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Hypervalent Phosphorus Compounds as Ligands

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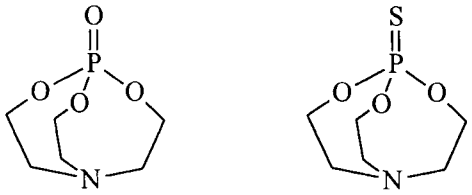
ABSTRACT: *Four new metal ion complexes with phosphatrane ligands have been isolated and characterized including* $AuBr_3(SP(OCH_2CH_2)_3N)$, $AuI_3(SP(OCH_2CH_2)_3N)$, $AuBr_3(OP(OCH_2CH_2)_3N)$ *and* $[MeHg(SP(OCH_2CH_2)_3N)](NO_3)$. *The phosphatranes are examples of hypervalent phosphorus ligands which are bound through oxygen or sulfur to the metal ion. These complexes are unique models for proposed intermediates in metal ion promoted phosphate ester substitution reactions.* © 1998 John Wiley & Sons, Inc. Heteroatom Chem 9: 699–702, 1998

INTRODUCTION

Metal ions catalyze phosphorus(V) substitution reactions including phosphate ester hydrolysis and phosphate ester transesterification [1–3]. In these reactions, it has been proposed that the metal ion binds to and stabilizes a hypervalent phosphorus transition state or intermediate. Circumstantial evidence for the presence of such intermediates in phosphate ester hydrolysis reactions has been presented. Sargeson and coworkers [4] observed the incorporation of more than one ^{18}O into a phosphate ester during hydrolysis implicating the existence of a hypervalent phosphorus intermediate. In addition, unusual product distributions have been explained by proposing metal ion bound hypervalent phosphorus intermediates [5,6]. Here, we show that metal ion complexes induce the formation of hypervalent phosphorus compounds. The isolation and characterization of several complexes with hypervalent phosphorus ligands are described.

RESULTS AND DISCUSSION

The majority of hypervalent phosphorus compounds that have been isolated contain electronegative substituents and one or more ring systems [7]. We began our search for hypervalent phosphorus ligands with the phosphate triesters **1** and **2** prepared by Verkade and coworkers (Scheme 1) [8–10]. These phosphate triesters are named "pro-phosphatranes" and form hypervalent phosphorus compounds upon formation of a P–N transannular bond to form "phosphatranes." The phosphatranes have characteristic NMR spectra including new ^1H-^{31}P and new ^{13}C-^{31}P coupling to the NCH_2 groups and a large upfield shift of the ^{31}P NMR resonance. Strong acids and alkyl-



1 **2**

SCHEME 1

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Dedicated to Prof. Robert R. Holmes on the occasion of his 70th birthday.
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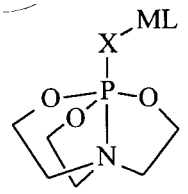
ating agents react at the oxygen or sulfur of **1** or **2**, respectively, and induce formation of a N-P transannular bond [8–10]. To date treatment of pro-phosphatranes with metal ions has failed to give phosphatranes. For example, **1** did not form a phosphatrane in the presence of Zn(II) and Co(II), as suggested by NMR spectroscopic data [10]. Our initial attempts to induce phosphatrane formation with metal ions also failed. When **1** was treated with an equivalent of $[Co(NH_3)_5(CF_3SO_3)](CF_3SO_3)_2$ in d^6-acetone, the ^{31}P NMR resonance broadened and shifted upfield by 1 ppm, consistent with binding of Co(III) to **1**. However, no new ^{31}P-^1H couplings were observed. Likewise when **1** was treated with an equivalent of $Lu(CF_3SO_3)_3$ in d^3-acetonitrile, the ^{31}P NMR resonance of **1** broadened and shifted upfield by approximately 1 ppm. However, no new ^{31}P-^1H couplings were observed, and the ^1H NMR of the triester was largely unchanged. This NMR spectroscopic data suggest that these two strongly Lewis acidic metal ions bind to **1** but do not induce phosphatrane formation. However, we cannot rule out that there is a weak transannular bond formed. Similar compounds that lack NMR spectroscopic evidence of phosphatrane formation may nonetheless have a weak transannular P–N bond as demonstrated by use of X-ray crystallography [11]. Alternately, we cannot rule out binding of the metal ion complexes to the amine of the triester although this site is highly sterically hindered.

