DALTON

Synthesis and characterization of dioxorhenium complexes derived from water-soluble diphosphine tetraphosphonates†

V. Sreenivasa Reddy,[a] Kattesh V. Katti *,[a] and Wynn A. Volkert[b]

[a] *Center for Radiological Research and Missouri University Research Reactor, Columbia, MO 65203, USA*

[b] *H. S. Truman Memorial VA Hospital, Columbia, MO 65203, USA*

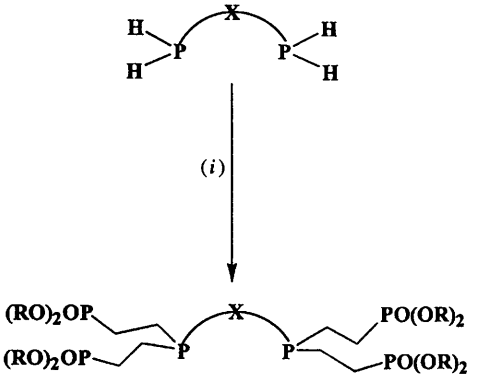
Water-soluble diphosphine tetraphosphonates $[(RO)_2OPCH_2CH_2]_2P–X–P[CH_2CH_2PO(OR)_2]_2$ (X = C_6H_4 or C_2H_4, R = Et or Me) were synthesized in near-quantitative yields by a base-catalysed Michael addition of appropriate P–H bonded compounds to vinylphosphonates in the presence of potassium *tert*-butoxide. The reactions of these compounds with $[ReO_2I(PPh_3)_2]$ in biphasic media (aqueous–organic) produced water-soluble dioxorhenium complexes of the type $[ReO_2\{[(RO)_2OPCH_2CH_2]_2P–X–P(CH_2CH_2PO(OR)_2]_2\}_2]^+$ in near-quantitative yields. The water-soluble phosphines and their rhenium complexes were characterized by IR, ^1H and ^{31}P NMR and high-resolution fast atom bombardment mass spectral analysis.

The chemistry of water-soluble transition metal/organometallic compounds has become a subject of burgeoning interest because of their usefulness in biphasic catalysis[1–4] and biomedicine.[5–8] Transition-metal complexes, in general, tend to exhibit instability in aqueous media because of complex redox reactions mediated by water. Characteristics including high aqueous solubility and kinetic inertness in water may be achieved by the use of appropriate ligands bound to specific transition metals. In this context the utility of sulfonated arylphosphines, as demonstrated by various workers, provides a viable pathway to produce water-soluble transition-metal compounds.[7–17] The application of mono-, di- or tri-sulfonated arylphosphines has become common in the development of water-soluble co-ordination compounds.[9–17] However, this methodology does suffer from some serious drawbacks. For example, it is extremely difficult to produce sulfonated arylphosphine ligands in high purity. In addition, the often encountered, sulfonated-assisted oxidation of phosphines poses complications in the utility of these ligands to synthesize transition-metal compounds (in high purity) for specific catalytic or biomedical applications.

Our current research interests are concerned with the development of ligand systems suitable for complexation reactions with technetium-99m and rhenium-186/188 with the ultimate objective of producing new diagnostic and therapeutic radiopharmaceuticals, respectively.[18–28] From this viewpoint, sulfonated arylphosphines, although highly soluble in water, are unsuitable because they display high lipophilicity. Therefore, it is expected that new developments in the design of water-soluble phosphines will result in greater strides in the areas of biphasic catalysis and also pharmaceutical sciences. As part of our ongoing research on fundamental main-group chemistry aimed at the design and development of new multifunctional ligand frameworks, we have recently discovered new classes of phosphines that have shown remarkable oxidative stability and solubility in aqueous media.[24–28] This paper will describe further developments on (*a*) new synthetic approaches to water-soluble phosphines and (*b*) biphasic reactions of these chelating bis(phosphines) with $[ReO_2I(PPh_3)_2]$ to produce water-soluble rhenium metal complexes.

