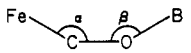
rings of these molecules that might reflect differences in intramolecular steric interactions. This boat conformation is shown schematically as **4** (side view). From the structures of **2** and **3**,



4

the following important comparisons can be made: (1) The Fe atom of **2** is displaced 0.19 Å further from the acyl [C(1), O(1), C(2), O(2)] plane than is the Fe atom of **3**. This result might reflect a steric repulsion between the bulky ring substituents of **2** and the ligands on the Fe atom greater than there is within **3**. (2) The values of the dihedral angles α and β of **2** are respectively 2.0 and 12°, larger than the corresponding angles in **3**. This result might indicate a steric repulsion between the axial F(2) atom and the axial C_5H_5 ligand of **2** greater than there is between the axial F(2) atom and the axial CO ligand of **3**.

Conclusion

The structure of a $[(\eta\text{-}C_5H_5)(OC)(\text{ferra }\beta\text{-diketonato})]BF_2$ complex that exhibits a carbonyl ligand stretching vibration at 2005 cm^{-1} reveals a boat-shaped ferra chelate ring having the C_5H_5 ligand in an axial site at the Fe atom. The alternate boat-shaped isomer having the CO ligand of the Fe atom in an axial site has been characterized previously. This isomer exhibits a carbonyl ligand stretching vibration at ca. 1960 cm^{-1}. Solution-phase and solid-state IR data now readily permit the determination of the identity and relative abundance of each boat-shaped isomer in this class of molecule for any combination of substituents on the ferra chelate ring.

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Registry No. **1**, 59125-00-7; **2**, 98778-63-3; boron trifluoride, 7637-07-2.

Supplementary Material Available: Lists of final atomic positional and thermal parameters before rounding, interatomic distances and angles, selected least-squares planes data, and final observed and calculated structure factors for complex **2** (28 pages). Ordering information is given on any current masthead page.

Contribution from the Laboratoire de Synthèse, Structure et Réactivité de Molécules Phosphorées, UA 454, and Laboratoire des Organométalliques, UA 477, Université Paul Sabatier, 31062 Toulouse Cedex, France

First Example of Prototropism in Iminobis(phosphines) Induced by Phosphorus Alkylation

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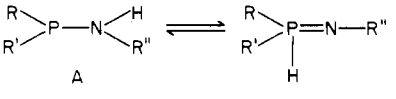
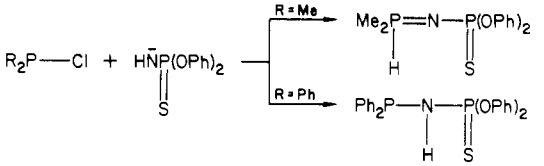
There are a few examples of tautomeric equilibrium in R_2PNHR systems. Depending on the nature of the R groups and on the temperature, the equilibrium is partially or totally shifted either to the aminophosphine form A or to the iminophosphorane form B.[2-8]

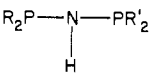


A B

The versatility of such a tautomerism has been illustrated by the attempted synthesis of ((dimethylphosphoranyl)amino)diphenoxyphosphine sulfide or ((diphenylphosphino)amino)diphenoxyphosphine sulfide:[2]



We report here a surprising prototropic rearrangement induced by alkylation of a phosphorus atom of iminobis(phosphines) **1** and **2** by triphenylcarbenium hexafluorophosphate or methyl trifluoromethanesulfonate. This type of reaction has permitted us to obtain unknown phosphoranimine–phosphonium salts which are potentially useful as synthetic reagents.



1, R = R' = Ph[9]
2, R = Ph, R' = *t*-Bu

Experimental Section

All experiments were performed under an atmosphere of dry argon or nitrogen. Dry and oxygen-free solvents were used at all times. $(C_6H_5)_2PCH_2P(C_6H_5)_2$, $(C_6H_5)_3C^+PF_6^-$, and $MeSO_3CF_3$ are commercially available and were used without further purification. Melting points are uncorrected. ^1H NMR spectra were recorded on a Varian T-60 or Bruker WM 250 spectrometer. ^1H chemical shifts are reported in ppm relative to Me_4Si as internal standard. ^{31}P NMR spectra were obtained on a Perkin-Elmer R 32 spectrometer at 36.4 MHz or Bruker WM 250 at 101.21 MHz. Downfield shifts are expressed with a positive sign, in ppm, relative to external 85% H_3PO_4. Infrared spectra were recorded on a Beckman IR 10 spectrometer, using polystyrene film for calibration. Mass spectra were obtained on a Ribermag R 10-10 E instrument.

