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Insertion of Carbon Fragments into P(III)–N Bonds in Aminophosphines and Aminobis(phosphines): Synthesis, Reactivity, and Coordination Chemistry of Resulting Phosphine Oxide Derivatives. Crystal and Molecular Structures of $(Ph_2P(O)CH_2)_2NR$ (R = Me, ^{n}Pr, ^{n}Bu), $Ph_2P(O)CH(OH)^nPr$, and *cis*-$[MoO_2Cl_2\{(Ph_2P(O)CH_2)_2NEt\text{-}\kappa O,\kappa O\}]$

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Reactions of *N*-aryl and *N*-alicyclic derivatives of aminophosphines with paraformaldehyde lead to methylene insertion into P–N bond followed by oxidation of phosphorus from the P(III) to P(V) state. When *N*-alkyl derivatives are reacted with paraformaldehyde, dimerization takes place to afford bis(phosphine oxide)s of the type $Ph_2P(O)CH_2N(R)CH_2P(O)Ph_2$ (R = Me, ^{n}Pr, ^{n}Bu). Aminobis(phosphines) also undergo methylene insertion when treated with paraformaldehyde to give bis(phosphine oxides) $Ph_2P(O)CH_2N(R)CH_2P(O)Ph_2$ (R = Me, Et, ^{n}Pr, ^{i}Pr, ^{n}Bu) in good yield. The reaction of aminophosphines with aromatic aldehydes ArCHO leads to insertion of "ArCH" into the P–N bond to give $Ph_2P(O)CH(R)N(H)Ph$ (R = C_6H_5, furfuryl, *o*-C_6H_4OH), but with aliphatic aldehydes such as butanal, P–N bond cleavage takes place to afford α-hydroxy phosphine oxide. The reaction of aminobis(phosphines) with both aromatic and aliphatic aldehydes leads to the formation of α-hydroxy phosphine oxides through P–N bond cleavage whereas the reaction with furfural leads to the P–N bond insertion. The structure of the α-hydroxy derivative $Ph_2P(O)CR(H)(OH)^nPr$ shows intermolecular hydrogen bonding between OH and P═O oxygen. The phosphine oxide derivatives act as bidentate ligands and form chelate complexes with Co(II), Mo(VI), Th(IV), and U(VI) derivatives. The crystal structure of the molybdenum complex, *cis*-$[MoO_2Cl_2\{(OPPh_2CH_2)_2NEt\text{-}\kappa O,\kappa O\}]$, shows the distorted octahedral geometry around Mo with two oxo groups cis to each other.

Introduction

Although the coordination chemistry of aminobis(phosphines) with the P−N−P framework is very extensive,[1] studies focused on the reactivity of P(III)−N bonds is limited.[2] This may be due to the sensitivity of P(III)−N bonds toward acid or base-catalyzed hydrolysis which results in the cleavage of P(III)−N bonds to give P(V) oxide with the liberation of secondary amines as shown in Scheme 1. This type of cleavage is illustrated in the reactions of aminobis(phosphines) with phosphoryl azides.[3] Similar P−N bond cleavage can also occur in the reactions of R_2PCl with amines in the presence of trace amounts of moisture wherein the initially formed P−N bond(s) cleave(s) to give the diphosphine monoxide as described in Scheme 2. King[4] and others[5]

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(1) (a) Knorr, M.; Storhmann, C. *Organometallics* **1999**, *18*, 248. (b) Ellermann, J.; Gabold, P.; Knoch, F. A.; Moll, M.; Pohl, D.; Sutter, J.; Bauer, W. *J. Organomet. Chem.* **1996**, *525*, 89. (c) Ellermann, J.; Schelle, C.; Knoch, F. A.; Moll, M.; Pohl, D. *Monatsh. Chem.* **1996**, *127*, 783. (d) Ellermann, J.; Utz, J.; Knoch, F. A.; Moll, M. *Z. Anorg. Allg. Chem.* **1996**, *622*, 1871. (e) Ellermann, J.; Sutter, J.; Schelle, C.; Knoch, F. A.; Moll, M. *Z. Anorg. Allg. Chem.* **1993**, *619*, 2006. (f) Arnold, D. I.; Cotton, F. A.; Kuehn, F. E. *Inorg. Chem.* **1996**, *35*, 4733, 5764. (e) Ellermann, J.; Schelle, C.; Moll, M.; Knoch, F. A.; Bauer, W. *Z. Anorg. Allg. Chem.* **1995**, *621*, 789. (f) Babu, R. P. K.; Krishnamurthy, S. S.; Nethaji, M. *Organometallics* **1995**, *14*, 2047.
(2) (a) Hudson, R. F.; Mancuso, A. *Phosphorus* **1972**, *1*, 271. (b) William, A. H.; Harry, H. S. *Inorg. Chem.* **1964**, *3*, 617. (c) Brudjebel, H.; Goncalves, H.; Mathis, F. *Bull. Chim. Soc. Fr.* **1974**, 7.
(3) Balakrishna, M. S.; Santarsiero, B. D.; Cavell, R. G. *Inorg. Chem.* **1994**, *33*, 3079.

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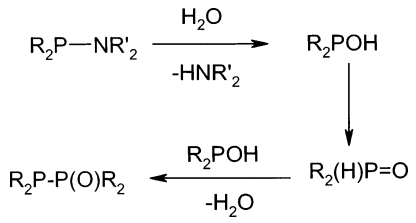
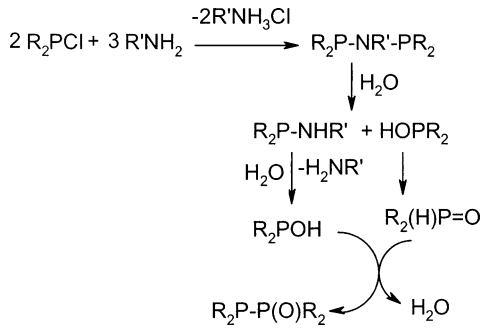
Scheme 1



Scheme 2



have also reported such P−N bond cleavage in metal complexes of aminobis(phosphines) in the presence of trace amounts of acid. In contrast, reports on the insertion of molecular fragments into P(III)−N bonds are rare. Hudson[6] and co-workers have reported the insertion of phenyl isocyanate into the P−N bond of $(EtO)_2PN(H)R$ which led to the isolation of isomeric $(EtO)_2PNRCON(H)Ph$ and $(EtO)_2PNPhCON(H)R$ involving a quaternized phosphorus intermediate.[6] Similarly the reaction of $P(NR_2)_3$ with CO_2 inserts carbon dioxide into the P−N bonds to afford mono-, $(R_2N)_2POOCNR_2$, and dicarbamates, $(R_2N)P(OOCNR_2)_2$.[7] Interestingly, such insertion into $O{=}P(NR_2)_3$ was unsuccessful. However, Cavell and co-workers[8] have reported the insertion of CO_2, COS, or CS_2 into the P(V)−N bond of $(CH_3)(CF_3)_2PN(CH_3)_2$, which yielded hexacoordinated phosphorus compounds. Recently we have described the first example of methylene insertion into the P(III)−N bond in the reaction of *N*-phenylaminodiphenylphosphine, $PhN(H)PPh_2$, with paraformaldehyde.[9] The interest for this investigation stems from the fact that such insertion reactions could lead to the isolation of phosphine oxide derivatives with a variety of substrates that can be used as source of organic fragments in synthesis. Further, such reactions generate a variety of phosphine oxide derivatives which can be potential herbicidal, antimicrobial, and neuroactive reagents.[10] Also, they can be used in some organic transformations such as formation of α-substituted phosphonates[11] and alkenes[12] and in the extraction of rare earths from radioactive wastes.[13]

As a part of our interest[9,14] and the others,[15] we have investigated the reactions of aminophosphines and aminobis(phosphines) with aldehydes in detail and herein we report the synthesis and X-ray structure of several phosphine oxide derivatives and their interactions with transition metals and lanthanides. The X-ray structure of a molybdenum complex is also described.

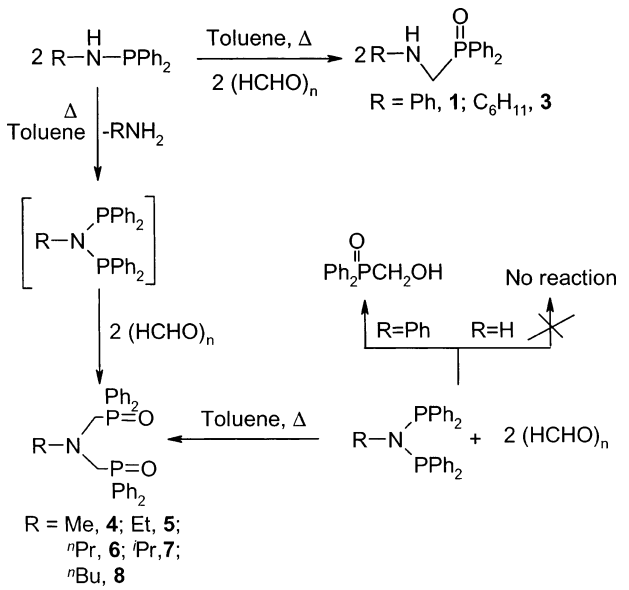
Results and Discussion

The stability of P(III)−N bonds in cyclic and acyclic phosphazanes depends to a large extent on the substituents on phosphorus and nitrogen.[16] The P(III)−N bonds are nominally single but show partial double bond character due to Npπ−Pdπ donor bonding. The P−N bonds can survive a variety of nucleophilic substitution reactions at phosphorus centers in both cyclic and acyclic phosph(V)azenes and phosph(III)azane systems.[16] However they are susceptible to acid/base-catalyzed hydrolysis reactions in the presence of one or more P−Cl bonds. In the absence of P−Cl bonds, P−N bonds are even stable to lithium reagents. The present investigation is aimed at further understanding of stability and reactivity of P−N bonds in aminophosphines.

