Rhenium complexes of *P,P,P′,P′*-tetrakis-(*o*-hydroxyphenyl)diphosphinoethane

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Abstract: Preparation of the hydrochloride salt of a new potentially hexadentate ligand precursor *P,P,P′,P′*-tetrakis(*o*-hydroxyphenyl)diphosphinoethane dihydrochloride (abbreviated $H_4P_2O_4{\cdot}2HCl$) is described. From $H_4P_2O_4{\cdot}2HCl$, neutral $[Re_2O_2Cl_2(PPh_3)_2(\mu\text{-}P_2O_4)]$ and dianionic $[Re_2O_2Br_4(\mu\text{-}P_2O_4)]^{2-}$ dinuclear rhenium(V) complexes were synthesized. The complexes have been characterized by elemental analysis, infrared spectroscopy, mass spectrometry, and $^1H/^{31}P\{^1H\}$ NMR spectra. $^{31}P\{^1H\}$ NMR revealed that only one isomer, presumably the *anti*, was present for $[Re_2O_2Cl_2(PPh_3)_2(\mu\text{-}P_2O_4)]$, and that two isomers, both *anti* and *syn* isomers, were observed for $[Re_2O_2Br_4(\mu\text{-}P_2O_4)]^{2-}$. The coligands ($PPh_3$ for the former, Br^- for the latter) of both complexes underwent ligand exchange with pyridine.

Key words: rhenium, *P,P,P′,P′*-tetrakis(*o*-hydroxyphenyl)diphosphinoethane, dimer, isomers.

Résumé : On décrit la préparation de sels d'un nouveau précurseur d'un coordinat potentiellement hexadentate, les dichlorhydrates de *P,P,P′,P′*-tétrakis(*o*-hydroxyphényl)diphosphinoéthane ($H_4P_2O_4{\cdot}2HCl$). À partir du $H_4P_2O_4{\cdot}2HCl$, on a synthétisé les complexes dinucléaires du rhénium neutre $[Re_2O_2Cl_2(PPh_3)_2(\mu\text{-}P_2O_4)]$ et dianionique $[Re_2O_2Br_4(\mu\text{-}P_2O_4)]^{2-}$. On a caractérisé les complexes par analyse élémentaire, spectroscopie infrarouge, spectrométrie de masse et spectroscopie RMN du $^1H/^{31}P\{^1H\}$. Les spectres RMN du $^{31}P\{^1H\}$ ont révélé qu'un seul isomère, probablement l'isomère *anti*, est présent dans le $[Re_2O_2Cl_2(PPh_3)_2(\mu\text{-}P_2O_4)]$ alors que deux isomères, les deux isomères *anti* et *syn*, sont présents dans le $[Re_2O_2Br_4(\mu\text{-}P_2O_4)]^{2-}$. Les co-coordinats ($PPh_3$ du premier et Br^- du dernier) des deux complexes subissent des échanges de coordinats avec la pyridine.

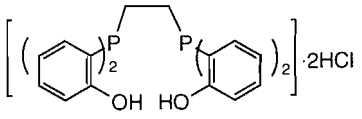
Mots clés : rhénium, *P,P,P′,P′*-tétrakis(*o*-hydroxyphényl)diphosphinoéthane, dimère, isomères.

[Traduit par la rédaction]

Introduction

The easy preparation of mixed (PO_2/HPO_2) complexes, $[MO(PO_2)(HPO_2)]$ (M = Re or Tc), from the direct interaction of a salt of bis(*o*-hydroxyphenyl)phenylphosphine ($H_2PO_2{\cdot}HCl$) with MO_4^-, suggests that this dihydroxylated phosphine is effective both as a reducing and a ligating agent, and that the combination of anchoring phenolate oxygen atoms and the softer phosphine P atoms stabilizes Re and Tc metal(V) centers (1). The ligand can both coordinate and reduce the metal center, a distinct advantage when considering potential ^{99m}Tc-radiopharmaceuticals where the only convenient source of ^{99m}Tc is $^{99m}TcO_4^-$ from a $^{99}Mo/^{99m}$Tc generator.

Deutsch and co-workers, working on Tc complexes with bidentate phosphine ligands such as DMPE, DEPE, DPPE (2, 3), showed that stable complexes of Tc in oxidation states from one to five can be formed with these ligands and auxiliary oxo or halo donor ligands. In our extended studies of functionalized phosphines, a novel, potentially hexadentate tetraprotic ligand, the dihydrochloride salt of *P,P,P′,P′*-tetrakis(*o*-hydroxyphenyl)diphosphinoethane ($H_4P_2O_4{\cdot}2HCl$) that contains two soft phosphine phosphorus donors and four hard phenolate oxygen anchors, has been synthesized. The classic hexadentate tetraprotic ligand, H_4edta, an N_2O_4 ligand, is known to form Tc complexes with such stoichiometries as $[TcO(edta)]^-$ (4) and $[Tc(\mu\text{-}O)(edta)]_2$ (5).



$H_4P_2O_4 \cdot 2HCl$

It was of interest to investigate the coordination chemistry of Tc/Re with this P_2O_4 donor set diphosphine ligand before pursuing the labeling of this ligand with ^{99m}Tc and evaluating its potential as an imaging agent. The results of the studies with Re are presented in this paper. Work with Tc is in progress and the results will be published elsewhere.

Experimental

Materials and methods

All chemicals were reagent grade and were used as received: phenol, PPh_3, dimethoxymethane, *n*-butyllithium, TMEDA (*N,N,N′N′*-tetramethylethylenediamine) (all above from Aldrich), $Cl_2PCH_2CH_2PCl_2$ (6), and NH_4ReO_4 (a gift from Johnson–Matthey, Inc.), $HCl_{(g)}$ (Matheson). $C_6H_5OCH_2OCH_3$ (mom-protected phenol) was prepared according to a published procedure (7), as was $[(n\text{-}Bu)_4N][ReOBr_4]$ (8).

Mass spectra were obtained with either a Kratos MS 50

Received December 5, 1995.

