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Staudinger Reactions of Aminophosphines. Influence of Phosphorus Basicity

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Products from the title reaction between the aminophosphines $(Me_2N)_3P$, $MeC(CH_2NMe)_3P$ and $P(NMeNMe)_3P$ and the azides PhN_3, $(PhO)_2P(O)N_3$ and $Ph_2P(O)N_3$ have been isolated and characterized by nmr (^1H, ^{31}P), ir, uv and mass spectroscopy. Also characterized are the intermediate adducts produced by reaction of the above aminophosphines with PhN_3. The proton decoupled ^{31}P nmr spectra of the compounds $(PhO)_2P(O)N{=}P(NMeNMe)_3P{=}NP(O)(OPh)_2$ and $Ph_2P(O)N{=}P(NMeNMe)_3P{=}NP(O)Ph_2$ were analyzed using computer simulation techniques and are described as AA'XX' systems in contrast to the spectral interpretation given the latter compound in a recent report (reference 3). The relative thermal stabilities of the adducts $(Me_2N)_3P{=}N{-}N{=}NPh$ (**1a'**), $MeC(CH_2NMe)_3P{=}N{-}N{=}NPh$ (**2a'**), and $P(NMeNMe)_3P{=}N{-}N{=}NPh$ (**3d'**) were found to be **1a'** >> **2a'** ≈ **3d'**. This behavior is ascribed to phosphorus lone pair basicity which is enhanced by repulsive interactions with a nitrogen lone pair in **1a'** but not in **2a'** or **3d'** because of molecular constraint. The uv spectra of the compounds $(Me_2N)_3P{=}NPh$, $MeC(CH_2NMe)_3P{=}NPh$, $PhN{=}P(NMeNMe)_3P{=}NPh$ and $P(NMeNMe)_3P{=}NPh$ are discussed in terms of the diminished σ basicity and greater π acidity of the bicyclic aminophosphines.

Introduction

Among the recent publications on the Staudinger reaction[1] (eq 1) between aminophosphines and organic azides[2-5] is the

$$R'N_3 + PR_3 \rightarrow R'N_3PR_3 \xrightarrow{-N_2} R'NPR_3 \tag{1}$$

report[3] that the bicyclic compound **3c** displays an effective isomerism as evidenced by the apparent pair of doublets which make up each branch of the proton-decoupled ^{31}P NMR spectrum. While the precise nature of this phenomenon was not ascertained, the possibility of rotational isomerization was not ruled out. Our interest in the electronic environment of bicyclic phosphorus compounds[6-8] led us to determine whether a similar phenomenon might be manifested in the proton NMR spectrum of **2a** at low temperature. Our failure to observe such an effect in this simpler molecule paralleled the findings of Goldwhite et al.[4] for compound **1a** and prompted us to reinvestigate the proton-decoupled ^{31}P NMR spectrum of **3c** with the result that a different conclusion has been drawn.

1	$(Me_2N)_3P$
1a	$(Me_2N)_3P{=}NPh$
1a'	$(Me_2N)_3P{=}NN{=}NPh$
1b	$(Me_2N)_3P{=}NP(O)(OPh)_2$
1c	$(Me_2N)_3P{=}NP(O)Ph_2$
2	$MeC(CH_2NMe)_3P$
2a	$MeC(CH_2NMe)_3P{=}NPh$
2a'	$MeC(CH_2NMe)_3P{=}NN{=}NPh$
2b	$MeC(CH_2NMe)_3P{=}NP(O)(OPh)_2$
2c	$MeC(CH_2NMe)_3P{=}NP(O)Ph_2$
3	$P(NMeNMe)_3P$
3a	$PhN{=}P(NMeNMe)_3P{=}NPh$
3b	$(PhO)_2P(O)N{=}P(NMeNMe)_3P{=}NP(O)(OPh)_2$
3c	$Ph_2P(O)N{=}P(NMeNMe)_3P{=}NP(O)Ph_2$
3d	$P(NMeNMe)_3P{=}NPh$
3d'	$P(NMeNMe)_3P{=}NN{=}NPh$

In the present work we also describe the preparation and properties of the new imido products **1b**, **1c**, **2a**, **2b**, **2c**, **3b**, and **3d** of Staudinger reactions between aminophosphines **1**–**3** and phenyl azide, PhN_3, diphenylphosphoryl azide, $(PhO)_2P(O)N_3$, and diphenylphosphinyl azide, $Ph_2P(O)N_3$. Also described are the new isolable azido adducts **2a'** and **3d'** obtained from the reactions of the aminophosphines **2** and **3** with phenyl azide.

Some recent work with the adducts produced in the first step of the Staudinger reaction has been concerned mainly with the kinetics of their decomposition[9,10] or with establishing their structure.[9,11] The idea that phosphorus basicity plays a large role in determining the stability of such adducts[9] led us to investigate qualitatively adducts **1a'**, **2a'**, and **3d'** with respect to their relative thermal stability.

Experimental Section

All solvents used were reagent grade and were stored over 4A molecular sieves. Prior to use the solvents were saturated with dry nitrogen. All reactions were carried out using Schlenk techniques under a dry nitrogen atmosphere with magnetic stirring. All recrystallizations were also done under nitrogen. Liquid reactants were handled using syringes while solids were manipulated in a nitrogen-filled drybag. Reactants **2**[12] and **3**[13] as well as phenyl azide[14] were prepared as described in the literature. Reactants **1**, diphenylphosphoryl azide, and diphenylphosphinyl azide were purchased from Aldrich Chemical Co., Inc. and used as received.

Melting points were obtained in open capillaries on a Thomas Uni-Melt apparatus and are uncorrected.

