

Reactions of the Dirhenium(II) Complex $\text{Re}_2\text{Cl}_4(\mu\text{-dppm})_2$ with Pyridinecarboxylic Acids. Examples of Bidentate O,O versus N,O Coordination and Tridentate O,N,O Coordination and Structural Isomers That Contain the Pyridine-2,6-dicarboxylate Ligand

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Received May 8, 2003

Pyridine-2-carboxylic acid, pyridine-2,3-dicarboxylic acid, and pyridine-2,4-dicarboxylic acid or their $[(\text{Ph}_3\text{P})_2\text{N}]^+$ salts react with the triply bonded dirhenium(II) complex $\text{Re}_2\text{Cl}_4(\mu\text{-dppm})_2$ ($\text{dppm} = \text{Ph}_2\text{PCH}_2\text{PPh}_2$) in refluxing ethanol to afford unsymmetrical substitution products of the type $\text{Re}_2(\eta^2\text{-}N,O)\text{Cl}_3(\mu\text{-dppm})_2$, where N,O represents a chelating pyridine-2-carboxylate ligand ($N,O = \text{O}_2\text{C-2-C}_5\text{H}_4\text{N}$ (**1**), $\text{O}_2\text{C-2-C}_5\text{H}_3\text{N(-3-CO}_2\text{Et)}$ (**3**), or $\text{O}_2\text{C-2-C}_5\text{H}_3\text{N(-4-CO}_2\text{H)}$ (**4**)). The carboxylate groups in the 3- and 4- positions are not bound to the metal centers; in the case of **3** this group undergoes esterification in the refluxing ethanol solvent. Structure determinations have shown that **1**, **3**, and **4** possess similar structures in which there is an axial Re-O (carboxylate) bond (collinear with the $\text{Re}\equiv\text{Re}$ bond) and the $\mu\text{-dppm}$ ligands are bound in a trans,cis fashion to the two Re atoms which have the ligand atom arrangement $[\text{P}_2\text{NOCiReReCl}_2\text{P}_2]$. The tridentate dianionic pyridine-2,6-dicarboxylate ligand (dipic) reacts with $\text{Re}_2\text{Cl}_4(\mu\text{-dppm})_2$ in ethanol at room temperature to give a compound $\text{Re}_2(\text{dipic})\text{Cl}_2(\mu\text{-dppm})_2$ (**6**) in which the dipic ligand is bound in a symmetrical $\eta^3\text{-(}O,N,O\text{)}$ fashion to one Re atom, with the N atom in an axial position (collinear with the $\text{Re}\equiv\text{Re}$ bond) and with preservation of the same trans,trans coordination of the $\mu\text{-dppm}$ ligands that is present in $\text{Re}_2\text{Cl}_4(\mu\text{-dppm})_2$. Under reflux conditions, this kinetic product isomerizes to the thermodynamically favored isomer **5** with an unsymmetrical structure in which the dipic ligand chelates to one Re atom (as in **1**, **3**, and **4**) and uses its other carboxylate group to bridge to the second Re atom. The isomerization of **6** to **5**, which also results in a change in the coordination of the pair of $\mu\text{-dppm}$ ligand to trans,cis, is believed to occur by a partial “merry-go-round” process, a mechanism that probably explains the structures of the thermodynamic products **1**, **3**, and **4**. The reaction of $\text{Re}_2\text{Cl}_4(\mu\text{-dppm})_2$ with pyridine-3-carboxylate gives the trans isomer of $\text{Re}_2(\mu\text{-}\eta^2\text{-O}_2\text{C-3-C}_5\text{H}_4\text{N})_2\text{Cl}_2(\mu\text{-dppm})_2$ (**2**) in which a pair of carboxylate bridges are present and the pyridine N atom is not coordinated. Single-crystal X-ray structural details are reported for **1–6**.

Introduction

Studies that involve the incorporation of multiply bonded dimetal units into supramolecular assemblies¹ have recently included the use of the 4-pyridinecarboxylate (isonicotinate) ligand to prepare a hybrid molecular square that is composed of alternating triply bonded dirhenium(II) and mononuclear

platinum(II) units at the corners of the square.² The key to this chemistry was the isolation of the synthon $\text{cis-Re}_2(\mu\text{-O}_2\text{C-4-C}_5\text{H}_4\text{N})_2\text{Cl}_2(\mu\text{-dppm})_2$ ($\text{dppm} = \text{Ph}_2\text{PCH}_2\text{PPh}_2$) in which the pyridyl nitrogen atoms are not coordinated to the dirhenium unit.² Although a couple of other dirhenium complexes that contain the isonicotinate ligand are known, specifically the trans isomer of $\text{Re}_2(\mu\text{-O}_2\text{C-4-C}_5\text{H}_4\text{N})_2\text{Cl}_2(\mu\text{-dppm})_2^3$ and the paramagnetic dirhenium(III,II) complex $\text{Re}_2\text{-}$

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$(\mu\text{-O}_2\text{C-4-C}_5\text{H}_4\text{N})\text{Cl}_4(\mu\text{-dppm})_2$,⁴ both of which are potentially capable of participating in the formation of mixed-metal assemblies, no other examples of pyridinecarboxylates of dirhenium are known. Since such compounds might exhibit interesting structural chemistry, and also be incorporated into homo- and heteronuclear assemblies in which diamagnetic and paramagnetic dirhenium cores are present, we have set out to examine the reactions of the triply bonded dirhenium(II) synthon $\text{Re}_2\text{Cl}_4(\mu\text{-dppm})_2$ ⁵⁻⁷ with a selection of pyridinemono- and dicarboxylate ligands. We have found that the substitution of one or two chloride ligands occurs and the pyridine carboxylate ligands are involved in a variety of chelating and/or bridging coordination modes to the dirhenium core. In addition, a pair of unusual structural isomers that contain the pyridine-2,6-dicarboxylate ligand have been isolated and characterized. The synthetic procedures and structures of the resulting complexes are reported.

Experimental Section

A. Starting Materials, General Procedures, and Physical Measurements. The complexes $\text{Re}_2\text{Cl}_4(\mu\text{-dppm})_2$ (dppm = $\text{Ph}_2\text{PCH}_2\text{PPh}_2$) and *cis*- $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_2(\mu\text{-dppm})_2$ were prepared by the usual methods.⁷ Samples of the pyridinecarboxylic acids and bis(triphenylphosphine)iminium chloride ([PPN]Cl) were purchased from Aldrich Chemical Co. The compound [PPN]Cl was used to prepare the [PPN]⁺ salts of acetic acid, pyridine-2-carboxylic acid, pyridine-3-carboxylic acid, and pyridine-2,6-dicarboxylic acid by use of the procedure we have described previously.³ In the case of [PPN]₂dipic, X-ray crystallography was used to confirm the identity of this compound (vide infra). 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.