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(electron impact ionization, EIMS) or a Kratos Concept II H32Q instrument (Cs^+-LSIMS with positive or negative ion detection). Only the most intense peaks are given where consistent isotopic patterns were observed. Infrared spectra were recorded as KBr pellets in the range 4000–400 cm^{-1} on a Perkin–Elmer PE 783 spectrophotometer and were referenced to polystyrene. Microanalyses were performed by Mr. P. Borda in this department. ^1H NMR spectra (300 MHz, 400 MHz, or 500 MHz) were recorded on Varian XL 300, Bruker WH-400 (^1H–^1H COSY), or Bruker AMX-500 ($^1H\{^{31}P\}$) spectrometers, respectively, with δ referenced to external TMS. $^{31}P\{^1H\}$ NMR spectra (81 MHz or 121 MHz) were recorded on Bruker AC-200E or Varian XL 300 spectrometers, respectively, with δ referenced to external H_3PO_4. The assignments were based on those for the unbound ligand and by comparison between analogous complexes.

(o-$C_6H_4OCH_2OCH_3$)$_2$$PCH_2CH_2P$($o$-$C_6H_4OCH_2OCH_3$)$_2$·0.5 H_2O ($(mom)_4P_2O_4$·0.5H_2O, mom = CH_2OCH_3)

This was prepared from $C_6H_5OCH_2OCH_3$ by modifying the procedure for $Ph_2P(o\text{-}C_6H_4\text{-}OCH_2OCH_3)$ ((mom)PO) (9). To an ice-cooled solution of methoxymethyl phenyl ether (21.8 g, 0.16 mol) in ca. 200 mL petroleum ether (bp 35–65°C, dried with anhydrous Na_2SO_4 overnight) was added a solution of 100 mL of 1.6 M n-BuLi in hexanes and 18.05 g TMEDA in 50 mL petroleum ether under N_2. The mixture was stirred for 4 h at room temperature. A yellow precipitate formed from the orange solution. This mixture was heated to ca. 40°C with stirring, and subsequently cooled to 0°C, at which point $Cl_2PCH_2CH_2PCl_2$ (9.30 g, 0.40 mol) in 20 mL petroleum ether was then added via a syringe. The mixture was stirred overnight, during which time it warmed to room temperature. The solvents were removed by rotary evaporation and to the residue was added Na_2HPO_4 (0.5 M, 200 mL). The reaction mixture was then extracted with Et_2O (2 × 200 mL) followed by $CHCl_3$ (2 × 100 mL). All the organic layers were combined, concentrated to a reddish oil under low pressure, diluted with MeOH (ca. 25 mL), and stored at −4°C overnight. A yellowish crude product was filtered off, washed with cold methanol (2 × 10 mL), and dried in vacuo. The yield of the off-white product was 11.5 g (45% based on $C_6H_5OCH_2OCH_3$). IR (cm^{-1}, KBr disk): 3060 (m, aromatic $\nu_{C\text{-}H}$); 3000–2800 (m, $\nu_{C\text{-}H}$, methyl and methylene of mom group); 1590, 1577, 1475, 1452, 1445, 1407 (all s). ^1H NMR ($CDCl_3$, 300 MHz): 7.24 (t, 4H, p-H), 7.14 (dd, 4H, o'-H), 7.03 (d, 4H, m-H), 6.91 (t, 4H, m'-H), 5.04 (s, 8H, OCH_2O), 3.17 (s, 12H, OCH_3), 2.28 (dd, 4H, backbone-CH_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121 MHz): −31.7 (s). Mass spectrum (EI), m/z: 638 ($[(mom)_4P_2O_4]^+$), 623 ($[(mom)_4P_2O_4 - CH_3]^+$). Anal. calcd. (found) for $C_{34}H_{41}O_{8.5}P_2$: C 63.06 (63.19), H 6.38 (6.24).

P,P,P',P'-Tetrakis(o-hydroxyphenyl)diphosphinoethane dihydrochloride salt ($H_4P_2O_4$·2HCl)

This was prepared from $(mom)_4P_2O_4$ by modifying the procedure for $Ph_2P(o\text{-}C_6H_4OH)$ or HPO (9). Anhydrous HCl gas was bubbled overnight, via a dispersion tube, into a stirred solution of $(mom)_4P_2O_4$ (7.36 g, 11.5 mmol) in 350 mL anhydrous methanol. (The white suspension dissolved to give a clear solution after 1 h, but became cloudy again overnight.) A fine white solid was removed by filtration, washed with ethanol (2 × 20 mL), and dried in vacuo. The yield was 3.95 g (74% based on $(mom)_4P_2O_4$). No recrystallization was necessary to obtain an analytically pure sample. IR (cm^{-1}, KBr disk): 3300–2500 (vs, b, $\nu_{O\text{-}H}$ and $\nu_{C\text{-}H}$); 1590, 1495, 1450 (all vs). ^1H NMR (DMSO-d_6, 300 MHz): 10.8 (br s, 4H, OH), 7.6–7.3 (overlapped multiplets, 8H), 7.0–6.8 (multiplet, 8H), 2.6 (br s, 4H, backbone-CH_2). $^{31}P\{^1H\}$ NMR (121 MHz): 43.5 (s, DMSO-d_6): −36.4 (s, py-d_5). EIMS, m/z: 462 ($[H_4P_2O_4]^+$), 368 ($[H_4P_2O_4 - C_6H_6O]^+$). Anal. calcd. (found) for $C_{26}H_{26}Cl_2O_4P_2$: C 58.33 (58.21), H 4.90 (4.84), Cl 13.24 (13.07).

