Heteroatomic Chelation of Mixed Phosphine (or Arsine) and Phosphine Oxide Ligands with Rhenium(V). Synthesis, Characterization, and X-ray Structural Investigations of New Rhenium(V) Metallacyclic Compounds: $(O)PPh_2(CH_2)_nEPh_2Re(O)Cl_3$ (E = P, As)

Kattesh V. Katti[*,†] and Charles L. Barnes[‡]

Departments of Radiology and Chemistry, University of Missouri, Columbia, Missouri 65211

Received January 23, 1992

The reactions of $(O)PPh_2CH_2PPh_2$ (1) and $(O)PPh_2CH_2CH_2AsPh_2$ (3) with $ReOCl_4^-$, generated from NH_4ReO_4 and concentrated HCl, produced $(O)PPh_2CH_2PPh_2Re(O)Cl_3$ (2) and $(O)PPh_2CH_2CH_2AsPh_2Re(O)Cl_3$ (4), respectively. The monoethoxy derivatives $(O)PPh_2CH_2PPh_2Re(O)(OEt)Cl_2$ (5) and $(O)PPh_2CH_2CH_2AsPh_2Re-(O)(OEt)Cl_2$ (6) were prepared by performing the above reactions in ethanol medium. The Re(V) complex Re-$(O)Cl_3(PPh_3)_2$ (7) undergoes ligand-exchange reactions with 1 or 3 to produce 2 and 4, respectively. The chemical compositions of all the new complexes have been established by analytical data and ^1H NMR, ^{31}P NMR, and IR spectroscopic data. The structure of 2 has been confirmed by an X-ray crystallographic study. The structure comprises the neutral monomeric complex $(O)PPh_2CH_2PPh_2Re(O)Cl_3$ with two crystallographically independent molecules in the asymmetric unit and a cocrystallized molecule of tetrahydrofuran. Crystal data: monoclinic space group $P2_1/c$, $a = 19.689$ (4) Å, $b = 20.030$ (3) Å, $c = 14.776$ (4) Å, $\beta = 91.329$ (10)°, $V = 5825.7$ (22) Å^3, $Z = 8$. The structure was solved by direct methods and was refined to $R = 0.048$.

Introduction

There is a burgeoning interest in the use of phosphine and arsine ligands to produce chelates of metallic radioisotopes for applications in nuclear medicine.[1] As part of our ongoing research in the development of new radiopharmaceuticals for applications in therapeutic and diagnostic nuclear medicine, we are presently exploring the chemistry of technetium-99m and rhenium-188/186 radioisotopes with new main group ligand systems.[2-4] In this connection, not only is a thorough understanding of the fundamental ligating chemistry of rhenium important to develop the rhenium-188/186 analogues but also the periodic relationship between Re and Tc can be advantageously used for the development of new technetium chemistry. The chemical and structural diversities of the functionalized phosphines have been extensively used in the development of new complexes of rhenium and related transition metals.[5,6] In particular, the ability of the electronic properties of triarylphosphines (e.g., PPh3) to stabilize rhenium in the +5 oxidation-state is well documented.[6-8] We have embarked upon a study involving the reactions of Re(V) precursors with mixed donor phosphorus ligands containing an arylphosphine or -arsine in combination with a phosphine oxide within the ligand backbone. In this paper, we report the synthesis and X-ray crystal structure investigation of heteroatomic chelated cyclometallaphosphine–phosphine oxide and analogous arsine complexes of Re(V), $(O)PPh_2(CH_2)_nEPh_2Re(O)Cl_3$ (E = P (2); E = As (4)). The efficacy of ligand-exchange reactions using the phosphine or arsine ligands $(O)PPh_2(CH_2)_nEPh_2$ (E = P, $n = 1$ (1); E = As, $n = 2$ (3)) is also demonstrated.

Experimental Section

All reactions were performed under anaerobic and anhydrous conditions using prepurified N_2 and conventional Schlenk techniques. Reagents such as PPh_3 and NH_4ReO_4 were purchased from Aldrich Chemical Co. The compounds $Ph_2AsCH_2CH_2PPh_2NSiMe_3$,[9] $(O)PPh_2CH_2PPh_2$ (1),[10] and $Re(O)Cl_3(PPh_3)_2$[11] were prepared according to literature methods.

Infrared spectra were obtained using Nujol mulls and KBr cells on a Mattson Galaxy 3000 spectrophotometer. ^{31}P and ^1H NMR spectra were obtained from a Bruker WH500 spectrometer using 85% H_3PO_4 and $SiMe_4$ as external standards, respectively.

Synthesis of $(O)PPh_2CH_2PPh_2Re(O)Cl_3$ (2). Compound 2 was produced in quantitative yields from the reaction of $ReOCl_4^-$ with $(O)PPh_2CH_2PPh_2$ (1) in THF.

(a) Generation of $ReOCl_4^-$. To a 250-mL round-bottom flask containing NH_4ReO_4 (2.760 g; 10.29 mmol) was added dropwise with stirring at 25 °C concentrated HCl (15 mL). The reaction mixture was stirred until a yellow homogeneous solution of $ReOCl_4^-$ was formed.

