

Reactions of the triply-bonded complex $cis\text{-Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_2(\mu\text{-dppm})_2$ with pyridine carboxylic acids. The isolation and structural characterization of a third structural isomer of $\text{Re}_2(\text{dipic})\text{Cl}_2(\mu\text{-dppm})_2$ (dipic = pyridine-2,6-dicarboxylate)

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The diamagnetic dirhenium(II) complexes $\text{Re}_2(\text{pic})\text{Cl}_3(\mu\text{-dppm})_2$ (**2**), $\text{Re}_2(\text{dipic})\text{Cl}_2(\mu\text{-dppm})_2$ (**3**), $\text{Re}_2(\text{HnicO})_2\text{Cl}_2(\mu\text{-dppm})_2$ (**4**) and $\text{Re}_2(\text{picO})_2(\mu\text{-dppm})_2$ (**5**) that are formed by the reactions of $cis\text{-Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_2(\mu\text{-dppm})_2$ (**1**) with picolinic acid (Hpic), dipicolinic acid (H_2dipic), 2-hydroxynicotinic acid (HnicOH) and 6-hydroxypicolinic acid (HpicOH) represent four different types of reaction products from the displacement of the *cis* acetate groups of **1**. All four compounds have been characterized by X-ray crystallography. Compound **2** can be prepared more logically and in higher yield from $\text{Re}_2\text{Cl}_4(\mu\text{-dppm})_2$. Compound **3**, which retains the same *cis,cis* coordination of $\mu\text{-dppm}$ ligands that is present in **1**, is the third structural isomer of $\text{Re}_2(\text{dipic})\text{Cl}_2(\mu\text{-dppm})_2$; the other two, which are prepared from $\text{Re}_2\text{Cl}_4(\mu\text{-dppm})_2$, contain *trans,trans* and *trans,cis* ligation by the pair of $\mu\text{-dppm}$ ligands. Compounds **4** and **5** are the first dirhenium(II) compounds that contain bridging 2-pyridonate ligands; in **4** the carboxylic acid group of $\mu\text{-HnicO}$ does not coordinate, whereas the $\mu\text{-picO}$ ligands in **5** are bound in a tridentate fashion and, consequently, the two axial Re–Cl bonds of **1** have been replaced by axial Re–O (carboxylate) coordination. Complexes **3–5** have quite accessible oxidation chemistry as shown by cyclic voltammetric measurements.

Introduction

The substitutional lability of the pair of acetate groups in the complex $cis\text{-Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_2(\mu\text{-dppm})_2$ (**1**)¹ towards monoanionic bridging ligands, especially other carboxylates, provides a convenient strategy for incorporating the triply bonded $[\text{Re}=\text{Re}]^{4+}$ unit into homometallic and heterometallic assemblies.^{2–4} The presence of a pendant coordinating group attached to the carboxylate moiety, as present in the isonicotinate and 4-(diphenylphosphino)benzoate ligands, has been used to prepare mixed Re_4Pt_2 ,³ Re_2Pd_2 ⁴ and Re_2Au_2 ⁴ assemblies, while bridging dicarboxylate ligands, such as terephthalate and *trans*-1,4-cyclohexanedicarboxylate, can be used to prepare either supramolecular triangles or “dimers-of-dimers”, the latter being linked through intermolecular hydrogen-bonds into zigzag chains.² These studies are of relevance to the growing body of work that has been focused on the incorporation of multiply bonded dimetal units into supramolecular assemblies.⁵

While the displacement of the acetate groups in **1** by isonicotinate to form $cis\text{-Re}_2(\mu\text{-O}_2\text{C-4-C}_5\text{H}_4\text{N})_2\text{Cl}_2(\mu\text{-dppm})_2$ leaves a pair of nitrogen atoms available for coordination to other metal units,³ studies have not yet been carried out of the reactions between **1** and pyridine-2-carboxylate ligands in which the nitrogen can also bind to the same dirhenium unit that is complexed by the carboxylate group. To ascertain whether this is the case, we have examined the reactions of **1** with picolinic acid, dipicolinic acid, 6-hydroxypicolinic acid and 2-hydroxynicotinic acid. The reaction course is different in each case, and the pyridine carboxylate ligands are found to bridge the dirhenium(II) unit and/or chelate to one of the metal centers.