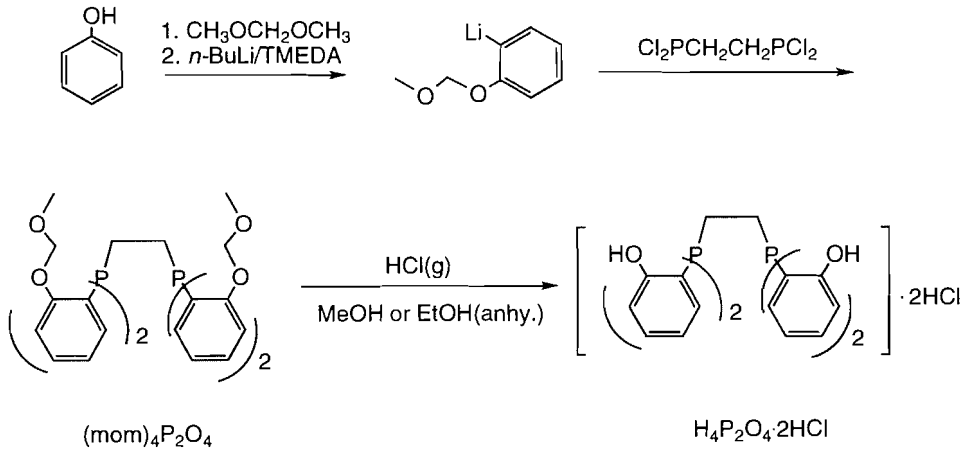
[$Re_2O_2Cl_2(PPh_3)_2(\mu\text{-}P_2O_4)$]

A mixture of $ReCl_4(PPh_3)_2$ (168 mg, 0.20 mmol), $H_4P_2O_4$·2HCl (109 mg, 0.20 mmol), and 8 drops of Et_3N in 15 mL ethanol was brought to reflux overnight. After the mixture was cooled to room temperature, a greenish yellow precipitate was isolated by centrifugation, washed with Et_2O, and dried in vacuo for 4 h. The yield was 40 mg (67%). The product was soluble in pyridine and DMSO (decomposes), slightly soluble in chloroform, but insoluble in diethyl ether. IR (cm^{-1}, KBr disk): 3060 (m, $\nu_{C\text{-}H}$); 1590, 1440 (both vs); 965 (s, $\nu_{Re=O}$). ^1H NMR (300 MHz, py-d_5): 7.70 (dd, 12H, o-H on PPh_3), 7.50 (dd, 2H), 7.40–7.20 (overlapped multiplets, 18H, m and p-H on PPh_3), 7.20 (d, 2H), 7.10 (d, 2H), 6.75 (m, 2H), 6.65 (t, 2H), 6.40 (t, 2H), 6.30 (t, 2H), 5.80 (dd, 2H), 2.85 (m, 2H, ethylene-H_A and -$H_{A'}$), 2.00 (d, 2H, ethylene-H_B and -$H_{B'}$). $^{31}P\{^1H\}$ NMR (81 MHz, py-d_5): 15.7, −11.3. LSIMS: m/z: 1459 ($[M + 1]^+$), 1423 ($[M - Cl]^+$), 1196 ($[M - PPh_3)]^+$), 1161 ($[M - Cl - PPh_3]^+$), 1124 ($[M - 2Cl - PPh_3]^+$), 645 ($[Re(P_2O_4)]^+$), 263 (PPh_3 + 1). Anal. calcd. (found) for $C_{62}H_{50}Cl_2O_6P_4Re_2$: C 51.07 (50.76), H 3.46 (3.59), Cl 4.86 (4.65).

[(n-Bu)$_4$N]$_2$[$Re_2O_2Br_4(\mu\text{-}P_2O_4)$]·$Me_2CO$

To a mixture of [(n-Bu)$_4$N][$ReOBr_4$] (77.6 mg, 0.10 mmol), [(n-Bu)$_4$N]Br (151 mg, 0.45 mmol), and $H_4P_2O_4$·2HCl (55.5 mg, 0.10 mmol) was added 20 mL toluene, and the mixture was refluxed for 2 h. From the resulting green oil, a green solid was precipitated with i-PrOH. Recrystallization from acetone gave emerald green crystals of the acetone solvate that were filtered, washed with cyclohexane, and dried in vacuo overnight. The yield was 31 mg (35%). The product was soluble in ethanol, acetone, chloroform, and dichloromethane, but insoluble in diethyl ether or cyclohexane. IR (cm^{-1}, KBr disk): 3060 (m, $\nu_{C\text{-}H}$); 2980, 2780 (s, $\nu_{C\text{-}H}$ of the n-Bu group), 960 (s, $\nu_{Re=O}$). ^1H NMR (500 MHz, acetone-d_6): 7.9–7.6 (overlapped m, 4H), 7.22 (t, ^1H), 7.16 (t, ^1H), 7.1–6.9 (overlapped m, 4H), 6.78 (t, 1H), 6.7–6.6 (overlapped m, 2H), 6.55 (t, ^1H), 6.2 (overlapped m, 2H), 4.14 (m, 2H, ethlyne-H_A and -$H_{A'}$), 3.45 (t, 16H, α-H of the n-Bu group), 2.65 (d, 2H, ethylene-H_B and -$H_{B'}$), 1.70 (quintet, 16H, β-H of the n-Bu group), 3.45 (sextet, 16H, γ-H of the n-Bu group), 0.95 (t, 24H, Me-H of the n-Bu group). $^{31}P\{^1H\}$ NMR (81 MHz, acetone-d_6): 18.0 (major); 17.0 (minor). LSIMS (+), m/z: 242 ($[(n\text{-}Bu)_4N]^+$), 645 ($[Re(P_2O_4)]^+$), 662 ($[ReO(HP_2O_4)]^+$); LSIMS (−), m/z: 645 ($[Re(P_2O_4)]^-$), 661 ($[ReO(P_2O_4)]^-$), 769 ($[ReO(P_2O_4) + 108]^-$). Anal. calcd. (found) for $C_{61}H_{98}Br_4N_2O_7P_2Re_2$: C 42.46 (42.62), H 5.72 (5.47), N 1.62 (1.71).

Scheme 1.



Results and discussion

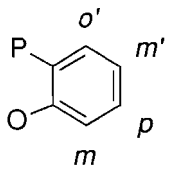
$H_4P_2O_4 \cdot 2HCl$

The new potentially hexadentate ligand $H_4P_2O_4 \cdot 2HCl$ was synthesized in a manner similar to that used to obtain the potentially tridentate $H_2PO_2 \cdot HCl$ (1). After protecting the phenol hydroxy group as a methoxymethyl (mom) ether (9), the mom-protected phenol was *ortho*-lithiated at low temperature under N_2, and 4 equivalents of it were then reacted with $Cl_2PCH_2CH_2PCl_2$ to give the mom-protected intermediate, $(mom)_4P_2O_4$. Upon treatment with anhydrous HCl gas in methanol or ethanol, the expected functionalized diphosphine was obtained as the dihydrochloride salt (Scheme 1).