In contrast, treatment of **1** or **2** with an equivalent of $AuBr_3$ produced new phosphatranes. The complexes **3** and **4** were isolated and found to be stable at room temperature as solids or for short periods in solution in dry acetonitrile or acetone. A large upfield shift of the ^{31}P NMR resonance was observed for both complexes consistent with a five-coordinate phosphorus center (Tables 1 and 2). The ^{31}P NMR chemical shifts are comparable to those observed for phosphatranes produced from protonation or alkylation of the chalcogenide [8–10]. In addition, new ^{31}P-^1H and ^{31}P-^{13}C NMR couplings to the NCH_2 groups were observed. These data are strong evidence for formulating **3** and **4** as phosphatrane complexes that contain a P–N transannular bond [11] with $AuBr_3$ bound to the oxygen of **1** or the sulfur of **2** (Scheme 2).

The gold complex **5** could be prepared by displacement of the phosphine ligand of $AuI_3(PEt_3)$ with one equivalent of **2** in acetonitrile solution at room temperature. ^1H and ^{31}P NMR spectra of the product were identical with those of **5** prepared from **2** and AuI_3. However this was a less effective preparation of pure **5**, as it was difficult to remove all traces of triethylphosphine. Complete displacement of the phosphine ligand attests to the fact that **2** is a good ligand for Au(III). Under conditions in which **2** completely displaces the phosphine ligand to form **5**, the simple phosphate triester $SP(OCH_3)_3$ did not react with $AuI_3(PET_3)$ to displace the phosphine ligand as determined by ^{31}P and ^1H NMR spectroscopy. Displacement of the triethylphosphine ligand is thus facilitated by the ability of the phosphate triester to form a phosphatrane. Steric differences between the two ligands is probably not responsible for the difference in coordination chemistry given that the cone angle of the phosphatrane is similar to that of the analogous acyclic phosphate triester [10]. However, the transannular bond makes the sulfur of the phosphatrane highly basic compared to the four-coordinate acyclic phosphate triesters [11]. This greater basicity would make the phosphatrane a better ligand for metal ions.

The $(CH_3)Hg^+$ cation, which has a strong affinity for sulfur ligands, formed a phosphatrane complex with **2**. A white precipitate (**6**) was isolated following treatment of **2** and $(Me)Hg(NO_3)$ in methylene chloride. ^1H, ^{31}P and ^{13}C NMR spectroscopy data all support the formation of a hypervalent phosphorus ligand (Tables 1 and 2).

To our knowledge, this report contains the first examples of metal ion complexes of hypervalent phosphorus compounds that are analogous to those proposed in phosphate ester hydrolysis. Other metal ion complexes of hypervalent phosphorus that con-



X=O, ML=$AuBr_3$ **3**
X=S, ML=$AuBr_3$ **4**
AuI_3 **5**
CH_3Hg **6**

SCHEME 2

TABLE 1 ^1H NMR Data for Phosphatranes and Pro-phosphatranes

Compound[a]	δ CH_2N	$^3J_{HH}$	$^3J_{PH}$
1	3.10 t	5.8	—
2	3.08 t	6.1	—
3	3.28 dt	6.0	1.6
4[b]	3.92 dt	6.4	4.9
5	3.51 dt	6.0	5.0
6	3.23 dt	6.0	3.0

[a]Spectra taken in d^3-acetonitrile unless noted.
[b]Spectrum taken in a^6-acetone.

TABLE 2 ^{13}C and ^{31}P NMR Data for Phosphatranes and Pro-phosphatranes

Compound[a]	$\delta^{31}P$	$\delta^{13}C(CH_2N)$	$^2J_{P\text{-}C}$
1	−6.5	49.0[b]	—
2	61.7	50.9[b]	—
3	−12.2	50.0	1.6
4[c]	0.9	—	4.9
5	1.4	50.2	5.0
6	21.8	49.0	3.0

[a]Spectra taken in a^3-acetonitrile unless noted.
[b]from reference 10 in $CDCl_3$
[c]Spectrum taken in d^6-acetone.

tain a metal–phosphorus bond (metallophosphoranes) have been reported, but these complexes are not models of those formed in substitution reactions at phosphate esters [12,13]. Only strongly Lewis acidic metal ions formed phosphatranes with **1** and **2**. It may be significant that all metal ion complexes that formed phosphatranes have a low coordination number (four or two coordinate). Both **1** and **2** are sterically bulky ligands with large cone angles. Future work will examine the reactivity of the metal ion phosphatrane complexes.