(b) Reaction of $ReOCl_4^-$ with 1. The phosphine–phosphine oxide ligand 1 (19.20 g; 48 mmol) in THF (100 mL) was added dropwise with stirring to $ReOCl_4^-$ as produced above. The reaction mixture immediately turned blue, and a blue precipitate of 2 deposited in the reaction mixture within 30 min. The solid was filtered off and washed with THF (2 × 25 mL) to remove the phosphine oxide byproduct (i.e. $(O)PPh_2CH_2PPh_2(O)$), and the light-blue residue was dried in vacuo to obtain 2 (yield 87%), mp 188 °C dec. Anal. Calcd for $C_{25}H_{22}Cl_3O_2P_2Re$: C, 42.33; H, 3.10; Cl, 15.00. Found: C, 42.17; H, 3.08; Cl, 15.12. MS(EI): m/z 708 (M$^+$).

Synthesis of $(O)PPh_2CH_2CH_2AsPh_2Re(O)Cl_3$ (4). The oxotetrachlororhenate(V) anion ($ReOCl_4^-$) was generated from NH_4ReO_4 (0.96 g; 3.57 mmol) and concentrated HCl (10 mL) as described above. A THF (100 mL) solution of 3 was added dropwise to the solution of $ReOCl_4^-$ at 25 °C, whereupon the reaction mixture turned blue and a blue precipitate appeared after 30 min. The precipitate was filtered off and washed with THF (2 × 25 mL) to obtain 4 (yield 78%), mp 220 °C dec. Anal. Calcd

---

* To whom correspondence should be addressed.
† Department of Radiology.
‡ Department of Chemistry.

(1) For leading references of technetium and rhenium chemistry with phosphine and arsine ligands, see: (a) Konno, T.; Heeq, M. J.; Stucky, J. A.; Kirchhoff, J. R.; Heinman, W. R.; Deutsch, E. *Inorg. Chem.* **1992**, *31*, 1173. (b) Konno, T.; Heeg, M. J.; Deutsch, E. *Inorg. Chem.* **1988**, *27*, 4113. (c) Konno, T.; Kirchhoff, J. R.; Heineman, W. R.; Deutsch, E. *Inorg. Chem.* **1989**, *28*, 1174. (d) Konno, T.; Heeg, M. J.; Deutsch, E. *Inorg. Chem.* **1989**, *28*, 1694. (e) Deutsch, E.; Ketring, A. R.; Libson, K.; Vanderheyden, J.-L.; Hirth, W. W. *Nucl. Med. Biol.* **1989**, *16*, 191.
(2) Singh, P. R.; Volkert, W. A.; Ketring, A. R.; Troutner, D. E.; Katti, K. K.; Katti, K. V. *J. Labelled Compd. Radiopharm.*, in press.
(3) Katti, K. V.; Singh, P. R.; Katti, K. K.; Kopicka, K.; Volkert, W. A.; Ketring, A. R. *J. Labelled Compd. Radiopharm.*, in press.
(4) Katti, K. V.; Singh, P. R.; Katti, K. K.; Volkert, W. A.; Ketring, A. R. *Int. J. Appl. Radiat. Isot.*, in press.
(5) Rouschias, G. *Chem. Rev.* **1974**, *74*, 531.
(6) Fergusson, J. E. *Coord. Chem. Rev.* **1966**, *1*, 459.
(7) Sergienko, V. S.; Koshits, M. A.; Mistryukov, V. E.; Kotegor, K. E. *Sov. J. Coord. Chem. (Engl. Transl.)* **1982**, *8*, 119.
(8) Sergienko, V. S.; Koshits, M. A. *Sov. J. Coord. Chem. (Engl. Transl.)* **1982**, *8*, 130.

(9) Katti, K. V.; Cavell, R. G. *Organometallics* **1989**, *8*, 2147.
(10) Grim, S. O.; Satek, L. C.; Tolman, C. A.; Jessen, J. P. *Inorg. Chem.* **1975**, *14*, 656 and references therein.
(11) Johnson, N. P.; Lock, C. J.; Wilkinson, G. *J. Chem. Soc.* **1964**, 1054.

Table I. Crystallographic Data for **2**

formula	$C_{25}H_{22}O_2P_2Cl_3Re\cdot^1/_2C_4H_8O$	V, Å^3	5825.7 (22)
fw	745.02	Z	8
cryst syst	monoclinic	T, °C	22 (1)
space group	$P2_1/c$ (No. 14)	μ, cm^{-1}	46.3
a, Å	19.689 (4)	d_{calcd}, g cm^{-3}	1.699
b, Å	20.030 (3)	R^a	0.048
c, Å	14.776 (4)	$R_w{}^b$	0.083
β, deg	91.329 (10)		

$^a R = \sum[|F_o|-|F_c|/\sum|F_o|$. $^b R_w = [\sum w(|F_o|-|F_c|)^2/\sum|F_o^2|]^{1/2}$, $w = 1/[\sigma^2|F_o| + 0.0008(F_o)^2]$.

for $C_{26}H_{24}Cl_3O_2PAsRe$: C, 40.70; H, 3.13; Cl, 13.87. Found: C, 40.59; H, 3.17; Cl, 13.69. MS(EI): m/z 766 (M$^+$).

Synthesis of (O)PPh$_2$CH$_2$PPh$_2$Re(O)(OEt)Cl$_2$ (5) and (O)PPh$_2$CH$_2$-CH$_2$AsPh$_2$Re(O)(OEt)Cl$_2$ (6). Complexes **5** and **6** were obtained in 88 and 83% yields, respectively, by carrying out the reactions of **1** or **3** with ReOCl$_4^-$ using absolute ethanol as the solvent. **5**: mp 210 °C dec. Anal. Calcd for $C_{27}H_{27}Cl_2O_3P_2Re$: C, 45.11; H, 3.75; Cl, 9.87. Found: C, 45.10; H, 3.68; Cl, 9.79. MS(EI): m/z 717 (M$^+$). **6**: mp 230 °C dec. Anal. Calcd for $C_{28}H_{29}Cl_2O_3AsPRe$: C, 43.29; H, 3.73; Cl, 9.13. Found: C, 43.18; H, 3.65; Cl, 9.15. MS(EI): m/z 775 M$^+$.