For the intermediate, $(mom)_4P_2O_4$, the EIMS shows the expected parent ion peak (*m/z*: 638, $[(mom)_4P_2O_4]^+$), along with fragments formed from the parent ion by the loss of $-CH_3$, $-OCH_3$, $-CH_2OCH_3$, and $-OCH_2OCH_3$ groups. In the $^{31}P\{^1H\}$ NMR spectrum ($CDCl_3$), a singlet at -31.7 ppm, typical for a phosphine P, is present (10). The ^1H NMR spectrum shows four hydrogen resonances at 7.24, 7.14, 7.03, and 6.91 ppm in the aromatic range, corresponding to *p*-, *o'*-, *m*-, and *m'*-*H* of the phenyl ring[3] (assigned from a ^1H–^1H COSY spectrum). The resonances corresponding to methyl and methylene H atoms of the mom protecting group, appear as singlets at 5.04 and 3.17, respectively. The two methylene H nuclei in each mom group of $(mom)_2PO_2$ gave an AB quartet (1), indicating nonequivalence of the two methylene hydrogens because of prochirality. This was not the case with $(mom)_4P_2O_4$, however; the four chemically equivalent backbone H atoms give a doublet of doublets due to unequal coupling to the two P nuclei.

As was seen in $H_2PO_2 \cdot HCl$ (1), the formulation of a hydrochloride salt for its hexadentate analogue $H_4P_2O_4 \cdot 2HCl$ is supported by the elemental analysis and by the ^{31}P chemical shift, characteristic of a phosphonium P (10) at +43.5 ppm in DMSO-d_6. This salt dissociated in its ligand-exchange reactions (vide infra) and in basic solution, as is indicated by the chemical shift of -36.4 ppm in the $^{31}P\{^1H\}$ NMR spectrum in py-d_5. EIMS shows the presence of $[H_4P_2O_4]^+$. The ^1H NMR spectrum in DMSO-d_6 shows four overlapped H resonances in the aromatic region and a broad backbone H resonance at 2.6 ppm with the expected integral ratio.

[3] This is designated as in the following diagram:



Synthesis of complexes

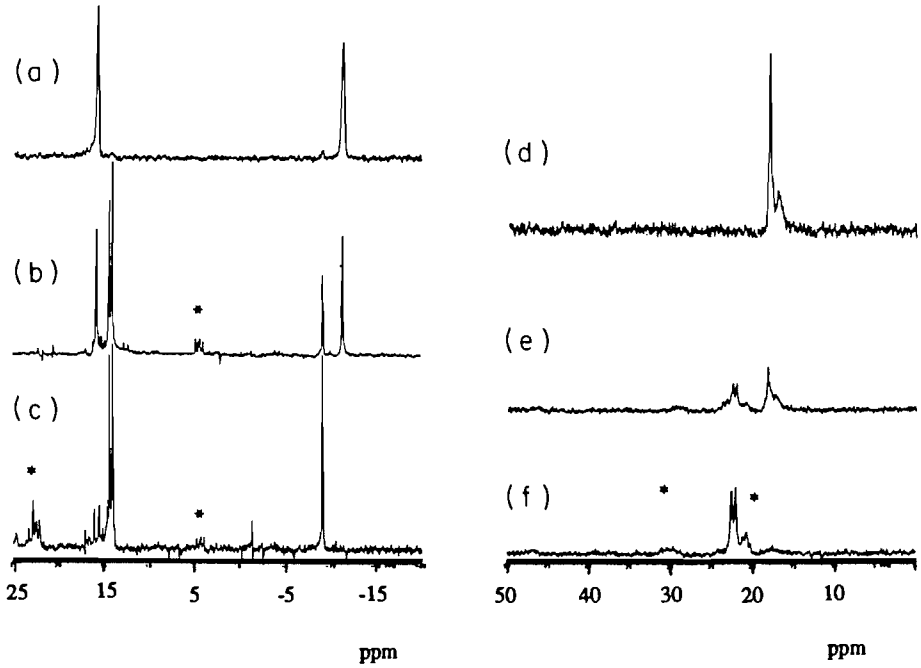
The phosphine hydrochloride salt $H_4P_2O_4 \cdot 2HCl$, when deprotonated by a base, reacted with $[ReCl_4(PPh_3)_2]$ forming a dinuclear complex $[Re_2O_2Cl_2(PPh_3)_2(\mu\text{-}P_2O_4)]$. Aerial oxidation was responsible for oxidizing Re(IV) to Re(V). In another trial without added base, the ligand did not react with the Re precursor; red crystals obtained from this trial were identified by X-ray crystallography as a partially oxidized mixture of *trans*-$[ReCl_4(PPh_3)_2]$ and *trans*-$[ReOCl_3(PPh_3)_2]$ (11, 12). A dinuclear dianionic complex $[Re_2O_2Br_4(\mu\text{-}P_2O_4)]^{2-}$ (as a $[(n\text{-}Bu)_4N]^+$ salt) was formed from the reaction of $[(n\text{-}Bu)_4N][ReOBr_4]$ with the ligand and added $[(n\text{-}Bu)_4N]Br$ in the absence of added base. These observations, taken together, suggest that an extra driving force is necessary to push forward the substitution reaction of $H_4P_2O_4$ with a precursor that contains PPh_3, consistent with observations reported for H_2PO_2 (1). In addition, chelation of the $P_2O_4^{4-}$ ligand to a single Re center is clearly not favored.

Both the dimetallic Re complexes are air stable in the solid state, and were characterized by elemental analysis, infrared spectroscopy, mass spectrometry, and $^1H/^{31}P\{^1H\}$ NMR spectroscopy. IR measurements confirmed the presence of Re=O multiple bonds and ensured that the multidentate ligands were coordinated as evidenced by the absorptions shifted in comparison with the free ligands. Both ^1H NMR and $^{31}P\{^1H\}$ spectra were very useful in verifying the diastereomeric structures of $[Re_2O_2Cl_2(PPh_3)_2(\mu\text{-}P_2O_4)]$ and $[(n\text{-}Bu)_4N]_2[Re_2O_2Br_4(\mu\text{-}P_2O_4)]$ (vide infra).