Infrared spectra, NMR spectra, and cyclic voltammetric measurements were carried out as described previously.⁸ Elemental microanalyses were done by Dr. H. D. Lee of the Purdue University Microanalytical Laboratory.

B. Synthesis of Pyridinecarboxylate Complexes of Dirhenium(II). (i) $\text{Re}_2[(\eta^2(N,O)\text{-O}_2\text{C-2-C}_5\text{H}_4\text{N})]\text{Cl}_3(\mu\text{-dppm})_2$ (**1**). A mixture of $\text{Re}_2\text{Cl}_4(\mu\text{-dppm})_2$ (100 mg, 0.078 mmol) and $[(\text{Ph}_3\text{P})_2\text{N}](\text{O}_2\text{C-2-C}_5\text{H}_4\text{N})$ (103 mg, 0.156 mmol) in ethanol (30 mL) was refluxed for 3 h. A green solid separated, and the mixture was then cooled and filtered. The solid residue was washed with ethanol (3 × 5 mL) and diethyl ether (3 × 5 mL) and dried in vacuo; yield 65 mg (61%). Recrystallization was carried out by the slow diffusion of hexane into a dichloromethane solution of **1** under $\text{N}_2(\text{g})$. Anal. Calcd for $\text{C}_{57}\text{H}_{50}\text{Cl}_5\text{NO}_2\text{P}_4\text{Re}_2$ (i.e., **1**· CH_2Cl_2): C, 47.07; H, 3.46; N, 0.96. Found: C, 47.17; H, 3.39; N, 0.97.

This same compound can be obtained by refluxing a mixture of $\text{Re}_2\text{Cl}_4(\mu\text{-dppm})_2$ (100 mg, 0.078 mmol) and pyridine-2-carboxylic acid (48 mg, 0.39 mmol) in ethanol (30 mL) for 1 day; yield 79

mg (74%). Recrystallization from dichloromethane/hexane gave single crystals of **1** without the presence of lattice solvent (as established by X-ray crystallography).

(ii) *trans*- $\text{Re}_2[\mu\text{-}\eta^2(O,O)\text{-O}_2\text{C-3-C}_5\text{H}_4\text{N}]\text{Cl}_2(\mu\text{-dppm})_2$ (**2**). The reaction between $\text{Re}_2\text{Cl}_4(\mu\text{-dppm})_2$ (100 mg, 0.078 mmol) and $[(\text{Ph}_3\text{P})_2\text{N}](\text{O}_2\text{C-3-C}_5\text{H}_4\text{N})$ (155 mg, 0.235 mmol) in refluxing ethanol (30 mL) for 3 h gave this orange product with a workup procedure similar to that used in section B(i); yield 82 mg (72%). Recrystallization was carried out from hexane/dichloromethane. Anal. Calcd for $\text{C}_{62}\text{H}_{52}\text{Cl}_2\text{N}_2\text{O}_4\text{P}_4\text{Re}_2$: C, 51.13; H, 3.60; N, 1.92. Found: C, 50.73; H, 3.73; N, 1.90.

(iii) $\text{Re}_2[\eta^2(N,O)\text{-O}_2\text{C-2-C}_5\text{H}_3\text{N(-3-COOEt)}]\text{Cl}_3(\mu\text{-dppm})_2$ (**3**). A mixture of $\text{Re}_2\text{Cl}_4(\mu\text{-dppm})_2$ (100 mg, 0.078 mmol) and pyridine-2,3-dicarboxylic acid (196 mg, 1.17 mmol) was refluxed in ethanol (30 mL) for 24 h and filtered, and the green solid was filtered off and worked-up as in section B(i); yield 81 mg (72%). Single crystals were obtained as for **1** and **2** by the slow diffusion of hexane into a dichloromethane solution of the complex under $\text{N}_2(\text{g})$. Anal. Calcd for $\text{C}_{60}\text{H}_{54}\text{Cl}_5\text{NO}_4\text{P}_4\text{Re}_2$ (i.e., **3**· CH_2Cl_2): C, 47.20; H, 3.57; N, 0.92. Found: C, 46.37; H, 3.37; N, 0.99.

(iv) $\text{Re}_2[\eta^2(N,O)\text{-O}_2\text{C-2-C}_5\text{H}_3\text{N(-4-CO}_2\text{H)}]\text{Cl}_3(\mu\text{-dppm})_2$ (**4**). The title complex was obtained by the reaction of $\text{Re}_2\text{Cl}_4(\mu\text{-dppm})_2$ (100 mg, 0.078 mmol) with pyridine-2,4-dicarboxylic acid (65 mg, 0.39 mmol) in ethanol (30 mL) for 24 h. Workup as in section B(i) afforded **4** as a purple solid; yield 85 mg (77%). Recrystallization from benzene/dichloromethane gave single crystals. Anal. Calcd for $\text{C}_{64}\text{H}_{56}\text{Cl}_5\text{NO}_4\text{P}_4\text{Re}_2$ (i.e., **4**· CH_2Cl_2 · C_6H_6): C, 48.75; H, 3.58; N, 0.89. Found: C, 49.57; H, 3.67; N, 1.01.

(v) $\text{Re}_2[\mu\text{-}\eta^3(O,N,O)\text{-}(\text{O}_2\text{C})_2\text{-2,6-C}_5\text{H}_3\text{N}]\text{Cl}_2(\mu\text{-dppm})_2$ (**5**) and $\text{Re}_2[\eta^3(O,N,O)\text{-}(\text{O}_2\text{C})_2\text{-2,6-C}_5\text{H}_3\text{N}]\text{Cl}_2(\mu\text{-dppm})_2$ (**6**). A mixture of $\text{Re}_2\text{Cl}_4(\mu\text{-dppm})_2$ (100 mg, 0.078 mmol) and $[(\text{Ph}_3\text{P})_2\text{N}]_2[(\text{O}_2\text{C})_2\text{-2,6-C}_5\text{H}_3\text{N}]$ (193 mg, 0.155 mmol) in ethanol (30 mL) was refluxed for 24 h. Workup as in section B(i) gave **5** as a green solid; yield 67 mg (62%). This product was recrystallized from hexane/dichloromethane to give X-ray-quality crystals. Anal. Calcd for $\text{C}_{57.50}\text{H}_{48}\text{Cl}_3\text{NO}_4\text{P}_4\text{Re}_2$ (i.e., **5**·0.5 CH_2Cl_2): C, 48.65; H, 3.41; N, 0.99. Found: C, 48.92; H, 3.58; N, 0.98.

This same product (**5**) was obtained, admixed with considerable quantities of unreacted $\text{Re}_2\text{Cl}_4(\mu\text{-dppm})_2$, when the dipicH_2 was used in place of [PPN]₂dipic; the reaction was carried out in refluxing ethanol for 3 days, but the conversion of $\text{Re}_2\text{Cl}_4(\mu\text{-dppm})_2$ to **5** by this method is quite low.

