Organometallic Phosphinimines as Building Blocks for Potential New Radiopharmaceuticals.

Synthesis, Structure and Reactivity of $\text{Ph}_3\text{P}=\text{NH}_2^+\text{ReO}_4^-$

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Reactions of the organometallic phosphinimine $\text{Ph}_3\text{P}=\text{N}-\text{SiMe}_3$ (**1**), with aqueous ReO_4^- and $^{188}\text{ReO}_4^-$ yield the ion pairs $\text{Ph}_3\text{P}=\text{NH}_2^+\text{MO}_4^-$ ($\text{M} = \text{Re}$ (**2**); ^{188}Re (**4**)). The ion pairs undergo dehydration upon heating to produce the neutral Re(VII) species: $\text{Ph}_3\text{P}=\text{N}-\text{MO}_3$ ($\text{M} = \text{Re}$ (**3**); ^{188}Re (**5**)). The solid state structure of $\text{Ph}_3\text{P}=\text{NH}_2^+\text{ReO}_4^-$ (**2**) shows the presence of hydrogen bonding between the iminato hydrogen and the rhenium oxo center. The relevance of such reactions for the design of new radiopharmaceuticals is discussed.

Introduction

There is a resurgence of interest in the use of organometallic phosphinimines (e.g.; $\text{Ph}_3\text{P}=\text{N}-\text{SiMe}_3$ (**1**)) as novel ligand systems for transition metals and actinide metals [1]. Phosphinimines of the type **1** have shown versatility in their ability to donate 1, 2, or 4 electrons to transition metals to produce kinetically stable compounds with most early transition metals. The N-Silylphosphinimines of the type **1** are prolific in their reactions with metal precursors because reactions with the metal halides proceeds through the facile elimination of Me_3SiX , whereas, metal oxides also react smoothly through the migration of Me_3Si from the iminato nitrogen onto the oxygen of the metal center. Despite the diversity in structure and reactivity of phosphinimines as noted above, there are no reports of the reactions of this class of ligand systems with metallic radioisotopes. The development of fundamental coordination chemistry of rhenium and technetium continue to make significant impact in the discovery of new radiopharmaceuticals of rhenium and technetium-99m for applications in nuclear medicine. A number of different ligand systems which include macrocyclic amines [2], aminethiols [3], amidethiols [4], isocyanides [5], boronic acid derivatives [6], phosphines [7], phos-

phonates [8] and many other ligand frameworks [9] have been used in the past to produce stable complexes of rhenium and technetium. In this communication, we report the use of an organometallic phosphinimine, $\text{Ph}_3\text{P}=\text{N}-\text{SiMe}_3$ (**1**), to produce complexes of rhenium $\text{Ph}_3\text{P}=\text{NH}_2^+\text{ReO}_4^-$ (**2**) and $\text{Ph}_3\text{P}=\text{N}-\text{ReO}_3$ (**3**) and also the corresponding ^{188}Re analogues $\text{Ph}_3\text{P}=\text{NH}_2^+^{188}\text{ReO}_4^-$ (**4**) and $\text{Ph}_3\text{P}=\text{N}^{188}\text{ReO}_3$ (**5**).

Results and Discussion

We have investigated the reaction of $\text{Ph}_3\text{P}=\text{N}-\text{SiMe}_3$ (**1**) with $\text{NH}_4^+\text{ReO}_4^-$ with the intent of extending the chemistry to the corresponding tetraoxo anion of ^{188}Re and $^{99\text{m}}\text{Tc}$ [10]. Aqueous solutions of NH_4ReO_4 on treatment with a solution of $\text{Ph}_3\text{P}=\text{N}-\text{SiMe}_3$ (**1**) in CH_3CN resulted in a near quantitative yield of the ion pair $\text{Ph}_3\text{P}=\text{NH}_2^+\text{ReO}_4^-$ (**2**) (Scheme 1) which was isolated as a colorless crystalline solid upon recrystallization from CH_3CN . Analytical, spectroscopic (^{31}P NMR and IR) data and single crystal X-ray crystallographic analysis (Fig. 1) confirmed its chemical constitution.