Infrared spectra were recorded with KBr pellets (±2 cm^{-1}) (except for compound **1a**) on a Beckman IR 4250 spectrophotometer. The infrared spectrum of compound **1a** was recorded as a smear between NaCl and polyethylene disks. Ultraviolet spectra were recorded on a Cary 14 spectrophotometer and were deconvoluted using LOGFIT.[15] Proton NMR spectra were obtained with a Varian HA-100 spectrometer on $CDCl_3$ solutions using TMS as an internal standard and lock. ^{31}P NMR spectra were obtained with a Bruker HX-90 spectrometer operating at 36.434 MHz in the Fourier transform mode locked on the ^2H resonance of the $CDCl_3$ sample solutions, and 85% H_3PO_4 in 1-mm capillaries was used as an external standard. The spectrometer was interfaced with a Nicolet Instruments 1080 minicomputer system. Mass spectra were obtained on an AEI MS902 high-resolution mass spectrometer, and exact masses were determined by utilizing the fragmentation patterns of known standards.

^{31}P NMR spectral calculations were executed with ITRCAL,[16] an implementation of the LAOCN3 algorithm on a minicomputer, for the laboratory real-time analysis of experimentally obtained spectra.

Compounds **1a**,[17] **3a**,[3] and **3c**[3] were prepared as previously described. Compound **3a** was recrystallized from boiling benzene in 50% yield; mp 253° (lit.[3] mp 243–244° dec). Compound **3c** was recrystallized from a boiling 2:1 toluene–ethyl acetate solution in 59% yield; mp 283° dec (lit.[3] mp 285–286° dec). The infrared spectrum of compound **1a** is as follows: 3065 (w), 3000 (m), 2910 (s), 2880 (s), 2840 (m), 2790 (m), 1590 (vs), 1557 (m), 1495 (vs), 1358 (vs, b), 1285 (s), 1190 (s), 1165 (m), 1063 (s), 972 (vs, b), 745 (m), 729 (s), 687 (m), 627 (m), 508 (m), 466 (m) cm^{-1}.

$(Me_2N)_3PNP(O)(OPh)_2$, 1b. A solution of 1.90 ml (8.82 mmol) of diphenylphosphoryl azide in 10 ml of toluene was added in ca. 1-ml increments over 20 min to a solution of 1.63 ml (10.0 mmol) of **1** in 10 ml of toluene at room temperature. Each addition to the colorless solution was accompanied by a yellow coloration and vigorous gas evolution. The solution became colorless again as the gas evolution subsided. During the reaction period the temperature of the solution rose noticeably. After addition was complete, the solvent was removed under vacuum leaving a clear yellow oil which, when triturated with pentane and cooled to −78°, changed into a white solid. Recrystallization from a boiling 3:1 hexane–benzene solution yielded 2.19 g (60%) of the product, mp 44–46°. *m/e* for P^+: 410.1621 ± 0.0021, exptl; 410.1637, calcd. Ir: 3060 (w), 3000 (w), 2920 (m), 2890 (m), 2795 (w), 1592 (m), 1489 (s), 1454 (m), 1400 (s), 1300 (s), 1240 (s), 1200 (vs, b), 1160 (s), 1067 (m), 1023 (m), 980 (s, b), 925 (s), 913 (s), 892 (vs), 766 (s), 742 (s), 714 (m), 691 (s), 617 (m), 585 (m), 567 (m), 530 (m), 511 (s), 474 (s), 457 (m) cm^{-1}.

(Me$_2$N)$_3$PNP(O)Ph$_2$, 1c. The solution formed by adding 0.81 ml (5.0 mmol) of **1** and 0.98 ml (5.0 mmol) of diphenylphosphinyl azide to 20 ml of benzene at room temperature was refluxed for 3 hr. The gas evolution which began upon heating subsided after about 5 min. The clear solution was cooled to room temperature and the solvent was removed under vacuum. After addition of 30 ml of heptane to the remaining yellow oil, the mixture was refluxed for 1 min. Upon cooling of the mixture to 0°, the white crystalline product (0.64 g, 35% yield) precipitated from the solution; mp 77–78°. *m/e* for P$^+$: 378.1742 ± 0.0019, exptl; 378.1738, calcd. Ir: 3070 (w), 3050 (w), 3000 (w), 2920 (m), 2890 (m), 2845 (m), 2800 (m), 1638 (m, b), 1479 (m), 1453 (m), 1434 (s), 1288 (vs, b), 1256 (vs, b), 1185 (vs, b), 1170 (vs, b), 1115 (s), 1102 (m), 1062 (m), 979 (vs), 809 (m), 741 (s), 712 (s), 693 (vs), 596 (m, b), 547 (vs), 490 (m), 465 (m), 449 (m) cm^{-1}.

MeC(CH$_2$NMe)$_3$PNPh, 2a. As in the above preparations, 1.00 ml (5.61 mmol) of **2** and 0.61 ml (5.6 mmol) of phenyl azide were added to 10 ml of toluene at room temperature and the solution was heated to 80° for 2 hr. After cooling of the solution to room temperature, the solvent was removed under vacuum, 15 ml of heptane was added to the remaining light yellow solid, and the mixture was refluxed for 1 min. Cooling the solution to room temperature and adding 15 ml of pentane caused precipitation of a pale yellow solid which was filtered, washed twice with pentane, and dried in vacuo yielding 1.20 g (78%) of the product, mp 68–69°. *m/e* for P$^+$: 278.1663 ± 0.0014, exptl; 278.1660, calcd. Ir: 3070 (w), 3010 (w), 2990 (w), 2985 (w), 2930 (m), 2855 (m, b), 1590 (s), 1563 (m), 1498 (vs), 1377 (vs), 1255 (m), 1208 (m), 1164 (s), 1137 (s), 1115 (s), 1090 (vs), 1068 (m), 1017 (m), 995 (m), 969 (s), 830 (m), 777 (m), 758 (s), 720 (vs, b), 691 (m), 657 (m), 534 (m), 508 (m), 470 (m) cm^{-1}.