When dichloromethane (10 mL) was used as the solvent for the reaction between $\text{Re}_2\text{Cl}_4(\mu\text{-dppm})_2$ (100 mg, 0.078 mmol) and [PPN]₂dipicolinate (136 mg, 0.109 mmol), an orange colored solution was formed when this mixture was stirred for 10 min at room temperature. The mixture was filtered and evaporated to dryness, and ³¹P{¹H} NMR spectroscopy of the orange residue showed the presence of a single dirhenium product (**6**) (AA'BB' multiplets centered at $\delta = -4.3$ and $\delta = -6.4$ with the most intense inner components at $\delta = -4.70$ and $\delta = -5.9$, respectively) in addition to [PPN]⁺ salts (Cl^- and dipic^{2-}). We have not yet been able to purify **6** from this particular reaction mixture. However, we find that when $\text{Re}_2\text{Cl}_4(\mu\text{-dppm})_2$ (100 mg, 0.078 mmol) is reacted with [PPN]₂dipic (387 mg, 0.312 mmol) in 25 mL of ethanol at room temperature for a period of 6 h, then pure **6** is formed in high yield; yield 80 mg (75%). Anal. Calcd for $\text{C}_{57}\text{H}_{47}\text{Cl}_2\text{NO}_4\text{P}_4\text{Re}_2$: C, 49.71; H, 3.44; N, 1.02; Cl, 5.15. Found: C, 49.07; H, 3.80; N, 0.96; Cl, 4.89.

When the insoluble red orange product **6** is suspended in fresh ethanol and the mixture refluxed for 24 h, it is converted quantitatively into green **5** (as shown by ³¹P NMR spectroscopy).

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Table 1. Crystallographic Data for the Salt [PPN]₂dipic·H₂O and Dirhenium(II) Complexes That Contain Pyridinecarboxylate Ligands

	[PPN] ₂ dipic· H ₂ O	1	1 ·CH ₂ Cl ₂	2	3 ·CH ₂ Cl ₂	4 ·CH ₂ Cl ₂ · C ₆ H ₆	5 ·0.5CH ₂ Cl ₂	6 ·3C ₆ H ₆
empirical formula	C ₈₅ H ₇₇ N ₃ O ₇ P ₄	C ₅₆ H ₄₈ Cl ₃ NO ₂ · P ₄ Re ₂	C ₅₇ H ₅₀ Cl ₃ NO ₂ · P ₄ Re ₂	C ₆₂ H ₅₂ Cl ₂ N ₂ O ₄ · P ₄ Re ₂	C ₆₀ H ₅₄ Cl ₅ NO ₄ · P ₄ Re ₂	C ₆₄ H ₅₆ Cl ₅ NO ₄ · P ₄ Re ₂	C _{57.50} H ₄₈ Cl ₃ NO ₄ · P ₄ Re ₂	C ₇₅ H ₆₅ Cl ₂ NO ₄ · P ₄ Re ₂
fw	1376.47	1369.67	1454.60	1456.32	1526.66	1576.73	1419.68	1611.56
space group	<i>Pnma</i> (No. 62)	<i>P1</i> (No. 2)	<i>P1</i> (No. 2)	<i>P2₁/n</i> (No. 14)	<i>P1</i> (No. 2)	<i>P2₁/c</i> (No. 14)	<i>C2/c</i> (No. 15)	<i>P2₁/c</i> (No. 14)
<i>a</i> , Å	21.2803(5)	11.0355(2)	12.0594(3)	11.5457(2)	12.7682(2)	16.3898(3)	22.9639(7)	17.4698(9)
<i>b</i> , Å	23.5958(4)	12.1148(3)	14.3049(4)	18.2181(4)	14.8301(2)	13.6250(3)	27.4965(9)	20.5735(14)
<i>c</i> , Å	14.4185(3)	21.2878(6)	15.5468(5)	13.8189(3)	15.9949(2)	26.8924(7)	19.2811(5)	21.2477(13)
α, deg	90	73.7737(9)	86.2266(13)	90	72.9221(10)	90	90	90
β, deg	90	78.0557(9)	89.7152(13)	106.8691(11)	85.2756(10)	101.4007(8)	119.2191(18)	102.921(5)
γ, deg	90	67.0559(17)	83.5631(12)	90	77.3973(10)	90	90	90
<i>V</i> , Å ³	7239.9(3)	2500.95(10)	2659.26(13)	2781.60(19)	2824.85(7)	5886.9(2)	10625.5(5)	7443.4(8)
<i>Z</i>	4	2	2	2	2	4	8	4
ρ _{calcd} , g/cm ⁻³	1.263	1.819	1.816	1.739	1.795	1.779	1.775	1.438
μ, mm ⁻¹	0.157	5.233	5.026	4.667	4.738	4.550	4.933	3.495
<i>R</i> (<i>F</i> _o) ^a	0.046	0.046	0.050	0.035	0.030	0.048	0.040	0.064
<i>R</i> _w (<i>F</i> _o ²) ^b	0.117	0.087	0.104	0.075	0.062	0.112	0.079	0.141
GOF	1.088	0.910	0.985	0.952	1.004	1.195	0.946	0.922

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

(vi) **Reaction of 1 with [PPN]₂O₂CCH₃.** A mixture of **1** (50 mg, 0.037 mmol) and [(Ph₃P)₂N]₂O₂CCH₃ (44 mg, 0.074 mmol) was refluxed in ethanol (15 mL) for 24 h. The insoluble orange product *cis*-Re₂(μ-O₂CCH₃)₂Cl₂(μ-dppm)₂ was filtered off, washed with ethanol (3 × 5 mL) and diethyl ether (3 × 5 mL), and dried in vacuo; yield 39 mg (80%). The identity of this product was established by a comparison of its spectroscopic and electrochemical properties with the literature data.⁷

C. X-ray Crystallography. Single crystals of composition [(Ph₃P)₂N]₂[(O₂C)₂-2,6-C₅H₃N]·H₂O, hereafter referred to as [PPN]₂dipic·H₂O, were grown by the slow diffusion of diethyl ether into an acetone solution of the compound, while X-ray-quality crystals of complexes of composition **1**, **1**·CH₂Cl₂, **2**, **3**·CH₂Cl₂, **4**·CH₂Cl₂·C₆H₆, and **5**·0.5CH₂Cl₂ were obtained as described in the individual synthetic procedures in section B. Crystals of composition **6**·3C₆H₆ were obtained by recrystallization of **6** from dichloromethane/benzene. In all instances, data collections were carried out at 150(±1) K with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) on a Nonius KappaCCD diffractometer. Lorentz and polarization corrections were applied to the data sets. The key crystallographic data are given in Table 1.