Synthesis of 2 from Ligand-Exchange Reactions between 1 and Re-(O)Cl$_3$(PPh$_3$)$_2$ (7). A solution of **1** (3.55 g; 8.87 mmol) in THF (100 mL) was added dropwise to a suspension of **7** (7.33 g; 8.80 mmol) in THF (50 mL) at 25 °C. The reaction mixture was heated under reflux for 6 h before the solvent was removed under vacuum to obtain a light blue solid which was washed with THF (4 × 25 mL) to produce **2** (yield 88%), mp 188 °C dec. Anal. Calcd for $C_{25}H_{22}Cl_3O_2P_2Re$: C, 42.33; H, 3.10; Cl, 15.00. Found: C, 42.30; H, 3.12; Cl, 15.02. The spectroscopic data were similar to those reported above. The ligand exchange between **3** and **7** was performed under conditions identical to those described above, and **4** was obtained in 89% yield; mp 221 °C dec. Anal. Calcd for $C_{26}H_{24}Cl_3O_2PAsRe$: C, 40.70; H, 3.13; Cl, 13.87. Found: C, 40.65; H, 3.15; Cl, 14.90. The spectroscopic data were similar to those described for **4**.
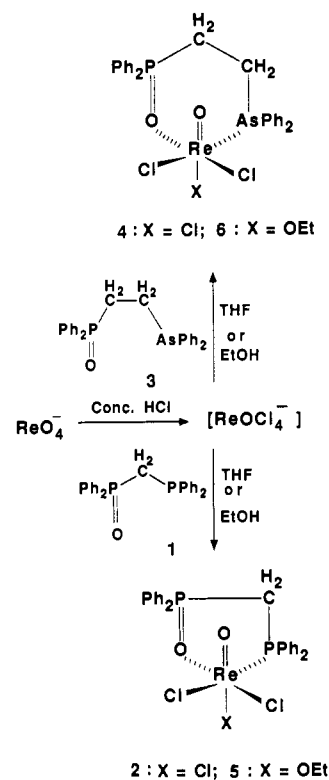
X-ray Data Collection and Processing

Light blue cubic crystals of **2** were isolated from slow evaporation of its THF solutions. All X-ray data were collected by using an Enraf-Nonius CAD4 diffractometer with Mo Kα radiation and a graphite monochromator at 22 (1) °C. Crystal data and details of data collection are given in Table I. The positional parameters are summarized in Table II. The unit cell dimensions were obtained from a least-squares fit to setting angles of 25 reflections. The crystals of **2** exhibited no significant decay under X-ray irradiation.

The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares methods, which minimized $\sum w(|F_o| - |F_c|)^2$ where $w^{-1} = (\sigma^2(\text{counting}) + (0.008(F_o^2)^2/4F_o^2$. Atomic scattering factors which included anomalous scattering contributions were from ref 12. All the hydrogen atoms were introduced in the last step of the refinement procedure in calculated positions. The final agreement factor (R) for **2** was 0.048, and the highest peak in the final difference Fourier map was 1.48 e Å^{-3}. The programs used for crystallographic computations are reported in ref 13. Listings of full experimental details, coordinates, temperature factors, and anisotropic temperature factors are deposited as supplementary material.
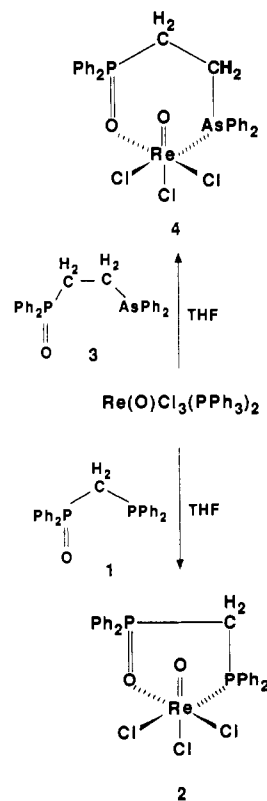
Results

The reactions of the heterodifunctional phosphine–phosphine oxide, Ph$_2$PCH$_2$PPh$_2$(O) (1), and arsine–phosphine oxide, Ph$_2$AsCH$_2$CH$_2$PPh$_2$(O)[14] (3), functionalized ligands with ReOCl$_4^-$ to produce the Re(V) metallacyclic compounds (O)PPh$_2$CH$_2$-PPh$_2$Re(O)Cl$_3$ (2) and (O)PPh$_2$CH$_2$CH$_2$AsPh$_2$Re(O)Cl$_3$ (4), respectively, are summarized in Scheme I. The reactions of **1** and **3** with ReOCl$_4^-$ in ethanol produced the corresponding

(12) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. IV (present distributor: D. Reidel, Dordrecht, The Netherlands).

(13) Gabe, E. J.; Le Page, Y.; Charland, J.-P.; Lee, F. E. *J. Appl. Crystallogr.* **1989**, *22*, 384.

(14) The phosphinimine of ARPHOS, Ph$_2$AsCH$_2$CH$_2$PPh$_2$(NSiMe$_3$), undergoes acid hydrolysis to produce **3** in nearly quantitative yields: Katti, K. V. Unpublished results.