Results and Discussion

New water-soluble diphosphine tetraphosphonates L^1–L^4 were synthesized by a base-catalysed Michael addition of phosphorus–hydrogen bonds to the vinylphosphonates as shown in Scheme 1. In all the cases the synthesis was performed in boiling tetrahydrofuran with potassium *tert*-butoxide as the base catalyst. The reactions with 1,2-bis(phosphino)benzene were complete in 6 h, whereas with 1,2-bis(phosphino)ethane the reactants needed to be refluxed for 6 d. All the new compounds were characterized by various spectroscopic and analytical techniques. Their oily nature coupled with the presence of small amounts (< 5%) of the unreacted vinylphosphonate precluded the determination of their chemical composition using analyses for C and H. However, their hydrophilic nature allowed their purity to be established *via* high-performance liquid chromatography (HPLC) analysis. On a Hamilton PRP-1 column, L^1–L^4 eluted as single chemical species, in a water–acetonitrile gradient (*e.g.* 95%:5%), demonstrating ≈97% purity of the individual compounds. Only trace amounts (< 3%) of the unreacted vinylphosphonate were observed in the solutions of L^1–L^4. The chemical compositions were further confirmed by high-resolution fast



	X	R
L^1	C_6H_4	Et
L^2	C_6H_4	Me
L^3	C_2H_4	Et
L^4	C_2H_4	Me

Scheme 1 (*i*) 4 CH_2=CHPO(OR)$_2$, KOBu^t–tetrahydrofuran (thf)

† Chemistry in Environmentally Benign Media. Part 4. Part 3 is ref. 28.

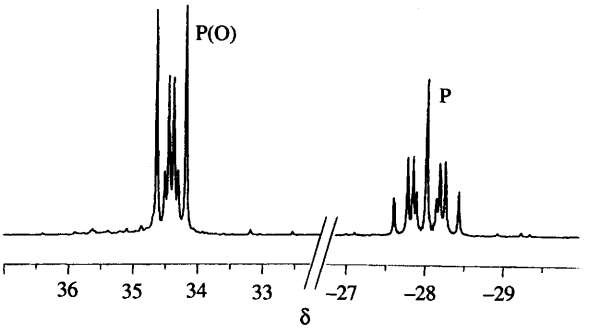
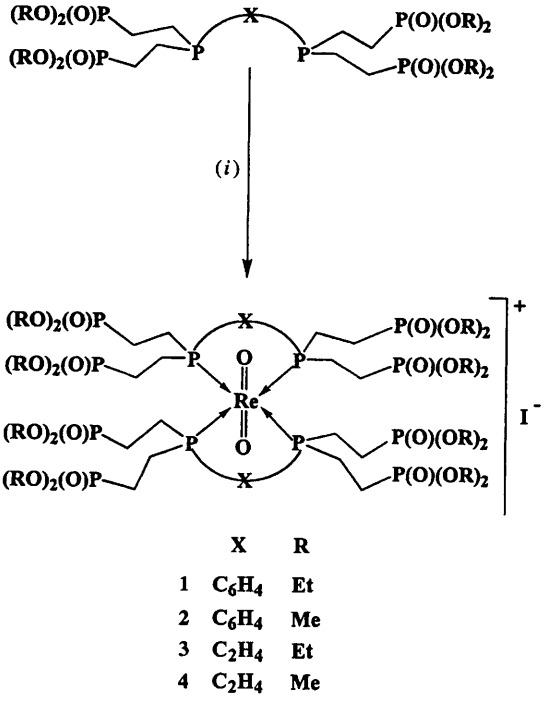


Fig. 1 The ^{31}P NMR (121.5 MHz) spectrum of compound L^1



	X	R
1	C_6H_4	Et
2	C_6H_4	Me
3	C_2H_4	Et
4	C_2H_4	Me

Scheme 2 (*i*) $\frac{1}{2}$ $[ReO_2I(PPh_3)_2]$

atom bombardment (HRFAB) mass spectral analysis. All the compounds show peaks corresponding to their parent ions, $[M + H]^+$.