Dinuclear (P_2O_4) Re complexes

Mass spectrometric data confirmed formation of dinuclear complexes when the expected parent ions and (or) their fragments were found, while microanalysis established the formulation of both compounds. The parent ion

Fig. 1. $^{31}P\{^1H\}$ NMR spectra (81 MHz) showing reactivity of the dinuclear complexes to pyridine (* decomposition products). (*a*) $[Re_2O_2Cl_2(PPh_3)_2(\mu\text{-}P_2O_4)]$ in py-d_5; (*b*) *a* after standing for 6 months; (*c*) *b* after being heated to 100°C then cooled to room temperature; (*d*) $[(n\text{-}Bu)_4N]_2[Re_2O_2Br_4(\mu\text{-}P_2O_4)]$ in acetone-d_6; (*e*) *d* after 3 drops of py-d_5 were added; (*f*) *e* after being heated to 60°C then cooled to room temperature.



$[Re_2O_2Cl_2(PPh_3)_2(\mu\text{-}P_2O_4) + 1]^+$ (*m/z* = 1459) was present in the +LSIMS spectrum of $[Re_2O_2Cl_2(PPh_3)_2(\mu\text{-}P_2O_4)]$; however, the stronger peaks were *m/z* = 263 (PPh_3), 645 ($[Re(P_2O_4)]^+$), and 1161 ($[M - Cl - PPh_3]^+$ or $[Re_2O_2Cl(PPh_3)(\mu\text{-}P_2O_4)]^+$), indicating that the monodentate Cl^- or PPh_3 ligands were subject to dissociation from the complex under the ionization conditions. For the positive ion detection mode LSIMS spectrum of $[(n\text{-}Bu)_4N]_2[Re_2O_2Br_4(\mu\text{-}P_2O_4]$, *m/z* = 242 ($[(n\text{-}Bu)_4N]^+$) was intense, and a much weaker peak for $[Re(P_2O_4)]^+$ was also found; in the negative ion detection mode, *m/z* = 79 (Br^-) was the most intense peak, with fragments found at *m/z* = 661 ($[ReO(P_2O_4)]^-$) and 769 ($[ReO(P_2O_4) + 108]^-$). The mass of 108 is that of the matrix, thioglycerol ($C_3H_8O_2S$). The dianionic parent ion $[Re_2O_2Br_4(\mu\text{-}P_2O_4)]^{2-}$ did not show in the negative ion mode, presumably due to a very strong interaction with the very polar matrix, thioglycerol, preventing the volatilization of the dianion.

There were similarities in the IR spectra of the two dinuclear complexes. Strong C–H stretching vibrations at 2960 and 2880 cm^{-1}, diagnostic for $[(n\text{-}Bu)_4N]^+$, were observed for $[(n\text{-}Bu)_4N]_2[Re_2O_2Br_4(\mu\text{-}P_2O_4)]$. Below 2000 cm^{-1}, almost all the absorptions in the spectrum of $[(n\text{-}Bu)_4N]_2[Re_2O_2Br_4(\mu\text{-}P_2O_4)]$ were observed in the spectrum of $[Re_2O_2Cl_2(PPh_3)_2(\mu\text{-}P_2O_4)]$ as well. The Re=O stretches for $[(n\text{-}Bu)_4N]_2[Re_2O_2Br_4(\mu\text{-}P_2O_4)]$) and $[Re_2O_2Cl_2(PPh_3)_2(\mu\text{-}P_2O_4)]$) were found at 960 and 965 cm^{-1}, respectively, in the normal range for six-coordinate Re^V=O complexes (13). The additional bands in $[Re_2O_2Cl_2(PPh_3)_2(\mu\text{-}P_2O_4)]$ originated from PPh_3 bound to the Re(V) center.

A seven-coordinate complex, as formed from Tc(V) and $edta^{4-}$ (4), did not seem feasible for Re(V) with $P_2O_4^{4-}$. In $[TcO(edta)]^-$, the two neutral tertiary amine N atoms are approximately opposite the oxo ligand, the Tc—N bonds being somewhat lengthened by the *trans* influence (14). Thus, one consideration for $P_2O_4^{4-}$ is that the phosphine P atom, which is much softer than the amine N atom, will be found in *cis* positions relative to the oxo group to avoid the *trans* influence (as soft, neutral donors usually do). The phenolate rings of $P_2O_4^{4-}$ are also considerably less flexible than the carboxylate arms of $edta^{4-}$.

The $^{31}P\{^1H\}$ NMR spectrum of $[Re_2O_2Cl_2(PPh_3)_2(\mu\text{-}P_2O_4)]$ showed two peaks of equal intensity, diagnostic for two nonequivalent phosphorus centers (Fig. 1*a*). This suggested that the two $\mu\text{-}P_2O_4^{4-}$ P nuclei were equivalent, as were the two PPh_3 P nuclei. Consistent with this, in the ^1H NMR spectrum (Fig. 2) there were eight types of aromatic hydrogen nuclei for the PO-phenyl rings of the complex, indicating that the four phenolate rings of the $\mu\text{-}P_2O_4^{4-}$ ligand were in two different environments, each including two equivalent rings. In this aromatic region, a doublet of doublets (7.70 ppm, *o*-H) and overlapped multiplets (~7.3 ppm, *m*-H and *p*-H) were also present, corresponding to the phenyl H nuclei of PPh_3 (Fig. 2). The four H and two P nuclei on the ethylene backbone form an AA′BB′XX′ spin system (one per diastereomer) because of chirality at the metal centre (Fig. 3, *anti*). The *syn* diastereomer was not present for this neutral dinuclear complex (vide infra). The appearance of two resonances (one triplet-like, the other doublet-like) corresponding to the H_A and H_B nuclei was complicated because of multiple couplings.