Scheme I

4 : X = Cl; 6 : X = OEt

2 : X = Cl; 5 : X = OEt

Scheme II

monoethoxy derivatives (O)PPh$_2$CH$_2$PPh$_2$Re(O)(OEt)Cl$_2$ (5) and (O)PPh$_2$CH$_2$CH$_2$AsPh$_2$Re(O)(OEt)Cl$_2$ (6), respectively (Scheme I). The Re(V)–phosphine complex Re(O)Cl$_3$(PPh$_3$)$_2$ (7) exchanges its nonchelating PPh$_3$ ligands with the chelating bifunctionalities of **1** and **3** to produce **2** and **4**, respectively, as described in Scheme II.

The detailed ^{31}P NMR, ^{1}H NMR, and IR spectroscopic analyses of **2**, **4**, **5**, and **6** have been obtained to support their

Table II. Positional Parameters and Their Estimated Standard Deviations for **2**

	x	y	z	B_{eq},[a] Å²		x	y	z	B_{eq},[a] Å²
Re(1)	0.33162 (3)	0.82817 (3)	0.06243 (4)	2.696 (24)	Cl(6)	0.15884 (23)	0.22029 (20)	1.1004 (3)	4.99 (20)
Cl(1)	0.34434 (21)	0.94002 (18)	0.0124 (3)	4.30 (18)	O(4)	0.0648 (5)	0.3416 (6)	1.1120 (8)	4.9 (5)
Cl(2)	0.39997 (19)	0.85724 (19)	0.19089 (24)	3.78 (16)	P(3)	0.10225 (18)	0.31360 (18)	0.9209 (3)	2.86 (16)
Cl(3)	0.34498 (22)	0.71465 (18)	0.1048 (3)	4.49 (19)	C(2)	0.1739 (6)	0.2736 (6)	0.8614 (10)	3.0 (6)
O(2)	0.2506 (4)	0.8372 (5)	0.0953 (7)	3.9 (5)	P(4)	0.25138 (17)	0.30511 (18)	0.90817 (25)	2.69 (15)
P(1)	0.28949 (18)	0.78778 (17)	−0.08607 (24)	2.63 (14)	O(3)	0.2387 (5)	0.3257 (4)	1.0045 (6)	3.1 (4)
C(1)	0.3659 (7)	0.7598 (7)	−0.1458 (9)	3.3 (6)	C(51)	0.0328 (8)	0.2547 (7)	0.9032 (11)	4.0 (7)
P(2)	0.44087 (18)	0.79407 (19)	−0.0968 (3)	3.01 (16)	C(52)	0.0102 (8)	0.2409 (9)	0.8187 (12)	5.1 (8)
O(1)	0.4265 (4)	0.8140 (4)	−0.0023 (7)	3.3 (4)	C(53)	−0.0405 (12)	0.1982 (10)	0.7981 (17)	8.6 (13)
C(11)	0.2334 (8)	0.7140 (7)	−0.0854 (10)	3.7 (6)	C(54)	−0.0722 (8)	0.1687 (10)	0.8767 (15)	6.7 (11)
C(12)	0.1972 (8)	0.7020 (10)	−0.0137 (11)	5.4 (9)	C(55)	−0.0535 (9)	0.1799 (9)	0.9646 (17)	6.9 (11)
C(13)	0.1498 (10)	0.6486 (11)	−0.0090 (14)	7.1 (11)	C(56)	0.0006 (9)	0.2254 (8)	0.9729 (12)	4.9 (8)
C(14)	0.1484 (10)	0.6086 (10)	−0.0845 (13)	7.0 (10)	C(61)	0.0774 (6)	0.3868 (6)	0.8570 (9)	2.6 (5)
C(15)	0.1881 (8)	0.6203 (10)	−0.1577 (14)	6.0 (10)	C(62)	0.0234 (7)	0.4257 (7)	0.8995 (11)	3.8 (7)
C(16)	0.2290 (9)	0.6739 (7)	−0.1612 (12)	4.7 (8)	C(63)	−0.0008 (8)	0.4808 (7)	0.8553 (12)	4.8 (8)
C(21)	0.2446 (8)	0.8452 (8)	−0.1610 (10)	3.9 (7)	C(64)	0.0247 (11)	0.4990 (9)	0.7740 (15)	7.3 (11)
C(22)	0.1769 (12)	0.8358 (9)	−0.1811 (14)	7.1 (12)	C(65)	0.0786 (11)	0.4632 (10)	0.7354 (13)	6.3 (10)
C(23)	0.1407 (11)	0.8818 (12)	−0.2350 (16)	8.6 (13)	C(66)	0.1036 (9)	0.4084 (9)	−0.7767 (12)	5.0 (8)
C(24)	0.1762 (10)	0.9334 (12)	−0.2743 (14)	7.4 (11)	C(71)	0.3133 (8)	0.2431 (7)	0.9019 (11)	4.1 (7)
C(25)	0.2450 (12)	0.9439 (10)	−0.2537 (14)	7.4 (11)	C(72)	0.3007 (9)	0.1786 (10)	0.9228 (18)	7.7 (13)
C(26)	0.2799 (9)	0.8989 (8)	−0.1987 (11)	4.9 (8)	C(73)	0.3516 (10)	0.1304 (9)	0.9248 (16)	7.2 (12)
C(31)	0.4696 (8)	0.8641 (8)	−0.1596 (11)	4.1 (7)	C(74)	0.4193 (10)	0.1478 (11)	0.8937 (15)	7.0 (11)
C(32)	0.4714 (10)	0.8643 (10)	−0.2534 (12)	6.1 (10)	C(75)	0.4329 (9)	0.2112 (10)	0.8720 (15)	6.5 (11)
C(33)	0.4886 (11)	0.9227 (13)	−0.2975 (13)	8.3 (13)	C(76)	0.3801 (7)	0.2577 (9)	0.8788 (14)	5.5 (9)
C(34)	0.5159 (11)	0.9743 (9)	−0.2487 (15)	7.2 (11)	C(81)	0.2782 (7)	0.3735 (7)	0.8441 (10)	3.5 (6)
C(35)	0.5158 (9)	0.9764 (8)	−0.1572 (12)	5.0 (8)	C(82)	0.2854 (10)	0.3657 (10)	0.7473 (12)	6.2 (10)
C(36)	0.4926 (8)	0.9204 (8)	−0.1128 (11)	4.6 (8)	C(83)	0.3005 (12)	0.4146 (11)	0.6898 (15)	7.5 (12)
C(41)	0.5052 (8)	0.7305 (8)	−0.1039 (10)	4.1 (7)	C(84)	0.3127 (11)	0.4779 (14)	0.7308 (15)	9.7 (14)
C(42)	0.4968 (11)	0.6701 (9)	−0.0693 (19)	8.6 (14)	C(85)	0.3079 (9)	0.4884 (9)	0.8221 (17)	7.2 (12)
C(43)	0.5422 (11)	0.6204 (10)	−0.0653 (18)	8.4 (13)	C(86)	0.2851 (8)	0.4358 (8)	0.8822 (13)	5.0 (8)
C(44)	0.6060 (11)	0.6366 (11)	−0.1057 (16)	8.2 (12)	O(S)	0.9009 (10)	1.0114 (10)	−0.0109 (14)	12.1 (12)
C(45)	0.6199 (10)	0.6969 (11)	−0.1380 (15)	7.1 (11)	C(1S)	0.8315 (12)	1.0175 (13)	0.0023 (21)	10.1 (18)
C(46)	0.5694 (8)	0.7438 (9)	−0.1344 (12)	4.9 (8)	C(2S)	0.8176 (13)	0.9508 (12)	0.0303 (23)	11.3 (18)
Re(2)	0.14555 (3)	0.33668 (3)	1.07560 (4)	3.00 (3)	C(3S)	0.8793 (17)	0.9265 (16)	0.0857 (23)	14.0 (22)
Cl(4)	0.15962 (20)	0.45073 (18)	1.0427 (3)	4.14 (17)	C(4S)	0.9262 (14)	0.9714 (16)	0.062 (3)	14.8 (22)
Cl(5)	0.21480 (22)	0.35450 (23)	1.2053 (3)	4.67 (20)					