The ^{31}P NMR spectra of compounds L^1–L^4 may be explained in terms of an AA′XX′X″X‴ spin pattern [A and A′ correspond to the two phosphorus(III) centres while the four phosphonate phosphorus(V) centres are labelled as X, X′, X″ and X‴ respectively]. A representative spectrum of L^1 is shown in Fig. 1. Complex multiplets observed at δ −28.0, −28.4, −19.2 and −19.5 for L^1–L^4 respectively may be attributed to P^{III} (*i.e.* A and A′) whereas, multiplets between δ 34 and 38 are assigned to P^V (Table 1). The resonances for P^{III} fall within the region noted for the closely related water-soluble hydroxymethyl-functionalized phosphines L^5–L^7 (Table 1). The ^1H NMR spectroscopic data for L^1 complement the proposed structures of these compounds (Scheme 1).

It is important to note that the reactions outlined in Scheme 1 demonstrate the efficacy with which the backbone that bridges the phoshporus(III) centres as well as the substituents on the phosphorus can be altered to produce a wide spectrum of functionalized bis(phosphines). This systematic tuning of substituents in L^1–L^4 should allow construction of frameworks with appropriate lipophilicities for use in radiopharmaceutical applications. Further, the chelating nature would provide useful avenues for the development of new classes of transition-metal complexes. In addition, the water-solubilities present unique prospects in reactions with transition-metal precursors under biphasic (*i.e.* aqueous–organic) conditions. For example, the chelating bis(phosphines) L^1–L^4, dissolved in water, react with $[ReO_2I(PPh_3)_2]$ dissolved in dichloromethane, to produce the corresponding water-soluble rhenium(V) complexes **1**–**4** in 80–85% yields. Detailed studies have confirmed the stoichiometry of 2 equivalents of L^1–L^4 with 1 equivalent of the rhenium(V) precursor (Scheme 2). The hydrophilic nature of **1**–**4** has presented significant problems in getting rid of water from these compounds. They tend to be waxy solids even after drying *in vacuo* for over 48 h. Attempts to crystallize them by slow evaporation of water or ethanol solutions have proven to be unsuccessful so far. The HRFAB mass spectral data confirm their chemical composition as formulated in Scheme 2. Positive-ion HRFAB gave signals corresponding to the respective parent cations in ≈100% intensities. These parent ions ($[M + H]^+$: *m*/*z* 1814.45 **1**, 1590.20 **2**, 1718.45 **3** and 1494.20 **4**) correspond to ^{185}Re. The ^{31}P NMR spectroscopic data for **1**–**4** suggest a considerable (≈45 ppm) downfield shift in comparison to those of the corresponding L^1–L^4 (Table 1). Similar chemical shift trends were also noted for the rhenium(V) complexes derived from the water-soluble hydroxymethylphosphines $P(CH_2OH)_3$ L^5, $E[P(CH_2OH)_2]_2$-1,2 (E = C_6H_4 L^6 or C_2H_4 L^7), Table 1.[25] A dramatic simplification, as compared to the complex AA′XX′X″X‴ spin pattern for L^1–L^4 (see above), in the ^{31}P spectral pattern of **1**–**4** is of note. A representative spectrum of **1**, shown in Fig. 2, demonstrates that the Re^V-bound phosphine centres resonate as a simple quintet whereas the four phosphonate groups resonate as a triplet. This simplicity, of a potentially second-order spectrum $[(AA'XX'X''X''')_2]$, may be explained in terms of its collapse to a six-spin AA′XX′X″X‴ pattern, presumably as a result of C_{2v} symmetry in the molecule. The six-spin AA′XX′X″X‴ system is expected to transform into an apparent first-order A_2X_4 spin pattern if the

Table 1 The ^{31}P NMR spectroscopic data for the phosphines and their rhenium complexes