For $[(n\text{-}Bu)_4N]_2[Re_2O_2Br_4(\mu\text{-}P_2O_4)]$, two peaks were observed in the $^31P\{^1H\}$ spectrum, one major and one minor, at 18.0 and 17.0 ppm, respectively (Fig. 1*d*). In the ^1H NMR spectrum, there were more than eight signals for the PO-phe-

Fig. 2. ^{1}H NMR spectra of $[Re_2O_2Cl_2(PPh_3)_2(\mu\text{-}P_2O_4)]$ (top, in py-d_5, 300 MHz) and $[(n\text{-}Bu)_4N]_2[Re_2O_2Br_4(\mu\text{-}P_2O_4)]$ (bottom, in acetone-d_6, 400 MHz), (# solvent or HOD; * impurity).

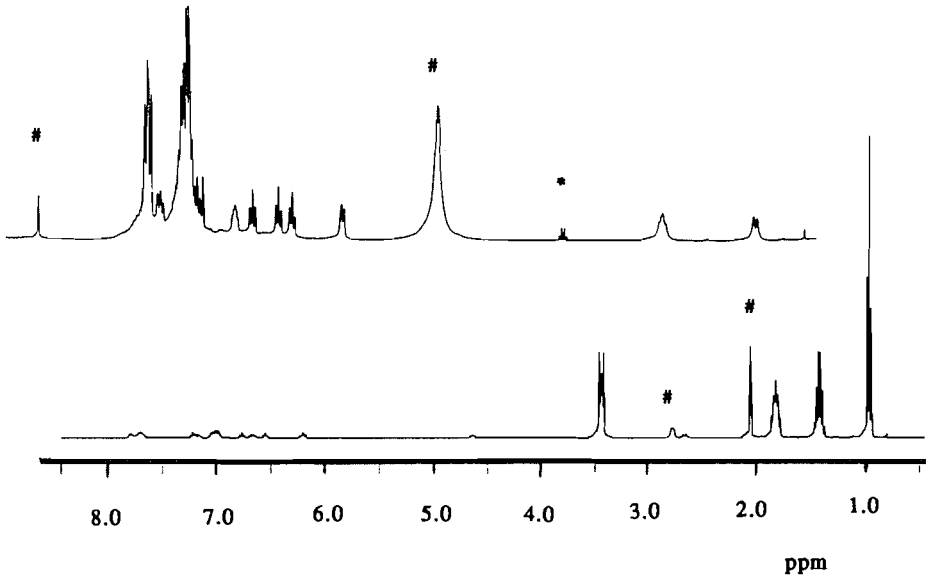
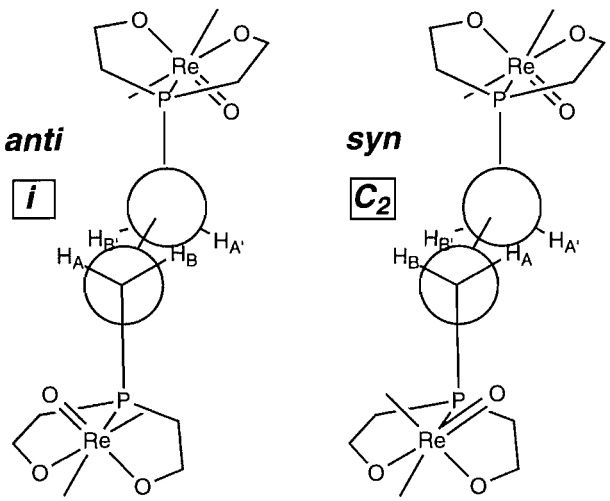


Fig. 3. Diastereomers of the dinuclear complexes showing the AA'BB'XX' system of the backbone (4H, 2P) in each.