Synthesis of $(t\text{-Bu})_2PNHPPH_2$ (2). Diphenylchlorophosphine (0.6 mL, 3.11 mmol) was added dropwise to a mixture of $(t\text{-Bu})_2PNH_2$ (0.5 g, 3.11 mmol) and triethylamine (0.43 mL, 3.11 mmol) in ether (2 mL) maintained at −70 °C. The reaction mixture was then stirred for 2 h at room temperature. After filtration and evaporation of the solvent under reduced pressure, the residue was recrystallized from toluene to give iminobis(phosphine) **2** as white crystals, mp 61 °C (0.8 g, 75% yield). IR (KBr): 980 (P–N) cm^{-1}. Anal. Calcd for $C_{20}H_{29}NP_2$: C, 69.54; H, 8.46; N, 4.06; P, 17.94. Found: C, 69.70; H, 8.40; N, 3.99; P, 17.78.

Reaction of 1 with Triphenylcarbenium Hexafluorophosphate. Triphenylcarbenium hexafluorophosphate (0.492 g, 1.27 mmol) in CH_2Cl_2 (4 mL) was added to a solution of iminobis(phosphine) **1** (0.490 g, 1.27 mmol) in CH_2Cl_2 (4 mL). After complete decoloration of the resulting mixture, the solvent was removed. Recrystallization of the residue from CH_3CN gave **3** as a white crystalline solid, mp 163–165 °C (0.835 g, 85% yield). IR (KBr): 1225 (P=N), 835 (P—N) cm^{-1}. Mass spectrum: *m/e* 628 (M^+). Anal. Calcd for $C_{43}H_{36}F_6NP_3$: C, 66.75; H, 4.69; N, 1.81; P, 12.01. Found: C, 66.38; H, 4.70; N, 1.79; P, 11.86.

Reaction of 1 with Methyl Trifluoromethanesulfonate. A mixture of **1** (0.492 g, 1.27 mmol) and methyl trifluoromethanesulfonate (0.208 g, 1.27 mmol) in CH_2Cl_2 (4 mL) was stirred for 1 h at room temperature. Evaporation of the solvent afforded **4** as an oil. IR (KBr): 1265 (P=N), 850 (P—N) cm^{-1}. Attempted crystallizations failed. However, a correct elemental analysis was obtained. Anal. Calcd for $C_{26}H_{24}F_3NO_3P_2S$: C, 56.83; H, 4.40; N, 2.55; P, 11.28. Found: C, 57.03; H, 4.52; N, 2.47; P, 11.02.

Reaction of 2 with Triphenylcarbenium Hexafluorophosphate. A so-

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Table I. ^1H and ^{31}P NMR Data[a,b]