Aminophosphines $Ph_2PN(H)R$ (R = Ph, Me, Et, ^{i}Pr, ^{n}Pr, ^{n}Bu) were prepared as described previously.[27] The cyclo-

(4) Newton, M. G.; King, R. B.; Chang, M.; Gimeno, J. *J. Am. Chem. Soc*. **1978**, *100*, 1632.
(5) Balakrishna, M. S.; Krishnamurthy, S. S. *Indian J. Chem*. **1991**, *30A*, 536.
(6) (a) Hudson, R. F.; Searle, R. J. G., *Chem. Commun*. **1967**, 1249. (b) Brown, C.; Hudson, R. F.; Searle, R. J. G. *Phosphorus* **1973**, *2*, 287.
(7) Aresta, M.; Quaranta, E. *J. Org. Chem*. **1988**, *53*, 4154.
(8) Cavell, R. G.; The, K. I.; van de Griend, L. *Inorg. Chem*. **1981**, *20*, 3813.
(9) Priya, S.; Balakrishna, M. S.; Mague, J. T. *Inorg. Chem. Commun*. **2001**, *4*, 437.
(10) Kafarski, P.; Mastalerz, P. Aminophosphonates. *Beitr. Wirkstofforsch*. **1984**, *21*, 1.
(11) Kumar, K. P.; Muthaiah, C.; Kumaraswamy, S.; Kumaraswamy, K. C. *Tetrahedron Lett*. **2001**, *42*, 3219.
(12) (a) Clayden, J.; Collington, E. W.; Lamont, R. B.; Warren, S. *Tetrahedron Lett*. **1993**, *34*, 2203. (b) Armstrong, D. R.; Barr, D.; Davidson, M. G.; Hutton, G.; O'Brien, P.; Snaith, R.; Warren, S. *J. Organomet. Chem*. **1997**, *529*, 29.
(13) (a) Archelas, E.; Buono, G.; Waegell, B. *Polyhedron* **1982**, *1*, 683. (b) Burger, L. L. *Nucl. Sci. Eng*. **1963**, *16*, 428. (c) Chmutova, M. K.; Kochetokova, N. E.; Myasoedev, B. F. *J. Inorg. Nucl. Chem*. **1978**, *40*, 1423.
(14) (a) Balakrishna, M. S.; Ramaswamy K.; Abhyankar, R. M. *J. Organomet. Chem*. **1998**, *560*, 131. (b) Balakrishna, M. S.; Abhyankar, R. M.; Mague, J. T. *J. Chem. Soc., Dalton Trans*. **1999**, 1407. (c) Balakrishna, M. S.; Panda, R.; Smith, D. C., Jr.; Klaman, A.; Nolan, S. P. *J. Organomet. Chem*. **2000**, *599*, 156. (d) Balakrishna, M. S.; Panda, R.; Mague, J. T. *Inorg. Chem*. **2001**, *40*, 5620. (e) Balakrishna, M. S.; Teipel, S.; Pinkerton, A. A.; Cavell, R. G. *Inorg. Chem*. **2001**, *42*, 2733. (f) Balakrishna, M. S.; Abhyankar, R. A.; Walwalker, M. G. *Tetrahedron Lett*. **2001**, *42*, 2733. (g) Balakrishna, M. S.; Walwalker, M. G. *J. Organomet. Chem*. **2001**, *628*, 76.
(15) (a) Tyka, R.; Hagele, G.; Peters, J. *Phosphorus Sulfur* **1987**, *34*, 31. (b) Claydon, J.; Warren, S. *Angew Chem., Int. Ed. Engl*. **1996**, *35*, 241 and references therein. (c) Muthiah, C.; Kumar, K. P.; Kumaraswamy, S.; Kumaraswamy, K. C. *Tetrahedron* **1998**, *54*, 14315.
(16) Balakrishna, M. S.; Reddy, V. S.; Krishnamurthy, S. S.; Nixon, J. F.; Burckett St. Laurent, J. C. T. R. *Coord. Chem. Rev*. **1994**, *129*, 1.
(17) Ewart, G.; Lane, A. P.; McKechnie, J.; Payne, D. S. *J. Chem. Soc*. **1964**, 1543.
(18) Panattoni, C.; Bandoli, G.; Bortolozzo, G.; Clemente, D. A.; Croatto, U. *J. Chem. Soc. A* **1970**, 2778.
(19) Rankin, D. W. H.; Robertson, H. E.; Seip, R.; Schmidbaur, H.; Blaschke, G.; *J. Chem. Soc., Dalton Trans*. **1985**, 827.
(20) Takaya, H.; Mashima, K.; Koyano, K.; Yagi, M.; Kumobayashi, H.; Taketomi, T.; Akutagawa, S.; Noyori, R. *J. Org. Chem*. **1986**, *51*, 629.
(21) Cameron, T. S.; Dahlen, B. *J. Chem. Soc., Perkin Trans. 2* **1975**, 1737.
(22) Butcher, R. J.; Penfold, B. R.; Sinn, E. *J. chem. Soc., Dalton Trans*. **1979**, 668.
(23) Florian, L. R.; Corey, E. R. *Inorg. Chem*. **1968**, *7*, 722.
(24) Wells, A. F. *Structural Inorganic Chemistry*, 3rd ed.; Clarendon Press: London, 1962; p 337.
(25) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960; p 260.
(26) Armarego, W. L. F.; Perrin, D. D. *Purification of Laboratory Chemicals*, 4th ed.; Butterworth-Heinemann Linacre House: Jordan Hill, Oxford, U.K., 1996.
(27) Wiegrabe, W.; Bock, H. *Chem. Ber*. **1968**, *101*, 1414.

Scheme 3



hexylamine derivative, $Ph_2PN(H)C_6H_{11}$ (**1**), was prepared in 80% yield by reacting chlorodiphenylphosphine with 2 equiv of cyclohexylamine in *n*-hexane.

Recently, we have described[9] the reaction of $Ph_2PN(H)$-Ph with paraformaldehyde to give phosphine oxide Ph_2P-$(O)CH_2N(H)Ph$. The product is a consequence of methylene insertion into a P−N bond followed by the oxidation of the P(III) center to P(V). The cyclohexylamine derivative **1** reacts in a fashion similar to afford $Ph_2P(O)CH_2N(H)C_6H_{11}$ (**3**) in 70% yield. The IR spectrum of **3** shows ν_{NH} at 3243 cm^{-1}; the low-frequency shift of 60 cm^{-1} when compared to the parent compound is attributed to the intermolecular hydrogen bonding (N−H···O═P) as reported earlier.[9] The ^{31}P NMR spectrum of **3** shows a single resonance at 30.6 ppm as expected. Interestingly, the reactivity of *n*-alkylaminophosphines, $Ph_2PN(H)R$ (R = Et, ^{n}Pr, ^{n}Bu), with paraformaldehyde differs significantly and gives exclusively the bis-(phosphine oxide) derivatives of the type $Ph_2P(O)CH_2N(R)$-$CH_2P(O)Ph_2$ in 60−70% yield. The formation of products, $Ph_2P(O)CH_2N(R)CH_2P(O)Ph_2$ (R = Et (**5**), ^{n}Pr (**6**), ^{n}Bu (**8**)), from the alkylaminophosphines may be due to the prior condensation of two alkylaminophosphines into the corresponding aminobis(phosphines) with the elimination of a molecule of alkylamine, which then reacts with paraformaldehyde to give the product as shown in Scheme 3. At high temperature, the condensation of *n*-alkylaminophosphines into the corresponding aminobis(phosphines) with elimination of alkylamine is reported.[17] The absence of ν_{NH} in the IR spectra of compounds **5**, **6**, and **8** confirms the dimerization of alkylaminophosphines and also the methylene insertion into the P−N bonds. The reaction of aminobis-(phosphines) $Ph_2PN(R)PPh_2$ (R = Me, Et, ^{n}Pr, ^{i}Pr, ^{n}Bu) with 2 equiv of paraformaldehyde facilitated methylene insertion into both the P−N bonds to give $Ph_2P(O)CH_2N(R)CH_2P$-$(O)Ph_2$ (R = Me (**4**), Et (**5**), ^{n}Pr (**6**), ^{i}Pr (**7**), ^{n}Bu (**8**)) in good yields. The ^{31}P NMR spectra of the compounds **4**−**8** show a single resonance in the range of 29−31 ppm. The ^1H NMR spectra of **4**−**8** show doublets in the range of 3−4 ppm for methylene protons with a $^2J_{PH}$ coupling of 5−6 Hz. Further confirmation of the structures of compounds **4**, **6**, and **8** comes from single-crystal X-ray diffraction studies.

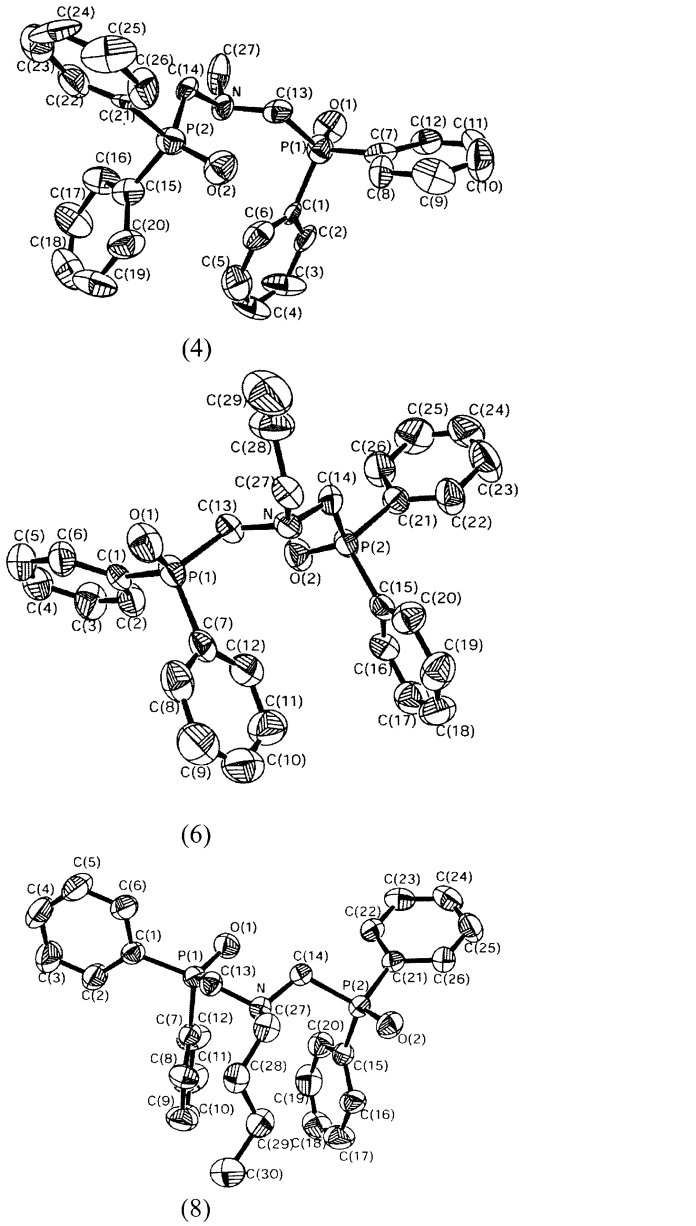


Figure 1. Perspective view of the compounds **4**, **6**, and **8** with atomic numbering scheme. Thermal ellipsoids are drawn with 50% probability level, and hydrogen atoms are omitted for clarity.