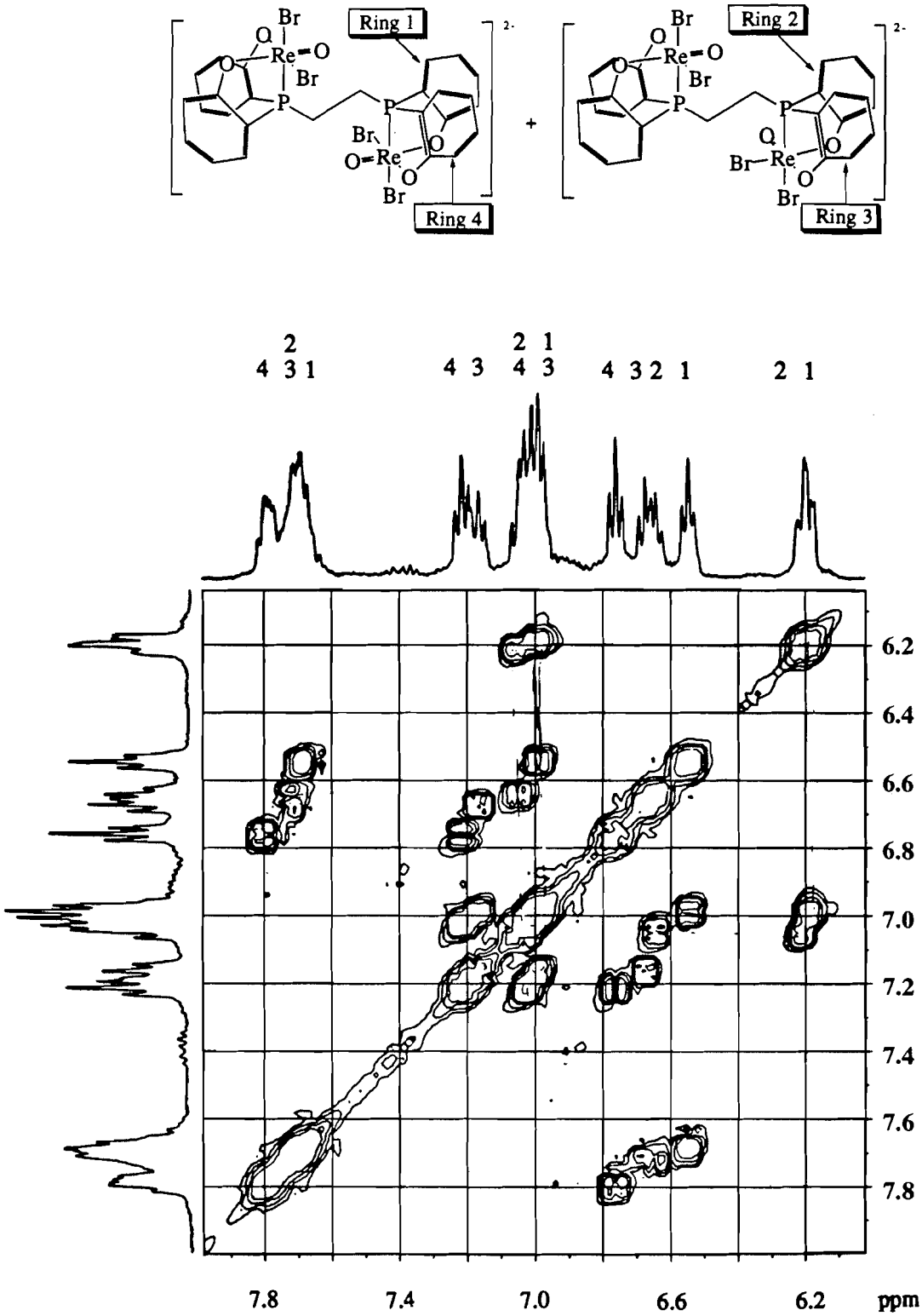


nyl rings in the complex (Fig. 2). In fact, 16 H signals (some of them overlapped) in the aromatic region (6.0–8.0 ppm) were correlated into four groups by a ^{1}H-^{1}H COSY experiment (Fig. 4), indicating that there were four PO-phenyl ring environments (numbered ring 1 to ring 4 as shown in Fig. 4). The H resonances corresponding to the *o'*-H of the four PO-phenyl rings were identified in the ^{1}H{^{31}P} NMR spectrum (each simplified from a multiplet to a doublet upon decoupling as shown in Fig. 5). The ^{1}H NMR signals corresponding to rings 1 and 4 were stronger in intensity than those of rings 2 and 3, and the ^{31}P NMR signal at 18.0 ppm was more intense than that at 17.0 ppm. Taken together, these data indicate that there are one major and one minor isomer present in the $[(n\text{-}Bu)_4N]_2[Re_2O_2Br_4(\mu\text{-}P_2O_4)]$ sample. In the ^{13}C{^{1}H} NMR spectrum, only eight signals were observed in the aromatic region, tentatively assigned to the major isomer eight PO-phenyl ring carbon atoms that had hydrogen atoms attached; those of the minor isomer, and quaternary carbons in both isomers, were not observed because the sample was too dilute. For the ethylene H nuclei, a similar AA'BB'XX' spin system was observed for $[(n\text{-}Bu)_4N]_2[Re_2O_2Br_4(\mu\text{-}P_2O_4)]$, and H_A and H_B were found to be coupled strongly to each other. The chemical shifts for the C_2H_4 ethylene H nuclei of the backbone of each isomer coincide since only two resonances are present. Upon phosphorus decoupling, both H_A and H_B signals appeared as doublets.

Two models, *anti* (*i*) and *syn* (C_2), proposed for the dinuclear complexes are shown in Fig. 3. Assumptions with adequate precedent have been used to formulate these models: neutral P donor(s) are *cis* to the Re=O, and the PO_2 donor set of each end of $P_2O_4^{4-}$ is facially coordinated. Both assumptions are based on the coordination of PO_2^{2-} in *fac*-$[ReZCl(PPh_3)(PO_2)]$ (Z = O or NPh) (1). In fact, P *trans* to M=O, M≡N, or M=NR has not been observed for complexes of this type (M = Re or Tc) incorporating phosphine (11, 15–22) or functionalized phosphine (1, 23, 24) ligands; the P donors are always *cis*.

The two models can be described as *syn* and *anti* with respect to the two Re=O groups, and they have C_2 and *i* symmetry, respectively (Fig. 3). With aid of a 3-D model, it is easy to reason why there is only one isomer for $[Re_2O_2Cl_2(PPh_3)_2(\mu\text{-}P_2O_4)]$, while there are two isomers for $[(n\text{-}Bu)_4N]_2[Re_2O_2Br_4(\mu\text{-}P_2O_4)]$, as shown in the ^{31}P NMR spectra (Figs. 1*a* and 1*d*, respectively). $[Re_2O_2Cl_2(PPh_3)_2(\mu\text{-}P_2O_4)]$ exists presumably as the *anti* isomer (*i* symmetry); the *syn* isomer is not feasible because of the two bulky PPh_3 groups. For this complex, a proposal with the two P donors *trans* to each other can also be rejected because the mutual P–P coupling is quite small. Either arrangement with the two P donors *trans* or *cis* to each other is possible based on modeling and has actually been observed for the complexes *fac*-$[ReZCl(PPh_3)(PO_2)]$ (Z = O or NPh) (1). In modeling $[Re_2O_2Br_4(\mu\text{-}P_2O_4)]^{2-}$, both *syn* and *anti* isomers are found to