MeC(CH$_2$NMe)$_3$PNP(O)(OPh)$_2$, 2b. A solution composed of 1.00 ml (5.61 mmol) of **2**, 1.21 ml (5.61 mmol) of diphenylphosphoryl azide, and 10 ml of toluene was heated to 80° for 1 hr. After cooling of the solution to room temperature, the addition of 30 ml of hexane caused the precipitation of a white solid. This mixture was heated to dissolve the solid, cooled to room temperature, and then placed in a −78° bath. The solid white precipitate was then filtered, washed twice with 25 ml of pentane, and dried in vacuo to yield 2.35 g (97%) of the product, mp 99–101°. *m/e* for P$^+$: 434.1622 ± 0.0022, exptl; 434.1637, calcd. Ir: 3060 (w), 3015 (w), 2970 (m), 2920 (m), 2870 (m), 2850 (m), 1598 (m), 1486 (vs), 1462 (m), 1435 (m), 1395 (m), 1350 (vs, b), 1247 (s), 1210 (vs, b), 1164 (s), 1125 (s), 1026 (m), 1018 (m), 1005 (m), 998 (m), 970 (m), 931 (vs), 909 (vs), 767 (vs), 737 (s), 728 (s), 689 (m), 640 (m), 578 (m), 522 (s), 483 (m), 447 (m) cm^{-1}.

MeC(CH$_2$NMe)$_3$PNP(O)Ph$_2$, 2c. A solution composed of 0.89 ml (5.0 mmol) of **2**, 0.98 ml (5.0 mmol) of diphenylphosphinyl azide, and 15 ml of toluene was heated to 80° for 3 hr. The precipitate obtained by cooling the solution to room temperature and then to −78° was collected and recrystallized upon cooling a boiling 10:1 pentane–toluene solution of the material to −10°. The off-white solid was filtered, washed with pentane, and dried in vacuo to yield 1.69 g (85%) of the product, mp 136–138°. *m/e* for P$^+$: 402.1741 ± 0.0020, exptl; 402.1738, calcd. Ir: 3070 (w), 2930 (m), 2860 (m), 1587 (w), 1468 (m), 1434 (m), 1325 (vs, b), 1215 (m), 1180 (s), 1114 (s), 993 (m), 966 (m), 735 (s), 712 (s), 690 (vs), 614 (m, b), 546 (vs), 527 (s), 490 (m), 464 (m), 426 (m) cm^{-1}.

(PhO)$_2$P(O)NP(NMeNMe)$_3$PNP(O)(OPh)$_2$, 3b. A solution of 1.18 g (5.00 mmol) of **3** and 2.16 ml (10.0 mmol) of diphenylphosphoryl azide in 15 ml of toluene was heated to 80° for 2 hr. Cooling the solution to room temperature and then to −78° caused a white solid to precipitate. Recrystallization from ethyl acetate followed by several washings with hexane and drying in vacuo yielded 2.90 g (80%) of the product, mp 118–119°. *m/e* for P$^+$: 730.1856 ± 0.0037, exptl; 730.1873, calcd. Ir: 3060 (w), 3000 (w), 2970 (w), 2930 (w), 1732 (m), 1590 (s), 1484 (s), 1455 (m), 1402 (s), 1357 (vs), 1250 (s), 1198 (vs), 1054 (m), 1020 (m), 978 (s), 929 (s), 911 (vs), 848 (s), 770 (s), 759 (s), 718 (s), 683 (s), 672 (s), 580 (m), 563 (m), 526 (s), 509 (s), 497 (s), 486 (s) cm^{-1}.

P(NMeNMe)$_3$PNPh, 3d. Upon addition of 0.57 g of compound **3d**' (see below) to 15 ml of toluene, gas bubbles began to form on the surface of the solid particles. The solid dissolved upon stirring at room temperature whereupon the solution was heated to 50° for 3 hr. Cooling the solution to room temperature and adding 35 ml of pentane caused a white solid to precipitate slowly. The mixture was further cooled to −78° and the solid produced was filtered, washed with pentane, and dried in vacuo yielding 0.18 g (34%) of the product, mp 123–125°. *m/e* for P$^+$: 327.1486 ± 0.0017, exptl; 327.1490, calcd. Ir: 3075 (w), 3050 (w), 2950 (m), 2930 (m), 2885 (m), 2780 (w), 1600 (s), 1507 (vs), 1477 (w), 1460 (w), 1431 (m), 1380 (vs), 1228 (m), 1185 (m), 1096 (s), 1050 (s), 933 (s), 787 (s), 752 (s), 729 (m), 693 (s), 634 (s), 598 (m), 553 (w), 498 (s) cm^{-1}.

Alternatively and more practically, compound **3a** could be synthesized from compound **3** and phenyl azide. A solution of 1.06 g (4.50 mmol) of **3** and 0.49 ml (4.5 mmol) of phenyl azide in 10 ml of benzene was heated to 40° for 2 hr and then cooled to room temperature. Filtering the solution and removing the solvent under vacuum gave a white solid. Unreacted **3** was sublimed out of the mixture at 65° at 0.1 Torr. The sublimate (0.284 g) was shown by ^{1}H NMR integration to be composed of about 2:1 **3d**–**3**. The remaining white solid (1.065 g) was shown to be about 20:1 **3d**–**3a** by the same method. The yield of the reaction was thus 9% **3**, 86% **3d**, and 5% **3a**.

(Me$_2$N)$_3$PN$_3$Ph, 1a'. To a solution of 0.68 ml (6.2 mmol) of phenyl azide in 25 ml of hexane at 0° was added dropwise 1.00 ml (6.15 mmol) of **1**. A bright yellow precipitate formed immediately upon adding each drop. The mixture was cooled to −78° and the solid was filtered, washed twice with hexane, and dried in vacuo yielding 1.42 g (82%) of product, mp 91–92°. *m/e* for P$^+$: 254.1659 ± 0.0013, exptl; 254.1660, calcd. Ir: 3070 (w), 3050 (w), 3010 (w), 2995 (w), 2910 (m), 2890 (m), 2835 (w), 2810 (w), 1590 (m), 1480 (s), 1456 (m), 1386 (s), 1296 (s), 1233 (s), 1185 (s), 1164 (vs), 1140 (vs), 1065 (s), 1005 (vs), 988 (vs, b), 829 (s), 772 (m), 753 (s), 737 (s), 693 (s), 664 (s), 596 (m), 545 (m), 521 (m), 464 (m) cm^{-1}.