The structure of [PPN]₂dipic·H₂O was solved by direct methods with the use of SIR 2002,⁹ while for the structures of **1**–**6** the structure solution program PATTY in DIRDIF99¹⁰ was used. The remaining atoms were located in succeeding difference Fourier syntheses. Hydrogen atoms were placed in calculated positions according to idealized geometries with C–H = 0.95 Å and *U*(H) = 1.3*U*_{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 SCALEPACK¹¹ was applied. The final refinements were performed by the use of the program SHELXL-97.¹² All non-hydrogen atoms were refined with anisotropic thermal parameters unless indicated otherwise. Crystallographic drawings were done using the program ORTEP.¹³

In most instances, the crystals were found to contain identifiable solvent molecules (see Table 1), the non-hydrogen atoms of which refined satisfactorily with anisotropic thermal parameters except in the case of **6**·3C₆H₆ where the three benzene molecules were refined isotropically. For compound **1**, structures were determined for crystals with and without lattice CH₂Cl₂. The salt of composition [PPN]₂dipic·H₂O contained a water molecule that was weakly H-bonded in a symmetrical fashion to the oxygen atoms O(21) and O(62) of the two carboxylate groups with distances O(1w)···O(21) and O(1w)···O(62) of 2.82 and 2.81 Å, respectively. The dirhenium unit in **2** was located about a center of inversion that was coincident with the center of the Re–Re bond. Consequently, atoms C(13) and N(13) of the pyridyl rings were modeled as a disorder involving half-atoms. In the structure of **3**·CH₂Cl₂, the dichloromethane molecule was disordered such that there were two half-carbon atoms (C(91A) and C(91B)) associated with two full chlorine atoms (Cl(91) and Cl(92)). The structure of **5**·0.5CH₂Cl₂ contained a well-behaved half molecule of dichloromethane that was located in the vicinity of a phenyl ring of one of the PPh₂ groups of a dppm ligand (atom P(3)). Each of the phenyl rings of this particular PPh₂ group were disordered such that there were two orientations for each ring. For one of the rings, two carbon atoms (C(311) and C(313)) were shared by the two orientations leaving the other four atoms of each ring as half-atoms (i.e. a total of eight atoms). The two orientations for the other disordered phenyl ring shared only one carbon atom (i.e., C(321) at full occupancy), leaving a total of 10 half-carbon atoms. All these carbon atoms refined satisfactorily with anisotropic thermal parameters. On the basis of chemically meaningful intermolecular distances involving atom Cl(92) of the half-CH₂Cl₂ solvent molecule, we conclude that it is associated with the half-phenyl ring C(311), C(31f), C(313), C(31h), C(31j), and C(31k), with nonbonding distances between these ring carbons and Cl(92) being in the range 3.71–4.92 Å. During the structure refinements of both [PPN]₂dipic·H₂O and **5**·0.5CH₂Cl₂, small amounts of badly disordered solvent molecules that could not be modeled satisfactorily were removed with use of the squeeze option in PLATON.¹⁴ The largest peaks remaining in the final difference maps of [PPN]₂dipic·H₂O and **1**–**6** (in the order given in Table 1) were 0.30, 1.74, 1.67, 1.51, 1.12, 1.17, 1.34, and 2.04 e/Å³, respectively.

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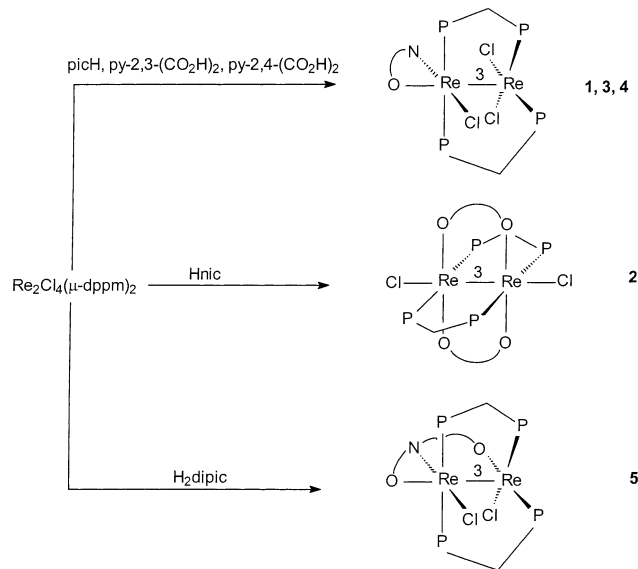
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Reactions of $\text{Re}_2\text{Cl}_4(\mu\text{-dppm})_2$

Scheme 1. Products Formed by the Reactions of $\text{Re}_2\text{Cl}_4(\mu\text{-dppm})_2$ with Pyridinecarboxylic Acids (or Their $[\text{PPN}]^+$ Salts) in Refluxing EtOH: $[\text{py-2-CO}_2]^-$ (**1**); $[\text{py-3-CO}_2]^-$ (**2**); $[\text{py-(3-CO}_2\text{Et)-2-CO}_2]^-$ (**3**); $[\text{py-(4-CO}_2\text{H)-2-CO}_2]^-$ (**4**); $[\text{py-2,6-(CO}_2)_2]^{2-}$ (**5**)



Results and Discussion

In all instances, the reactions of $\text{Re}_2\text{Cl}_4(\mu\text{-dppm})_2$ with pyridinecarboxylic acids, or their $[\text{PPN}]^+$ salts, afford the unsymmetrical dirhenium(II) complexes **1–5** that are shown in Scheme 1. These reactions were carried out under similar conditions, namely, reflux in ethanol for periods of 3–24 h; the longer reaction times were typically used with the dicarboxylic acids. Only one of these products is of a type that has been obtained previously, namely, the nicotinate complex $\text{trans-Re}_2(\mu\text{-O}_2\text{C-3-C}_5\text{H}_4\text{N})_2\text{Cl}_2(\mu\text{-dppm})_2$ (**2**), which is similar to the analogous isonicotinate complex $\text{trans-Re}_2(\mu\text{-O}_2\text{C-4-C}_5\text{H}_4\text{N})_2\text{Cl}_2(\mu\text{-dppm})_2$.³ The cis isomer of the isonicotinate has also been prepared and structurally characterized,² as have both the cis and trans isomers of the acetate complex $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_2(\mu\text{-dppm})_2$.^{3,7} While the trans isomer of the acetate (and propionate) complex readily isomerizes to the more thermodynamically stable cis isomer, the trans isomer of the nicotinate (reported here) and the isonicotinate³ are much more stable to isomerization and, therefore, could be useful synthons for preparing mixed-metal assemblies based upon a $\text{trans-Re}_2(\mu\text{-O}_2\text{CR})_2\text{Cl}_2(\mu\text{-dppm})_2$ template. Such studies are now underway.