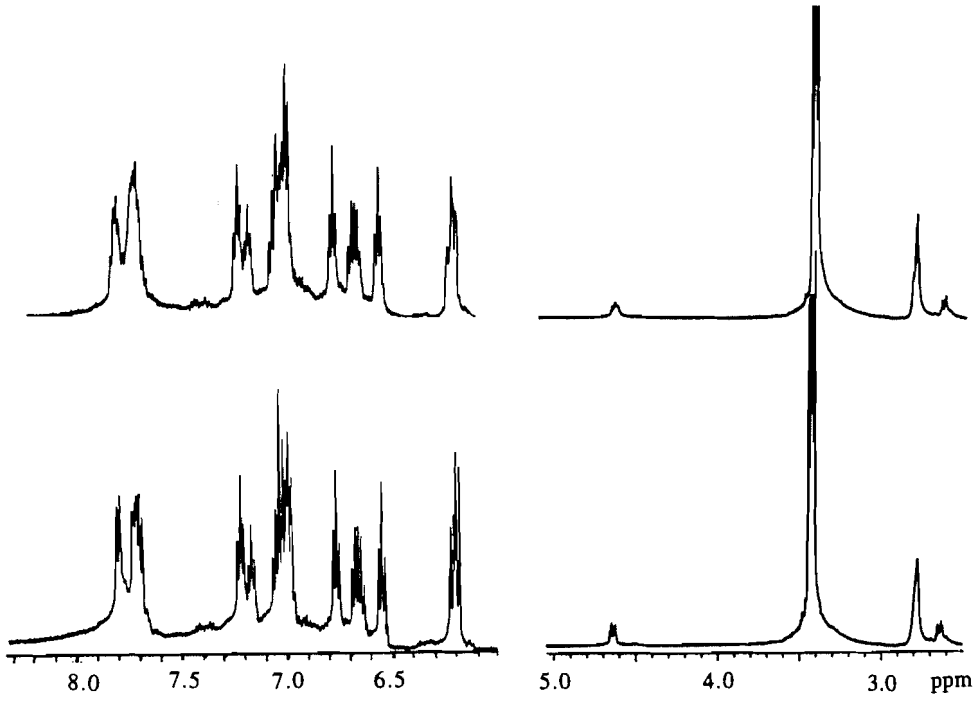
Fig. 4. The proposed isomers and the ^1H–^1H COSY spectrum (400 MHz) of $[(n\text{-}Bu)_4N]_2[Re_2O_2Br_4(\mu\text{-}P_2O_4)]$ (aromatic region); the correlated H resonances are designated by the same number as the respective PO phenyl ring.



be feasible as Br^- is much less bulky, and this might be the case as indicated by the NMR results.

The two P signals at 15.7 and −11.3 ppm in the $^{31}P\{^1H\}$ NMR spectrum (Fig. 1*a*) for $[Re_2O_2Cl_2(PPh_3)_2(\mu\text{-}P_2O_4)]$ are assigned to the P nuclei of the $\mu\text{-}P_2O_4^{4-}$ and PPh_3 ligands, respectively. Phenolato-anchored phosphine P nuclei experience a greater deshielding effect than the PPh_3 ligand in such complexes as $[ReZCl(PO_2)(PPh_3)]$ (Z = O or NPh) (1), due to

Fig. 5. ^1H (top) and $^1H\{^{31}P\}$ (bottom) NMR spectra (500 MHz) of $[(n\text{-}Bu)_4N]_2[Re_2O_2Br_4(\mu\text{-}P_2O_4)]$ (aromatic and ethylene regions).



stronger donation (25). This $\mu\text{-}P_2O_4^{4-}$ P chemical shift was found to be quite close to that of $[(n\text{-}Bu)_4N]_2[Re_2O_2Br_4(\mu\text{-}P_2O_4)]$, at 18.0 (major) and 17.0 (minor) ppm (Fig. 1*d*). Further support for this assignment is depicted by Fig. 1*c*, where the PPh_3 P signal is identified by its replacement with py-d_5.

Reactivity with pyridine

The replacement of PPh_3 in $[Re_2O_2Cl_2(PPh_3)_2(\mu\text{-}P_2O_4)]$ with pyridine (py-d_5) was monitored in the $^{31}P\{^1H\}$ NMR spectrum by the appearance of a free PPh_3 singlet at −9.1 ppm, and by the decrease in intensity of the upfield P signal (−11.3 ppm, bound PPh_3) in the original spectrum (Fig. 1*c*). The substitution is very slow (Fig. 1*b*); however, after the solution was heated to 100°C and then cooled to room temperature, the substitution was complete, at which time the bound PPh_3 P signal (−11.3 ppm) disappeared completely, and the downfield P signal (15.7 ppm) was replaced by two singlets (14.3 and 14.0 ppm). Clearly, the PPh_3 ligands in the complex are labile and the assignment of the bound PPh_3 in the original $^{31}P\{^1H\}$ NMR spectrum is verified. No attempt was made to fully characterize the new complex formed with pyridine; however, *syn* and *anti* isomers would be consistent with the appearance of the two singlets at 14.3 and 14.0 ppm.

Pyridine (py-d_5, 3 drops) was added to $[(n\text{-}Bu)_4N]_2[Re_2O_2Br_4(\mu\text{-}P_2O_4)]$ in acetone-d_6. Changes in the ^{31}P resonances were also observed in the $^{31}P\{^1H\}$ NMR spectrum: the original peaks were reduced in intensity, while two new singlets appeared (Fig. 1*e*). After heating to 60°C for 10 min and then cooling to room temperature (the solution changed to yellowish green from the original emerald green), these spectral changes were complete, whereupon the original P signals (18.0 and 17.0 ppm) disappeared completely, giving rise to two singlets at 22.1 and 22.6 ppm (Fig. 1*f*). The dianionic complex is also labile to substitution. Again, similar *syn* and *anti* isomers would be consistent with the substituted products.

Conclusion

The hydrochloride salt of a new ligand, the potentially hexadentate and tetraprotic $H_4P_2O_4{\cdot}2HCl$, was synthesized and characterized. With this salt, neutral $[Re_2O_2Cl_2(PPh_3)_2(\mu\text{-}P_2O_4)]$ and dianionic $[Re_2O_2Br_4(\mu\text{-}P_2O_4)]^{2-}$ dinuclear rhenium(V) complexes were synthesized and characterized. The rigidity of the ligand frame and (or) *trans* influence make it impossible for all the donor atoms to bind a single $Re^V{=}O$ centre. However, this ligand can bridge two Re(V) centers, incorporating monodentate oxo, chloro, and PPh_3 ligands to complete the coordination sphere of each Re(V). These complexes are important since they provide useful information about the coordination preference of the $P_2O_4^{4-}$ ligand. Work on the $^{99}Tc/^{99m}Tc$ complex of this ligand and its radiopharmaceutical chemistry is in progress.

Acknowledgments

We wish to thank the Natural Sciences and Engineering Research Council of Canada, the British Columbia Health Research Foundation, and the Du Pont Merck Pharmaceutical Company for operating grants, Johnson Matthey, Inc. for NH_4ReO_4, and Mr. G. Clentsmith and Professor M. D. Fryzuk for a sample of $Cl_2PCH_2CH_2PCl_2$.

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