[a] B_{eq} is the mean of the principal axes of the thermal ellipsoid.

Table III. Phosphorus-31 NMR,[a] Proton NMR,[b] and IR[c] Spectroscopic Data for Rhenium(V) Complexes

	^{31}P			^{1}H			IR, cm^{-1}
compound	$\delta_{P^{III}}$	δ_{P^V}	$^2J_{PP}$, Hz	δ_{CH_2}	$J_{P^{III}H}$, Hz	J_{P^VH}, Hz	$\nu(Re=O)$
(O)PPh₂CH₂PPh₂ (**1**)	−28.7	27.4	50.0	3.07 (dd)	1.20	12.10	
(O)PPh₂CH₂PPh₂Re(O)Cl₃ (**2**)	−15.58	59.45	17.25	3.23 (dd)	9.15	11.10	965
(O)PPh₂CH₂CH₂AsPh₂Re(O)Cl₃ (**4**)[b]		60.10		2.23 (m)			970
				2.67 (m)			
(O)PPh₂CH₂PPh₂Re(O)Cl₂(OEt) (**5**)[b,d]	−17.10	61.00	17.00	3.40 (br)			955
				3.45 (br)			
(O)PPh₂CH₂CH₂AsPh₂Re(O)Cl₂(OEt) (**6**)[b,e]		60.50		2.30 (m)			960
				2.70 (m)			

[a] All spectra in CDCl₃; ppm vs 85% H₃PO₄. [b] All spectra in CDCl₃; ppm vs SiMe₄; the insolubility of **4–6** in CDCl₃ (or CD₃OD) has resulted in poorly resolved spectra with broad lines. [c] Recorded in KBr cells. [d] −OC₂H₅: δ_{CH_2} = 1.51 (br); δ_{CH_3} = 0.17 (br). [e] −OC₂H₅: δ_{CH_2} = 1.55 (br); δ_{CH_3} = 0.19 (br).

structural formulations (Table III). The X-ray crystal structure of **2** confirms its chemical constitution. The spectroscopic and X-ray crystal structural data (Tables III–V) are considered in the Discussion.