Single-crystal X-ray structure determinations on **1–5** have confirmed the structures that are represented in Scheme 1. The ORTEP¹³ representations of the structures are shown in Figures 1–5; in all cases the important bond distances and angles are given in the captions to the figures. In addition, the structural identity of $[\text{PPN}]_2\text{dipic}$, which was used in the synthesis of compound **5**, was confirmed by X-ray crystallography. Crystallographic details for this crystal are given in Table 1, and full structural data are provided as Supporting Information.

The structure of the dirhenium units in the crystals of **1** and $\mathbf{1}\cdot\text{CH}_2\text{Cl}_2$ are essentially identical; the structure shown in Figure 1 is of the molecule $\text{Re}_2(\text{pic})\text{Cl}_3(\mu\text{-dppm})_2$ (pic = pyridine-2-carboxylate) that is present in $\mathbf{1}\cdot\text{CH}_2\text{Cl}_2$. The

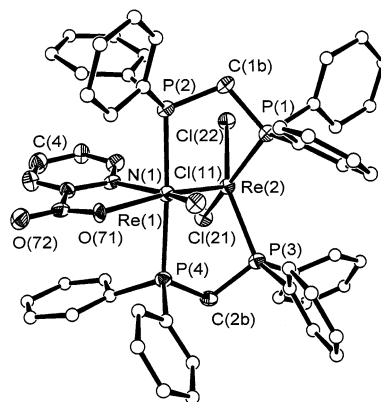


Figure 1. ORTEP¹³ representation of the structure of the complex $\text{Re}_2(\text{pic})\text{Cl}_3(\mu\text{-dppm})_2$ as present in $\mathbf{1}\cdot\text{CH}_2\text{Cl}_2$. Thermal ellipsoids are drawn at the 50% probability level except for the phenyl carbon atoms of the dppm ligands which are circles of arbitrary radius. Selected bond distances (Å) and angles (deg) are as follows: $\text{Re}(1)\text{--Re}(2)$ 2.2937(4), $\text{Re}(1)\text{--N}(1)$ 2.129(6), $\text{Re}(1)\text{--Cl}(11)$ 2.3863(19), $\text{Re}(1)\text{--O}(71)$ 2.234(4), $\text{Re}(1)\text{--P}(2)$ 2.4638(18), $\text{Re}(1)\text{--P}(4)$ 2.4816(18), $\text{Re}(2)\text{--P}(1)$ 2.3836(19), $\text{Re}(2)\text{--P}(3)$ 2.3890(19), $\text{Re}(2)\text{--Cl}(21)$ 2.4283(18), $\text{Re}(2)\text{--Cl}(22)$ 2.4003(18), $\text{O}(71)\text{--C}(7)$ 1.278(9), $\text{O}(72)\text{--C}(7)$ 1.217(9); $\text{N}(1)\text{--Re}(1)\text{--Cl}(11)$ 149.21(15), $\text{P}(2)\text{--Re}(1)\text{--P}(4)$ 172.23(6), $\text{P}(1)\text{--Re}(2)\text{--Cl}(21)$ 157.32(7), $\text{P}(3)\text{--Re}(2)\text{--Cl}(22)$ 145.99(6), $\text{P}(1)\text{--Re}(2)\text{--P}(3)$ 109.30(7), $\text{O}(71)\text{--Re}(1)\text{--Re}(2)$ 168.58(12).

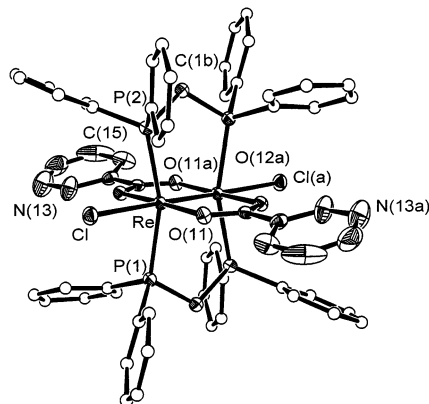


Figure 2. ORTEP¹³ representation of the structure of the dirhenium complex $\text{Re}_2(\mu\text{-nic})_2\text{Cl}_2(\mu\text{-dppm})_2$ (**2**). Thermal ellipsoids are drawn at the 50% probability level except for the phenyl carbon atoms of the dppm ligands which are circles of arbitrary radius. Selected bond distances (Å) and angles (deg) are as follows: $\text{Re}\text{--Re}(a)$ 2.2931(3), $\text{Re}\text{--O}(11)$ 2.134(3), $\text{Re}\text{--O}(12)$ 2.108(3), $\text{Re}\text{--P}(1)$ 2.4252(12), $\text{Re}\text{--P}(2)$ 2.4358(12), $\text{Re}\text{--Cl}$ 2.5993(11); $\text{O}(11)\text{--Re}\text{--O}(12)$ 177.93(11), $\text{P}(1)\text{--Re}\text{--P}(2)$ 161.20(4), $\text{Cl}\text{--Re}\text{--Re}(a)$ 178.83(3).

structure is noteworthy in that the trans sets of $\text{Re}\text{--P}$ bonds that are present in $\text{Re}_2\text{Cl}_4(\mu\text{-dppm})_2$ have become a trans and cis set in $\text{Re}_2(\text{pic})\text{Cl}_3(\mu\text{-dppm})_2$. The $\text{Re}\text{--Re}$ distances in **1** and $\mathbf{1}\cdot\text{CH}_2\text{Cl}_2$ differ by about 0.012 Å, the values being 2.2816(4) Å for **1** and 2.2937(4) Å for $\mathbf{1}\cdot\text{CH}_2\text{Cl}_2$, while the axial $\text{Re}\text{--O}$ bond distance ($\text{Re}(1)\text{--O}(71)$) is the same in these two structures (2.232(4) and 2.234(4) Å, respectively). Accordingly, the variation in $\text{Re}\text{--Re}$ distances does not reflect any significant difference in the $\text{Re}\text{--O}$ (carboxylate) binding.