The structures of $Ph_2P(O)CH_2N(R)CH_2P(O)Ph_2$ (R = Me (**4**), ^{n}Pr (**6**), ^{n}Bu (**8**)) with atom numbering schemes are shown in Figure 1. The crystal data and selected bond lengths and bond angles for **4**, **6**, and **8** are given in the Tables 1−3, respectively. All the three structures show a distorted tetrahedral geometry about the phosphorus centers and pyramidal environment around the nitrogen center with the sum of the angles in the range 332−335°. The two P═O bonds are mutually anti to each other in all three compounds. The P═O bond distances in **4** (1.486(11), 1.471(12) Å), **6** (1.483(4), 1.488(5) Å), and **8** (1.487(1), 1.481(1) Å) are longer than that in Ph_3PO (1.46 Å),[18] while they are shorter when compared with ^{t}Bu_3PO (1.590 Å)[19] and BINAPO

Table 1. Crystallographic Data for **4**, **6**, **8**, and **26**

	4	**6**	**8**	**14**	**26**
empirical formula	$C_{27}H_{27}NO_2P_2$	$C_{29}H_{31}NO_2P_2$	$C_{30}H_{33}NO_2P_2$	$C_{16}H_{19}O_2P$	$C_{28}H_{29}Cl_2MoNO_4P_2 \cdot 0.3CH_2Cl_2$
fw	459.44	487.49	501.51	274.28	697.84
cryst system	orthorhombic	orthorhombic	triclinic	monoclinic	orthorhombic
space group	*Pna*2$_1$ (No. 33)	*P*2$_1$*cn* (No. 1)	*P*-1 (No. 2)	*P*2$_1$/*n* (No. 14)	*Pbca* (No. 61)
a (Å)	10.354(1)	8.468(8)	8.053(2)	10.595(1)	16.822(8)
b (Å)	28.375(5)	15.126(1)	10.287(2)	10.422(1)	16.191(11)
c (Å)	8.275(2)	20.262(2)	16.264(3)	13.952(2)	23.722(13)
α (deg)			85.72(3)		
β (deg)			89.53(3)	94.333(8)	
γ (deg)			89.81(3)		
V (Å^3)	2431.2(7)	2595.2(4)	1343.5(5)	1536.2(3)	6461.0(6)
Z	4	4	2	4	1
D_{calcd} (g cm^{-1})	1.255	1.248	1.240	1.186	1.435
μ(Mo Kα)[a] (mm^{-1})	0.2	0.194	0.2	0.2	0.8
temp (K)	293	293	293	293	293
R[b]	0.085	0.0521	0.0395	0.0441	0.069
R_w[c]	0.1349	0.1045	0.1122	0.1100	0.238
weight for *a*, *b*	0.0227, 0.000		0.0439, 0.753		0.1431, 0.000

[a] Graphite monochromated. [b] $R = \sum|F_o - F_c|/\sum|F_o|$. [c] $R_w = [\sum w(F_o^2 - F_c^2)/\sum w(F_o^2)^2]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$. $P = 1/3[F_o^2 + 2F_c^2]$.

Table 2. Selected Bond Distances (Å) for **4**, **6**, and **8**

bond dists	**4**	**6**	**8**
P(1)−O(1)	1.486(11)	1.483(4)	1.487(2)
P(1)−C(1)	1.827(15)	1.821(7)	1.816(2)
P(1)−C(7)	1.815(17)	1.808(6)	1.805(2)
P(1)−C(13)	1.808(15)	1.821(7)	1.820(2)
P(2)−O(2)	1.471(12)	1.488(5)	1.481(2)
P(2)−C(14)	1.819(14)	1.807(7)	1.823(2)
P(2)−C(15)	1.829(18)	1.806(7)	1.805(2)
P(2)−C(21)	1.806(17)	1.818(6)	1.816(2)
N−C(13)	1.464(18)	1.460(8)	1.464(3)
N−C(14)	1.452(18)	1.468(8)	1.464(3)
N−C(27)	1.467(19)	1.487(8)	1.482(3)

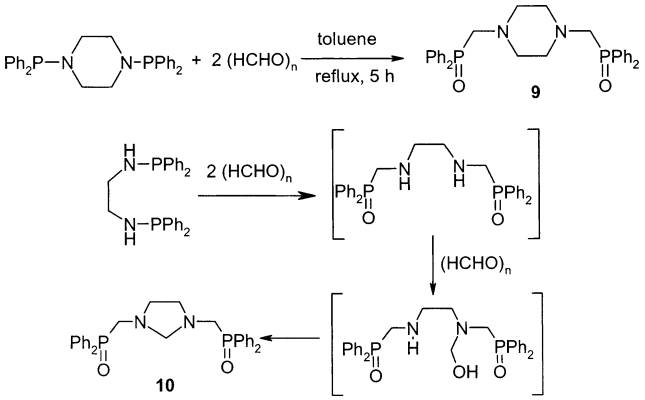
Table 3. Selected Bond Angles (deg) for **4**, **6**, and **8**

bond angles	**4**	**6**	**8**
O(1)−P(1)−C(1)	110.6(7)	112.0(3)	112.9(1)
O(1)−P(1)−C(7)	110.3(7)	110.8(3)	112.6(1)
O(1)−P(1)−C(13)	117.5(7)	115.8(3)	114.1(1)
C(1)−P(1)−C(7)	109.0(7)	107.5(3)	106.4(1)
C(1)−P(1)−C(13)	107.2(7)	107.3(3)	102.3(1)
C(7)−P(1)−C(13)	101.6(7)	102.6(3)	107.8(1)
O(2)−P(2)−C(14)	114.5(6)	114.6(3)	115.1(1)
O(2)−P(2)−C(15)	111.6(9)	112.6(3)	112.3(1)
O(2)−P(2)−C(21)	113.6(7)	111.6(3)	110.9(1)
C(14)−P(2)−C(15)	107.6(7)	100.9(3)	105.7(1)
C(14)−P(2)−C(21)	102.3(7)	109.2(3)	103.8(1)
C(15)−P(2)−C(21)	106.6(9)	107.2(3)	108.3(1)
C(13)−N−C(14)	110.9(11)	111.1(5)	110.5(2)
C(13)−N−C(27)	111.7(11)	112.4(5)	110.5(2)
C(14)−N−C(27)	111.7(11)	111.4(5)	111.8(1)

(1.506 Å).[20] The P−C bond distances are comparable with literature values.[21] The N−C bond distances are in the range of 1.452−1.482 Å, slightly longer when compared to the same in $Ph_2P(O)CH_2N(H)Ph$ (1.441(2) and 1.375(2) Å).[9]

The reaction of $Ph_2PN(H)PPh_2$ with paraformaldehyde afforded $Ph_2P(O)CH_2OH$. The formation of $Ph_2P(O)CH_2OH$ could be due to the initial cleavage of the P−N bond to form Ph_2POH and then $Ph_2P(O)H$, which reacts with paraformaldehyde to give $Ph_2P(O)CH_2OH$. In contrast, $Ph_2PN(Ph)PPh_2$ did not react with paraformaldehyde even under vigorous conditions and the unreacted starting materials are recovered. The controlled methylene insertion into one of the P−N bonds to make mixed-valent phosphine derivatives of the type $Ph_2P(O)CH_2N(R)PPh_2$ have been unsuccessful.

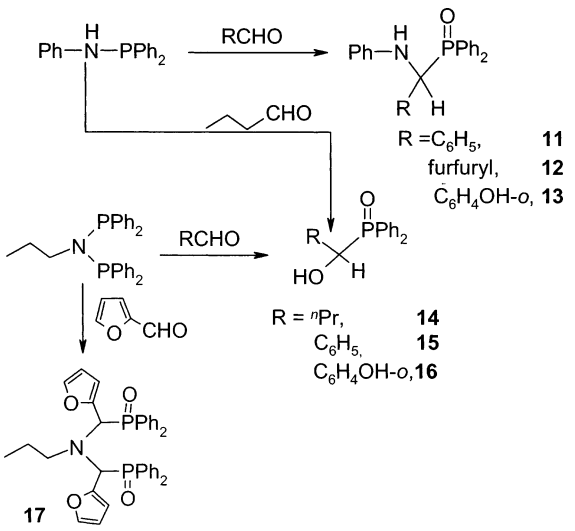
Scheme 4



N,*N*′-Bis(diphenylphosphino)piperazine reacts with 2 equiv of paraformaldehyde to give the methylene-inserted product, $Ph_2P(O)CH_2N(C_2H_4)_2NCH_2P(O)Ph_2$ (**9**), in good yield. The ^{31}P NMR spectrum of the product **9** shows a single resonance at 27.3 ppm, while the ^{1}H NMR spectrum shows a doublet at 4.23 ppm with $^2J_{PH}$ coupling of 5.2 Hz for methylene protons. When bis(diphenylphosphino)ethylenediamine was treated with paraformaldehyde in 1:2 molar ratio, apart from the two methylene groups inserted into two P−N bonds, another methylene bridge was established between the two nitrogen centers. This may result from nucleophilic addition at N to give NCH_2OH, which further condenses with NH of the substrate to give the product **10** as shown in Scheme 4. The ^{31}P NMR spectrum of **10** shows a single resonance at 28.3 ppm. The methylene groups inserted between P−N bonds appear as doublets at 3.44 ppm in its ^{1}H NMR spectrum with $^2J_{PH}$ coupling of 7.19 Hz, whereas the bridging methylene group appears as a singlet at 3.59 ppm.

When aromatic aldehydes are treated with aminophosphines, a "CH(R)" group is inserted into the P−N bond followed by oxidation of phosphorus from P(III) to P(V). The reaction of RCHO (R = Ph, OC_4H_3, C_6H_4OH-*o*) with $Ph_2PN(H)Ph$ afforded $Ph_2P(O)CH(R)N(H)Ph$ (R = Ph (**11**), OC_4H_3 (**12**), C_6H_4OH-*o* (**13**)) in 65−89% yields as shown in Scheme 5. The IR spectra of **11**−**13** show ν_{NH} around 3300−3390 cm^{-1}. The ^{31}P NMR spectra of **11**−**13** show

Scheme 5



single resonances in the range of 30−37 ppm while their ^{1}H NMR spectra show doublets around 5.3−5.5 ppm with $^2J_{PH}$ couplings in the range of 7−12 Hz for CH protons.

The reaction of butyraldehyde with $Ph_2PN(H)Ph$ afforded $Ph_2P(O)CH(OH)^nPr$ (**14**) in 89% yield as shown in Scheme 5. In this reaction, the P−N bond cleavage takes place instead of P−N bond insertion. The IR spectrum of **14** shows a band at 3207 cm^{-1} corresponding to an OH group. The ^{31}P NMR spectrum of **14** exhibits a single resonance at 31.3 ppm whereas the ^{1}H NMR spectrum shows a doublet for the CH proton at 4.41 ppm with a $^2J_{PH}$ coupling of 10.3 Hz.