MeC(CH$_2$NMe)$_3$PN$_3$Ph, 2a'. To a solution of 1.00 ml (5.61 mmol) of **2** in 25 ml of pentane at 0° was added dropwise 0.62 ml (5.6 mmol) of phenyl azide. The solution became turbid but cleared after 5 min. The solvent was removed under vacuum at 0° and the remaining yellow liquid was cooled at −10° for 4 days. During this time, a bright yellow solid formed which was washed with cold pentane, filtered, and dried in vacuo at 0° yielding 1.09 g (64%) of product, mp 82–83° dec. Ir: 3070 (w), 2950 (m), 2870 (m), 2815 (w), 1590 (w), 1478 (m), 1454 (m), 1403 (vs), 1391 (m), 1351 (m), 1227 (s), 1160 (s), 1140 (vs, b), 1068 (m), 1027 (vs), 990 (s), 975 (s), 962 (s), 854 (s), 770 (m), 740 (s), 694 (m), 607 (m), 556 (m), 538 (m), 527 (m), 468 (m), 449 (m) cm^{-1}.

P(NMeNMe)$_3$PN$_3$Ph, 3d'. To a solution of 0.70 g (3.0 mmol) of **3** in 25 ml of diethyl ether at 0° was added dropwise 0.65 ml (5.9 mmol) of phenyl azide. The solution was kept at −5° for 14 hr and filtered while cold. The solvent was removed under vacuum leaving a light yellow solid which was washed with hexane, filtered, and dried in vacuo. Proton NMR spectral analysis indicated the presence of compound **3d**' only; yield 0.57 g (54%); mp 83–85° dec. Ir: 3070 (w), 3020 (w), 2960 (w), 2940 (m), 2930 (m), 2885 (m), 2785 (w), 1592 (w), 1478 (m), 1462 (s), 1429 (m), 1414 (s), 1227 (vs), 1164 (vs), 1144 (vs), 1095 (m) 1066 (m), 1047 (s), 1024 (s), 930 (vs, b), 839 (s), 758 (s), 743 (m), 688 (m), 630 (s, b), 589 (m), 544 (w), 520 (w), 492 (s), 436 (w) cm^{-1}. The same reaction in either hexane or acetonitrile gave only **3d**' in yields of 27% and 95%, respectively.

Compounds **2a**' and **3d**' were unstable in the mass spectrometer, decomposing on the heated probe (60°) to give nitrogen gas and the compounds **2a** and **3d**, respectively, which were identified by their parent ions.

Results and Discussion

^{31}P NMR Assignments. The upfield shift of the ^{31}P resonances from the aminophosphines **1**–**3** to the corresponding aminophosphine oxides is also seen in the imides produced in the Staudinger reaction (Table I) and this is consistent with oxidation of the phosphorus. The assignments were based mainly on the fewer proton couplings expected in the proton-undecoupled ^{31}P NMR spectra of the >P(O)N phosphorus (there being at most only four protons within a distance of three bonds) compared to those of the amino-bound phosphorus which in all cases was only three bonds removed from at least nine equivalent protons. The proton-undecoupled

Table I. ^{31}P NMR Chemical Shifts and P–P Coupling Constants[a]

Compd		No.	$\delta(P(N<)_3)$	$\delta(>P(O)N)$	$^2J_{PP}$ ($^3J_{PP}$)[b]
$(Me_2N)_3PY$	Y = lone pair	**1**	−122.0[c]		
	$Y = N_3Ph$	**1a′**	−42.8 (−41.2)[d]		
	Y = NPh	**1a**	−19.5		
	$Y = NP(O)(OPh)_2$	**1b**	−23.5	+11.3	64.5
	$Y = NP(O)Ph_2$	**1c**	−25.1	−9.2	22.2
	Y = O		−24.8		
$MeC(CH_2NMe)_3PY$	Y = lone pair	**2**	−83.5[c]		
	$Y = N_3Ph$	**2a′**	−33.7		
	Y = NPh	**2a**	−11.5		
	$Y = NP(O)(OPh)_2$	**2b** ·	−13.8	+12.0	74.4
	$Y = NP(O)Ph_2$	**2c**	−14.6	−10.9	24.4
	Y = O		−18.2[c]		
$YP(NMeNMe)_3PZ$	Y = Z = lone pair	**3**	−107.4[c]		
	Y = Z = NPh	**3a**	+6.0 (+6.6)[e]		
	$Y = Z = NP(O)(OPh)_2$	**3b**	−1.0[f]	+13.9[f]	74.0 (107.5)[f]
	$Y = Z = NP(O)Ph_2$	**3c**	−2.5[f]	−12.2[f]	19.9 (110.5)[f]
	Y = Z = O		−8.6		
	Y = lone pair $Z = N_3Ph$	**3d′**	*g*		(74.4)
	Y = lone pair Z = NPh	**3d**	*h*		(78.2)

[a] Samples were contained in 10-mm o.d. tubes at 25° except as noted. δ in ppm; J_{PP} in Hz. [b] J_{PP}: ±1.1 Hz. [c] In C_6D_6; this work. [d] Reference 5. [e] Reference 3. [f] Calculated values from ITRCAL (see text); values of $^5J_{PP}$ and $^7J_{PP}$ were much less than the experimental error and are assumed to be 0. The rms error for **3b** is 0.30 while that for **3c** is 0.63. [g] $\delta(^{31}P^{III})$ −102.0, $\delta(^{31}P^{V})$ −25.4. [h] $\delta(^{31}P^{III})$ −96.8, $\delta(^{31}P^{V})$ +1.8.