Experimental

A Starting materials, reaction procedures, and physical measurements

The dirhenium(II) complex $cis\text{-Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_2(\mu\text{-dppm})_2$ (**1**) was prepared by the literature method.¹ The ligands

picolinic acid (Hpic, py-2-CO₂H), dipicolinic acid (H_2dipic , py-2,6-(CO₂H)₂), 2-hydroxypyridine, 2-hydroxynicotinic acid (HnicOH) and 6-hydroxypicolinic acid (HpicOH) were obtained from Aldrich Chemical Co. All other reagents and organic solvents were purchased from commercial sources and were used without further purification. Solvents were deoxygenated by purging with dinitrogen prior to use and all reactions were carried out under an atmosphere of dinitrogen. NMR spectra and cyclic voltammograms were determined as described previously.⁶ Elemental microanalyses were done by Dr H. D. Lee of the Purdue University Microanalytical Laboratory.

B Reactions of $cis\text{-Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_2(\mu\text{-dppm})_2$ (**1**) with pyridine carboxylic acids

(i) **Synthesis of $\text{Re}_2(\text{pic})\text{Cl}_3(\mu\text{-dppm})_2$ (**2**).** A mixture of picolinic acid (46 mg, 0.374 mmol) and **1** (100 mg, 0.075 mmol) was stirred in 30 mL of ethanol and then slowly brought to reflux. After one day, the mixture was cooled to r.t. and the insoluble green solid was filtered off and washed with cold ethanol (3 × 5 mL) and diethyl ether (3 × 5 mL). Yield of **2**: 48 mg (47%). Recrystallization from dichloromethane–hexanes gave single crystals of **2** which were shown by X-ray crystallography to be identical to the product formed by the reaction of $\text{Re}_2\text{Cl}_4(\mu\text{-dppm})_2$ with picolinic acid or the salt $[(\text{Ph}_3\text{P})_2\text{N}]\text{pic}$.⁷

(ii) **Synthesis of $\text{Re}_2(\text{dipic})\text{Cl}_2(\mu\text{-dppm})_2$ (**3**).** A mixture of **1** (100 mg, 0.075 mmol) and dipicolinic acid (63 mg, 0.377 mmol) in ethanol (30 mL) was refluxed for one day. Work-up as in section B(i) gave **3** as a red solid. Yield of **3**: 75 mg (76%). This product was recrystallized from dichloromethane–hexanes. Calc. for $\text{C}_{58}\text{H}_{49}\text{Cl}_4\text{NO}_4\text{P}_4\text{Re}_2$ (i.e. $3\cdot\text{CH}_2\text{Cl}_2$): C, 47.64; H, 3.38; N, 0.96. Found: C, 47.09; H, 3.65; N, 0.95%. ¹H NMR spectrum (δ in CDCl_3): 9.0–6.5 (m, 43 H, dipic and Ph of dppm), 5.98 and 4.50 (m, 4H, CH_2 of dppm). ³¹P{¹H} NMR spectrum (δ in CDCl_3): +5.48 (d), +1.78 (d), –4.43 (d), –9.43 (d). Cyclic voltammogram (0.1 M $\text{Bu}_4\text{NPF}_6\text{-CH}_2\text{Cl}_2$ at 25 °C, Pt-bead electrode, $\nu = 200 \text{ mV s}^{-1}$): $E_{1/2}(\text{ox}) = +0.73 \text{ V vs. Ag/AgCl}$.

(iii) **Synthesis of $\text{Re}_2(\text{HnicO})_2\text{Cl}_2(\mu\text{-dppm})_2$ (**4**).** A mixture of **1** (100 mg, 0.075 mmol) and 2-hydroxynicotinic acid (53 mg,

0.381 mmol) was refluxed in ethanol (30 mL) for 3 days. Work-up as in section B(i) gave **4** as an orange solid. Yield of **4**: 93 mg (83%). This product was recrystallized from dichloromethane–hexanes. Calc. for $C_{62}H_{52}Cl_2N_2O_6P_4Re_2$: C, 50.04; H, 3.52; N, 1.88. Found: C, 49.11; H, 3.63; N, 1.66%. 1H NMR spectrum (δ in $CDCl_3$): 12.73 (s, 2H, CO₂H of HnicO), 8.8–6.4 (m, 46H, HnicO and Ph of dppm), 5.02 (m, 4H, CH₂ of dppm). $^{31}P\{^1H\}$ NMR spectrum (δ in $CDCl_3$): –12.58, –13.20, –14.43 and –15.05 (components of an AA'BB' pattern). Cyclic voltammogram (0.1 M $Bu_4^+NPF_6^-CH_2Cl_2$ at 25 °C, Pt-bead electrode, $v = 200$ mV s^{–1}): $E_{1/2}(ox)(1) = +0.53$ V and $E_{1/2}(ox)(2) = +1.30$ V vs. Ag/AgCl.