The structure reveals the presence of hydrogen bonding between the iminato hydrogens and the oxygen atoms of the ReO_4^- anion. The P–N bond length (1.636(7) Å) (Table I) found in the Re(VII) ion pair **2** is within the range observed for a recently reported non-metallated free phosphinimine ion pair of the type: $\text{R}_2\text{R}'\text{P}=\text{NH}_2^+\text{Cl}$ [11]. The absence of any significant elongation of the P–N bond in **2**

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Scheme 1.

Fig. 1. ORTEP drawing of $\text{Ph}_3\text{P}=\text{NH}_2^+\text{ReO}_4^-$ (**4**) showing 50% thermal ellipsoids. The interaction between O(1) or O(3) and the imine N is through hydrogen bonding.

as compared to the free phosphinimine may suggest some delocalization of electronic charge from the Re(VII) center onto the P–N bond. This is further indicated by the fact that the P–N bond length in **2** is very similar to the P–N bond lengths reported for a number of phosphinimine complexes of early transition metals [1]. The ion pair is soluble in ethyl alcohol and other common organic solvents (*e.g.*, CHCl_3 , toluene and THF). The addition of water to the CH_3CN solutions of **2** (1:1) did not result in the dissociation of the ion pair and such solutions also did not show a temperature dependency of the ^{31}P NMR chemical shifts. The ion pair **2** has a sharp melting point of 160 °C and remelts without decomposition at the same temperature. It is non-hygroscopic and can be stored in an open atmos-

Table I. Selected bond distances [Å] and angles [°].

Distances	
Re–O(1)	1.710(8)
Re–O(2)	1.690(7)
Re–O(2)	1.699(8)
Re–O(2)	1.727(7)
P–N	1.636(7)
P–C(1)	1.794(8)
P–C(7)	1.769(8)
P–C(13)	1.806(8)
Angles	
O(1)–Re–O(2)	108.7(4)
O(1)–Re–O(3)	112.3(5)
O(1)–Re–O(4)	108.3(4)
O(2)–Re–O(3)	108.9(5)
O(2)–Re–O(4)	108.9(4)
O(3)–Re–O(4)	109.6(4)
N–P–C(1)	107.3(4)
N–P–C(7)	114.3(4)
N–P–C(13)	107.0(4)
C(1)–P–C(7)	111.0(4)
C(1)–P–C(13)	108.4(3)
C(7)–P–C(13)	108.6(4)
P–C(1)–C(2)	119.8(6)
P–C(1)–C(6)	119.8(6)
P–C(7)–C(8)	118.1(7)
P–C(7)–C(12)	124.1(7)
P–C(13)–C(14)	119.4(6)
P–C(13)–C(18)	119.7(7)

phere for months. The dual neutral and ionic type of solubility properties, the melting behavior and the unusual stability of this salt in alcohol is noteworthy. The toluene or acetonitrile solution of **2** upon boiling for 4–6 h produced the neutral Re(VII) phosphinimine complex $\text{Ph}_3\text{P}=\text{N}-\text{ReO}_3$ (**3**) in near quantitative yields. The neutral complex **3** was also obtained in 60% yield by heating the solid ion pair **2** *in vacuo* at 185 °C for 1.5 h. The electron impact mass spectrum of **3** showed the parent ion (510; 80%) and the solution molecular weight measurements of **3** revealed that it is monomeric in solution.

Roesky *et al.* have reported an approach to the formation of **3** in 38% yield from the reaction of $\text{Ph}_3\text{P}=\text{N}-\text{SiMe}_3$ with Re_2O_7 [12]. Our methodology to produce **3** serves as a model to extend the reactions of $\text{Ph}_3\text{P}=\text{N}-\text{SiMe}_3$ with the tetraoxo anions of $^{99\text{m}}\text{Tc}$ or ^{188}Re . The extension of this chemistry to produce the $^{99\text{m}}\text{Tc}$ or ^{188}Re analogues of **2** and **3** would also be worthwhile in the context of developing organic soluble $^{99\text{m}}\text{Tc}$ or ^{188}Re .