The reaction of $^nPrN(PPh_2)_2$ with RCHO (R = ^{n}Pr, Ph, C_6H_4OH-*o*) yielded α-hydroxy phosphine oxides $Ph_2P(O)CH(OH)R$ (R = ^{n}Pr (**14**), Ph (**15**), C_6H_4OH-*o* (**16**)) in 40−45% yields. The formation of these products may be due to the prior cleavage of the P−N bond to form $Ph_2P(O)H$, which then reacts with aldehyde to give $Ph_2P(O)CH(OH)R$. Compounds **14**−**16** show ν_{OH} around 3200−3250 cm^{-1} in their IR spectra. The ^{31}P NMR spectra of **14**−**16** show a single resonance in the range of 30−37 ppm, and the ^{1}H NMR spectra show doublets around 4.4−5.5 ppm for the CH proton with $^2J_{PH}$ couplings in the range 5−10 Hz. The structure of **14** is confirmed by a single-crystal X-ray diffraction study. The crystal data, bond distances, and bond angles for **14** are listed in Tables 1 and 4, and a perspective view of the molecule is shown in Figure 2. The structure of **14** shows distorted tetrahedral geometry around the phosphorus center. The P═O bond length is 1.486(2) Å, and the P−C bond distances are in the range 1.802(3)−1.829(3) Å. Compound **14** exists as a dimer in the crystal due to intermolecular O−H···O═P hydrogen bonding between H (from OH) of one molecule and O (from P═O) of an adjacent molecule (d(O···O) = 2.682(3) Å, d(H(111)−O) = 1.91(3) Å; the O−H···O bond angle is 167(4)°). The anti conformation of the OH group and P═O oxygen of the adjacent molecule facilitates this type of strong intermolecular hydrogen bonding. The reaction of $^nPrN(PPh_2)_2$ with furfural is different from other aldehydes, but it is similar to that with paraformaldehyde. When $^nPrN(PPh_2)_2$ is treated with 2 equiv of

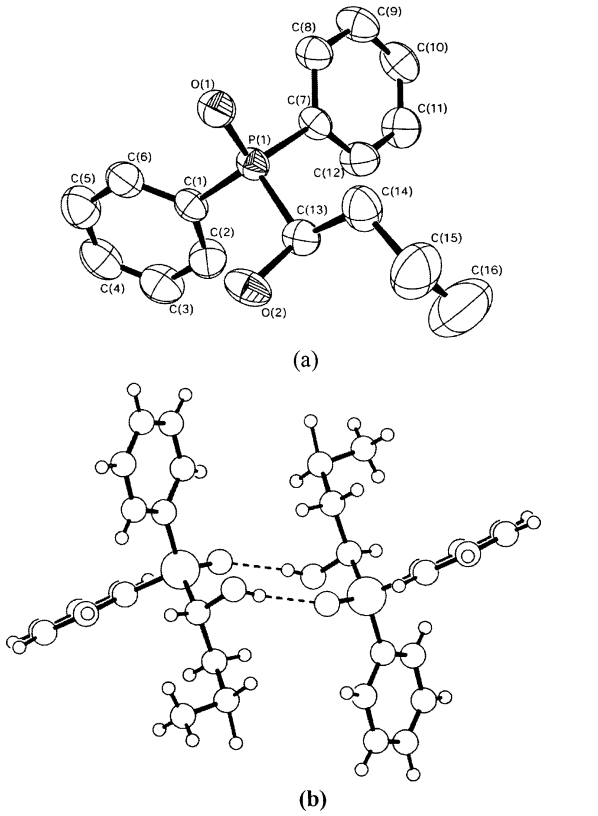


Figure 2. (a) Perspective view of the compound **14** with atomic numbering scheme. Thermal ellipsoids are drawn with 50% probability level, and hydrogen atoms are omitted for clarity. (b) Intermolecular H-bonding interaction between O−H···O═P of another molecule.

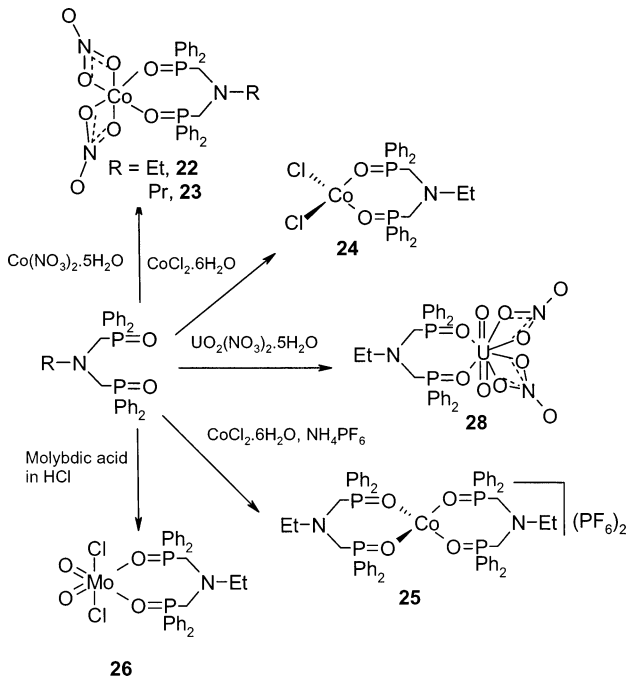
Table 4. Selected Bond Distances (Å) and Bond Angles (deg) for **14**

Bond Distances			
P(1)−O(1)	1.486(2)	P(1)−C(13)	1.829(3)
P(1)−C(1)	1.802(3)	O(2)−C(13)	1.419(4)
P(1)−C(7)	1.811(3)		
Bond Angles			
O(1)−P(1)−C(1)	111.3(1)	C(7)−P(1)−C(13)	106.5(1)
O(1)−P(1)−C(7)	110.7(1)	P(1)−C(13)−O(2)	108.5(2)
O(1)−P(1)−C(13)	114.0(1)	P(1)−C(13)−C(14)	111.5(2)
C(1)−P(1)−C(7)	107.9(1)	O(2)−C(13)−C(14)	113.7(3)
C(1)−P(1)−C(13)	106.2(1)		

furfural, it afforded $(Ph_2P(O)CH(OC_4H_3))_2N^nPr$ (**17**) in 37% yield. The IR spectrum of **17** shows ν_{PO} at 1187 cm^{-1}. The ^{31}P NMR spectrum of the compound **17** shows a single resonance at 29.8 ppm, and the ^{1}H NMR spectrum shows a doublet at 5.53 ppm for the CH proton with a $^2J_{PH}$ coupling of 5.99 Hz.

Coordination Chemistry of the Phosphine Oxides. The phosphine oxides readily react with oxophilic metals to give coordination complexes. When the compound $Ph_2P(O)CH_2NHPh$ (**2**) is treated with group 12 metal precursors MX_2 (M = Zn, Cd; X = acetate and M = Hg; X = iodide), tetrahedral complexes $[(Ph_2P(O)CH_2NHPh)MX_2]$ (M = Zn (**18**), Cd (**19**); X = $COOCH_3^-$ and M = Hg (**20**); X = I^-) were obtained in good yield. The IR spectra of the complexes **18**−**20** show shifts for both ν_{NH} and ν_{PO} as compared to the free ligand **2** indicating the interaction of nitrogen and oxygen with the metal centers. The ^{1}H NMR spectra of the complexes **18**−**20** show broad singlets for the NH protons

Scheme 6



which are deshielded compared to the free ligand while their ^{31}P NMR spectra show single resonances around 29−31 ppm.

The reaction of 2 equiv of $Ph_2P(O)CH_2NHPh$ (**2**) with $Co(NO_3)_2{\cdot}6H_2O$ gave a purple colored octahedral complex, $[Co(NO_3)_2\{Ph_2P(O)CH_2NHPh\}_2]$ (**21**). When an ethanolic solution of $Co(NO_3)_2{\cdot}6H_2O$ was treated with equimolar quantity of $(Ph_2P(O)CH_2)_2NR$ (R = Et (**5**), ^{n}Pr (**6**)) purple colored, octahedral chelate complexes of the type $[Co(NO_3)_2(Ph_2P(O)CH_2)_2NR]$ (R = Et (**22**), ^{n}Pr (**23**)) are obtained in quantitative yield as shown in Scheme 6. In the octahedral cobalt complexes, the oxygen atoms of the nitrate groups occupy four coordinating sites and the other two sites are filled by the oxygen atoms of the phosphine oxides. The ^{31}P NMR spectra of the products show broad singlets implying both the phosphorus atoms are equivalent. Further structural confirmation for **21**−**23** comes from ^{1}H NMR, IR spectra, and microanalytical data (vide infra).

The reaction of **5** with $CoCl_2{\cdot}6H_2O$ in equimolar ratio in ethanol leads to the formation of a dark blue tetrahedral complex, $[CoCl_2(Ph_2P(O)CH_2)_2NEt]$ (**24**). The ^{31}P NMR spectrum of the compound **24** shows a broad singlet at 34.0 ppm. When $CoCl_2{\cdot}6H_2O$ was treated with 2 equiv of **5** in the presence of NH_4PF_6, the tetrahedral ionic complex $[Co\{(Ph_2P(O)CH_2)_2NEt\}_2](PF_6)_2$ (**25**) was obtained. The magnetic measurements confirm the presence of high-spin Co(II) centers in complexes **21**−**25** (see Experimental Section). The broadening of signals in both ^{31}P NMR and ^{1}H NMR spectra is due to the presence of paramagnetic Co(II) species.

The electronic spectra of free ligands **2**, **5**, and **6** and the complexes **22**−**25** were recorded in ethanol, while CH_2Cl_2 was used for recording the spectrum of the complex **21**. The free ligands exhibit n → π^* and $\pi \rightarrow \pi^*$ transitions in the UV region near 224 and 266 nm, respectively. The octahedral (**21**−**23**) and the tetrahedral complexes (**24** and **25**) display ligand-based transitions in the UV region (222−264 nm).

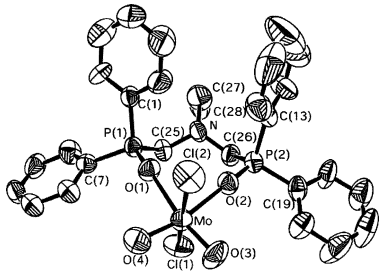


Figure 3. Perspective view of the complex **26** with atomic numbering scheme. Thermal ellipsoids are drawn with 50% probability level, and hydrogen atoms are omitted for clarity.