(iv) Synthesis of $Re_2(picO)_2(\mu-dppm)_2$ (5**).** A mixture of **1** (100 mg, 0.075 mmol) and 6-hydroxypicolinic acid (26 mg, 0.187 mmol) in 30 mL of ethanol was refluxed for 2 days, then cooled to r.t., and filtered. The dark red filtrate was evaporated to dryness under a reduced pressure and the residue extracted into 10 mL of dichloromethane. The dichloromethane extracted was allowed to evaporate under a reduced pressure to afford red microcrystals. Yield of **5**: 96 mg (90%). This product was recrystallized from dichloromethane–hexanes. Calc. for $C_{62}H_{52}N_2O_7P_4Re_2$ (i.e. **5**·H₂O): C, 51.95; H, 3.66; N, 1.95. Found: C, 51.51; H, 3.70; N, 1.84%. 1H NMR spectrum (δ in $CDCl_3$): 8.0–6.7 (m, br, 46H, picO and Ph of dppm), 6.08 and 5.28 (m, 4H, CH₂ of dppm). $^{31}P\{^1H\}$ NMR spectrum (δ in $CDCl_3$): +19.8 and +1.2 (m, br). Cyclic voltammogram (0.1 M $Bu_4^+NPF_6^-CH_2Cl_2$ at 25 °C, Pt-bead electrode, $v = 200$ mV s^{–1}): $E_{1/2}(ox)(1) = +0.15$ V and $E_{1/2}(ox)(2) = +1.13$ V vs. Ag/AgCl.

Compound **5** is also obtained when the complex $Re_2Cl_4(\mu-dppm)_2$ is reacted with 6-hydroxypicolinic acid in refluxing ethanol with use of these same reaction conditions and work-up.⁸ This sample was recrystallized from dichloromethane–hexanes. Yield: 32%. The identities of single crystals selected from samples of both **5** and **5**·H₂O were established by X-ray crystallography and these were shown to be essentially identical with the exception of the presence of a water molecule in the latter crystal. Only structural data for **5** are reported and discussed herein. Full crystallographic data for **5**·H₂O are available in the CIF file.

(v) Reaction of **1 with 2-hydroxypyridine.** The reaction of these reagents in refluxing ethanol for 3 days left an orange solid that was shown by $^{31}P\{^1H\}$ NMR spectroscopy and cyclic voltammetry to be unreacted **1**. Based upon the amount recovered (>90%), 2-hydroxypyridine does not appear to react under these conditions.

C X-Ray crystallography

Single crystals of composition $Re_2(dipic)Cl_2(\mu-dppm)_2 \cdot 2CH_2Cl_2$ (**3**·2CH₂Cl₂), $Re_2(HnicO)_2Cl_2(\mu-dppm)_2$ (**4**), $Re_2(picO)_2(\mu-dppm)_2$ (**5**) and $Re_2(picO)_2(\mu-dppm)_2 \cdot H_2O$ (**5**·H₂O) were obtained by slow diffusion of hexanes into dichloromethane solutions of the complexes **3–5** under a dinitrogen atmosphere.

The crystals were mounted on glass fibers in random orientations. The data collections were carried out at 150(±1) K with graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å) on a Nonius KappaCCD diffractometer. Lorentz and polarization corrections were applied to all data sets. The key crystallographic data for **3**·2CH₂Cl₂, **4** and **5** are given in Table 1.

The structures were solved using the structure solution program PATTY in DIRDIF-99.⁹ The remaining atoms were located in succeeding difference Fourier syntheses. Hydrogen atoms were placed in calculated positions according to idealized geometries with $U(H) = 1.3U_{eq}(C)$. They were included in

the refinement but constrained to ride on the atom to which they are bonded. An empirical absorption correction using SCALEPACK¹⁰ was applied in all cases. The final refinements were performed by the use of the program SHELXL-97.¹¹ All non-hydrogen atoms were refined with anisotropic thermal parameters unless indicated otherwise. Crystallographic drawings were done using the program ORTEP.¹²