compd	signal	^1H NMR, ppm	^{31}P NMR, ppm	coupling const, Hz
$[(CH_3)_3C]_2P_aNHP_bPh_2$ **2**	$C(CH_3)_3$	0.89 (d)	P_a, +84.5	$^3J_{PH}$ = 13.8
	NH	3.00 (b s)	P_b, +42	J_{PP} = 220
	Ph	7.30 (m)		
$Ph_2P_a(H)=N-P_b(CPh_3)Ph_2$, PF_6^- **3**	H	6.08 (d)	P_a, +7.50	$^1J_{PH}$ = 504
	Ph	7.15 (m)	P_b, +29.80	J_{PP} = 16.4
$Ph_2P_a(H)=N-P_b(CH_3)Ph_2$, $CF_3SO_3^-$ **4**	CH_3	2.40 (d)	P_a, +6.50	$^1J_{PH}$ = 509
	Ph	7.75 (m)	P_b, +25.80	$^2J_{PH}$ = 13
	H	8.60 (d)		J_{PP} = 16.9
$[(CH_3)_3C]_2P_a(H)=N-P_b(CPh_3)Ph_2$, PF_6^- **5**	$C(CH_3)_3$	1.01 (d)	P_a, +45.70	$^1J_{PH}$ = 456
	H	5.20 (d)	P_b, +20.80	$^3J_{P_aH}$ = 18
	Ph	7.45 (m)		J_{PP} = 31
$[(CH_3)_3C]_2P_a(H)=N-P_b(CH_3)Ph_2$, $CF_3SO_3^-$ **6**	$C(CH_3)_3$	1.18 (d)	P_a, +47.10	$^1J_{PH}$ = 444.2
	CH_3	2.32 (d)	P_b, +23.07	$^2J_{PH}$ = 11
	H	7.71 (d)		$^3J_{P_aH}$ = 15
	Ph	7.62 (m)		J_{PP} = 17.9
$[(CH_3)_3C]_2P_a(CH_3)-N=P_b(H)Ph_2$, $CF_3SO_3^-$ **6'**	$C(CH_3)_3$	1.25 (d)	P_a, +56.13	$^1J_{PH}$ = 498.1
	CH_3	1.52 (d)	P_b, +5.10	$^2J_{PH}$ = 11
	H	7.60 (d)		$^3J_{P_aH}$ = 13.8
	Ph	7.62 (m)		J_{PP} = 15
$Ph_2P_a(CH_3)-N(CH_3)-P_bPh_2$, $CF_3SO_3^-$ **8**	$N-CH_3$	2.98 (t)	P_a, 55.20 (d)	$^2J_{PH}$ = 12
	$P-CH_3$	3.03 (d)	P_b, 59.06 (d)	$^3J_{PH}$ = 10
	Ph	7.98 (m)		J_{PP} = 88.20
$Ph_2P(=O)-N(CH_3)-PPh_2$, $CF_3SO_3^-$ **9**	$P-CH_3$	2.92 (d)	58.16	$^2J_{PH}$ = 12
	$N-CH_3$	3.18 (t)		$^3J_{PH}$ = 10
	Ph	8.01 (m)		
$Ph_2P_aCH_2P_bPh_2$, $CF_3SO_3^-$ **11**	$P-CH_3$	2.53 (d)	P_a, +22 (d)	$^2J_{PCH_2}$ = 15
	$P-CH_2-P$	3.82 (d like)	P_b, −28.05 (d)	$^2J_{PCH_3}$ = 14
	Ph	7.60 (m)		J_{PP} = 58.5
$Ph_2P_aCH_2P_bPh_2$, PF_6^- **12**	$P-CH_2-P$	3.79 (d like)	P_a, +31.15	$^2J_{P_aH}$ = 11.9
	Ph	7.45 (m)	P_b, −24.50	$^2J_{P_bH}$ < 0.5
				J_{PP} = 59

[a] Spectra were recorded on a solution of the compound in CH_2Cl_2. [b] Abbreviations: d = doublet; t = triplet; s = singlet; m = unresolved multiplet; b s = broad singlet.

lution of triphenylcarbenium hexafluorophosphate (0.229 g, 0.58 mmol) in 2 mL of CH_2Cl_2 was added dropwise to a solution of iminobis(phosphine) **2** (0.200 g, 0.58 mmol) in 3 mL of CH_2Cl_2. After complete decoloration of the resulting mixture, the solvent was removed. Recrystallization of the residue from toluene gave **5** as white crystals, mp 175–177 °C (0.314 g, 70% yield). IR (KBr): 1300 (P=N), 840 (P—N) cm^{-1}. Mass spectrum: *m/e* 588 (M^+). Anal. Calcd for $C_{39}H_{44}F_6NP_3$: C, 63.84; H, 6.04; N, 1.91; P, 12.66. Found: C, 63.57; H, 6.12; N, 1.88; P, 12.41.

Reaction of 2 with Methyl Trifluoromethanesulfonate. To a solution of iminobis(phosphine) **2** (0.200 g, 0.58 mmol) in 2 mL of CH_2Cl_2 was added dropwise methyl trifluoromethanesulfonate (0.095 g, 0.58 mmol) at room temperature or at −10 °C. The mixture was stirred for 15 min. After evaporation of the solvent, a 20/80 mixture of **6** and **6'** was obtained as a white powder. Attempted separations of the two isomers failed. Anal. Calcd for $C_{22}H_{32}F_3NO_3P_2S$: C, 51.86; H, 6.33; N, 2.75; P, 12.16. Found: C, 52.11; H, 6.44; N, 2.73; P, 11.91.