Table II. ^{1}H NMR Chemical Shifts and P–H Coupling Constants[a]

Compd	$\delta(^1H_{NMe})$	$\delta(^1H_{NCH_2})$ ($\delta(^1H_{CMe})$)	$\delta(^1H_{C_6H_5})$[b]	$^3J_{PNCH_3}$ ($^3J_{PNCH_2}$) [$^3J_{PH} + {}^4J_{PH}$][c]
1	2.48			9.0
1a′	2.75[d]		7.30	9.0
1a	2.67[e]		6.86	9.5
1b	2.60		7.10	10.0
1c	2.62		7.86, 7.32	10.0
2	2.52	2.56 (0.83)		17.0 (3.5)
2a′	2.69	3.14 (0.96)	7.34	12.0 (7.0)
2a	2.62	3.08 (0.91)	6.90	12.0 (7.0)
2b	2.59	3.01 (0.87)	7.16	13.0 (7.0)
2c	2.63	3.04 (0.88)	7.85, 7.32	13.5 (7.0)
3	2.83			[15.0]
3a	2.98		7.05	[11.0]
3b	2.85		7.24	[12.0]
3c	2.92		7.78, 7.38	[12.0]
3d′	*f*		7.38	
3d	*g*		6.84	

[a] Probe temperature 34°; J_{PH} values are within ±0.02 Hz; δ in ppm. [b] All C_6H_5 resonances appeared as complex multiplets. [c] Resonances appeared as pseudotriplets. [d] Reference 5 reports $\delta(^1H_{NMe})$ 2.60, $\delta(^1H_{C_6H_5})$ 6.8–7.2, and $^3J_{PH} = 10.0$ Hz for neat liquid. [e] Reference 5 reports $\delta(^1H_{NMe})$ 2.30, $\delta(^1H_{C_6H_5})$ 6.1–6.9, and $^3J_{PH} = 9.8$ Hz for neat liquid. [f] $P(NMe_bNMe_a)_3P{=}N_3Ph$: $\delta(^1H_{Me_a})$ 2.94 (d, 10.3 Hz), $\delta(^1H_{Me_b})$ 2.90 (doublet of doublets; 14.5, 1.5 Hz). [g] $P(NMe_bNMe_a)_3P{=}NPh$: $\delta(^1H_{Me_a})$ 2.95 (d, 10.0 Hz), $\delta(^1H_{Me_b})$ 2.95 (doublet of doublets; 14.5, 1.5 Hz).

^{31}P NMR spectrum of **2c** in Figure 1a is illustrative of this point while the decoupled spectrum is shown in Figure 1b. Table II contains the chemical shifts of the proton resonances and the magnitudes of the measurable P–H couplings. Also of aid in the ^{31}P NMR assignments was the expectation that the chemical shift of the $P(N<)_3$ phosphorus would not change appreciably among the imido derivatives and this is apparent from a comparison of compounds **1a**, **2a**, and **3a** (where the assignment is unambiguous) to the respective **b** and **c** analogues. The ^{31}P chemical shifts for the $P(N<)_3$ phosphorus atoms in the imido compounds **1a–c** and **2a–c** and to a lesser extent **3a–d** are similar to those of the corresponding aminophosphine oxides and probably reflect the isoelectronic character of the P═O and P═NR links.[4] The presence of the additional nitrogens in the phenyl azido groups in **1a′**, **2a′**, and **3d′** apparently causes a smaller upfield shift of the $P(N<)_3$ phosphorus resonance, however.

The magnitudes of $^2J_{PP}$ are about three times larger for the diphenylphosphoryl imido derivatives (**1b**, **2b**, **3b**) than for the diphenylphosphinyl imido derivatives (**1c**, **2c**, **3c**). This is reasonably ascribed to the increased s character in the P–N bond of the >P(O)N moiety and the higher positive charge on this phorphorus, both effects being induced by the greater electron-withdrawing power of the phenoxy relative to the phenyl group.

The proton decoupled ^{31}P spectrum of **3b** (Figure 2a) reveals six peaks in each branch which is typical of an AA′XX′ system in which both $J_{AX'}$ and $J_{XX'}$ are near zero. Inspection of the pertinent equations governing the AA′XX′ system[18] allows the determination of $^3J_{PP}$ ($J_{AA'}$) and $^2J_{PP}$ (J_{AX}) provided that $^5J_{PP}$ ($J_{AX'}$) and $^7J_{PP}$ ($J_{XX'}$) are zero. The values which were calculated by this method for compound **3b** closely approximate those obtained by calculation of the spectrum using the program ITRCAL, which utilizes the method of Castellano and Bothner-By.[19] In addition to the experimentally observed chemical shifts for the phosphorus atoms, estimates of the four coupling constants were necessary for the program input. The $^2J_{PP}$ coupling value for **2b** was used for **3b** while the 140-Hz coupling observed earlier in our laboratories for $O{=}P(OCH_2)_3P{=}O$[20] was taken to approximate $^3J_{PP}$. That substantial