Table 5. Selected Bond Distances (Å) and Bond Angles (deg) for **26**

Bond Distances			
Mo−O(1)	2.170(7)	P(1)−C(25)	1.816(7)
Mo−O(2)	2.163(7)	P(1)−C(1)	1.794(11)
Mo−O(3)	1.664(9)	P(2)−O(2)	1.497(7)
Mo−O(4)	1.674(9)	P(2)−C(26)	1.815(11)
Mo−Cl(1)	2.405(4)	P(2)−C(13)	1.795(14)
Mo−Cl(2)	2.378(4)	N−C(25)	1.435(13)
P(1)−O(1)	1.486(7)	N−C(26)	1.446(14)

Bond Angles			
O(1)−Mo−O(2)	77.3(3)	O(3)−Mo−O(4)	102.5(4)
O(1)−Mo−O(3)	168.1(3)	O(3)−Mo−Cl(1)	93.4(3)
O(1)−Mo−O(4)	89.4(4)	O(3)−Mo−Cl(2)	94.2(3)
O(1)−Mo−Cl(1)	85.0(2)	O(4)−Mo−Cl(1)	94.5(3)
O(1)−Mo−Cl(2)	85.2(2)	O(4)−Mo−Cl(2)	94.9(3)
O(2)−Mo−O(3)	90.7(3)	Cl(1)−Mo−Cl(2)	166.3(1)
O(2)−Mo−O(4)	166.8(4)	C(26)−N−C(25)	116.3(9)
O(2)−Mo−Cl(1)	84.5(2)	C(26)−N−C(27)	112.9(9)
O(2)−Mo−Cl(2)	84.1(2)	C(25)−N−C(27)	116.8(10)

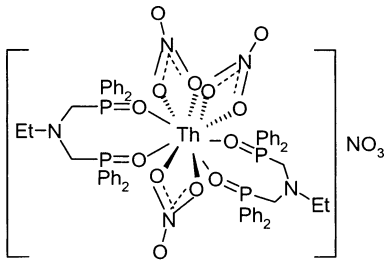
Also, both octahedral and tetrahedral complexes show two closely spaced weak d−d transitions in the visible region. The two visible energy bands observed near 520 nm and 528−554 nm of the octahedral complexes **21**−**23** are assigned to $^4T_{1g}(F) \rightarrow {}^4T_{2g}$ and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transitions, respectively. The visible energy transitions of the tetrahedral complexes **24** and **25** are substantially red shifted (644−674 nm) with appreciable intensity enhancement compared to the octahedral complexes **21**−**23**. The observed bands are assigned to $^4A_2 \rightarrow {}^4T_1(P)$ and $^4A_2 \rightarrow {}^4T_1(F)$ transitions.

The reaction of an ethanolic solution of $(Ph_2P(O)CH_2)_2NEt$ (**5**) with molybdic acid in acidic medium gave Mo(VI) chelate complex *cis*-$[MoO_2Cl_2\{(Ph_2P(O)CH_2)_2NEt\text{-}\kappa O,\kappa O\}]$ (**26**). The ^{31}P NMR spectrum of complex **26** shows a single resonance at 38.9 ppm with a coordination shift of 9 ppm. The structure of the molybdenum complex **26** is confirmed by a single-crystal X-ray diffraction study. The crystal data and bond distances and angles are listed in Tables 1 and 5, respectively. A perspective view of the complex with atomic numbering scheme is shown in Figure 3. The structure of **26** shows a distorted octahedral environment around Mo in which the ligand coordinates to the metal in a chelate bidentate mode via the oxygen centers. Both the oxo ligands and phosphine oxide are in mutually cis orientations while the chloro ligands are in mutually trans dispositions. The $Mo-O_{oxo}$ bond distances in **26** (1.664(9) and 1.674(9) Å) fall within the range of 1.63−1.73 Å[22] and are comparable to those in $[MoO_2X_2\{Ph_3P(O)\}_2]$ (X = Cl and Br) (1.70, 1.67 and 1.69, 1.73 Å)[22] but shorter when compared to the $Mo-O_{oxo}$ distances observed in $[MoO_2Cl_2(OHCN(CH_3)_2)_2]$

(1.68 Å).[23] The Mo−Cl(1) bond distance of 2.405(4) Å is slightly longer than the Mo−Cl(2) (2.378(4) Å) bond distance. However, both Mo−Cl distances in complex **26** are longer than those observed in tetrahedrally coordinated MoO_2Cl_2 (gas-phase structure 2.281(3) Å)[24] and in $[MoO_2Cl_2(OHCN(CH_3)_2)_2]$ (2.341(7) Å).[23]

The O−Mo−O angles show large distortions from 90° (O(1)−Mo−O(2) = 77.3(3)°; O(3)−Mo−O(4) = 102.5(4)°) similar to analogous Mo(VI) complexes containing $Ph_3P{=}O$.[22] The Mo−O_{oxo} (Mo−O(3) and Mo−O(4)) bond distances are shorter; the wider angle involves the shorter Mo−O bond distances and is probably due to the O−O repulsion. The nonbonding O(3)···O(4) distance is 2.604 Å, which is less than 2.8 Å[25] (twice the van der Waals radius of oxygen).

The reaction of **5** with $Th(NO_3)_4{\cdot}5H_2O$ affords a 10-coordinate complex, $[Th(NO_3)_3\{(Ph_2P(O)CH_2)_2NEt\}_2](NO_3)$ (**27**). The ^{31}P NMR spectrum of the complex **27** shows a single resonance at 40.1 ppm with a coordination shift of 11 ppm. The IR and ^1H NMR spectral data and the microanalytical data for the product **27** support the proposed structure. The FAB mass spectrum shows *m*/*z* at 1364 (100%) corresponding to the cation.



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The reaction of the ligand **5** with uranyl nitrate in equimolar ratio in dichloromethane afforded the 8-coordinate complex, *trans*-$[UO_2(NO_3)_2\{(Ph_2P(O)CH_2)_2$-NEt-$\kappa O,\kappa O\}]$ (**28**) as shown in Scheme 6. The ^{31}P NMR spectrum of the complex **28** shows a single resonance at 41.8 ppm, which is considerably deshielded from the free ligand with a coordination shift of 12.3 ppm. The IR spectrum shows ν_{PO} at 1175 cm^{-1} with the low-frequency shift of 14 cm^{-1} attributed to the coordination.

Conclusion

The reactions of both aminophosphines and aminobis(phosphines) with paraformaldehyde lead to the insertion of methylene groups into the P−N bond(s). Similar reactions with other alkyl and aryl aldehydes afford either P−N inserted products or α-hydroxy phosphine oxides through P−N bond cleavage. The reactions of aminobis(phosphines) with both aromatic and aliphatic aldehydes lead to the formation of α-hydroxy phosphine oxides through P−N bond cleavages whereas the reaction with furfural affords P−N insertion product. These reactions do not depend on the acidic proton on nitrogen as reported earlier,[6] but they mainly depend on the oxidation state of phosphorus atom. Also, the reactivity depends on the substituents on nitrogen, but the influence of phosphorus substituents in these reactions is yet to be explored. The α-hydroxy phosphine oxides obtained from these reactions are similar to Horner−Wittig intermediates in the formation of alkenes from the corresponding alkylphosphine oxides. Further research to understand the influence of phosphorus substituents in this type of reaction is underway in our laboratory.

Experimental Section

All manipulations were performed under rigorously anaerobic conditions using Schlenk techniques. All the solvents were purified by conventional procedures and distilled prior to use.[26] The aminophosphines, $RN(H)PPh_2$ (R = Et, ^{n}Pr, ^{n}Bu, Ph[27]), bis(diphenylphosphino)amines, $RN(PPh_2)_2$ (R = H,[28] Me, Et, ^{n}Pr, ^{n}Bu, Ph,[17] ^{i}Pr[29]), $Ph_2PN(H)CH_2CH_2N(H)PPh_2$,[27] and bis(diphenylphosphino)piperazine,[30] $Ph_2PN(C_2H_4)_2NPPh_2$, were prepared according to the literature procedures. The ^1H and ^{31}P NMR spectra were recorded using Varian VXR 300 and Bruker AMX 400 spectrometers operating at the appropriate frequencies using tetramethylsilane and 85% H_3PO_4 as internal and external references, respectively. Positive shifts lie downfield in all cases. IR spectra were recorded on a Nicolet Impact 400 FT IR instrument in KBr disks. The electronic absorption spectra were recorded on a JASCO V 570 UV−visible spectrometer. Magnetic moment measurements were carried out on a Faraday balance at 303 K. Microanalyses were performed on a Carlo Erba model 1112 elemental analyzer. The FAB mass spectra were recorded on JEOL SX 102/DA-6000 mass spectrometer/data system using argon/xenon (6 kV, 10 mA) as FAB gas and high-resolution mass spectra (HRMS) on a MASCPEC (msco/9849) system. Melting points were recorded in capillary tubes and are uncorrected.

Preparation of $Ph_2PN(H)C_6H_{11}$ (1). To a stirring ice-cold solution of cyclohexylamine (5.8 g, 59 mmol) in *n*-hexane (100 mL) was added dropwise chlorodiphenylphosphine (5.9 g, 27 mmol) in *n*-hexane (40 mL), and the reaction mixture was stirred at room-temperature overnight. Amine hydrochloride was removed by filtration, and the filtrate was concentrated and cooled to 0 °C overnight to give **1** as an analytically pure white crystalline solid. Yield: 80% (6.1 g, 21 mmol). Mp: 49−51 °C. Anal. Calcd for $C_{18}H_{22}NP$: C, 76.29; H, 7.83; N, 4.94. Found: C, 76.31; H, 7.69; N, 5.02. IR (KBr disk; cm^{-1}): ν_{NH} 3303 s. ^1H NMR ($CDCl_3$): δ 0.95−2.59 (m, *cyclohexyl*, 11H), 7.21−7.55 (m, *phenyl*, 10H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 36.1 (s).

Preparation of $C_6H_{11}N(H)CH_2P(O)Ph_2$ (3). A mixture of **1** (0.5 g, 1.60 mmol) and paraformaldehyde (0.057 g, 1.60 mmol) in toluene (10 mL) was heated to reflux for 4 h. The solution was then cooled to room temperature, concentrated to 4 mL, and cooled to 4 °C, whereupon an analytically pure crystalline product of **3** precipitated out. Yield: 70% (0.153 g, 0.488 mmol). Mp: 86−90 °C. Anal. Calcd for $C_{19}H_{24}NOP$: C, 72.82; H, 7.72; N, 4.47. Found: C, 72.94; H, 7.49; N, 4.59. IR (KBr disk; cm^{-1}): ν_{NH} 3243 s, ν_{PO} 1183 vs. ^1H NMR (CD_2Cl_2): δ 0.97−2.44 (m, *cyclohexyl*, 11H), 3.22 (d, $^2J_{PH}$ = 9.6 Hz, C*H*$_2$, 2H), 7.2−7.8 (m, *phenyl*, 10H). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 29.9 (s).