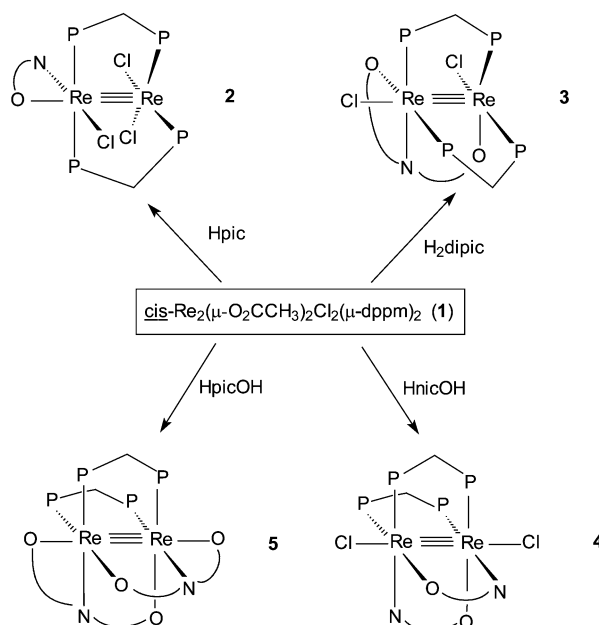
The structure solutions and refinements of all three compounds proceeded without significant problem. The crystal of **3** contained well behaved dichloromethane solvent, the non-hydrogen atoms of which were refined with anisotropic thermal parameters. During the structure refinement of **5**, a small amount of residual electron density, probably associated with disordered dichloromethane solvent, was adjusted using the SQUEEZE option in PLATON.¹³ The largest peaks remaining in the final difference maps of **3**·2CH₂Cl₂, **4** and **5** were 1.79, 1.82 and 1.26 e Å^{–3}, respectively.

CCDC reference numbers 212135–212138.

See <http://www.rsc.org/suppdata/dt/b3/b306331n/> for crystallographic data in CIF or other electronic format.

Results and discussion

The reactions of *cis*- $Re_2(\mu-O_2CCH_3)_2Cl_2(\mu-dppm)_2$ (**1**) with picolinic acid (Hpic), dipicolinic acid (H₂dipic), 2-hydroxynicotinic acid (HnicOH) and 6-hydroxypicolinic acid (HpicOH) give four different types of products as shown in Scheme 1. However, in all cases, the two *cis* acetato groups of **1** are displaced in refluxing ethanol. Complex **2**, which is formed in <50% yield from picolinic acid, has been prepared previously⁷ by the reaction of $Re_2Cl_4(\mu-dppm)_2$ with Hpic or [PPN]pic (where PPN = [(Ph₃P)₂N]⁺). Its formation from **1** attests to its stability, since the reaction mechanism must involve the sacrifice of a portion of the starting material **1** in order to provide the extra chloride ligand that is incorporated into the product. The structure of **2**, which was established by X-ray crystallography, shows that there has been a switch from a *cis,cis* coordination of the μ -dppm ligands in **1** to a *trans,cis* arrangement in **2** (see Scheme 1). This compound is not discussed further (see ref. 7 for additional details). In the case of **3–5**, a *cis,cis* coordination of the dppm ligands is retained as confirmed by X-ray crystal structure determinations of all three complexes (Figs. 1–3).



Scheme 1 Products formed by the reactions of *cis*- $Re_2(\mu-O_2CCH_3)_2Cl_2(\mu-dppm)_2$ (**1**) with pyridine carboxylic acids in refluxing ethanol.

Table 1 Crystallographic data for the dirhenium(II) complexes $\text{Re}_2(\text{dipic})\text{Cl}_2(\mu\text{-dppm})_2 \cdot 2\text{CH}_2\text{Cl}_2$ ($3 \cdot 2\text{CH}_2\text{Cl}_2$), $\text{Re}_2(\text{HnicO})_2\text{Cl}_2(\mu\text{-dppm})_2$ (**4**), and $\text{Re}_2(\text{picO})_2(\mu\text{-dppm})_2$ (**5**)

	$3 \cdot 2\text{CH}_2\text{Cl}_2$	4	5
Formula	$\text{C}_{59}\text{H}_{51}\text{Cl}_6\text{NO}_4\text{P}_4\text{Re}_2$	$\text{C}_{62}\text{H}_{52}\text{Cl}_2\text{N}_2\text{O}_6\text{P}_4\text{Re}_2$	$\text{C}_{62}\text{H}_{50}\text{N}_2\text{O}_6\text{P}_4\text{Re}_2$
Formula weight	1547.08	1488.32	1415.40
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$ (no. 14)	$P2_1/c$ (no. 14)	$P2_1/n$ (no. 14)
$a/\text{\AA}$	19.4967(4)	13.0405(3)	12.1326(3)
$b/\text{\AA}$	15.3146(3)	22.9844(5)	21.4366(5)
$c/\text{\AA}$	19.7094(4)	19.7779(3)	23.4676(6)
$\beta/^\circ$	93.0862(8)	107.5243(15)	104.9374(11)
Z	4	4	4
$V/\text{\AA}^3$	5876.4(2)	5652.9(2)	5897.2(3)
$D/\text{g cm}^{-3}$	1.749	1.749	1.594
$\mu(\text{Mo-K}\alpha)/\text{mm}^{-1}$	4.601	4.597	4.313
Reflections:			
collected	45465	43144	24531
independent	13990	13025	13040
observed [$I > 2\sigma(I)$]	10360	6795	8688
No. of variables	685	703	685
R_{int}	0.072	0.090	0.047
$R(F_o)^a$	0.044	0.045	0.041
$R_w(F_o^2)^b$	0.104	0.117	0.076
GOF	0.982	1.031	0.913