Compound	δ(^{31}P)	δ(^{31}P=O)
L^1 $C_6H_4\{P[CH_2CH_2PO(OEt)_2]_2$-1,2$\}_2$	−28.0 (m)	34.4 (m)
L^2 $C_6H_4\{P[CH_2CH_2PO(OMe)_2]_2$-1,2$\}_2$	−28.4 (m)	37.6 (m)
L^3 $C_2H_4\{P[CH_2CH_2PO(OEt)_2]_2$-1,2$\}_2$	−19.2 (m)	34.8 (m)
L^4 $C_2H_4\{P[CH_2CH_2PO(OMe)_2]_2$-1,2$\}_2$	−19.5 (m)	37.5 (m)
L^5 $P(CH_2OH)_3$	−24.0 (s)[a]	—
L^6 $C_6H_4[P(CH_2OH)_2$-1,2$]_2$	−31.2 (s)[b]	—
L^7 $C_2H_4[P(CH_2OH)_2$-1,2$]_2$	−25.1 (s)[a]	—
1 $[ReO_2(C_6H_4\{P[CH_2CH_2PO(OEt)_2]_2$-1,2$\}_2)_2]I$	22.0 (qnt)	31.2 (t)
2 $[ReO_2(C_6H_4\{P[CH_2CH_2PO(OMe)_2]_2$-1,2$\}_2)_2]I$	21.4 (q)	34.0 (t)
3 $[ReO_2(C_2H_4\{P[CH_2CH_2PO(OEt)_2]_2$-1,2$\}_2)_2]I$	20.0 (q)	31.2 (t)
4 $[ReO_2(C_2H_4\{P[CH_2CH_2PO(OMe)_2]_2$-1,2$\}_2)_2]I$	20.2 (q)	34.5 (t)
5 $[ReO_2\{P(CH_2OH)_3\}_4]I$	27.7 (s)[d]	—
6 $[ReO_2\{C_6H_4[P(CH_2OH)_2$-1,2$]_2\}_2]I$	24.2 (s)[d]	—
7 $[ReO_2\{C_2H_4[P(CH_2OH)_2$-1,2$]_2\}_2]I$	29.8 (s)[d]	—

[a] Ref. 29. [b] From ref. 23. [c] From ref. 25.

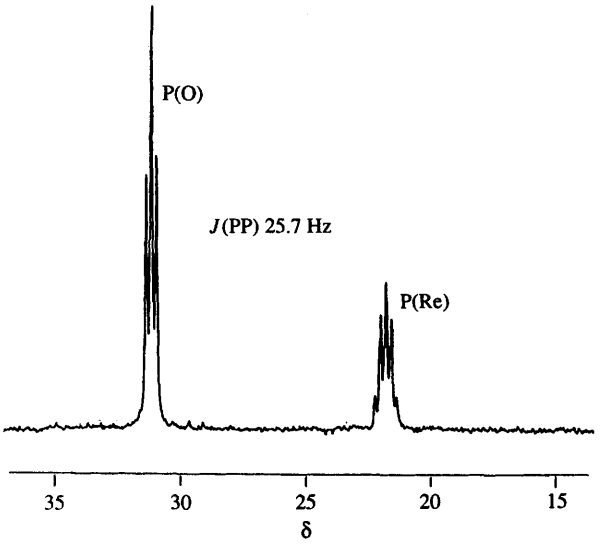


Fig. 2 The ^{31}P NMR (121.5 MHz) spectrum of compound **1**

chemical shift differences within each of As and Xs are minimum or equal to zero. A similar explanation may be advanced for the observed simplicity in the ^{31}P NMR spectra of **2**–**4**. The A_2X_4 pattern noted for **1**–**4** also suggests that the two bis(phosphines) in these compounds are disposed in a *trans* arrangement. An A_2B_2 pattern for the phosphorus(III) nuclei would be apparent for a less likely *cis* disposition of the bis(phosphines).