For triply bonded $[\text{Re}_2]^{4+}$ complexes there is no electronic barrier to rotation about the $\text{Re}\text{--Re}$ bond¹⁵ and, as expected, there is a pronounced staggering of the two $[\text{ReL}_4]$ units both

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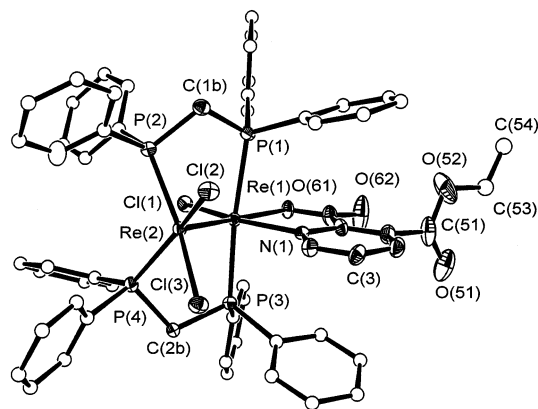


Figure 3. ORTEP¹³ representation of the structure of the dirhenium complex $\text{Re}_2[(\text{O}_2\text{C}-2-(\text{EtO}_2\text{C}-3\text{-py})]\text{Cl}_3(\mu\text{-dppm})_2$ as present in $3 \cdot \text{CH}_2\text{Cl}_2$. Thermal ellipsoids are drawn at the 50% probability level except for the phenyl carbon atoms of the dppm ligands and of the ethyl ester groups which are circles of arbitrary radius. Selected bond distances (Å) and angles (deg) are as follows: Re(1)–Re(2) 2.2752(2), Re(1)–N(1) 2.143(3), Re(1)–Cl(1) 2.3931(9), Re(1)–O(61) 2.221(2), Re(1)–P(1) 2.4625(9), Re(1)–P(3) 2.4635(9), Re(2)–P(2) 2.3851(10), Re(2)–P(4) 2.4032(9), Re(2)–Cl(3) 2.4127(9), Re(2)–Cl(2) 2.4036(9), O(61)–C(61) 1.267(5), O(62)–C(61) 1.221(5); N(1)–Re(1)–Cl(1) 155.85(8), P(1)–Re(1)–P(3) 171.69(3), P(2)–Re(2)–Cl(3) 156.10(3), P(4)–Re(2)–Cl(2) 152.01(3), P(2)–Re(2)–P(4) 108.27(3), O(61)–Re(1)–Re(2) 175.83(6).

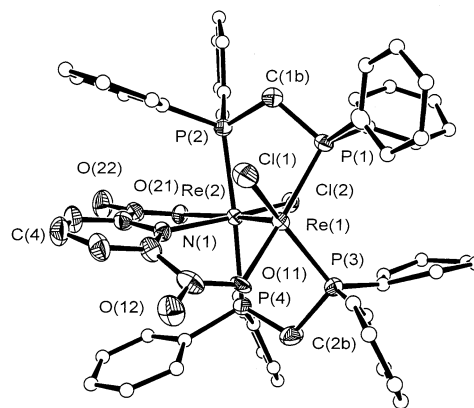


Figure 5. ORTEP¹³ representation of the structure of the dirhenium complex $\text{Re}_2(\text{dipic})\text{Cl}_2(\mu\text{-dppm})_2$ as present in $5 \cdot 0.5\text{CH}_2\text{Cl}_2$. Thermal ellipsoids are drawn at the 50% probability level except for the phenyl carbon atoms of the dppm ligands which are circles of arbitrary radius. Selected bond distances (Å) and angles (deg) are as follows: Re(1)–Re(2) 2.2512(3), Re(2)–N(1) 2.188(4), Re(2)–Cl(2) 2.3941(13), Re(2)–O(21) 2.197(3), Re(2)–P(2) 2.4623(14), Re(2)–P(4) 2.4775(14), Re(1)–P(1) 2.3836(14), Re(1)–P(3) 2.3516(14), Re(1)–Cl(1) 2.4128(15), Re(1)–O(11) 2.103(3), O(11)–C(7) 1.300(7), O(12)–C(7) 1.229(7), O(21)–C(8) 1.290(6), O(22)–C(8) 1.225(7); N(1)–Re(2)–Cl(2) 160.20(12), P(2)–Re(2)–P(4) 173.34(5), P(1)–Re(1)–O(11) 162.33(11), P(3)–Re(1)–Cl(1) 145.59(6), P(1)–Re(1)–P(3) 107.45(5), O(21)–Re(2)–Re(1) 168.09(9).

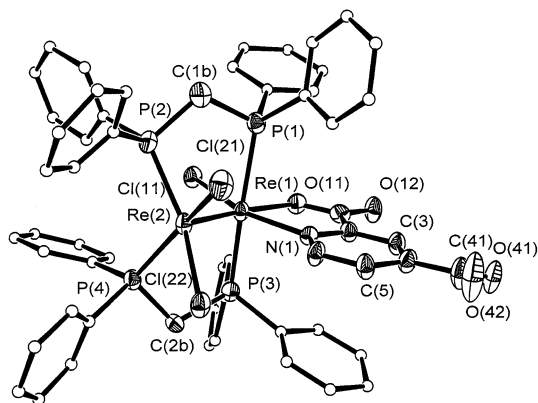


Figure 4. ORTEP¹³ representation of the structure of the dirhenium complex $\text{Re}_2[(\text{O}_2\text{C}-2-(\text{HO}_2\text{C}-4\text{-py})]\text{Cl}_3(\mu\text{-dppm})_2$ as present in $4 \cdot \text{CH}_2\text{Cl}_2 \cdot \text{C}_6\text{H}_6$. Thermal ellipsoids are drawn at the 50% probability level except for the phenyl carbon atoms of the dppm ligands which are circles of arbitrary radius. Selected bond distances (Å) and angles (deg) are as follows: Re(1)–Re(2) 2.2713(5), Re(1)–N(1) 2.147(7), Re(1)–Cl(11) 2.403(2), Re(1)–O(11) 2.240(6), Re(1)–P(1) 2.481(2), Re(1)–P(3) 2.443(2), Re(2)–P(2) 2.397(3), Re(2)–P(4) 2.401(2), Re(2)–Cl(21) 2.387(2), Re(2)–Cl(22) 2.428(2), O(11)–C(11) 1.284(11), O(12)–C(11) 1.242(11); N(1)–Re(1)–Cl(11) 155.78(18), P(1)–Re(1)–P(3) 169.40(8), P(2)–Re(2)–Cl(22) 153.71(8), P(4)–Re(2)–Cl(21) 155.34(9), P(2)–Re(2)–P(4) 106.00(8), O(11)–Re(1)–Re(2) 175.26(15).

in **1** and $1 \cdot \text{CH}_2\text{Cl}_2$. This can be gauged by considering the four torsion angles P(2)–Re(1)–Re(2)–P(1), Cl(11)–Re(1)–Re(2)–P(3), P(4)–Re(1)–Re(2)–Cl(21), and N(1)–Re(1)–Re(2)–Cl(22) (see Figure 1); the average of these torsion angles (χ_{av}) in **1** and $1 \cdot \text{CH}_2\text{Cl}_2$ is 33.4 and 53.8°, respectively, signifying that the *cis*- ReP_2Cl_2 units in these two structures are similarly twisted away from a fully eclipsed conformation relative to the *trans*- ReP_2NCl unit at the coordinatively saturated Re center. Variations in the torsion angles are the consequence of a low barrier to rotation about the $\text{Re}=\text{Re}$ bond and the actual values for **1** and $1 \cdot$

CH_2Cl_2 presumably reflect small differences in intermolecular packing forces. The fact that the Re–Re distance in **1** is a little shorter than in $1 \cdot \text{CH}_2\text{Cl}_2$ could in part be a consequence of a slightly more favorable conformation for

the fused five-membered RePCH_2PRe rings in the former crystal as well as a minimization of intramolecular repulsion forces. Of further note are differences in some of the bond angles associated with the *coordinatively unsaturated* atom Re(2) in these two structures. These differences, which reflect the ease of distorting the pyramidal geometry¹⁶ about Re(2), could also contribute to a slight difference in the Re–Re bond distances.