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

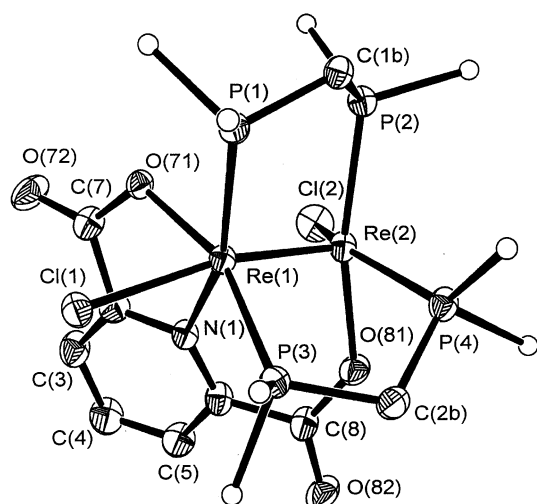


Fig. 1 ORTEP¹² representation of the structure of the dirhenium(II) complex $\text{Re}_2(\text{dipic})\text{Cl}_2(\mu\text{-dppm})_2$ as present in $3 \cdot 2\text{CH}_2\text{Cl}_2$. Thermal ellipsoids are drawn at the 50% probability level. The phenyl carbon atoms of the dppm ligands have been omitted for clarity except for the carbon atoms that are bound to phosphorus (these are shown as circles of arbitrary radius). Selected bond distances (Å) and bond angles ($^\circ$): Re(1)–Re(2) 2.2583(3), Re(1)–Cl(1) 2.5753(13), Re(1)–N(1) 2.185(4), Re(1)–O(71) 2.061(4), Re(1)–P(1) 2.4596(13), Re(1)–P(3) 2.4430(14), Re(2)–Cl(2) 2.3672(14), Re(2)–O(81) 2.107(4), Re(2)–P(2) 2.3642(14), Re(2)–P(4) 2.3630(14), C(7)–O(71) 1.307(6), C(7)–O(72) 1.211(6), C(8)–O(81) 1.281(7), C(8)–O(82) 1.228(7); Re(2)–Re(1)–Cl(1) 168.15(3), N(1)–Re(1)–P(1) 159.40(12), O(71)–Re(1)–P(3) 158.51(11), N(1)–Re(1)–O(71) 75.91(15), Cl(2)–Re(2)–P(4) 145.42(5), O(81)–Re(2)–P(2) 166.10(11). The torsion angles P(1)–Re(1)–Re(2)–P(2), O(71)–Re(1)–Re(2)–Cl(2), N(1)–Re(1)–Re(2)–O(81) and P(3)–Re(1)–Re(2)–P(4) are 21.29(5), 30.69(10), 43.47(14) and 24.12(5) $^\circ$, respectively.

The structure of **3** (Fig. 1) shows an unsymmetrical $\eta^3\text{-O,N,O'}$ coordination of the dipic ligand which bridges the two Re atoms. This stable compound is the third isomeric form of $\text{Re}_2(\text{dipic})\text{Cl}_2(\mu\text{-dppm})_2$; two other isomers (**6** and **7**) have previously been prepared by the reaction of $\text{Re}_2\text{Cl}_4(\mu\text{-dppm})_2$ with $[\text{N}(\text{PPh}_3)_2]\text{dipic}$ in ethanol.⁷ At room temperature the kinetic isomer **6** is isolated, but it converts quantitatively to the thermodynamically stable isomer **7** when refluxed in ethanol. We have found no conditions that lead to the interconversion of **3** and **7**. The Re–Re triple bond distance in **3** is 2.2583(3) Å, a value that is very similar to the distances in **6** (2.2750(10) Å)⁷