Recent X-ray crystallographic investigations in our laboratory have demonstrated that the products from the reactions of bis(phosphines) of the type $(HOH_2C)_2P–E–P(CH_2OH)_2$ (E = C_2H_4 or C_6H_4) with rhenium(V), palladium(II) or platinum(II) precursors are exclusively cationic species similar to the ones outlined in Scheme 2.[23–26] The co-ordination chemistry of Re^V, Pd^{II} and Pt^{II}, with the hydroxymethylphosphines L^5–L^7,[23–26] not only complements the formulation of cationic structures for compounds **1**–**4**, as outlined in Scheme 2, but more importantly suggests the propensity of the water-soluble phosphines L^1–L^4 with $[ReO_2I(PPh_3)_2]$ to produce the cationic complexes exclusively.

The reactions outlined in Scheme 2 are 'strictly' biphasic because upon simple shaking of solutions of L^1–L^4 (in aqueous media) and the metal precursor (in organic media) more than 98% of the metal complexes **1**–**4** are transferred into the aqueous phase enabling easy isolation upon simple separation from the organic phase. A similar observation was recently made for the reactions of bis(phosphines) L^6 and L^7 with late-transition-metal precursors to afford several water-soluble complexes of Pd^{II} and Pt^{II}.[23,24] The rhenium(V) complexes **1**–**4** are stable in aqueous media for several weeks. This remarkable kinetic inertness may be attributed to the high nucleophilicity of the phosphorus centres in the these diphosphine tetraphosphonate ligands (*i.e.*, L^1–L^4). Phosphine ligands with high nucleophilicity are expected to participate in efficient π-back bonding interactions with metal centres enabling the formation of strong and kinetically inert M–P bonds.

Experimental

All reactions were carried out under purified nitrogen by standard Schlenk techniques. Solvents were purified and dried by standard methods and distilled under nitrogen prior to use. Reagents such as $[ReO_2I(PPh_3)_2]$, CH_2=CHPO(OEt)$_2$ and KOBu^t (1.0 mol dm^{-3} solution in thf) obtained from Aldrich Chemical Co. and 1,2-bis(phosphino)benzene and 1,2-bis(phosphino)ethane from Strem Chemical Inc. were used without further purification. The compound CH_2=CHPO(OMe)$_2$ was obtained from Fluka Chemical Co. Nuclear magnetic resonance spectra were recorded on a Bruker ARX-300 spectrometer using D_2O as a solvent, ^1H chemical shifts are reported in ppm, downfield from external standard $SiMe_4$, ^{31}P NMR (121.5 MHz) with 85% H_3PO_4 as external standard and positive chemical shifts downfield of the standard. Infrared spectra were recorded using Nujol mulls and KBr cells on a Mattson Galaxy-3000 spectrophotometer, mass spectra at Washington University, St. Louis, Missouri. All the FAB data correspond to the ^{185}Re isotope.

Syntheses

C_6H_4{P[$CH_2CH_2PO(OEt)_2$]$_2$}$_2$-1,2 L^1. To a thf solution (25 cm^3) of diethyl vinylphosphonate (0.141 mmol) was added 1,2-bis(phosphino)benzene (0.035 mmol) at room temperature *via* a syringe. A 1 mol dm^{-3} solution of KOBu^t (4 cm^3) in thf was added dropwise with constant stirring at 25 °C, followed by reflux for 6 h. Solvent was removed *in vacuo* and the residue extracted by diethyl ether. Removal of ether *in vacuo* afford compound L^1 in quantitative yield as a viscous colourless oil. HRFAB: *m/z* 799.2583 ([*M* + H]$^+$); calc. for $C_{30}H_{60}O_{12}P_6$ 798.2510. NMR: ^1H, δ 1.17 [td, *J*(HH) 7.0, *J*(PH) 5.4 Hz, 24 H, CH_2CH_3], 1.78 (m, 8 H, PCH_2CH_2), 1.94 (m, 8 H, PCH_2CH_2), 4.0 (m, 16 H, OCH_2CH_3) and 7.47 (m, 4 H, C_6H_4); ^{31}P, δ 34.4 (m, 4P, P^V) and −28.0 (m, 2P, P^{III}).