Simple mixing of an aqueous solution of $^{188}\text{ReO}_4^-$ with a CH_3CN solution of $\text{Ph}_3\text{P}=\text{N}-\text{SiMe}_3$ (**1**) at

25 °C produced the ^{188}Re analogue of the ion pair **2** in 98% yields (Scheme 1). Upon heating the toluene extract of $\text{Ph}_3\text{P}=\text{NH}_2^{+188}\text{ReO}_4^-$ (**4**), at 80 °C for 30 min the tracer level analogue of **3**, $\text{Ph}_3\text{P}=\text{N}^{188}\text{ReO}_3$ (**5**), was obtained in >95% yields. The ion pair and the neutral complex **5** were found to be quite stable in dry toluene with minimal or no decomposition occurring for up to 18 h. The TLC R_f values of **5** matched closely with those of its non-tracer analogue **3**. The TLC R_f values (Table I) for **2** and its ^{188}Re analogue **4** are in perfect agreement to indicate that the species formed at the tracer level is indeed the one identified to be $\text{Ph}_3\text{P}=\text{NH}_2^{+}\text{ReO}_4^-$ at the non-tracer level. The thin layer chromatographic scanning of **4** and **5** eluted in acetone and ethyl acetate showed sharp single peaks which indicate that both the ion pair and the neutral complexes of ^{188}Re were singular chemical species. The complexes are generally insoluble in aqueous media because they contain three phenyl groups bound to phosphorus.

Conclusions

$^{99\text{m}}\text{Tc}$ and ^{188}Re are commonly used radioisotopes for diagnosis and therapy of cancer in nuclear medicine. In most parts of the world these two radioisotopes are readily available in their tetraoxo anion (*i.e.*, MO_4^-) form. The direct interaction of MO_4^- ($\text{M} = \text{Re}$ and ^{188}Re) with an organometallic phosphinimine to produce a complex of rhenium as demonstrated in this communication, may set a new trend in the application of unconventional ligand systems in the development of a new generation of radiopharmaceuticals. The substitutional chemistry of the tetrahedral P(V) center in **1** is extensive and such tuning of substituents on the phosphorus may become the most practical approach to develop new classes of radiopharmaceuticals with improved biolocalization and biodistribution characteristics.

Experimental

The trimethylsilylphosphinimine $\text{Ph}_3\text{P}=\text{N}-\text{SiMe}_3$ (**1**) was prepared according to reported procedures [13]. NH_4ReO_4 was used as supplied by Aldrich U.S.A. $\text{NH}_4^{+188}\text{ReO}_4^-$ was obtained from a $^{188}\text{W}/^{188}\text{Re}$ generator as supplied by the University of Missouri Research Reactor.

Preparation of $\text{Ph}_3\text{P}=\text{NH}_2^{+}\text{ReO}_4^-$ (**2**)

To a CH_3CN (100 ml) solution of $\text{Ph}_3\text{P}=\text{N}-\text{SiMe}_3$ (**1**) (4.11 g, 11.77 mmol) was added an aqueous solution (10 ml) of NH_4ReO_4 (3.15 g, 11.77 mmol) dropwise at 25 °C. The mixture was stirred for 1 h before the volatiles and the aqueous solvents were removed *in vacuo* to produce a white crystalline solid of $\text{Ph}_3\text{P}=\text{NH}_2^{+}\text{ReO}_4^-$ (**2**). The final purification of **2** was achieved by recrystallization from CH_3CN ; cooling the solutions to 0 °C produced cubic shaped X-ray quality crystals of **2** (86%), m.p. 160 °C. ^{31}P NMR (CDCl_3 ; 85% H_3PO_4) δ 35.10; IR (Nujol) ν_{NH_2} 3176 cm^{-1} .

Analysis

Calcd	C 40.89	H 3.20	N 2.65%,
Found	C 40.85	H 3.15	N 2.62%.