Discussion

The heterodifunctional ligands (O)PPh₂CH₂PPh₂ (**1**) and (O)PPh₂CH₂CH₂AsPh₂ (**3**) react with ReOCl₄⁻ to give the new Re(V) metallacyclic compounds (O)PPh₂CH₂PPh₂Re(O)Cl₃ (**2**) and (O)PPh₂CH₂CH₂AsPh₂Re(O)Cl₃ (**4**) in good yields (Scheme I). These reactions proceeded to completion only when ligands **1** and **3** were used in an excess (at least 3-fold) over the ReOCl₄⁻ stoichiometry. In the reactions shown in Scheme I, it was not necessary to generate ReOCl₄⁻ separately; good yields of **2** and **4** were obtained by introducing concentrated HCl to mixtures of **1** or **3** and NH₄ReO₄ in THF. The substitution of one of the chlorines in **2** and **4** with an ethoxy group to produce (O)PPh₂-CH₂PPh₂Re(O)(OEt)Cl₂ (**5**) and (O)PPh₂CH₂CH₂AsPh₂Re-

(O)(OEt)Cl₂ (**6**) was achieved by performing these reactions in EtOH. The reactions of **1** and **3** with the acidified ReO₄⁻ are comparable to the reactions of a nonchelating triarylphosphine (e.g., PPh₃) which produced Re(O)Cl₃(PR₃)₂ under similar experimental conditions.[5,6,11]

The chemical compositions of **2**, **4**, **5**, and **6** were obtained from analytical and mass spectrometric data. Strong bands at 965 and 970 cm⁻¹ attributable to $\nu(Re=O)$ were observed in the IR spectra of **2** and **4** (Table III).[15–20] The IR spectra of the corresponding monoethoxy derivatives **5** and **6** consisted of bands

(15) Cianti, G.; Alfonso, G.; Romiti, P.; Sironi, A.; Freni, M. *Inorg. Chim. Acta* **1983**, *72*, 29.

(16) Lock, C. J. L.; Wan, C. *Can. J. Chem.* **1975**, *53*, 1548.

(17) Albano, V. G.; Bellon, P. L.; Ciani, G. *J. J. Organomet. Chem.* **1971**, *31*, 75.

(18) Doedens, R. J.; Ibers, J. A. *Inorg. Chem.* **1967**, *6*, 204.

(19) Corfield, P. W. R.; Doedens, R. J.; Ibers, J. A. *Inorg. Chem.* **1967**, *6*, 197.

(20) Rossi, R.; Marchi, A.; Magon, L.; Casellato, U.; Tamburini, S.; Graziani, R. *J. Chem. Soc., Dalton Trans.* **1991**, 263.

Table IV. Selected Bond Distances (Å) and Bond Angles (deg) for 2A

Distances			
Re(1)–Cl(1)	2.374 (4)	Re(1)–O(1)	2.137 (9)
Re(1)–Cl(2)	2.374 (4)	Re(1)–P(1)	2.464 (4)
Re(1)–Cl(3)	2.371 (4)	P(1)–C(1)	1.849 (14)
Re(1)–O(2)	1.688 (9)	C(1)–P(2)	1.767 (14)
Angles			
Cl(1)–Re(1)–Cl(2)	87.45 (14)	Cl(1)–Re(1)–O(1)	83.53 (3)
Cl(1)–Re(1)–Cl(3)	167.18 (15)	P(1)–Re(1)–O(1)	80.6 (3)
Cl(1)–Re(1)–O(2)	95.5 (4)	Re(1)–O(1)–P(2)	130.1 (6)
Cl(1)–Re(1)–P(1)	93.92 (13)	P(1)–C(1)–P(2)	111.6 (7)

Table V. Selected Bond Distances (Å) and Bond Angles (deg) for 2B

Distances			
Re(2)–Cl(4)	2.353 (4)	Re(2)–O(3)	2.146 (9)
Re(2)–Cl(5)	2.353 (4)	Re(2)–P(3)	2.464 (4)
Re(2)–Cl(6)	2.373 (4)	P(3)–C(2)	1.861 (13)
Re(2)–O(4)	1.694 (9)	C(2)–P(4)	1.776 (13)
Angles			
Cl(4)–Re(2)–Cl(6)	166.49 (15)	Cl(4)–Re(2)–O(4)	97.2 (4)
Cl(5)–Re(2)–Cl(6)	87.92 (16)	P(3)–Re(2)–O(3)	79.0 (3)
Cl(4)–Re(2)–P(3)	91.75 (13)	Re(2)–O(3)–P(4)	130.6 (6)
Cl(4)–Re(2)–O(3)	83.83 (25)	P(3)–C(2)–P(4)	108.5 (7)

at 955 and 960 cm^{-1}, respectively. This modest decrease in the ν(Re=O) frequencies on going from 2 to 5 (or 4 to 6) may be rationalized in terms of the disposition of the ethoxy group trans to the Re=O core in the ethoxy derivatives:
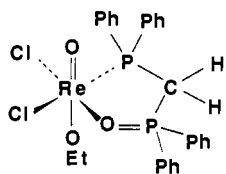
The ^{1}H NMR spectrum of 2 consisted of doublet of doublet signals for the methylene, P^{V}CH_2P^{III}, protons because of the differences in the coupling constants ($^2J_{P^{III}-H}$ vs $^2J_{P^V-H}$) (Table III). A similar observation has been made on a number of transition metal complexes of mixed phosphine–phosphinimine ligands.[9] The detailed ^{1}H NMR spectroscopic analysis may add further evidence for the disposition of the OEt groups in 5 and 6 with respect to the Re≡O core. However, the extreme insolubility of 4, 5, and 6 in common organic solvents has resulted in broad line shapes, precluding the complete interpretation of all the P–H and the H–H coupling constants. For the same reasons, the OCH_2CH$_3$ protons are poorly resolved and appear as broad humps in the ^{1}H NMR spectra of 5 and 6. The ^{31}P NMR spectra of 2 and 5 (Table II) consisted of two doublets centered at –15.58 (–17.10 for 5) and 59.45 (61.0 for 5) ppm and can be analyzed in terms of an AX spin system with a $^2J_{P_AP_X}$ value of 17.2 Hz (17.0 Hz for 5). The upfield (–15.58 in 2 and –17.10 ppm in 5) and the down field (59.45 in 2 and 61.0 ppm in 5) doublet signals were assigned to the phosphine (Ph$_2$P) and phosphine oxide (P(O)) centers, respectively. The chemical shifts of the lone phosphine oxide centers in 4 (60.0 ppm) and 6 (60.5 ppm) compare well with the assignments made for 2 and 5 and show the consistency of the chemical shifts of chemically similar Ph$_2$P(O) or Ph$_2$P type phosphorus centers in all these compounds. The selected ^{1}H NMR spectroscopic data for 2, 4, 5, and 6 are summarized in Table III.