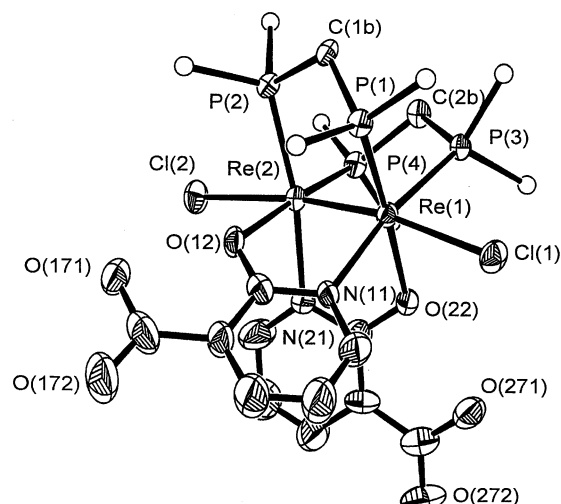


Fig. 2 ORTEP¹² representation of the structure of the dirhenium(II) complex $\text{Re}_2(\text{HnicO})_2\text{Cl}_2(\mu\text{-dppm})_2$ (**4**). The thermal ellipsoids are drawn at the 50% probability level. The phenyl carbon atoms of the dppm ligands have been omitted for clarity except for the carbon atoms that are bound to phosphorus (these are shown as circles of arbitrary radius). Selected bond distances (Å) and bond angles ($^\circ$): Re(1)–Re(2) 2.3035(6), Re(1)–Cl(1) 2.562(3), Re(1)–N(11) 2.231(9), Re(1)–O(22) 2.154(8), Re(1)–P(1) 2.413(3), Re(1)–P(3) 2.411(3), Re(2)–Cl(2) 2.539(3), Re(2)–N(21) 2.214(9), Re(2)–O(12) 2.184(8), Re(2)–P(2) 2.409(3), Re(2)–P(4) 2.418(3), C(12)–O(12) 1.296(15), C(22)–O(22) 1.299(15), C(17)–O(171) 1.317(19), C(17)–O(172) 1.260(18), C(27)–O(217) 1.351(18), C(27)–O(272) 1.209(15); Re(2)–Re(1)–Cl(1) 170.29(17), Re(1)–Re(2)–Cl(2) 171.67(8), N(11)–Re(1)–P(3) 170.9(3), O(22)–Re(1)–P(1) 170.6(2), N(21)–Re(2)–P(2) 170.1(3), O(12)–Re(2)–P(4) 173.4(2). The torsion angles P(1)–Re(1)–Re(2)–P(2), N(11)–Re(1)–Re(2)–O(12), O(22)–Re(1)–Re(2)–N(21) and P(3)–Re(1)–Re(2)–P(4) are 21.32(10), 20.92(35), 19.63(35) and 20.40(10) $^\circ$, respectively.

and **7** (2.2512(3) Å).⁷ All three complexes possess staggered rotational geometries, the χ_{av} values for the usual torsion angles¹⁴ being 29.9, 45.8 and 42.8 $^\circ$, respectively. Since there is no electronic barrier to rotation in triply bonded $[\text{Re}_2]^{4+}$ complexes,¹⁴ these variations in χ_{av} are to be expected since they largely reflect the minimization of intramolecular non-bonded repulsions, and the various conformation demands of the different five- and six-membered rings that are contained within these complexes. The small differences in Re–Re distances are most likely a result of the differences in the axial ligation that

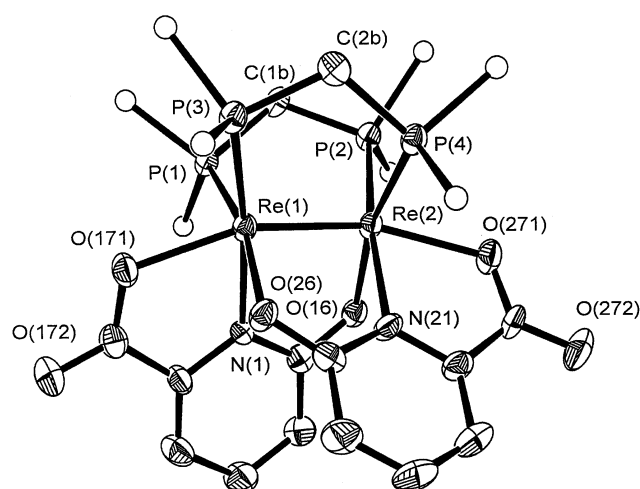
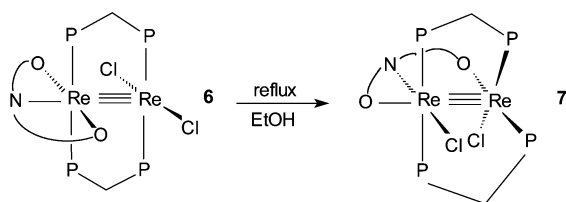