Preparation of $\text{Ph}_3\text{P}=\text{N}-\text{ReO}_3$ (**3**)

A solution of **2** (2.55 g, 5.0 mmol) in acetonitrile (100 ml) was heated under reflux for 6 h before the solvent was removed *in vacuo* to obtain a colorless solid of $\text{Ph}_3\text{P}=\text{N}-\text{ReO}_3$ (**3**). Recrystallization of **3** from CH_3CN produced analytically pure **3**. Yield 78%; m.p. 192 °C (decomp.), Lit. m.p. [27] 193 °C (decomp.). ^{31}P NMR (CDCl_3 ; 85% H_3PO_4) δ 38.2.

Analysis for $\text{C}_{18}\text{H}_{15}\text{NPrReO}_3$

Calcd	C 42.35	H 2.96	N 2.74%,
Found	C 42.29	H 2.93	N 2.72%.

Roesky *et al.* [12] have independently reported the formation of **3** ($\delta^{31}\text{P} = 37.9$) in 38% yield from the reaction of Re_2O_7 with $\text{Ph}_3\text{P}=\text{N}-\text{SiMe}_3$.

Preparation of $\text{Ph}_3\text{P}=\text{NH}_2^{+188}\text{ReO}_4^-$ (**4**)

Typically the ^{188}Re complex was prepared by mixing 100 μCi (370 kBq) of $^{188}\text{ReO}_4^-$ in a 0.1 ml saline solution with $\text{Ph}_3\text{P}=\text{N}-\text{SiMe}_3$ (**1**) (10–15 mg) in a 1 ml toluene solution. The mixture was vortexed for 1 min at r.t. 5 min following vortexing, an aliquot of the organic layer was removed and the radiochemical purity (RCP) of the ^{188}Re complex **2** was measured. Caution: Rhenium-188 is a β emitter ($E = 1.12$ MeV; $t_{1/2} = 17$ h). All work has been done in laboratories approved for the use of radioactive materials.

Preparation of $\text{Ph}_3\text{P}=\text{N}-^{188}\text{ReO}_3$ (**5**)

A toluene extract of $\text{Ph}_3\text{P}=\text{NH}_2^{+188}\text{ReO}_4^-$ (2 ml; 100–150 μCi) was heated at 80 °C for 30 min. An aliquot of the solution was used to determine the radiochemical purity (RCP) (95%) of $\text{Ph}_3\text{P}=\text{N}-^{188}\text{ReO}_3$ by radiographic scanning methods as described below.

Table II. TLC R_f values for Re^a - and $^{188}\text{Re}^b$ -phosphiniminato complexes.

Complex	Acetone	R_f values	
		Saline	Ethyl acetate
$\text{NH}_4^+\text{ReO}_4^-$	0.97	0.90	0.0
$\text{Ph}_3\text{P}=\text{NH}_2^+\text{ReO}_4^-$	0.85	0.88	0.80
$\text{Ph}_3\text{P}=\text{NH}_2^{+188}\text{ReO}_4^-$	0.86	0.88	0.80
$\text{Ph}_3\text{P}=\text{N}-\text{ReO}_3$	0.82	0.0	0.75
$\text{Ph}_3\text{P}=\text{N}-^{188}\text{ReO}_3$	0.82	0.0	0.73

^a R_f values determined by conventional TLC chromatography; ^b R_f values determined by radiographic scanning of the chromatographic strips (see Experimental for details).

Chromatographic and radiographic scanning studies

The radiochemical purity (RCP) of the ^{188}Re complexes were determined by paper chromatography (PC) and on instant thin layer chromatography-silica gel (ITLC-SG). PC and ITLC-SG analysis involved spotting 10 μl of the complex near the bottom (origin) of the strips. The strips were then developed in 0.9% aqueous saline, ethyl acetate and acetone. Determination of the R_f 's and quantitation of the migration of activity on the paper strips were made using AMBIS radiochromatographic scanning system and/or by cutting 1 cm sections of the strips and counting each section in a NaI well counter. The RCP's of the samples at r.t. were measured for 24 h to study their stability as a function of time. The complexes were formed in typically >95% yields and showed no significant decomposition over a period of 24 h. Blanks of $^{188}\text{ReO}_4^-$ were done on PC and ITLC-SG. Typically, $\text{NH}_4^{+188}\text{ReO}_4^-$ showed an R_f of 0.97 in acetone, an R_f of 0.00 in ethyl acetate and an R_f of 0.9 in saline on both paper and thin layer-silica gel strips.