The aforementioned observations regarding the structures of **1** and $1 \cdot \text{CH}_2\text{Cl}_2$ are supported by a structure determination we carried out on a crystal of composition $2\text{Re}_2(\text{pic})\text{Cl}_3(\mu\text{-dppm})_2 \cdot \text{Re}_2\text{Cl}_6(\mu\text{-dppm})_2 \cdot 2.172\text{CH}_2\text{Cl}_2$ that was obtained on one occasion when we recrystallized a sample of **1** from dichloromethane/benzene. The presence of $\text{Re}_2\text{Cl}_6(\mu\text{-dppm})_2$, whose structure has been reported previously,¹⁷ presumably arose from the oxidation of a small amount of the $\text{Re}_2\text{Cl}_4(\mu\text{-dppm})_2$ starting material. This is a well-known transformation,¹⁷ but it is unclear why it occurs in the present instance. The crystal structure was determined and refined satisfactorily; full details are provided as Supporting Information. The $\text{Re}_2(\mu\text{-Cl})_2\text{Cl}_4(\mu\text{-dppm})_2$ molecule is located about an inversion center (the Re–Re distance is 2.7101(7) Å) while the molecule of $\text{Re}_2(\text{pic})\text{Cl}_3(\mu\text{-dppm})_2$ in the asymmetric unit is similar to that present in the crystals of **1** and $1 \cdot \text{CH}_2\text{Cl}_2$ (Figure 1). The value for the Re–Re distance (2.2841(5) Å) is between that found in **1** and $1 \cdot \text{CH}_2\text{Cl}_2$, and

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Table 2. Selected Spectroscopic and Electrochemical Data for Dirhenium(II) Complexes Containing Pyridinecarboxylate Ligands

compd no.	chem shift, δ^a		CV half-wave potentials, V^b		
	$^{31}\text{P}\{^1\text{H}\}\text{NMR}^c$	$^1\text{H NMR}^d$	$E_{p,a}$	$E_{1/2}(\text{ox})$	$E_{1/2}(\text{red})$
1	+7.7 (m), -6.1 (m)	+6.17 (m, 2H, dppm), ^e +6.02 (m, 2H, dppm) ^e	+1.30	+0.64 (75) ^f	
2	+4.4 (s) ^g	+4.93 (br, 4H, dppm)		+1.11 (90)	-0.12 (80)
3	+7.7 (m), -6.2 (m)	+6.23 (m, 2H, dppm), ^e +6.07 (m, 2H, dppm), ^e +4.18 (q, 2H, OCH_2CH_3), +1.21 (t, 3H, OCH_2CH_3)	+1.45	+0.78 (100) ^f	
4	+7.8 (m), -5.7 (m)	+6.17 (m, 2H, dppm), ^e +6.04 (m, 2H, dppm) ^e	+1.30	+0.66 (60) ^f	
5	+13.5 (m), -3.15 (m) ^h	+5.73 (m, 4H, dppm)	+1.50	+0.69 (130) ^f	
6	-4.3 (m), -6.4 (m)	+5.16 (m, br, 4H, dppm)	\sim +1.2 ⁱ	+0.32 (160) ^f	

^a NMR spectra recorded on CDCl_3 solutions unless otherwise noted. Abbreviations: s = singlet; t = triplet; q = quartet; m = multiplet. ^b Data are given for dirhenium-centered processes and are based upon single scan cyclic voltammograms (scan rate (ν) = 200 mV/s) measured on 0.1 M TBAH/ CH_2Cl_2 solutions at a Pt-bead electrode and referenced to the Ag/AgCl electrode. Under our experimental conditions $E_{1/2} = +0.47$ V for the ferrocenium/ferrocene couple. $E_{1/2}$ values are for one-electron processes with $i_{p,a} = i_{p,c}$, and numbers in parentheses are the approximate values of $\Delta E_p (=E_{p,a} - E_{p,c})$ for the reversible processes. ^c The spectra of compounds **1**, **3**, **4**, and **6** appear as simple AA'BB' patterns; the approximate centers of the two multiplets are given. ^d Resonances for the phenyl groups of dppm and pyridyl ring protons are not given. ^e Multiplets of an ABX₄ pattern. ^f This $E_{1/2}$ value was determined from a single-scan CV with a switching potential of \sim +0.9 V, i.e., less than the onset of the irreversible oxidation ($E_{p,a}$). ^g Spectrum recorded in CD_2Cl_2 . ^h The multiplet centered about $\delta = +13.5$ has the appearance of a doublet-of-doublets while that at $\delta = -3.15$ approximates to a quartet-of-doublets. ⁱ This oxidation is actually two closely spaced processes with $E_{p,a}$ values of \approx 1.01 and \approx 1.35 V; there is a weak coupled reduction process at $E_{p,c} \approx +0.8$ V and a chemical product wave at $E_{p,c} \approx -0.02$ V.

so is the value of χ_{av} (42.7°) for the four torsion angles mentioned above.

The complexes **3** and **4**, which are formed by reacting $\text{Re}_2\text{Cl}_4(\mu\text{-dppm})_2$ with pyridine-2,3-dicarboxylic acid and pyridine-2,4-dicarboxylic acid, have structures very similar to that of **1** (see Figures 3 and 4). The carboxylate groups in the 3 and 4 positions of **3** and **4** are not involved in coordination to the dirhenium unit. In the case of **3**, the carboxylic acid group in the 3 position of the free ligand is converted into the ethyl ester under the reflux conditions used, while the crystals of **4** contain dirhenium units that are linked into infinite chains through intermolecular hydrogen bonds that are formed between the atom O(12) of the coordinated carboxylate group in the 2 position and the "free" carboxylic acid group in the 4 position (O(41)) of a neighboring molecule. The hydrogen-bonded distance O(12)⋯O(41) is 2.69 Å. The Re–Re bond distance in the crystals of **3**· CH_2Cl_2 and **4**· CH_2Cl_2 · C_6H_6 are 2.2752(2) and 2.2713(5) Å, respectively, and are similar to the Re–Re triple bond distances in **1** and **1**· CH_2Cl_2 albeit a little shorter by 0.01–0.02 Å. Very similar staggered geometries are found in **1**, **3**, and **4**. The close similarities in the electronic and molecular structures of these three complexes are also reflected by the similarity of their $^{31}\text{P}\{^1\text{H}\}$ NMR spectra and cyclic voltammetric properties (Table 2). The latter show two one-electron oxidations, which is typical of $[\text{Re}\equiv\text{Re}]^{4+}$ complexes,¹⁵ although the $[\text{Re}_2]^{6+}/[\text{Re}_2]^{5+}$ process is clearly irreversible (Table 2).