EXPERIMENTAL

All ^1H, ^{13}C, and ^{31}P NMR spectra were recorded by use of a Varian 400 XL spectrometer. Chemical shifts are given in ppm with positive values denoting a downfield shift from the reference ($SiMe_4$ or 85% phosphoric acid). Elemental analyses were performed by E&R Microanalytical Laboratories.

All syntheses were carried out under an inert N_2 atmosphere using standard Schlenk techniques. All solvents were dried before use. CH_2Cl_2 was distilled from P_2O_5; acetonitrile and methylene chloride from CaH_2. $AuBr_3$ and AuI_3 were purchased from Strem Chemicals, and all other reagents were purchased from Aldrich chemicals and used as received. $[Co(NH_3)_5(CF_3SO_3)](CF_3SO_3)_2$ [14], $AuI_3(P(CH_2\text{-}CH)_3)_3$ [15], $MeHg(NO)_3$ [16], and the phosphatranes **1** and **2** [8–10] were prepared as reported previously.

^{31}P NMR spectroscopy was used to monitor binding of **1** or **2** by metal ion complexes. For these experiments, solutions were 10 mM in **1** or **2** and in metal complex.

Synthesis of **3**

To a Schlenk flask under nitrogen was added $AuBr_3$ (0.185g, 0.423 mmol) and **1** (0.0820 g, 0.425 mmol) and 30 mL of methylene chloride. The reaction mixture was stirred at room temperature for 40 minutes. Diethyl ether was added to precipitate the light reddish-brown product. The precipitate was recrystallized from a 1:1 methylene chloride diethyl ether mixture to give orange-brown microcrystals in 40% yield. ^1H NMR (acetonitrile-d^3): 3.28 (dt, 6H, $J_{P\text{-}H}$ = 1.6 Hz, $J_{H\text{-}H}$ = 6.0 Hz), 4.28 (dt, 6H, $J_{P\text{-}H}$ = 16.4 Hz, $J_{H\text{-}H}$ = 6.0 Hz). $^{13}C\{^1H\}$ NMR (acetonitrile-d^6): 50.0 (d, $J_{P\text{-}C}$ = 5.5 Hz, NCH_2), 65.8 (d, $J_{P\text{-}C}$ = 7.8 Hz, OCH_2). $^{31}P\{^1H\}$ NMR (acetonitrile-d^3): −12.2. Anal calcd. for $C_6H_{12}NO_4PBr_3Au$: C, 11.44; H 1.92; N, 2.22. Found: C, 11.27; H, 1.86; N, 2.10.

Synthesis of 4

To a Schlenk flask under nitrogen was added $AuBr_3$ (0.523 g, 1.20 mmol) and **2** (0.251 g, 1.20 mmol) and 30 mL diethyl ether. The solution was stirred for 1 hour, and a brown precipitate was formed. The precipitate was filtered, washed with diethyl ether, and dried under vacuum. An orange brown powder was isolated in 65% yield. ^1H NMR (acetone-d^6): 3.92 (q, 6H, $J_{H\text{-}H}$ = 6.4, $J_{P\text{-}H}$ = 4.9 Hz, NCH_2), 4.68 (dt, 6H, $J_{H\text{-}H}$ = 6.4 Hz, $J_{P\text{-}H}$ = 16.6 Hz, OCH_2). ^{31}P NMR (acetone-d^6): 0.9. Anal calcd for $C_6H_{12}NO_3PSBr_3Au$: C, 11.16; H 1.87; N, 2.16. Found: C, 11.30; H, 1.89; N, 2.14

Synthesis of 5

To a Schlenk flask under nitrogen was added AuI_3 (0.205g, 0.355 mmol), **2** (0.0742g, 0.355 mmol) and 35 mL of methylene chloride. The solution was stirred at room temperature for 1 hour and diethyl ether was added to precipitate a reddish brown solid. The solid was washed with diethyl ether and dried in vacuo. The reddish-brown solid was isolated in 75% yield. ^1H NMR (acetonitrile-d^3): 3.51 (q, 6H, $J_{P\text{-}H}$ = 5.0, $J_{H\text{-}H}$ = 6.0), 4.40 (dt, 6H, $J_{P\text{-}H}$ = 16.4, $J_{H\text{-}H}$ = 6.0). $^{13}C\{^1H\}$ NMR (acetonitrile-d^3): 50.2 (d, $J_{P\text{-}C}$ = 13.5 Hz, NCH_2), 65.0 (d, $J_{P\text{-}C}$ = 13.5 Hz, OCH_2). $^{31}P\{^1H\}$ NMR (acetonitrile-d^3): 1.4.