Fig. 3 ORTEP¹² representation of the structure of the dirhenium(II) complex $\text{Re}_2(\text{picO})_2(\mu\text{-dppm})_2$ (**5**). The thermal ellipsoids are drawn at the 50% probability level. The phenyl carbon atoms of the dppm ligands have been omitted for clarity except for the carbon atoms that are bound to phosphorus (these are shown as circles of arbitrary radius). Selected bond distances (Å) and bond angles (°): Re(1)–Re(2) 2.3194(3), Re(1)–O(171) 2.175(3), Re(1)–N(1) 2.154(4), Re(1)–O(26) 2.096(3), Re(1)–P(1) 2.3873(13), Re(1)–P(3) 2.4091(15), Re(2)–O(271) 2.171(3), Re(2)–N(21) 2.157(4), Re(2)–O(16) 2.113(4), Re(2)–P(2) 2.3998(13), Re(2)–P(4) 2.3820(15), C(17)–O(171) 1.287(6), C(17)–O(172) 1.247(6), C(27)–O(271) 1.284(6), C(27)–O(272) 1.238(6); Re(2)–Re(1)–O(171) 157.82(11), Re(1)–Re(2)–O(271) 158.37(10), N(1)–Re(1)–P(3) 167.41(11), O(26)–Re(1)–P(1) 165.59(11), N(21)–Re(2)–P(2) 167.87(12), O(16)–Re(2)–P(4) 165.84(10), O(171)–Re(1)–N(1) 74.04(14), O(271)–Re(2)–N(21) 73.74(14). The torsion angles N(1)–Re(1)–Re(2)–O(16), O(26)–Re(1)–Re(2)–N(21), P(1)–Re(1)–Re(2)–P(2) and P(3)–Re(1)–Re(2)–P(4) are 10.79(14), 9.39(16), 14.08(5) and 13.61(5)°, respectively.

occurs between **3**, **6** and **7**. What is very unusual is that **3**, **6** and **7** contain the three possible types of coordination behavior for a pair of $\mu\text{-dppm}$ ligands in a dimetal complex, *i.e.* *cis,cis*-, *trans,trans*- and *trans,cis*-, respectively.



All three isomeric dipic complexes possess distinctly different $^3\text{P}\{^1\text{H}\}$ NMR spectra as a consequence of differences in P–P coupling associated with the *cis,cis*-, *trans,trans*-, and *trans,cis* coordination of the $\mu\text{-dppm}$ ligands. In the case of **3**, the four P resonances that are associated with the four chemically and magnetically inequivalent P atoms have the appearance of doublets (see Experimental section); the inner pair at $\delta +1.78$ and -4.43 have $^2J_{\text{P-P}} \approx 77$ Hz while those at $\delta +5.48$ and -9.43 have $^2J_{\text{P-P}} \approx 85$ Hz. The cyclic voltammograms of the three isomers (recorded in 0.1 M $\text{Bu}_4\text{NPF}_6\text{-CH}_2\text{Cl}_2$) each show a quasi reversible one-electron process that is associated with the $[\text{Re}_2]^{5+}/[\text{Re}_2]^{4+}$ couple and has an $E_{1/2}$ value of +0.73, +0.32 and +0.69 V vs. Ag/AgCl for **3**, **6** and **7**, respectively. This surprisingly large variation must reflect differences in energy of the HOMO (primarily the metal δ^* orbital), which is influenced by the differences in the ligand sets and coordination numbers at the two metal centers in each of the complexes. However, it is not obvious that **3** should be the hardest to oxidize.

Complexes **4** and **5** both contain a pair of *cis* 2-pyridonate ligands (Figs. 2 and 3) that bridge in a head-to-tail fashion. In compound **4**, the carboxylic acid group in the 3-position

of each HnicO ligand is not involved in coordination to the dirhenium(II) unit. Since the distances between the oxygen atoms O(171) and O(271) of the two $-\text{CO}_2\text{H}$ groups and the corresponding atoms O(12) and O(22) of the 2-pyridonate moieties are quite short (2.540 and 2.586 Å, respectively), this implies that intramolecular $\text{O-H} \cdots \text{O}$ hydrogen bonds are participating in the formation of planar six-membered rings $\text{O-H} \cdots \text{O-C-C-C}$ (see Fig. 2). In the ^1H NMR spectrum of **4** (recorded in CDCl_3) the ‘free’ acid groups appear as a singlet at $\delta +12.73$. The structure of **5** resembles that of **4** except that the two terminal Re–Cl bonds are replaced by Re–O bonds formed by the carboxylic acid groups of the bridging tridentate 6-hydroxypicolinic acid ligand. The Re–Re distances in **4** and **5** are very similar (2.3035(6) and 2.3194(3) Å, respectively) but are longer than the distance in **3** (2.2583(3) Å). This reflects the presence of two axial Re–Cl or Re–O bonds in **4** and **5** in contrast to **3** which has only one Re–Cl axial bond. While **4** and **5** both have staggered rotation geometries, the value of χ_{av} for **4** (20.6°) is close to twice that in **5** (12.0°), reflecting the much more rigid nature of the tridentate $\mu\text{-picO}$ ligands compared to bidentate $\mu\text{-HnicO}$. Compounds **4** and **5** are the first examples of complexes of dirhenium(II) that contain 2-pyridonate ligands, although a variety of dirhenium(III) complexes are known.^{15–17}