Mono- and Dialkylation of 7 with Methyl Trifluoromethanesulfonate. To a solution of (methylimino)bis(phosphine) **7** (0.176 g, 0.441 mmol) in 2 mL of CH_2Cl_2 was added dropwise methyl trifluoromethanesulfonate (0.072 g, 0.441 mmol) at room temperature. After the usual workup and recrystallization from 50/50 hexane/toluene, **8** was obtained as a white powder, mp 42–43 °C (0.2 g, 80% yield). IR (KBr): 850 (P—N) cm^{-1}. Anal. Calcd for $C_{27}H_{26}F_3NO_3P_2S$: C, 57.55; H, 4.65; N, 2.49; P, 11.00. Found: C, 57.81; H, 4.72; N, 2.46; P, 10.72.

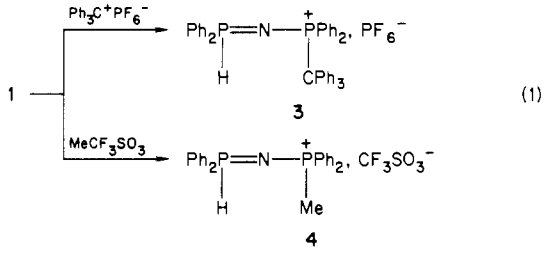
In the same way, but with an excess of $CH_3SO_3CF_3$ (0.290 g, 1.6 mmol), **9** was obtained as a deliquescent powder (0.2 g, 60% yield). IR (KBr): 865 (P—N) cm^{-1}. Anal. Calcd for $C_{29}H_{29}F_6NO_6S_2P_2$: C, 47.87; H, 4.02; N, 1.93; P, 8.52. Found: C, 47.98; H, 4.10; N, 1.86; P, 8.29.

Alkylation of Methylenebis(phosphine) (10). To a solution of **10** (0.700 g, 1.823 mmol) in CH_2Cl_2 (2 mL) was added dropwise, at 0 °C, a solution of triphenylcarbenium hexafluorophosphate (0.710 g, 1.823 mmol) in CH_2Cl_2 (3 mL). After complete decoloration of the resulting mixture, the solvent was removed. The residue was dissolved in dichloroethane (1 mL), and **12** was precipitated with toluene (2 mL). After filtration and several rinses with ether **12** was obtained as a white powder, mp 145 °C (0.85 g, 60% yield). Mass spectrum: *m/e* 399 (M^+). Anal. Calcd for $C_{27}H_{25}F_3O_3P_2S$: C, 59.12; H, 4.59; P, 11.30. Found: C, 59.40; H, 4.62; P, 11.10.

To a solution of **10** (0.325 g, 0.846 mmol) in CH_2Cl_2 (2 mL) was added dropwise, at 0 °C, methyl trifluoromethanesulfonate (0.139 g, 0.848 mmol). After the mixture was stirred for 2 h at room temperature, the solvent was removed. Recrystallization of the residue from a 1/1 hexane/toluene solution gave **11** as white crystals, mp 164 °C (0.418 g, 90% yield). Mass spectrum: *m/e* 627 (M^+). Anal. Calcd for $C_{44}H_{37}F_6P_3$: C, 68.39; H, 4.83; P, 12.03. Found: C, 68.52; H, 4.80; P, 11.89.

Results and Discussion

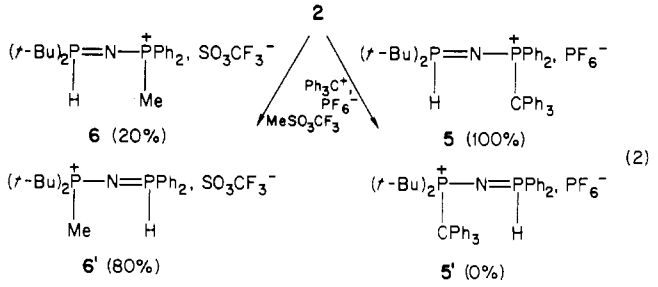
When iminobis(phosphine) **1** was allowed to react with triphenylcarbenium hexafluorophosphate and methyl trifluoromethanesulfonate, in acetonitrile solution, at room temperature, products **3** and **4** were formed in near-quantitative yield (eq 1).