Compound L^2 was synthesized by a similar procedure using dimethyl vinylphosphonate (0.141 mmol) and 1,2-bis(phosphino)benzene (0.035 mmol) in the presence of one molar solution of KOBu^t (4 cm^3) in thf. HRFAB: *m/z* 687.1326 ([*M* + H]$^+$); calc. for $C_{22}H_{44}O_{12}P_6$ 686.1258. NMR: ^1H, δ 1.74 (m, 8 H, PCH_2CH_2), 1.92 (m, 8 H, PCH_2CH_2), 3.57 [d, *J*(HH) 6.4, 12 H, OCH_3], 3.61 [d, *J*(PH) 6.4 Hz, 12 H, OCH_3] and 7.48 (m, 4 H, C_6H_4); ^{31}P, δ 37.6 (m, 4P, P^V) and −28.4 (m, 2P, P^{III}).

C_2H_4{P[$CH_2CH_2PO(OEt)_2$]$_2$}$_2$-1,2 L^3. To a thf solution (25 cm^3) of diethyl vinylphosphonate (0.141 mmol) was added 1,2-bis(phosphino)ethane (0.035 mmol) at room temperature also in thf solution. A 1 mol dm^{-3} solution of KOBu^t (4 cm^3) in thf was added dropwise with constant stirring at 25 °C followed by reflux for 6 d [reaction was incomplete even after 5 d (^{31}P NMR spectroscopy)]. Solvent was removed *in vacuo* and the residue extracted with diethyl ether. Removal of ether *in vacuo* afforded compound L^3 in quantitative yield as a viscous colourless oil. HRFAB: *m/z* 751.2578 ([*M* + H]$^+$); calc. for $C_{26}H_{60}O_{12}P_6$ 750.2510. NMR: ^1H, δ 1.23 [t, *J*(HH) 7.0 Hz, 24 H, OCH_2CH_3], 1.62 (m, 8 H, PCH_2CH_2), 1.85 (m, 8 H, PCH_2CH_2) and 4.0 (m, 16 H, OCH_2CH_3); ^{31}P, δ 34.8 (m, 4P, P^V) and −19.2 (m, 2P, P^{III}).

Compound L^4 was synthesized by a similar procedure as described above for L^3 using dimethyl vinylphosphonate (0.141 mmol) and 1,2-bis(phosphino)ethane (0.035 mmol) in the presence of a 1 mol dm^{-3} solution of KOBu^t (4 cm^3) in thf. HRFAB: *m/z* 639.1323 ([*M* + H]$^+$); calc. for $C_{18}H_{44}O_{12}P_6$ 638.1258. NMR: ^1H, δ 1.62 (m, 8 H, PCH_2CH_2PO), 1.78 (m, 4 H, PCH_2CH_2P), 1.90 (m, 8 H, PCH_2CH_2PO) and 3.65 [d, *J*(HH) 10.9 Hz, 24 H, OCH_3]; ^{31}P, δ 37.5 (m, 4P, P^V) and −18.4 (m, 2P, P^{III}).

[ReO_2(X{P[$CH_2CH_2PO(OR)_2$]$_2$}$_2$-1,2)$_2$]I (X = C_6H_4, R = Et 1 or Me 2; X = C_2H_4, R = Et 3 or Me 4). An aqueous solution (20 cm^3) of X{P[$CH_2CH_2PO(OR)_2$]$_2$-1,2} (2.0 mmol) was added dropwise to the rhenium(V) precursor [ReO_2-$I(PPh_3)_2$] (1.0 mmol) in dichloromethane (20 cm^3) at 25 °C with constant stirring. Stirring was continued for 1 h and the aqueous layer separated from the organic layer. The aqueous solution was concentrated to ≈5 cm^3 *in vacuo* and evaporated slowly at room temperature to give yellow complex(es) **1**–**4** in ≈80–85% yield(s).