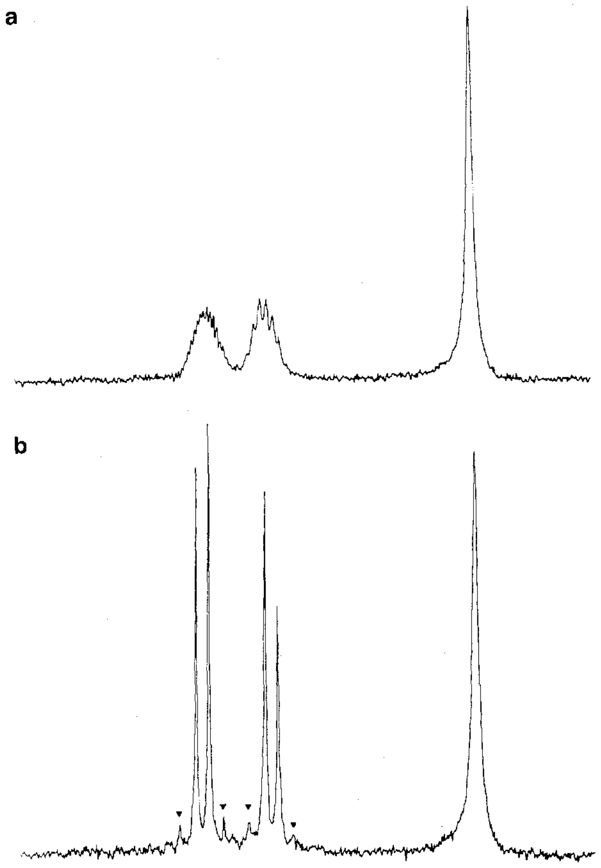

Figure 1. (a) Proton-undecoupled ^{31}P NMR spectrum of compound **2c**. The fine structure of the downfield doublet arises from the greater number of protons coupled to the $P(N<)_3$ phosphorus compared to the $>P(O)N$ phosphorus. (b) Proton-decoupled ^{31}P NMR spectrum of compound **2c**. Spinning side bands are marked with ▼.

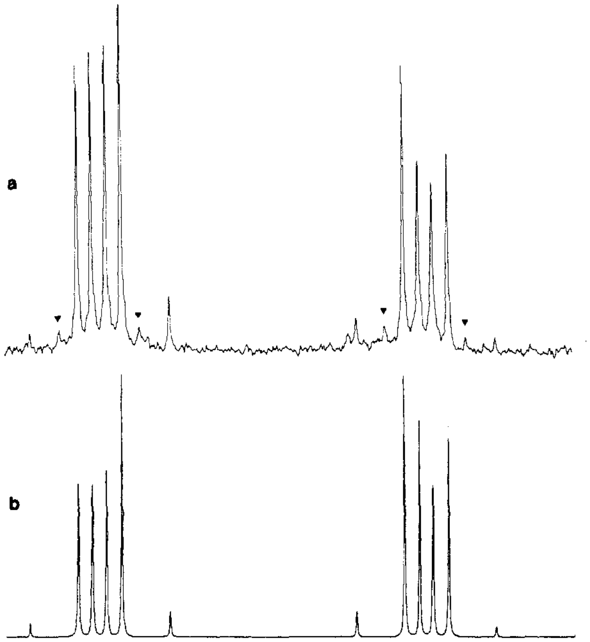

Figure 2. (a) Proton-decoupled ^{31}P NMR spectrum of compound **3b**. The peaks marked with ▼ are spinning side bands as determined by varying the sample spin rate. (b) ITRCAL-generated ^{31}P NMR spectrum of compound **3b**.

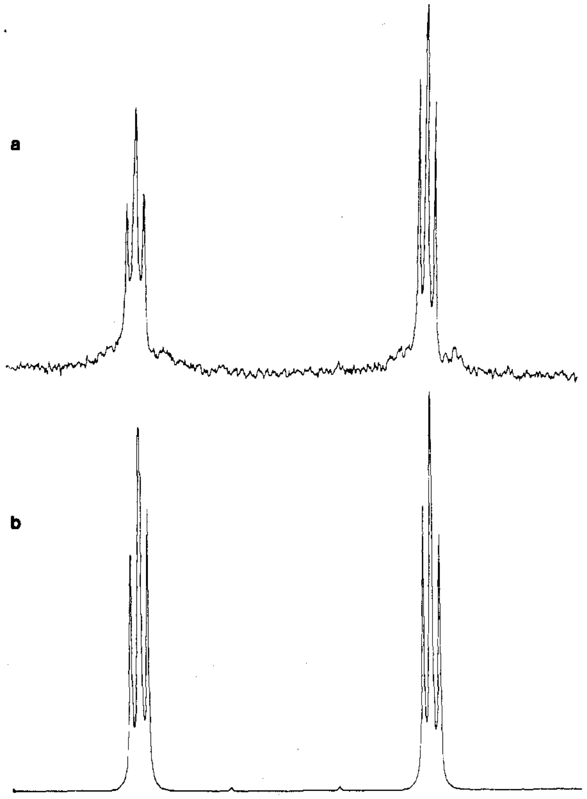

Figure 3. (a) Proton-decoupled ^{31}P NMR spectrum of compound **3c**. The outermost lines are not observable above the spectrum noise and the separation between the central two lines is not resolvable. (b) ITRCAL-generated ^{31}P NMR spectrum of compound **3c**. Noteworthy are the small outermost lines.

coupling is to be expected for such bridgehead phosphorus atoms is also suggested by the pseudotriplet observed in the ^{1}H NMR spectra of **3**, **3a–c**, and the bis(chalcogenide)[21] and the bis(triethylalane)[22] derivatives of **3**. The relative contributions of through-bond and direct through-space interactions[22,23] are not possible to assess presently. Values of $^{5}J_{PP}$ and $^{7}J_{PP}$ were initially set at 0 and the calculated values (Table I) confirmed that they were indeed negligible. The chemical shifts, coupling constants, and rms error are given in Table I while the calculated spectrum of **3b** shown in Figure 2b is seen to be well matched with the experimentally obtained spectrum (Figure 2a).

Using the value of $^{2}J_{PP}$ obtained from **2c** and the $^{3}J_{PP}$ value found for **3b** as initial values of the coupling constants in **3c** (with the long-range couplings set at 0) the two- and three-bond P–P couplings shown in Table I were calculated. The agreement of the calculated and the observed spectrum is seen to be excellent in Figure 3. The overlap in the central two lines of each branch leading to the apparent triplets stems from the larger difference between $^{3}J_{PP}$ and $^{2}J_{PP}$ in **3c** than in **3b**. The theoretical difference in transition frequencies for the two innermost lines is 1.8 Hz in **3c** (which is unresolvable due to line broadening) and 23.0 Hz in **3b** calculated from the previously mentioned equations.[18] Moreover, as the difference between $^{3}J_{PP}$ and $^{2}J_{PP}$ increases, the intensities of the two innermost lines increase and the intensities of the two outermost lines decrease. In **3c**, the intensities of these two outermost lines are so small (Figure 3b) that they are undetectable above the experimental spectrum noise (Figure 3a). The near-equality in $^{3}J_{PP}$ for **3b** and **3c** is indicative of the expected similarity in the electronic environments of the two caged molecules.