(1)

They were readily identified by NMR [^1J(PH) = 504 and 509 Hz for **3** and **4**, respectively] and infrared [ν(P=N) = 1225 (**3**), 1265 (**4**) cm^{-1}] spectroscopy.

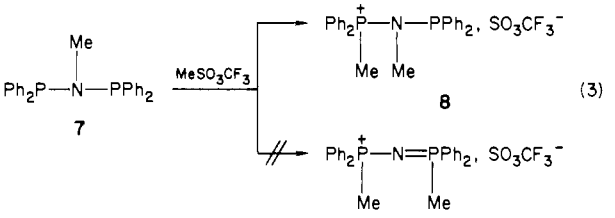
Interestingly, when triphenylcarbenium hexafluorophosphate was added to iminobis(phosphine) **2**, a single isomer **5** was obtained but, in contrast, the two possible isomers **6** and **6'** were formed in a 20/80 ratio when the methylating agent was used (eq 2). The



(2)

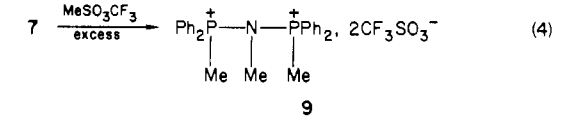
structures of the different isomers were assigned on the basis of ^{31}P chemical shifts in comparison with those of **3** and **4** (see Table I).

Since the isomeric ratio is directed by the alkylating agent used, it seems quite likely that the first step of the reaction involves the quaternization of a phosphorus atom. In the case of the trityl group, steric hindrance prevents the attack on the *tert*-butyl-substituted phosphorus atom and thus we only observed the formation of isomer **5**. On the other hand, the preferential attack of the methyl cation is probably directed by the difference in the nucleophilicities of the two phosphorus centers. To explain the prototropic rearrangement, one could postulate that the presence of a phosphorus cation decreases the basicity of the nitrogen atom and thus the proton migrates to the second phosphorus atom, which has become the more basic center of the molecule. This hypothesis has been confirmed with use of (methylimino)bis(phosphine) **7**. Indeed, alkylation of **7** with a stoichiometric amount of methyl trifluoromethanesulfonate led to **8** (eq 3).



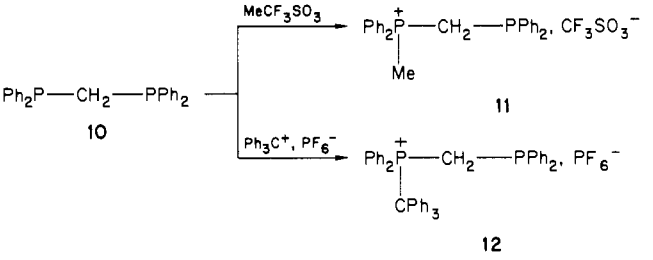
(3)

Note that an excess of methylating agent gave rise to the corresponding β-diphosphonium salt **9** (eq 4) and only a very few examples of such β-dications are known.[10]



(4)

Moreover, we have investigated the behavior of the analogous methylenebis(phosphine) **10** toward alkylating agents and we have only observed the formation of products **11** and **12** (eq 5).



(5)

This last result is in perfect agreement with the postulated mechanism since it is obvious that the acidity of the protons bonded to the carbon atom could not be sufficient for them to undergo prototropism.

Registry No. **1**, 2960-37-4; **2**, 100311-90-8; **3**, 100311-92-0; **4**, 100311-94-2; **5**, 100311-96-4; **6**, 100311-98-6; **6'**, 100312-08-1; **7**, 2960-43-2; **8**, 100312-00-3; **9**, 100312-02-5; **10**, 2071-20-7; **11**, 100312-04-7; **12**, 100312-06-9; Ph_2PCl, 1079-66-9; $(t\text{-}Bu)_2PNH_2$, 17858-28-5; Ph_3C^+,PF_6^-, 437-17-2; $MeOSO_2CF_3$, 333-27-7.

(10) See for example: Drach, B.; Zhumuro, I.; Kirsanov, A. *Zh. Obshch. Khim.* **1967**, *37*, 2524.