol wt, 681 (cryoscopic in benzene), 646 (mass spectrum).

Mesityl((trimethylsilyl)imino)((trimethylsilyl)methylene)phosphorane (3). A sample of dimer **2** (10.5 g, 0.016 mol) was heated under a dynamic vacuum in a flask on which was mounted a 10-cm distillation column. Some sublimation of **2** occurred along with the distillation of a colorless liquid (7.5 g; bp 91–93 °C (0.03 mm)) which was shown by NMR to be a mixture of **2** and **3**. After the mixture was left standing overnight at room temperature, dimer **2** crystallized, and the supernatant liquid was removed by means of a pipette. Analysis by NMR spectroscopy (Table I) confirmed that the liquid product was compound **3** (3.3 g, 31% yield) of good purity. Complete crystallization to dimer **2** occurred when the product was allowed to stand for several days at room temperature.

***P*-Mesityl-*P*-methoxy-*P*-((trimethylsilyl)methyl)-*N*-(trimethylsilyl)phosphinimine (4).** A freshly prepared sample of **3** (3.0 g, 9.3 mmol) was dissolved in CH_2Cl_2 (10 mL) and treated at 0 °C with anhydrous methanol (0.38 mL, 9.3 mmol). After being stirred for 20 min at 0 °C, the mixture was allowed to warm to room temperature. Solvent removal followed by distillation gave **4** as a colorless liquid (2.8 g, 85% yield; bp 89–90 °C (0.02 mm)). Anal. Calcd: C, 57.42; H, 9.64. Found: C, 57.57; H, 9.85.

***P*-Bromo-*P*-mesityl-*P*-((trimethylsilyl)methyl-*N*-(trimethylsilyl)phosphinimine (5).** With use of our previously reported procedure,[7] phosphine **1** (37.0 g, 93 mmol) in benzene (200 mL) was treated at 0 °C with a solution of bromine (16 g, 100 mmol) in benzene (75 mL). After being stirred at 0 °C for 4 h, the mixture was warmed to room temperature. Removal of solvent and Me_3SiBr under reduced pressure left compound **5** as a spectroscopically pure orange liquid. Attempted distillation caused partial decomposition so that the distillate (bp 124 °C (0.02 mm)) contained small amounts of **2** and **3** in addition to **5**. Heating of a neat sample of **5** at higher temperature (ca. 160 °C) resulted in extensive decomposition to a complex mixture of products.

***P*-Mesityl-*P*-((trimethylsilyl)methyl)-*P*-(2,2,2-trifluoroethoxy)-*N*-(trimethylsilyl)phosphinimine (6).** A sample of the *P*-bromophosphinimine **5** (15.9 g, 40 mmol) was prepared as described above and was dissolved in Et_2O (60 mL). A solution of $LiOCH_2CF_3$ (40 mmol, prepared from *n*-BuLi and CF_3CH_2OH) in Et_2O (30 mL) was then added with stirring at 0 °C. The mixture was warmed to room temperature and stirred overnight. Most of the Et_2O was removed under vacuum, and hexane (100 mL) was added. Filtration, followed by solvent removal, and distillation gave **6** as a colorless liquid (11.0 g, 65% yield; bp 95–96 °C (0.03 mm)). Anal. Calcd: C, 51.04; H, 7.85. Found: C, 52.04; H, 7.92.

PCPN Dimer 7. A sample of the P_2N_2 dimer **2** (~2 g) was heated in a sealed, evacuated ampule at 145 °C for 2 h. Quantitative conversion to the isomer **7** was indicated by NMR, expecially ^{31}P, spectroscopy (Table I). Analytically pure crystals of **7** were obtained by recrystallization from hexane at -15 °C: mass spectrum, *m/e* (relative intensity) 646 (4), 631 (9), 559 (10), 513 (12), 486 (17), 441 (15), 411 (10), 410 (20), 409 (10), 395 (12), 368 (10), 353 (4), 337 (10), 336 (15), 324 (5), 323 (5), 322 (5), 310 (5), 309 (13), 308 (15), 130 (20), 73 (100), 59 (20), 45 (32). Anal. Calcd: C, 59.39; H, 9.35; mol wt, 646. Found: C, 59.01; H, 9.31; mol wt, 646 (mass spectrum), 613 (cryoscopic in benzene). Compound **7** was also formed quantitatively when a freshly

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prepared sample of monomer **3** was heated at 145 °C for 2 h in a sealed tube. Heating of **7** under a dynamic vacuum, as described above for **2**, resulted only in sublimation of **7**; no formation of the monomer **3** was observed.

Acknowledgment. We thank the U.S. Office of Naval Research, the Robert A. Welch Foundation, and the U.S. Army Research Office for generous financial support of this research.

Registry No. **1**, 85336-22-7; **2**, 86563-48-6; **3**, 86563-49-7; **4**, 86563-50-0; **5**, 86563-51-1; **6**, 86563-52-2; **7**, 86563-53-3.