Single crystal X-ray structural analysis of $\text{Ph}_3\text{P}=\text{NH}_2^+\text{ReO}_4^-$ (2)

Crystal data for $\text{C}_{18}\text{H}_{15}\text{NPREO}_4$ (4): orthorhombic P2₁2₁2 (No. 19), $a = 11.1809(9)$; $b = 11.4598(11)$; $c = 14.5957(9)$ Å; $V = 1870.2(3)$ Å³; $Z = 4$; $D_{\text{calcd}} = 1.870$ g cm⁻³, λ (MoK α) = 0.70930 Å, $\mu = 6.69$ mm⁻¹. An Enraf-Nonius CAD-4 diffractometer was used to collect 3622 independent reflections on a colorless cubic shaped crystal. Of these 3215 were observed ($I \geq 2.5 \sigma(I)$). The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included in idealized positions. $R = 0.029$, $R_w = 0.042$.

Table III. Atomic parameters x , y , z and B_{iso} . E.S.D.s. refer to the last digit printed.

	x	y	z	B_{iso}
Re	0.34177(3)	0.28070(3)	0.138223(19)	2.762(14)
O1	0.1892(7)	0.2718(7)	0.1340(6)	5.9(4)
O2	0.3844(9)	0.2918(9)	0.2489(5)	6.5(4)
O3	0.3952(9)	0.3975(8)	0.0794(6)	6.7(4)
O4	0.4003(7)	0.1539(7)	0.0927(5)	5.0(3)
P	0.99840(16)	0.97329(15)	0.14356(13)	2.57(7)
N	1.0577(6)	1.0640(7)	0.0699(5)	3.6(3)
C1	1.1111(7)	0.9397(7)	0.2270(5)	2.6(3)
C2	1.2295(7)	0.9675(7)	0.2097(6)	3.4(3)
C3	1.3169(9)	0.9346(9)	0.2751(8)	4.7(4)
C4	1.2841(9)	0.8739(8)	0.3496(7)	4.0(4)
C5	1.1647(10)	0.8439(10)	0.3660(6)	4.8(5)
C6	1.0798(8)	0.8752(8)	0.3055(6)	3.5(3)
C7	0.8667(7)	1.0253(7)	0.1969(6)	3.1(3)
C8	0.7591(9)	1.0257(8)	0.1449(8)	4.3(4)
C9	0.6579(9)	1.0754(9)	0.1816(10)	5.2(5)
C10	0.6602(10)	1.1189(8)	0.2679(11)	5.8(6)
C11	0.7585(10)	1.1206(9)	0.3205(9)	5.0(5)
C12	0.8633(9)	1.0741(8)	0.2839(6)	3.7(3)
C13	0.9627(7)	0.8414(7)	0.0816(5)	2.8(3)
C14	0.8765(8)	0.7665(7)	0.1160(6)	3.2(3)
C15	0.8571(9)	0.6593(8)	0.0739(7)	4.3(4)
C16	0.9229(12)	0.6310(8)	-0.0031(6)	5.0(5)
C17	1.0058(14)	0.7029(11)	-0.0369(7)	5.7(5)
C18	1.0277(10)	0.8119(9)	0.0047(7)	4.5(4)

B_{iso} is the mean of the principal axes of the displacement ellipsoid.

The final difference map had maximum and minimum densities of +0.870 and -1.130 eÅ⁻³, respectively. The positional parameters and their estimated standard deviations are summarized in Table III. Atomic scattering factors and anomalous dispersion corrections were taken from the International Table for X-Ray Crystallography [14]. All calculations were performed with NRCVAX [15].

Further details may be obtained from: Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, by quoting the Registry-No. CSD 57422, the names of the authors and the journal citation.

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