Complex **1**: HRFAB *m/z* 1814.4549 ([*M* + H]$^+$) (calc. for $C_{60}H_{120}O_{26}P_{12}Re$ 1813.4556); ν(O=Re=O) (Nujol) 842 cm^{-1};

^{1}H NMR, δ 1.14 [dt, *J*(HH) 7.1, *J*(PH) 16.1, 48 H, OCH_2CH_3], 1.60 (m, 32 H, PCH_2CH_2), 3.0 (m, 32 H, PCH_2CH_2), 3.90 (m, 32 H, OCH_2CH_3) and 8.20 (m, 8 H, C_6H_4); ^{31}P NMR, δ 31.2 [t, *J*(PP) 25.7, 8P, P^V] and 22.0 [(qnt, *J*(PP) 25.7 Hz, 4P, P^{III}].

Complex **2**: HRFAB *m/z* 1590.1980 ([*M* + H]$^+$) (calc. for $C_{44}H_{88}O_{26}P_{12}Re$ 1589.1973); ν(O=Re=O) (Nujol) 812 cm^{-1}; ^{1}H NMR, δ 1.7 (m, 16 H, PCH_2CH_2), 2.9 (m, 16 H, PCH_2CH_2), 3.46 [d, *J*(PH) 11.0, 24 H, OCH_3], 3.52 [d, *J*(HH) 11.0, 24 H, OCH_3] and 8.20 (m, 8 H, C_6H_4); ^{31}P NMR, δ 34.0 [t, *J*(PP) 36.4, 8P, P^V] and 21.4 [qnt, *J*(PP) 36.4 Hz, 4P, P^{III}].

Complex **3**: HRFAB *m/z* 1718.4590 ([*M* + H]$^+$) (calc. for $C_{52}H_{120}O_{26}P_{12}Re$ 1717.4477) ν(O=Re=O) (Nujol) 847 cm^{-1}; ^{1}H NMR, δ 1.22 (m, 48 H, CH_2CH_3), 2.0–2.5 (m, 40 H, CH_2CH_2) and 4.0 (m, 32 H, OCH_2CH_3); ^{31}P NMR, δ 31.2 [t, *J*(PP) 24.0, 8P, P^V] and 20.0 [qnt, *J*(PP) 24.0 Hz, 4P, P^{III}].

Complex **4**: HRFAB *m/z* 1494.2001 ([*M* + H$^+$]) (calc. for $C_{36}H_{88}O_{26}P_{12}Re$ 1493.1973); ν(O=Re=O) (Nujol) 818 cm^{-1}; ^{1}H NMR, δ 2.1 (m, 16 H, PCH_2CH_2PO), 2.3 (m, 16 H, PCH_2CH_2PO), 2.5 (m, 8 H, PCH_2CH_2P), 3.65 [d, *J*(PH) 11.0, 24 H, OCH_3] and 3.69 [d, *J*(PH) 11.0, 24 H, OCH_3]; ^{31}P NMR, δ 34.5 [t, *J*(PP) 24.7, 8P, P^V] and 20.5 [qnt, *J*(PP) 24.7 Hz, 4P, P^{III}].

Acknowledgements

This work was supported by funds provided by the Department of Energy Grant No. DEFG0289E R60875, Du Pont-Merck pharmaceuticals and by the Departments of Radiology and Research Reactor, University of Missouri. We would like to thank one of the referees for helpful suggestions.