General Procedure for the Preparation of $RN(CH_2P(O)Ph_2)_2$ (R = Me, Et, ^{n}Pr, ^{i}Pr, ^{n}Bu). To a solution of $RN(PPh_2)_2$ (0.50 mmol) in 7 mL of toluene was added paraformaldehyde (1.0 mmol), and the mixture was heated to reflux for 4 h. The solution was then cooled to room temperature, solvent was removed under

(28) Noeth, H.; Meinel, L. *Z. Anorg. Allg. Chem.* **1967**, *349*, 225.
(29) Balakrishna, M. S.; Prakasha, T. K.; Krishnamurthy, S. S.; Siriwardane, U.; Hosmane, N. S. *J. Organomet. Chem.* **1990**, *390*, 203.
(30) Thomas, C. J.; Rao, M. N. S. *Z. Anorg. Allg. Chem.* **1993**, *619*, 433.

reduced pressure, and the residue obtained was washed with *n*-hexane (3 × 5 mL) and then dissolved in a mixture of CH_2Cl_2−*n*-hexane (2:1) and kept at −15 °C for 2 days to give colorless crystals of the products.

$MeN(CH_2P(O)Ph_2)_2$ (4). Yield: 79% (0.182 g, 0.40 mmol). Mp: 149−152 °C. Anal. Calcd for $C_{27}H_{27}NO_2P_2$: C, 70.58; H, 5.92; N, 3.05. Found: C, 69.17; H, 5.96; N, 3.04. IR (KBr disk; cm^{-1}): ν_{PO} 1189 s. ^1H NMR (CD_2Cl_2): δ 2.62 (s, C*H*$_3$, 3H), 3.63 (d, PC*H*$_2$N, 4H, $^2J_{PH}$ = 6 Hz), 7.20−7.95 (m, *phenyl*, 10H). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 29.8 (s). MS (HRMS): *m*/*z* 459.5.

$EtN(CH_2P(O)Ph_2)_2$ (5). Yield: 73% (0.167 g, 0.35 mmol). Mp: 148−152 °C. Anal. Calcd for $C_{28}H_{29}NO_2P_2$: C, 71.03; H, 6.17; N, 2.96. Found: C, 70.48; H, 6.15; N, 3.19. IR (KBr disk; cm^{-1}): ν_{PO} 1189 s. ^1H NMR ($CDCl_3$): δ 0.91 (t, C*H*$_3$, 3H, $^3J_{HH}$ = 6.95 Hz), 3.06 (q, CH_2, 2H, $^3J_{HH}$ = 6.93 Hz), 3.69 (d, PC*H*$_2$N, 4H, $^2J_{PH}$ = 5.86 Hz), 7.20−7.90 (m, *phenyl*, 10H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 29.5 (s).

$^nPrN(CH_2P(O)Ph_2)_2$ (6). Yield: 73% (0.167 g, 0.34 mmol). Mp: 154−156 °C. Anal. Calcd for $C_{29}H_{35}NO_2P_2$: C, 71.45; H, 6.41; N, 2.87. Found: C, 70.81; H, 6.25; N, 2.43. IR (KBr disk; cm^{-1}): ν_{PO} 1178 s. ^1H NMR ($CDCl_3$): δ 0.95 (t, C*H*$_3$, 3H, $^3J_{HH}$ = 7.25 Hz), 1.67 (sextet, C*H*$_2$, 2H, $^3J_{HH}$ = 7.25 Hz), 3.30 (t, C*H*$_2$, 2H, $^3J_{HH}$ = 7.25 Hz), 4.08 (d, PC*H*$_2$N, 4H, $^2J_{PH}$ = 5.85 Hz), 7.75−8.20 (m, *phenyl*, 10H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 29.1 (s).

$^iPrN(CH_2P(O)Ph_2)_2$ (7). Yield: 67% (0.152 g, 0.31 mmol). Mp: 150−154 °C. Anal. Calcd for $C_{29}H_{35}NO_2P_2$: C, 71.45; H, 6.41; N, 2.87. Found: C, 70.81; H, 6.25; N, 2.73. IR (KBr disk; cm^{-1}): ν_{PO} 1183 s. ^1H NMR ($CDCl_3$): δ 0.83 (d, C*H*$_3$, 6H, $^3J_{HH}$ = 7.25 Hz), 2.31 (m, C*H*, 1H), 3.66 (d, PC*H*$_2$N, 4H, $^2J_{PH}$ = 6.18 Hz), 7.75−8.20 (m, *phenyl*, 10H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 30.0 (s).

$^nBuN(CH_2P(O)Ph_2)_2$ (8). Yield: 75% (0.165 g, 0.33 mmol). Mp: 178−180 °C. Anal. Calcd for $C_{30}H_{37}NO_2P_2$: C, 71.84; H, 6.63; N, 2.79. Found: C, 72.16; H, 6.81; N, 2.51. IR (KBr disk; cm^{-1}): ν_{PO} 1190 s. ^1H NMR ($CDCl_3$): δ 0.72 (t, C*H*$_3$, 3H, $^3J_{HH}$ = 7.32 Hz), 0.99 (sextet, C*H*$_2$, 2H, $^3J_{HH}$ = 7.5 Hz), 1.25 (m, C*H*$_2$, 2H), 2.97 (t, C*H*$_2$, 2H, $^3J_{HH}$ = 7.14 Hz), 3.72 (d, PC*H*$_2$N, 4H, $^2J_{PH}$ = 5.5 Hz), 7.30−7.80 (m, *phenyl*, 10H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 29.2 (s).

The reactions of aminophosphines $RN(H)PPh_2$ (R = Et, ^{n}Pr, and ^{n}Bu) with paraformaldehyde also gave compounds **5**, **6,** and **8**. The typical procedure is as follows: A solution of $RN(H)PPh_2$ (1.5 mmol) and paraformaldehyde (1.50 mmol) in toluene (7 mL) was heated to reflux for 5 h. The reaction mixture was cooled to room temperature, and the solvent was removed under reduced pressure to give a white residue which was redissolved in a mixture of CH_2Cl_2−*n*-hexane (2:1) and cooled to −10 °C for 2 days to give analytically pure samples of **5**, **6**, and **8** in 70% (0.165 g, 0.31 mmol), 68% (0.247 g, 0.51 mmol), and 66% (0.248 g, 0.50 mmol) yields, respectively.

Preparation of $Ph_2P(O)CH_2N(C_2H_4)_2NCH_2P(O)Ph_2$ (9). To a solution of bis(diphenylphosphino)piperazine (0.20 g, 0.44 mmol) in 7 mL of toluene was added paraformaldehyde (0.028 g, 0.88 mmol), heated under reflux conditions for 5 h. The solution was then cooled to room temperature, the solvent was removed under reduced pressure, and the residue washed with *n*-hexane (3 × 5 mL) and redissolved in a mixture of CH_2Cl_2−*n*-hexane (3:1) to give the analytically pure product of **9**. Yield: 73% (0.160 g, 0.31 mmol). Mp: 238−240 °C (dec). Anal. Calcd for $C_{30}H_{32}N_2O_2P_2$: C, 70.03; H, 6.27; N, 5.44. Found: C, 69.48; H, 6.15; N, 5.48. IR (KBr disk; cm^{-1}): ν_{PO} 1184 vs. ^1H NMR ($CDCl_3$): δ 2.57 (s, C*H*$_2$, 4H), 3.19 (d, PC*H*$_2$N, 2H, $^2J_{PH}$ = 6.96 Hz), 7.41−7.82 (m, *phenyl*, 10H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 27.2 (s).

Preparation of $Ph_2P(O)CH_2N(CH_2)_3NCH_2P(O)Ph_2$ (10). A mixture of bis(diphenylphosphino)ethylenediamine (0.20 g, 0.44 mmol) and paraformaldehyde (0.028 g, 0.88 mmol) in 7 mL of toluene was heated under reflux conditions for 4 h. The solution was then cooled to room temperature, solvent was removed under reduced pressure, and the residue obtained was washed with hexane (4 × 3 mL) and redissolved in a mixture of CH_2Cl_2−hexane (2:1) to give the crystalline product of **10**. Yield: 55% (0.130 g, 0.26 mmol). Mp: 132−134 °C. Anal. Calcd for $C_{29}H_{30}N_2O_2P_2$: C, 69.59; H, 6.04; N, 5.60. Found: C, 69.32; H, 6.01; N, 5.33. IR (KBr disk; cm^{-1}): ν_{PO} 1171 s. ^1H NMR ($CDCl_3$): δ 2.87 (s, C*H*$_2$, 4H), 3.44 (d, PC*H*$_2$N, 4H, $^2J_{PH}$ = 7.19 Hz), 3.59 (s, C*H*$_2$, 2H), 7.26−7.89 (m, *phenyl*, 20H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 28.3 (s).

General Procedure for Preparation of $Ph_2P(O)CH(R)NHPh$ (R = Ph, OC_4H_3 (Furfuryl), C_6H_4OH-*o*). A mixture of $Ph_2PN(H)Ph$ (0.400 g, 1.44 mmol) and 1 equiv of aldehyde RCHO (R = ^{n}Pr, Ph, OC_4H_3, C_6H_4OH-*o*) was stirred at room temperature for 12 h. The resultant slurry was subjected to vacuum to remove any volatiles, and the residue obtained was washed with *n*-hexane (3 × 5 mL) and crystallized in a mixture of CH_2Cl_2−*n*-hexane (2:1) at 0 °C to give analytically pure products.

$Ph_2P(O)CH(Ph)N(H)Ph$ (11). Yield: 81% (0.451 g, 1.17 mmol). Mp: 197−200 °C (dec). Anal. Calcd for $C_{25}H_{22}NOP$: C, 78.31; H, 5.78; N, 3.65. Found: C, 78.01; H, 5.65; N, 3.17. IR (KBr disk; cm^{-1}): ν_{NH} 3387 s, ν_{PO} 1177 vs. ^1H NMR ($CDCl_3$): δ 5.39 (br m, N*H* and C*H*, N*H*−D_2O exchangeable, 2H), 6.58−7.92 (m, *phenyl*, 20H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 32.7 (s). MS (FAB): 384 (*m*/*z* + 1).

$Ph_2P(O)CH(OC_4H_3)N(H)Ph$ (12). Yield: 67% (0.360 g, 0.96 mmol). Mp: 202−205 °C. Anal. Calcd for $C_{23}H_{20}NO_2P$: C, 73.98; H, 5.39; N, 3.75. Found: C, 73.05; H, 5.53; N, 3.40. IR (KBr disk; cm^{-1}): ν_{NH} 3372 s, ν_{PO} 1184 vs. ^1H NMR ($CDCl_3$): δ 4.95 (br m, N*H*, D_2O exchangeable, 1H), 5.34 (m, C*H*, 1H), 6.16−7.88 (m, *phenyl* and *furfuryl*, 18H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 30.3 (s). MS (FAB): 374 (*m*/*z* + H).