Complexes of Functional Phosphines. 6.[1] Five-Membered Palladium or Platinum Metallocycles Resulting from Nucleophilic Attack of α-Phosphino Carbanions on Organonitriles. Synthesis and Crystal Structure of *trans*-$\overline{\mathrm{Pt[Ph_2PC(COOC_2H_5)C(Ph)N}}\mathrm{H]_2}$ and $\mathrm{Pd(\overline{C\ N})Cl[\mu\text{-}Ph_2PCH_2C(\overline{NH)C(CN)PPh_2]P}d(\overline{C\ N})}$ [$\overline{\mathrm{C\ N}} = o\text{-}\mathrm{C_6H_4CH_2N(CH_3)_2}$]

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Received February 24, 1983

Reaction of 2 equiv of $\mathrm{Li(Ph_2PCHY)}$ (Y = CN, COOEt) with $\mathrm{PtCl_2(PhCN)_2}$ proceeds via nucleophilic attack on the coordinated nitriles afforded *trans*-$\overline{\mathrm{Pt[Ph_2PC(Y)C(Ph)N}}\mathrm{H]_2}$ (Y = CN, **1**; Y = COOEt, **2**). The crystal and molecular structure of **2** has been determined by X-ray diffraction methods. The compound crystallizes in the space group $P2_1/c$ of the monoclinic system with two formula units in a cell of dimensions a = 10.064 (3) Å, b = 23.272 (3) Å, c = 8.964 (1) Å, and β = 77.28 (1)°. The structure has been refined by least-squares methods to a final value of the conventional R factor of 0.047 on the basis of 3163 independent intensities. The molecule is centrosymmetric. The coordination about platinum is square planar, and there are only small deviations from planarity in the two metallocycles. The Pt–P bonds (2.280 (3) Å) and the Pt–N bonds (1.992 (8) Å) fall in a normal range; the shortness of the C(Ph)N bonds (1.32 (1) Å) suggests electron delocalization within the $\overset{\frown}{\mathrm{P\ N}}$ chelate. An isoelectronic unsaturated metallocycle was found in $\mathrm{Pd(\overline{C\ N})Cl[\mu\text{-}Ph_2PCH_2C(\overline{NH)C(CN)PPh_2]P}d(\overline{C\ N})}$ (**5**; $\overline{\mathrm{C\ N}} = o\text{-}\mathrm{C_6H_4CH_2N(CH_3)_2}$), the formation of which is interpreted as resulting from nucleophilic attack of the uncoordinated nitrile in the complex $\mathrm{(\overline{C\ N})Pd(Cl)Ph_2PCH_2CN}$ by "$\mathrm{(\overline{C\ N})Pd(Ph_2PCHCN)}$" (**6**), itself generated by reaction of $\mathrm{[(\overline{C\ N})Pd(\mu\text{-}Cl)]_2}$ with 2 equiv of $\mathrm{Li(Ph_2PCHCN)}$. The structure of complex $\mathbf{5}\cdot\mathrm{2CH_2Cl_2}$ was determined by single-crystal X-ray diffraction methods and refined to conventional R = 0.024. The compound crystallizes in the monoclinic crystal system of space group $P2_1$ with a = 10.234 (7) Å, b = 23.743 (10) Å, c = 10.663 (7) Å, β = 107.06 (2)°, and Z = 2. The molecule consists of two $\mathrm{(\overline{C\ N})Pd}$ cyclopalladated moieties linked by the bridging six-electron donor multifunctional anionic ligand μ-$\mathrm{[Ph_2P(1)CH_2C(NH^-)CH(CN)P(2)Ph_2]}$. This original ligand is P(1) bonded to Pd(1) [Pd(1)–P(1) = 2.255 (2) Å] and (P(2),N) bonded in a chelate manner to Pd(2) [Pd(2)–P(2) = 2.239 (2), Pd(2)–N(3) = 2.092 (6) Å]. The coordination about Pd(1) is completed by a Cl ligand [Pd(1)–Cl = 2.405 (2) Å], trans with respect to P(1). The $\overline{\mathrm{P(2)N}}$ unsaturated chelating moiety about Pd(2) is characterized by a short C(2)N(3) bond (1.30 (1) Å) resembling the situation found in **2**. The electron delocalization in **2** and **5** is related to the structural and spectroscopic data of the molecules. Spectroscopic (IR and ^{1}H, ^{13}C, and ^{31}P{^{1}H} NMR) data in solution are consistent with the solid-state structure of the new compounds.

Introduction

The coordination properties of functional phosphines $\mathrm{R_2P{\sim}Y}$ toward transition metals attract considerable interest because of the structural features, the reactivity, and catalytic applications of the resulting complexes.[3-12] One of the obvious parameters controlling the bonding modes of the ligand is the nature of the function Y. For example, we have recently shown that (diphenylphosphino)aceto-

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