Synthesis of 6

To a methylene chloride solution containing $CH_3Hg(NO_3)$ (0.195 g, 0.702 mmol) was added a methylene chloride solution of **2** (0.147g, 0.703 mmol). The solution was stirred for 1 hour at room temperature, and a white precipitate was formed. The solid was filtered, and washed with methylene chloride under nitrogen, and dried under vacuum. The white microcrystalline solid was isolated in 73% yield. ^1H NMR (acetonitrile-d^3): 0.86 (s, 3H, $J_{Hg\text{-}H}$ 188 Hz, $HgCH_3$), 3.23 (dt, 6H, $J_{P\text{-}H}$ = 3.0, $J_{H\text{-}H}$ = 6.0 Hz, NCH_2), 4.23 (dd, 6H, $J_{P\text{-}H}$ = 17.6, $J_{H\text{-}H}$ = 6.0 Hz,

OCH_2). $^{13}C\{^1H\}$ NMR (acetonitrile-d^3): 25.3 (s, $HgCH_3$), 49.0 (d, $J_{P\text{-}C}$ = 9.1 Hz, NCH_2), 64.9 (d, $J_{P\text{-}C}$ = 11 Hz, OCH_2). $^{31}P\{^1H\}$NMR (acetonitrile-d^3): 21.8. Anal calcd for: $C_7H_{15}O_6N_2PSHg$: C, 17.27; H, 3.11; N, 5.75. Found: C, 17.41; H, 3.06; N, 5.73.

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REFERENCES

[1] S. Kuusela, H. Lonneberg: in H. Sigel, A. Sigel (eds), *Metal Ions in Biological Systems,* Dekker, New York, vol. 32, ch. 7 (1996).
[2] J. R. Morrow: in H. Sigel, A. Sigel (eds), *Metal Ions in Biological Systems,* Dekker, New York, vol. 33, ch. 19 (1996).
[3] J. Chin, *Acc. Chem. Res., 24,* 1991, 145.
[4] D. R. Jones, L. F. Lindoy, A. M. Sargeson, *J. Am. Chem. Soc., 105,* 1983, 7327.
[5] S. H. Gellman, R. Petter, R. Breslow, *J. Am. Chem. Soc., 108,* 1986, 2388.
[6] J. R. Morrow, W. C. Trogler, *Inorg. Chem., 28,* 1989, 2330.
[7] R. R. Holmes, *Pentacoordinated Phosphorus,* American Chemical Society, Washington, DC, vols. 1 and 2 (1990).
[8] L. E. Carpenter II, B. de Ruiter, D. van Aken, H. M. Buck, J. G. Verkade, *J. Am. Chem. Soc., 108,* 1989, 4918.
[9] L. E. Carpenter II, J. G. Verkade, *J. Am. Chem. Soc. 107,* 1985, 7084.
[10] D. S. Milbrath, J. G. Verkade, *J. Am. Chem. Soc., 77,* 1979, 6607.
[11] J. G. Verkade, *Acc. Chem. Res., 26,* 1993, 483.
[12] J.-S. Tang, M. A. H. Laramay, V. Young, S. Ringrose, R. A. Jacobson, J. G. Verkade, *J. Am. Chem. Soc., 114,* 1992, 3129.
[13] A. J. Arduengo III, M. Lattman, H. V. R. Dias, J. C. Calabrese, M. Kline, *J. Am. Chem. Soc. 113,* 1991, 1799.
[14] G. G. Schlessinger: in S. Y. Tyree, Jr., ed., McGraw Hill, NY, *Inorg. Syntheses,* vol. 9, 1967, 161.
[15] F. G. Mann, D. Purdie, *J. Am. Chem. Soc.,* 1940, 62 1235.
[16] R. D. Bach, H. B. Vardhan: in J. M Shreeve, ed., John Wiley & Sons, NY, *Inorg. Syntheses,* vol 24, 1986, 143.