References

1 B. Cornils and E. Wiebus, *CHEMTECH*, 1995, **25**, 33 and refs. therein.
2 *Proceedings of NATO Advanced Research Workshop Aqueous Organometallic Chemistry and Catalysis*, Debrecen, 29th August–1st September, 1994, Preprints.
3 P. Kalck and F. Monteil, *Adv. Organomet. Chem.*, 1994, **34**, 219.
4 W. A. Herrmann and C. W. Kohlpaintner, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 1524.
5 W. A. Volkert and E. Deutsch, *Advances in Metals in Medicine*, Eds. M. J. Abrams and B. Murrer, JAI Press, Connecticut, 1993, vol. 1, pp. 115–153.
6 W. A. Volkert, J. Simon, A. R. Ketring, R. A. Holmes, J. C. Lattimer and L. A. Corwin, *Drugs of the Future*, 1989, **14**, 799.
7 R. W. Kozak, R. W. Atcher, O. A. Gansow, A. M. Friedman, J. J. Hines and T. A. Waldmann, *Proc. Natl. Acad. Sci. USA*, 1986, **83**, 473.
8 W. A. Volkert, W. F. Goeckeler, G. J. Ehrhardt and A. R. Ketring, *J. Nucl. Med.*, 1990, **1**, 80.
9 J. Chatt, G. J. Leigh and R. M. Slade, *J. Chem. Soc., Dalton Trans.*, 1973, 2021.
10 S. Ahrland, J. Chatt, N. R. Davies and A. A. Williams, *J. Chem. Soc.*, 1958, 276.
11 A. F. Borowski, D. J. C. Hamilton and G. Wilkinson, *Nouv. J. Chim.*, 1978, **2**, 137.
12 F. Joo and M. T. Beck, *React. Kinet. Catal. Lett.*, 1975, **2**, 257.
13 R. T. Smith and M. C. Baird, *Transition Met. Chem.*, 1981, **6**, 187.
14 E. G. Kuntz, *Chemtech*, 1987, **17**, 570.
15 E. G. Kuntz, Rhone-Poulenc Ind., *Fr. Pat.*, 2 349 562, 1976.
16 E. G. Kuntz, Rhone-Poulenc Ind., *Fr. Pat.*, 2 366 237, 1976.
17 E. G. Kuntz, Rhone-Poulenc Ind., *Fr. Pat.*, 2 733 516, 1976.
18 K. K. Katti, P. R. Singh, M. Wang, W. A. Volkert, T. J. Hoffman, A. R. Ketring and K. V. Katti, *Appl. Radiat. Isot.*, 1995, **46**, 53.
19 K. V. Katti, P. R. Singh, W. A. Volkert, A. R. Ketring and K. K. Katti, *Appl. Radiat. Isot.*, 1992, **43**, 1151.
20 W. A. Volkert, P. R. Singh, K. K. Katti, A. R. Ketring and K. V. Katti, *J. Labelled Compd. Radiopharm.*, 1993, **32**, 15.
21 M. Corlija, K. V. Katti, W. A. Volkert, T. J. Hoffman, C. Higginbotham and R. A. Holmes, *J. Nucl. Biol. Med.*, 1992, **36**, 296.
22 K. V. Katti, P. R. Singh, K. K. Katti, K. Kopicka, W. A. Volkert and A. R. Ketring, *J. Labelled Compd. Radiopharm.*, 1993, **32**, 407.
23 V. S. Reddy, K. V. Katti and C. L. Barnes, *Inorg. Chim. Acta*, 1995, **240**, 367.
24 V. S. Reddy, K. V. Katti and C. L. Barnes, *J. Chem. Soc., Dalton Trans.*, 1996, 1301.
25 V. S. Reddy, D. E. Berning, K. V. Katti, W. A. Volkert, A. R. Ketring and C. L. Barnes, *Inorg. Chem.*, 1996, **35**, 1753.
26 D. E. Berning, K. V. Katti, P. R. Singh, C. Higginbothom, V. S. Reddy and W. A. Volkert, *J. Nucl. Med. Biol.*, in the press.
27 K. V. Katti, V. S. Reddy and P. R. Singh, *Chem. Soc. Rev.*, 1995, 97.
28 K. V. Katti, *Curr. Sci.*, 1996, **70**, 219.
29 J. W. Ellis, K. N. Harrison, P. A. Hoye, A. G. Orpen, P. G. Pringle and M. B. Smith, *Inorg. Chem.*, 1992, **31**, 3026.

Received 4*th March* 1996; *Paper* 6/01542E