The heteroatomic chelated metallacyclic compounds 2, 4, 5, and 6 are the first examples of Re(V) centers involved in chelate formations with a phosphine or arsine and phosphine oxides. In order to gain structural insights into such compounds, a detailed X-ray structural analysis of 2 has been undertaken. The structure comprises the neutral monomeric complex (O)PPh$_2$CH$_2$PPh$_2$-Re(O)Cl$_3$ (2) with two crystallographically independent molecules

2 A

2 B
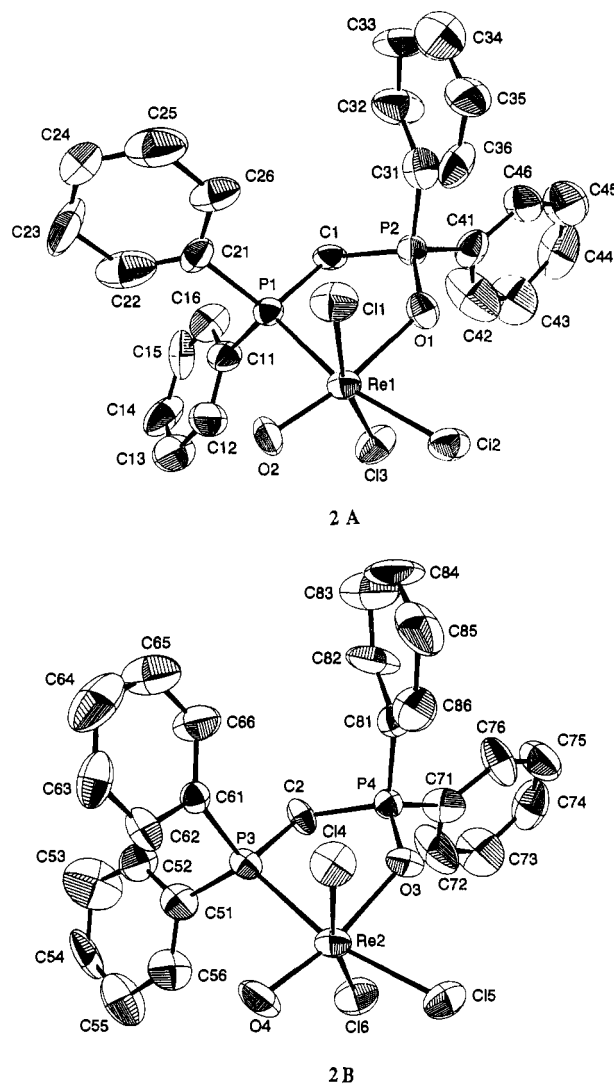
Figure 1. ORTEP drawing of (O)PPh$_2$CH$_2$PPh$_2$Re(O)Cl$_3$, showing 50% probability ellipsoids for the two crystallographically independent molecules 2A and 2B in the asymmetric unit.

in the asymmetric unit and a cocrystallized molecule of tetrahydrofuran. Figure 1 shows the ORTEP drawing for the two independent molecules 2A and 2B, and the skeletal bond distances and angles are listed in Tables IV and V. The rhenium(V) in 2 is in a distorted octahedral environment with the (O)PPh$_2$CH$_2$-PPh$_2$ fragment chelating in a cis fashion via O(1) and P(1) to form a five-membered metallacyclic compound. The Re(1)–Cl(2) bond length (2.374 Å) is identical to that for Re(1)–Cl(1) and is not significantly different from the Re(1)–Cl(3) (2.371 Å) bond lengths. This suggests that the phosphine moiety has no trans influence on the Cl(2) that is trans to it. The Re(1)–P(1) bond length (2.464 Å) is in the normal range that is found in a number of other rhenium(IV) phosphine complexes.[15–19] The rhenium–oxygen bond length (i.e., Re(1)–O(2) = 1.691 Å) is very similar to those observed in a number of monooxo–Re(V)–phosphine complexes[15–19] and also in the Re(V) complexes of bis(diphenylphosphino)amine ligands.[20] The nature of the donor atoms trans to the Re–O bond does not seem to have profound effects on the Re–O bond lengths in Re(V)–phosphine and related complexes.

It is noteworthy that the mixed phosphine–phosphine oxide ligands[21] (e.g., 1) and also the closely related phosphine–

(21) (a) Grim, S. O.; Satek, L. C.; Tolman, C. A.; Jesson, J. P. *Inorg. Chem.* **1975**, *14*, 656. (b) Carr, S. W.; Colton, R. *Aust. J. Chem.* **1981**, *34*, 35. (c) Grim, S. O.; Walton, E. D. *Inorg. Chem.* **1980**, *19*, 1982.

phosphinimine ligands[22] (e.g., $RN=PPh_2CH_2PPh_2$) have been shown to bind in a cis fashion with a number of early and late transition metals. The cis disposition of the Re(V)–oxo group with respect to the phosphine as seen in the structure of **2** (Figure 1) suggests that the first step in the complex formation may involve a strong adduct of Re(V) with the phosphine unit of **1**. In a subsequent metallacyclic formation, the strong trans influence of the Re–O(oxide) bond may result in the disposition of the loosely bound P(O) group trans to Re(O) while maintaining the cis relationship with the phosphine group.