We therefore conclude that it is not necessary to postulate the presence of any unusual steric or electronic phenomena in order to rationalize the ^{31}P NMR spectra of compounds **3b** and **3c**. A factor in the earlier interpretation[3] of the ^{31}P spectrum of **3c** was the absence of the undetectable outer lines,

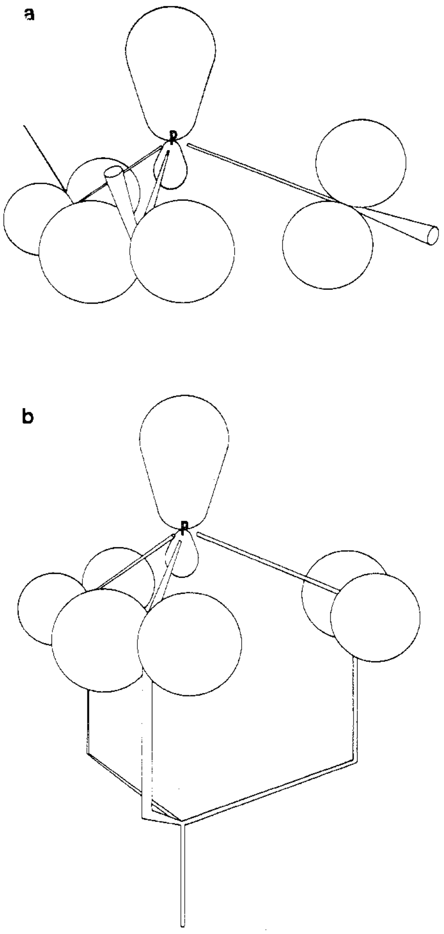

Figure 4. (a) Lone-pair orbital configuration approached by $O{=}P(OPh)_3$.[6] (b) Lone-pair orbital configuration approached by $O{=}P(OCH_2)_3CMe$.[6]

which do appear for **3b**, however.

Phosphorus Basicity. It has been proposed[9] that electron-donating groups attached to phosphorus enhance the stability of the azido adducts formed in the Staudinger reaction. Our interest in these adducts stemmed from the apparent decreases in phosphorus basicities displayed by cyclic compared to acyclic phosphorus esters[6] and **3** compared to **1**.[21] Using ^1H NMR spectroscopy to monitor decomposition rates of the adducts **1a**', **2a**', and **3d**' in $CDCl_3$ solutions at 34°, it was qualitatively determined that the order of thermal stability was **1a**' >> **2a**' ≈ **3d**'. That is, during the 6.5 hr required to decompose both **2a**' and **3d**' completely to **2a** and **3d**, there was no appreciable decomposition of **1a**' detected.

A rationale for the above order is based on lone-pair electron repulsion effects.[7] The spatial arrangements of the largely unhybridized lone pairs on each nitrogen in **1** are very probably different from those in **2** and **3**. Thus in the phosphite and phosphate esters $XP(OMe)_3$ and $XP(OCH_2)_3CMe$ (X = lone pair or oxygen) the p-orbital conformations approach those shown in Figure 4a and b,[6,7] respectively, and presumably **1** resembles $P(OMe)_3$ while **2** and **3** are comparable to $P(OCH_2)_3CMe$ in this regard. By symmetry, one p-orbital lone pair in **1** is capable of interacting with the phosphorus lone pair in a repulsive manner (Figure 4a), raising the energy of the latter and rendering it more basic toward a phenyl azido moiety. In **2** the nitrogen lone pairs are constrained to be orthogonal to the phosphorus lone pair (Figure 4b) and this is nearly the case in **3**, in which some pyramidal character of the nitrogens is present owing to the vicinal methyl steric interactions.[12b] The decreased interaction of the phosphorus lone pair with the nitrogen p lone pairs in **2** and **3** allows no enhancement of the phosphorus basicity and consequently the phenyl azido adducts **2a**' and **3d**' are destabilized relative to **1a**'.

Table III. Uv Spectra Analyzed Using LOGFIT

Compd	Solvent	λ_{max}, nm	ϵ_{max}, M^{-1} cm^{-1}
1a'[a]	Et_2O	224	11500
		259	4200
		286	6000
		298	5900
		318	12500
1a[b]	Et_2O	256	18600
		266	1400
		284	1600
		296	1300
		307	800
2a	Et_2O	249	20300
		255	1800
		278	1800
		288	1400
		297	1300
3a	THF	249	38900
		255	11900
		263	2300
		274	3100
		285	2300
		293	1300
3d	THF	248	19500
		258	3100
		276	1300
		287	1200
		296	500

[a] Reference 5 reports λ (ε): 223 (12400), 290 (13400), 300 (14900), 310 (14200) in Et_2O. [b] Reference 5 reports λ (ε): 257 (16900), 290 (2060) in Et_2O.

Opening of the OPO angles upon polarization of the phosphorus lone pair by a Lewis acid results in a smaller POC angle in $AP(OCH_2)_3CMe$ than in $AP(OMe)_3$ (A = Lewis acid) because of molecular constraint in the former ester.[6] The rehybridization of oxygen from sp^2 toward sp^3 could decrease the basicity of phosphorus since lone pairs in sp^3 hybrids are expected to be less effective in donating π density to the phosphorus than when contained in a p orbital. From the available structural data on monomeric aminophosphorus systems[12b] there appears to be no marked decrease in the ring PNC angles or the NPN angles upon contraining acyclic molecules into bicyclic analogues. It is therefore presently not possible to conclude whether or not such a "hinge effect" also contributes to the decreased basicity of **2** and **3**.