$Ph_2P(O)CH(C_6H_4OH$-*o*$)N(H)Ph$ (13). Yield: 89% (0.510 g, 1.28 mmol). Mp: 144−148 °C. Anal. Calcd for $C_{25}H_{22}NO_2P$: C, 75.18; H, 5.55; N, 3.51. Found: C, 74.82; H, 5.32; N, 3.26. IR (KBr disk; cm^{-1}): ν_{OH} 3390 br s, ν_{NH} 3220 s, ν_{PO} 1150 vs. ^1H NMR ($CDCl_3$): δ 4.83 (br s, N*H*, D_2O exchangeable), 5.46 (dd, C*H*, 1H, $^2J_{PH}$ = 12.0 Hz, $^3J_{HH}$ = 3.0 Hz), 6.58−7.86 (m, *phenyl*, 19H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 37.9 (s).

General Procedure for the Reaction of $^nPrN(PPh_2)$ with RCHO (R = ^{n}Pr, Ph, OC_4H_3, C_6H_4OH-*o*). A mixture of $Ph_2PN(^nPr)PPh_2$ (0.400 g, 0.94 mmol) and 2 equiv of aldehyde RCHO (R = ^{n}Pr, Ph, OC_4H_3, C_6H_4OH-*o*) was stirred at room temperature for 24 h. The resultant slurry was subjected to vacuum to remove any volatiles, and the residue obtained was washed with *n*-hexane (3 × 5 mL) and crystallized in a mixture of CH_2Cl_2−*n*-hexane (2:1) at 0 °C to give analytically pure products.

$Ph_2P(O)CH(OH)CH_2CH_2CH_3$ (14). Yield: 41% (0.210 g, 0.77 mmol). Mp: 116−118 °C. Anal. Calcd for $C_{16}H_{19}O_2P$: C, 70.06; H, 6.98. Found: C, 70.67; H, 6.87. IR (KBr disk; cm^{-1}): ν_{OH} 3207 s, ν_{PO} 1179 vs. ^1H NMR ($CDCl_3$): δ 0.85 (t, C*H*$_3$, 3H, $^3J_{HH}$ = 6.32 Hz), 1.38 (m, C*H*$_2$, 2H), 1.65 (m, C*H*$_2$, 2H), 1.73 (br s, O*H*, D_2O exchangeable, 1H), 4.41 (d, C*H*, 2H, $^2J_{PH}$ = 10.32 Hz), 7.43−7.89 (m, *phenyl*, 10H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 31.3 (s).

The compound **14** is also obtained by the treatment of $Ph_2PN(H)Ph$ (0.400 g, 1.44 mmol) with butyraldehyde (0.104 g, 1.44 mmol) at room temperature. Yield: 89% (0.350 g, 1.28 mmol).

$Ph_2P(O)CH(OH)Ph$ (15). Yield: 42% (0.240 g, 0.78 mmol). Mp: 164−166 °C (dec). Anal. Calcd for $C_{18}H_{17}O_2P$: C, 74.01; H, 5.56. Found: C, 73.66; H, 5.29. IR (KBr disk; cm^{-1}): ν_{OH} 3388 s,

ν_{PO} 1163 vs. ^{1}H NMR ($CDCl_3$): δ 1.83 (br s, OH, D_2O exchangeable), 5.48 (d, C*H*, 1H, $^2J_{HH}$ = 5.24 Hz), 7.13−7.90 (m, *phenyl*, 15H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 30.6 (s).

$Ph_2P(O)CH(OH)C_6H_4OH$-*o* (16). Yield: 41% (0.250 g, 0.77 mmol). Mp: 90−92 °C. Anal. Calcd for $C_{19}H_{17}O_3P$: C, 70.37; H, 5.28. Found: C, 70.25; H, 5.33. IR (KBr disk; cm^{-1}): ν_{OH} 3229 br s, ν_{PO} 1139 vs. ^{1}H NMR ($CDCl_3$): δ 4.01 (br s, OH, D_2O exchangeable), 5.45 (d, C*H*, 1H, $^2J_{PH}$ = 5.86 Hz), 6.67−7.82 (m, *phenyl*, 14H), 9.65 (br s, O*H*, D_2O exchangeable). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 37.4 (s).

$(Ph_2P(O)CH(OC_4H_3))_2N^nPr$ (17). Yield: 37% (0.210 g, 0.34 mmol). Mp: 152−155 °C (dec). Anal. Calcd for $C_{37}H_{35}NO_4P_2$: C, 71.72; H, 5.69; N, 2.26. Found: C, 71.65; H, 5.49; N, 2.17. IR (KBr disk; cm^{-1}): ν_{PO} 1187 vs. ^{1}H NMR ($CDCl_3$): δ 0.52 (t, CH_3, 3H, $^3J_{HH}$ = 8.99 Hz), 1.25 (sextet, CH_2, 2H, $^3J_{HH}$ = 8.99 Hz), 2.14 (t, CH_2, 2H, $^3J_{HH}$ = 8.99 Hz), 5.53 (d, C*H*, 2H, $^2J_{PH}$ = 5.99 Hz.), 6.23−7.91 (m, *phenyl* and *furfuryl*, 26H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 29.8 (s). MS (FAB): 620 (*m*/*z* + H).

Preparation of Zinc, Cadmium, and Mercury Complexes, $Ph_2P(O)CH_2NHPh{\cdot}MX_2$ (M = Zn, Cd; X = CH_3COO^- and M = Hg; X = I^-). To a solution of an appropriate metal precursor (0.10 g) in methanol (10 mL) was added to a stoichiometric amount of the ligand also in methanol (5 mL), and the solution was stirred for overnight. The solvent was removed completely under reduced pressure, and the residue obtained was washed with hexane to give the products.

$[(Ph_2P(O)CH_2NHPh)Zn(CH_3COO)_2]$ (18). Yield: 82% (0.191 g, 0.37 mmol). Mp: 114−117 °C. Anal. Calcd for $C_{23}H_{24}NO_5PZn{\cdot}H_2O$: C, 54.29; H, 5.15; N, 2.75. Found: C, 54.26; H, 4.97; N, 2.65. IR (KBr disk; cm^{-1}): ν_{OH} 3329 br, ν_{NH} 3242 s, ν_{CO} 1600 s, ν_{PO} 1169 s. ^{1}H NMR ($CDCl_3$): δ 2.03 (s, CH_3, 3H), 3.95 (d, PCH_2N, 2H, $^2J_{PH}$ = 8.40 Hz), 4.41 (br s, N*H*, 1H), 7.49−7.93 (m, *phenyl*, 15H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 30.4 (s).

$[(Ph_2P(O)CH_2NHPh)Cd(CH_3COO)_2]$ (19). Yield: 70% (0.150 g, 0.26 mmol). Mp: 74−76 °C. Anal. Calcd for $C_{23}H_{24}NPO_5Cd{\cdot}2H_2O$: C, 48.14; H, 4.92; N, 2.44. Found: C, 48.03; H, 4.78; N, 2.64. IR (KBr disk; cm^{-1}): ν_{OH} 3323 br s, ν_{NH} 3242 s, ν_{CO} 1600 s, ν_{PO} 1167 s. ^{1}H NMR ($CDCl_3$): δ 2.05 (s, CH_3, 3H), 3.94 (m, PCH_2N, 2H), 6.65−7.83 (m, *phenyl*, 15H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 29.8 (s).

$[(Ph_2P(O)CH_2NHPh)HgI_2]$ (20). Yield: 95% (0.160 g, 0.21 mmol). Mp: 106−109 °C. Anal. Calcd for $C_{19}H_{18}NOPHgI_2$: C, 29.96; H, 2.38; N, 1.84. Found: C, 29.78; H, 2.43; N, 1.85. IR (KBr disk; cm^{-1}): ν_{NH} 3348 s, ν_{PO} 1143 s. ^{1}H NMR ($CDCl_3$): δ 3.94 (d, PCH_2N, 2H, $^2J_{PH}$ = 11.7 Hz), 6.74−7.91 (m, *phenyl*, 15H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 29.8 (s).

Preparation of $[Co(O_2NO)_2\{Ph_2P(O)CH_2N(H)Ph\}_2]$ (21). To an ethanolic solution (5 mL) of ($Co(NO_3)_2{\cdot}6H_2O$ (0.050 g, 0.17 mmol) was added $Ph_2P(O)CH_2NHC_6H_5$ (0.106 g, 0.340 mmol) also in ethanol (10 mL), and the mixture was stirred for 2 h at room temperature. The resultant purple colored solution was evaporated to dryness and washed with *n*-hexane (3 × 5 mL) to get crystalline product **21**. Yield: 81% (0.110 g, 0.138 mmol). Mp: 128−131 °C (dec). Anal. Calcd for $C_{38}H_{34}N_4O_8P_2Co$: C, 57.22; H, 4.55; N, 7.02. Found: C, 56.69; H, 4.66; N, 6.96. IR (KBr disk; cm^{-1}): ν_{NH} 3369 br m, ν_{NO_3} 1435 s, ν_{PO} 1163 s. UV−vis [λ (nm) (ϵ, M^{-1} cm^{-1})] (CH_2Cl_2): 544 (71); 520 (49), 289 (7892), 243 (40 588), 222 (61 274). μ_s (303 K): 4.2 μ_B.

Preparation of $[Co(O_2NO)_2\{(Ph_2P(O)CH_2)_2NR\}]$ (R = Et, ^{n}Pr). ($Co(NO_3)_2{\cdot}6H_2O$ (0.100 g, 0.34 mmol) in ethanol (7 mL) was combined with 2 equiv of the ligand ($Ph_2P(O)CH_2)_2NR$ (R = Et, ^{n}Pr) also in ethanol (10 mL), and the purple colored solution was stirred at room temperature for 2 h. The reaction mixture was concentrated to 5 mL, triturated with few drops of *n*-hexane, and kept at room temperature to give the crystalline products.

$[Co(O_2NO)_2\{(Ph_2P(O)CH_2)_2NEt\}]$ (22). Yield: 99% (0.230 g, 0.34 mmol). Mp: 150−152 °C (dec). Anal. Calcd for $C_{28}H_{31}N_3O_8P_2Co{\cdot}H_2O$: C, 49.86; H, 4.63; N, 6.23. Found: C, 49.99; H, 4.49; N, 6.17. IR (KBr disk; cm^{-1}): ν_{NO_3} 1455 s, ν_{PO} 1143 s. ^{1}H NMR (CD_3OD): δ 0.68 (br, CH_3, 3H), 3.32 (br, CH_2, 2H), 3.80 (br, PCH_2N, 4H), 7.43 (br, *phenyl*, 12H), 7.69 (br, *phenyl*, 8H). $^{31}P\{^1H\}$ NMR (CD_3OD): δ 33.7 (br s). UV−vis [λ (nm) (ϵ, M^{-1} cm^{-1})] (C_2H_5OH): 528 (20); 520 (21), 264 (5165), 225 (21 907). μ_s (303 K): 4.1 μ_B.