By making use of the Pauling equation (i.e., bond length = A + B log (bond order), where A and B are refined by fixing Re–O single and double bonds), we can derive a value of 2.78 for the bond order of Re–O(oxide) in **2**. In this calculation, a value of 2.04 Å for an Re^V–O single bond[23] and a value of 1.765 Å for a double bond[24] are used. Similar triple-bond characters for the Re^V–O(oxide) bonds have been noted in a number of Re(V) complexes.[20,23,24]

Ligand-Exchange Reactions

Oxotrichlorobis(triphenylphosphine)rhenium(V) reacts with **1** or **3** to give the metallacycles **2** and **4**, respectively, in nearly quantitative yields (Scheme II). These ligand-exchange reactions clearly demonstrate the usefulness of the cooperative chelating effects of the π-acid phosphine (or arsine) and the electron-donating properties of the phosphine oxide in **1** and **3** to produce the metallacycles **2** and **4**, respectively, through the exchange of nonchelating PPh_3 groups of **7**. The melting points and the analytical and spectroscopic data for **2** and **4** as obtained from these reactions are very similar to the data for **2** and **4** produced directly from the reactions of **1** and **3** with $ReOCl_4^-$ (Scheme I). This suggests that different routes as outlined in Schemes I and II produce the Re(V) complexes **2** and **4** with similar geometrical dispositions of substituents around the octahedral metal center. In particular, the formation of **2** from $Re(O)Cl_3(PPh_3)_2$ (**7**) (Scheme I), which has been confirmed to have the phosphine unit cis to the Re–oxo core and the phosphine oxide trans to the Re–oxo core (Figure 1), suggests a major rearrangement of substituents around the Re(V) center in **2** as compared to its precursor **7**. The propensity of the phosphine (PPh_2) and the phosphine oxide (P(O)) functionalities of **1** to bind to the Re(V) core through a cis disposition and also the strong trans influence of the Re–oxide unit, which can dispose the loosely coordinated P(O) group trans to the oxo atom, are presumably responsible for these

rearrangements. The reactions outlined in Scheme II to produce **2** and **4** demonstrate an alternative pathway involving mild reaction conditions as compared to the harsh pH requirements of the reactions presented in Scheme I. The concept of ligand-exchange reactions is of considerable importance in the development of new radiopharmaceuticals of technetium-99m and rhenium-188/186.[27] We have successfully extended the methodology shown in Scheme II to the reactions of $^{99m}Tc(O)(PPh_3)_2$-Cl_3 with **1** and **3** to produce the radioactive analogues of **2** and **4**, respectively.[28]

Summary

The reactions described in Schemes I and II demonstrate a new methodology to stabilize Re(V) through heteroatomic chelation. The extreme hydrolytic stability of **2**, **4**, **5**, and **6** under neutral and acidic pH conditions is unique and important for extending such reactions to produce the radioactive analogues of these compounds using $^{188/186}Re$ and ^{99m}Tc precursors. Our preliminary studies suggest that the reactions shown in Scheme I can be performed with $^{188}ReOCl_4^-$ and $^{99m}TcOCl_4^-$ to produce a new genre of radiopharmaceuticals.[28] The chemical flexibility of the ligand backbones of **1** and **3** can be achieved by tuning the substituents on the phosphorus and also by varying the alkane chain lengths. Development of the transition metal chemistry of such skeletally modified ligands is underway.

Supplementary Material Available: Tables of crystallographic details, positional and thermal parameters, temperature factor expressions, and bond distances and angles (9 pages). Ordering information given on any current masthead page.

(22) Katti, K. V.; Cavell, R. G. *Comments Inorg. Chem.* **1990**, *10*, 53.
(23) Cotton, F. A.; Lippard, S. J. *Inorg. Chem.* **1965**, *4*, 1621.
(24) Lock, C. J. L.; Turner, G. *Acta Crystallogr., Sect. B* **1978**, *34*, 923.
(25) Chatt, J.; Garforth, J. D.; Johnson, N. P.; Rowe, G. A. *J. Chem. Soc.* **1965**, 1012.
(26) Cotton, F. A.; Lippard, S. J. *Inorg. Chem.* **1966**, *5*, 9.

(27) (a) Schwartz, D. A.; Abrams, M. J.; Hauser, M. M.; Gaul, F. E.; Larsen, S.-K.; Rauth, D.; Zubieta, J. A. *Bioconjugate Chem.* **1991**, *2*, 333. (b) Vanderheyden, J.-L.; Rao, T. N.; Kasina, S.; Wester, D.; Su, F.-M.; Fritzberg, A. R. In *Technetium and Rhenium in Chemistry and Nuclear Medicine*; Nicolini, M., Bandoli, G., Mazzi, U., Eds.; Raven Press: New York, 1990; pp 615–621. (c) Abrams, M. J.; Juweid, M.; Tenkate, C. J.; Schwartz, D. A.; Hauser, M. M.; Gaul, F. E.; Fuccello, A. J.; Rubin, R. H.; Straus, W. H.; Fischman, A. J. *J. Nucl. Med.* **1990**, *31*, 2022.
(28) Details of the radiochemical studies will be published elsewhere.