The basicity of an unoxidized phosphorus atom in **3** is apparently severely altered upon oxidation of the other. This was demonstrated by the inability to form the bis(phenyl azido) derivative of **3** in either hexane, diethyl ether, or acetonitrile using 2:1 phenyl azide:**3** ratios under mild conditions. An attempt to adduct the uncoordinated phosphorus of **3d** under the same conditions in chloroform solution gave no evidence of reaction and phenyl azide was recovered.

Monitoring the reaction of a 2:1 phenyl azide–**3** mixture in $CDCl_3$ solution at 34° by ^1H NMR spectroscopy showed only the presence of **3**, **3d**', **3d**, and **3a**. A 1:1 phenyl azide–**3** mixture under the same conditions showed only **3**, **3d**', and **3d** to be present in the reaction mixture. This ratio in C_6D_6 at 34° produced the same results, in contrast to previous work[3] in which it was reported that only unreacted **3** and the bis(phenylimido) derivative **3a** were found. Evidently, the monoazide **3d**' forms first followed by fairly rapid decomposition to **3d**. Compound **3d** then could react with more phenyl azide to give the very unstable adduct, $PhN_3P(NMeNMe)_3PNPh$, which under these conditions rapidly decomposes to **3a**. This behavior is in accord with the idea that the electron-withdrawing properties of the phenylimido group in **3d** reduce the basicity of the phosphorus at the opposite end of the cage.

Uv Spectra. The uv absorption spectra of compounds **1a'**, **1a**, **2a**, **3a**, and **3d** were analyzed using the program LOGFIT[15] and the relevant parameters are listed in Table III. Although the spectra for **1a'** and **1a** generally resembled those reported earlier,[5] the present analysis indicates the presence of additional bands. Compounds **2a'** and **3d'**, in accordance with their previously described instability, decomposed so rapidly in ether or THF solutions that meaningful spectra could not be obtained.

The greater electron-withdrawing character of **2** and **3** relative to that of **1** is undoubtedly responsible for the hypsochromic shift in the spectra of compounds **2a**, **3a**, and **3d** compared to those of compound **1a**. A similar absorption shift toward higher energies from aniline to the anilinium ion has been ascribed to the absence of a nitrogen lone-pair interaction with the aromatic π system in the latter.[24] In the present cases, the decreased availability of the imido nitrogen lone pair(s) for this electron interaction in **2a** and **3a** could arise from lower σ basicity and/or the higher π acidity of **2** and **3**, respectively.

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Registry No. $(Me_2N)_3P$, 1608-26-0; $(Me_2N)_3P{=}NPh$, 35589-04-9; $(Me_2N)_3P{=}NN{=}NPh$, 55215-22-0; $(Me_2N)_3P{=}NP(O)(OPh)_2$, 56727-71-0; $(Me_2N)_3P{=}NP(O)Ph_2$, 56727-72-1; $MeC(CH_2NMe)_3P$, 14418-26-9; $MeC(CH_2NMe)_3P{=}NPh$, 56727-73-2; $MeC(CH_2NMe)_3P{=}NN{=}NPh$, 56727-74-3; $MeC(CH_2NMe)_3P{=}NP(O)(OPh)_2$, 56727-75-4; $MeC(CH_2NMe)_3P{=}NP(O)Ph_2$, 56727-76-5; $P(NMeNMe)_3P$, 3478-74-8; $PhN{=}P(NMeNMe)_3P{=}NPh$, 42975-97-3; $(PhO)_2P(O)N{=}P(NMeNMe)_3P{=}NP(O)(OPh)_2$, 56727-77-6; $Ph_2P(O)N{=}P(NMeNMe)_3P{=}NP(O)Ph_2$, 42975-98-4; $P(NMeNMe)_3P{=}NPh$, 56727-78-7; $P(NMeNMe)_3P{=}NN{=}NPh$, 56727-79-8; $Ph_2P(O)N_3$, 4129-17-3; PhN_3, 622-37-7; $(PhO)_2P(O)N_3$, 26386-88-9; ^{31}P, 7723-14-0.

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Ligand Field Theory of Metal Sandwich Complexes. Magnetic Properties of f^x Configurations

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The magnetic behavior of the bis(cyclooctatetraene) derivatives of the lanthanide and actinide series is discussed in terms of a pseudoaxial ($C_{\infty v}$) ligand field model. A molecular orbital approach is used to deduce the ordering of the dominantly f-orbital levels and to estimate the required ligand field parameters. The temperature dependence and anisotropy of the magnetic moments are thereby calculated for the f^1, f^2, f^3, and f^4 configurations and compared with the experimental results.

Introduction

In 1968 the first proposed f-orbital aromatic system, bis(cyclooctatetraene)uranium(IV), $U(COT)_2$, was synthesized by Streitwieser and Müller-Westerhoff.[1] Since then $U(COT)_2$ and its 5f analogues have been extensively studied[2-8] and bis(cyclooctatetraene) derivatives of the An^{IV} elements are now also known for Th, Pa, Np, and Pu, while for U, Np, and Pu a number of alkyl-substituted bis(cyclooctatetraene) species have been investigated.[9-11] These studies have mostly been directed toward elucidating the nature of the interaction between the An^{IV} f orbitals and the π systems of the formally aromatic cyclooctatetraenyl dianion rings, chiefly by NMR and magnetic susceptibility measurements, and the state of knowledge concerning the bonding in $U(COT)_2$ has recently been summarized by Streitwieser et al.[8]

Bis(cyclooctatetraene)uranium(IV) belongs[12] to the point group D_{8h} and the principal f orbital–π ligand interaction was considered to be that between the ligand e_{2u} combination and the f_{xyz}, $f_{z(x^2-y^2)}$ orbitals of the metal, this being similar in character to the e_{1g} ligand–d_{xz}, d_{yz} metal interaction known to be important for the metallocenes. In a molecular orbital description the basis set for the actinide elements should include the 5f, 6d, 7s, and 7p levels, but it seems probable that only the lowest of these—the 5f orbitals—are appreciably involved in bonding in $U(COT)_2$ and its analogues.[1,8] In D_{8h} symmetry the π-type orbitals of the two cyclooctatetraene rings