$[Co(O_2NO)_2\{(Ph_2P(O)CH_2)_2N^nPr\}]$ (23). Yield: 87% (0.201 g, 0.30 mmol). Mp: 174−176 °C. Anal. Calcd for $C_{29}H_{31}N_3O_8P_2Co$: C, 51.95; H, 4.66; N, 6.27. Found: C, 51.73; H, 4.61; N, 6.02. IR (KBr disk; cm^{-1}): ν_{NO_3} 1473 s, ν_{PO} 1143 s. ^{1}H NMR (CD_3OD): δ 0.27 (br, CH_3, 3H), 1.01 (br, CH_2, 2H), 1.12 (br, CH_2, 2H), 3.80 (br, PCH_2N, 4H), 7.39 (br, *phenyl*, 12H), 7.67 (br, *phenyl*, 8H). $^{31}P\{^1H\}$ NMR (CD_3OD): δ 33.5 (br s). UV−vis [λ (nm) (ϵ, M^{-1} cm^{-1})] (C_2H_5OH): 528 (24); 520 (21), 264 (5330), 225 (22 474). μ_s (303 K): 4.3 μ_B.

$[CoCl_2\{(Ph_2P(O)CH_2)_2NEt\}]$ (24). $CoCl_2{\cdot}6H_2O$ (0.100 g, 0.40 mmol) in ethanol (10 mL) was added to $(Ph_2P(O)CH_2)_2NEt$ (0.199 g, 0.40 mmol), also in ethanol (10 mL), and the blue solution was stirred at room temperature for 3 h. The solvent was removed from the reaction mixture, and the residue was washed with diethyl ether (3 × 5 mL) to give the product **24**. Yield: 60% (0.168 g, 0.25 mmol). Mp: 220−222 °C (dec). Anal. Calcd for $C_{28}H_{29}NO_4P_2CoCl_2{\cdot}4H_2O$: C, 49.79; H, 5.52; N, 2.07. Found: C, 49.38; H, 5.31; N, 1.92. IR (KBr disk; cm^{-1}): ν_{PO} 1143 s. $^{31}P\{^1H\}$ NMR (CD_3OD): δ 34.0 (br s). UV−vis [λ (nm) (ϵ, M^{-1} cm^{-1})] (C_2H_5OH): 674 (138); 644 (136), 264 (2667), 224 (19 178). μ_s (303 K): 4.4 μ_B.

$[Co\{(Ph_2P(O)CH_2)_2NEt\}_2](PF_6)_2$ (25). To an ethanolic (5 mL) solution of $CoCl_2{\cdot}6H_2O$ (0.05 g, 0.20 mmol) was added $(Ph_2P(O)CH_2)_2NEt$ (0.198 g, 0.42 mmol), also in ethanol (7 mL), and the mixture was stirred for 4 h at room temperature. To the reaction mixture was added NH_4PF_6 (0.068 g, 0.42 mmol), and the turbid solution was stirred for a further 4 h at room temperature. The blue turbid solution was filtered, and solvent was removed from the filtrate under vacuum to give the light blue colored product **25**. Yield: 61% (0.250 g, 0.193 mmol). Mp: 144−147 °C (dec). Anal. Calcd for $C_{56}H_{58}N_2P_6O_4CoF_{12}$: C, 51.90; H, 4.51; N, 2.16. Found: C, 51.70; H, 4.35; N, 2.06. IR (KBr disk; cm^{-1}): ν_{PO} 1180 s. UV−vis [λ (nm) (ϵ, M^{-1} cm^{-1})] (C_2H_5OH): 674 (106); 662 (104), 266 (6701), 226 (23 546). μ_s (303 K): 4.3 μ_B.

Preparation of $[MoO_2Cl_2\{(Ph_2P(O)CH_2)_2NEt\}]$ (26). Molybdic acid (0.50 g, 3.34 mmol) was dissolved in concentrated hydrochloric acid (4 mL), and $(Ph_2P(O)CH_2)_2NEt$ (1.64 g, 3.34 mmol) in a minimum amount of ethanol was added. The precipitated solid was filtered out and washed with water, dried, and further recrystallized from dichloromethane at room temperature. Yield: 61% (1.590 g, 2.10 mmol). Mp: 188−190 °C. Anal. Calcd for $C_{28}H_{29}NO_4P_2MoCl_2{\cdot}CH_2Cl_2$: C, 45.99; H, 4.12; N, 1.85. Found: C, 45.68; H, 4.10; N, 1.76. IR (KBr disk; cm^{-1}): ν_{PO} 1184 s. ^{1}H NMR ($CDCl_3$): δ 0.54 (t, CH_3, 3H, $^3J_{HH}$ = 6.98 Hz), 1.98 (q, CH_2, 2H, $^3J_{HH}$ = 6.98 Hz.) 3.98 (s, PCH_2N, 2H), 7.11−8.06 (m, *phenyl*, 20H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 38.9 (s).

Preparation of $[Th(NO_3)_3\{(Ph_2P(O)CH_2)_2NEt\}_2]NO_3$ (27). A solution of the dioxide $EtN(CH_2P(O)Ph_2)_2$ (0.166 g, 0.35 mmol) in ethanol (5 mL) was added to a solution of $Th(NO_3)_4{\cdot}5H_2O$ (0.100 g, 0.17 mmol) also in ethanol (10 mL). The clear solution was allowed to stir at room temperature for 4 h, during which time the product precipitated out was filtered and dried. The product was

recrystallized from CH_2Cl_2−diethyl ether (1:1) mixture. Yield: 80% (0.200 g, 0.14 mmol). Mp: 141−144 °C. Anal. Calcd for $C_{56}H_{68}N_6O_{16}P_4Th$: C, 47.13; H, 4.09; N, 5.89. Found: C, 47.25; H, 3.98; N, 6.05. IR (KBr disk; cm^{-1}): ν_{NO_3} 1519 s, ν_{PO} 1134 s. ^1H NMR ($CDCl_3$): δ 0.41 (t, C*H*$_3$, 3H, $^3J_{HH}$ = 6.59 Hz), 1.75 (q, C*H*$_2$, 2H, $^3J_{HH}$ = 6.59 Hz), 3.90 (s, PC*H*$_2$N, 4H), 7.26−7.72 (m, *phenyl*, 20H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 40.1 (s). MS (FAB): 1364 (m/z − 1).

Preparation of $[UO_2(NO_3)_2\{(Ph_2P(O)CH_2)_2NEt\}]$ (28). A solution of the ligand $EtN(CH_2P(O)Ph_2)_2$ (0.047 g, 0.09 mmol) in CH_2Cl_2 (10 mL) was added to $UO_2(NO_3)_2$ (0.050 g, 0.09 mmol) also in CH_2Cl_2 (10 mL), and the reaction mixture was stirred at room temperature for 12 h, during which time an analytically pure yellow crystalline product was separated from the reaction mixture. The product was isolated by filtration and dried under vacuum. Yield: 52% (0.045 g, 0.052 mmol). Mp: 199−200 °C (dec). Anal. Calcd for $C_{28}H_{29}N_3O_{10}P_2U$: C, 38.77; H, 3.37; N, 4.84. Found: C, 38.43; H, 3.62; N, 4.58. IR (KBr disk; cm^{-1}): ν_{NO_3} 1439 s, ν_{PO} 1175 s. ^1H NMR ($CDCl_3$): δ 0.76 (t, C*H*$_3$, 3H, $^3J_{HH}$ = 8.00 Hz), 2.39 (q, C*H*$_2$, 2H, $^3J_{HH}$ = 8.00 Hz), 4.06 (s, PC*H*$_2$N, 4H), 7.26−8.16 (m, *phenyl*, 20H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 41.8 (s).

X-ray Crystallography. Crystals of the compounds **4**, **6**, **8**, **14**, and **26** obtained as described above were mounted on Pyrex filaments with epoxy resin. An Enraf-Nonius CAD-4 diffractometer (for compound **26**) and Nonius MACH3 diffractometer (for the compounds **4**, **6**, **8**, and **14**) were used for the unit cell determination and intensity data collection. The initially obtained unit cell parameters were refined by accurately centering randomly selected reflections. General procedures for crystal alignment and collection of intensity data on the Enraf-Nonius CAD-4 diffractometer have been published.[31] The initial orthorhombic cell obtained by the CAD-4 software for **26** was confirmed by the observation of *mmm* diffraction symmetry. Periodic monitoring of check reflections showed stability of the intensity data. Details of the crystal and data collection are given in the Tables 1 and 4. The data were corrected for Lorentz and polarization effects.[32] The calculations were performed with the SHELXTL PLUS[33] program package for the compounds **4**, **8**, and **26**, whereas for the compounds **6** and **14** the structures were solved by direct methods (SHELXS-97) and refined using SHELXL-97 software.[34] The non-hydrogen atoms were geometrically fixed and allowed to refine using riding model. For **26**, an empirical (ψ-scans) absorption correction was employed.[35]

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Supporting Information Available: X-ray crystallographic files in CIF format for the structure determinations of $MeN(CH_2P(O)Ph_2)_2$ (**4**), $^nPrN(CH_2P(O)Ph_2)_2$ (**6**), $^nBuN(CH_2P(O)Ph_2)_2$ (**8**), $Ph_2P(O)CH(OH)CH_2CH_2CH_3$ (**14**), and $[MoO_2Cl_2\{(Ph_2P(O)CH_2)_2NEt\}]$ (**26**). This material is available free of charge via the Internet at http://pubs.acs.org.

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(31) Harms, K.; Wocadlo, S. *Program to Extract Intensity Data from Enraf-Nonius CAD-4 Files*; University of Marburg: Marburg, Germany, 1987.

(32) Burla, M. C.; Camalli, M.; Cascarano, G.; Giacovazzo, C.; Polidori, G.; Spagna, R.; Viterbo, D. *J. Appl. Crystallogr.* **1989**, *22*, 389.

(33) *SHELXTL PLUS*, version 5.1; Bruker AXS: Madison, WI, 1995.

(34) Sheldrick, G. M. *SHELXL-97. Program for crystal structure refinement*; University of Gottingen: Gottingen, Germany, 1997.

(35) Mague, J. T.; Lloyd, C. L. *Organometallics* **1988**, *7*, 983.