The cyclic voltammograms of **4** and **5** (recorded in 0.1 M $\text{Bu}_4\text{NPF}_6\text{-CH}_2\text{Cl}_2$) each show two one-electron processes that can be assigned to the $[\text{Re}_2]^{6+}/[\text{Re}_2]^{5+}$ and $[\text{Re}_2]^{5+}/[\text{Re}_2]^{4+}$ couples. These processes are more accessible in **5** than **4** (*e.g.* a $E_{1/2}(\text{ox})$ value of +0.15 V in **5** vs. +0.53 V in **4**) but the unsymmetrical nature of these complexes and delocalization within the $\mu\text{-HnicO}$ and $\mu\text{-picO}$ ligands makes it difficult to attribute these shifts just to variations in the nature of the axial interactions (*i.e.* Re–Cl in **4** vs. Re–OC(O)– in **5**). The coordination of the carboxylate groups in **5** is quite strong as shown by the Re–O (carboxylate) distances of 2.175(3) and 2.171(3) Å. Also, the Re–N and Re–O distances associated with the bridging 2-pyridonate units in this complex are shorter than the comparable distances in **4** by between 0.04 and 0.09 Å (see Figs. 2 and 3).

Concluding remarks

The isolation and structural characterization of **3** is noteworthy because it provides the third structural isomer of $\text{Re}_2(\text{dipic})\text{-Cl}_2(\mu\text{-dppm})_2$. The kinetic isomer **6** has been shown to convert quantitatively to the thermodynamically stable form **7**. Like isomer **7**, compound **3** contains a similar but not identical coordination of the tridentate dipic ligand such that it chelates to one Re center and uses its second carboxylate group to bridge to the other Re atom. The flexibility of $[\text{dipic}]^{2-}$ enables it to bind to the $[\text{Re}_2(\mu\text{-dppm})_2]^{4+}$ core such that it can allow for either *cis,cis*-, *trans,trans*- or *trans,cis*- arrangements of the adjacent ReP_2 units. Also of note is our isolation of the first dirhenium(II) complexes (**4** and **5**) that contain 2-pyridonate bridging ligands. In one of these, compound **4**, a free carboxylic acid group is present on each of the monoanionic HnicO ligands, while in **5** the dianionic picO ligands are coordinated in a tridentate fashion. Interestingly, we find that **1** does not react with 2-hydroxypyridine (Hhp) with use of the same reaction conditions that gave **4** and **5**. Apparently, this ligand is not able to protonate the $\mu\text{-acetate}$ ligands in refluxing ethanol and facilitate their loss as acetic acid in order to form $\text{Re}_2(\mu\text{-hp})_2\text{-Cl}_2(\mu\text{-dppm})_2$. In a previous study,¹⁸ we found that 6-(diphenylphosphine)-2-pyridone (pyphosH), which is a phosphine substituted 2-hydroxypyridine ligand, reacts with the dirhenium(III) complexes $(\text{Bu}_4\text{N})_2\text{Re}_2\text{Cl}_8$, $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_4\text{Cl}_2$ or *cis*- $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_2(\text{H}_2\text{O})_2$ to afford the reduced dirhenium(II) complex $\text{Re}_2\text{Cl}_2(\mu\text{-pyphos})_2(\text{pyphosH})$. However, a structural study showed that there is at best only weak $\text{Re} \cdots \text{O}$ bonding (the

Re–O distances are in the range 2.42–2.98 Å in this molecule).¹⁸ Therefore, **4** and **5** constitute the first bona-fide examples of 2-pyridonate *N,O* bridged dirhenium(II) complexes. We should now be in a position to develop this chemistry further by synthesizing a range of compounds with substituents in the 3-, 4- and 5- positions of the rings (as we have done in the case of **4**) which can bind other dimetal or monometal species to form supramolecular assemblies. This possibility is attractive in the case of Re_2^{4+} because of the accessibility of the paramagnetic Re_2^{5+} core.²

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