Complex **2**, which is formed by the reaction between $\text{Re}_2\text{Cl}_4(\mu\text{-dppm})_2$ and (PPN)nic in refluxing ethanol, is similar to the related compound $\text{trans-Re}_2(\mu\text{-O}_2\text{C-4-C}_5\text{H}_4\text{N})_2\text{Cl}_2(\mu\text{-dppm})_2$ that is prepared by an analogous reaction using the (PPN)⁺ salt of isonicotinate.³ The related cis isomer of the isonicotinate complex can be obtained² by the reaction between $\text{cis-Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_2(\mu\text{-dppm})_2$ and isonicotinic acid. The structure of **2**, which is shown in Figure 2, is similar to that of the analogous μ -acetato complex $\text{trans-Re}_2(\mu\text{-O}_2\text{-CCH}_3)_2\text{Cl}_2(\mu\text{-dppm})_2$.³ The Re–Re distance in the latter complex (2.2763(7) Å)³ is similar to that in **2** (2.2931(3) Å). The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows a singlet at $\delta = +4.4$

(Table 2), similar to the chemical shift reported for $\text{trans-Re}_2(\mu\text{-O}_2\text{C-4-C}_5\text{H}_4\text{N})_2\text{Cl}_2(\mu\text{-dppm})_2$ ($\delta = +3.7$). In addition, the CV properties of **2** (Table 2) are typical of those reported for other carboxylate complexes of the type $\text{trans-Re}_2(\mu\text{-O}_2\text{-CR})_2\text{Cl}_2(\mu\text{-dppm})_2$,^{3,7} thereby confirming that the trans structure is retained in solution.

The green colored complex **5**, which is formed by the use of a procedure very similar to that by which $\text{Re}_2\text{Cl}_4(\mu\text{-dppm})_2$ is converted to **1–4** (i.e. reflux in ethanol), is the most interesting compound of this group, and its characterization provides insights into the reason **1** and **3–5** have such unsymmetrical structures. The use of [PPN]₂dipic rather than dipicH₂ is much preferred in the preparation of **5** (see Experimental Section) since the reaction with the free acid is very slow. The structure of **5** as present in a crystal of composition **5**·0.5 CH_2Cl_2 is shown in Figure 5. The Re–Re bond distance of 2.2512(3) Å accords with the retention of a Re≡Re bond and is similar to the distances in **1**, **3**, and **4** (range 2.27–2.29 Å), albeit a little shorter. The structure of **5** also resembles those of **1**, **3**, and **4** in the environment about the coordinatively saturated Re atom, i.e., that with the atom set [ReCINP₂O] in which there is a pair of trans Re–P bonds and an axially bound O atom from the carboxylate group in the 2 position of the pyridyl ring. This structure differs from **1**, **3**, and **4** in that the second carboxylate group (that in the 6 position) has displaced one of the Cl atoms bound to the coordinatively unsaturated Re atom to form a pyridine carboxylate bridge between the two metal centers (Figure 5). This leads to the formation of a stable, puckered, six-membered ReNCC(O)ORe ring and results in the retention of a staggered rotational geometry ($\chi_{av} = 42.8^\circ$) and a cis arrangement of Re–P bonds, as is the case in **1**, **3**, and **4**.

When the reaction between $\text{Re}_2\text{Cl}_4(\mu\text{-dppm})_2$ and [PPN]₂dipic is carried out in ethanol or dichloromethane at room temperature, a single product (**6**) is isolated as orange crystals. It converts quantitatively to **5** when heated (as a suspension in ethanol) for 24 h. Microanalytical data indicate that it has the same composition as **5**, and this has been

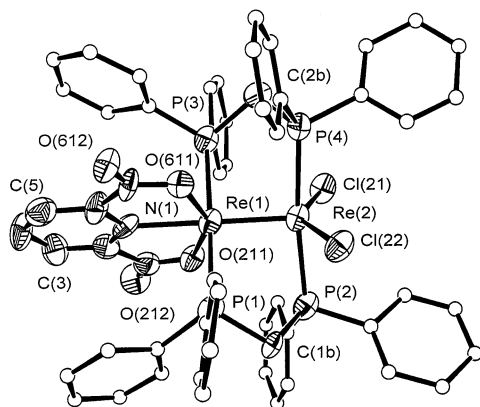


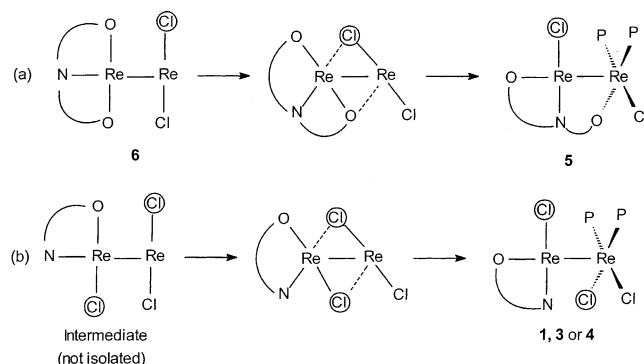
Figure 6. ORTEP¹³ representation of the structure of the dirhenium complex $\text{Re}_2(\text{dipic})\text{Cl}_2(\mu\text{-dppm})_2$ as present in $6 \cdot 3\text{C}_6\text{H}_6$. Thermal ellipsoids are drawn at the 50% probability level except for the phenyl carbon atoms of the dppm ligands which are circles of arbitrary radius. Selected bond distances (Å) and angles (deg) are as follows: $\text{Re}(1)\text{--Re}(2)$ 2.2750(10); $\text{Re}(1)\text{--N}(1)$ 2.210(13), $\text{Re}(1)\text{--O}(211)$ 2.085(9), $\text{Re}(1)\text{--O}(611)$ 2.115(10), $\text{Re}(1)\text{--P}(1)$ 2.439(4), $\text{Re}(1)\text{--P}(3)$ 2.452(4), $\text{Re}(2)\text{--P}(2)$ 2.413(5), $\text{Re}(2)\text{--P}(4)$ 2.418(5), $\text{Re}(2)\text{--Cl}(21)$ 2.353(4), $\text{Re}(2)\text{--Cl}(22)$ 2.375(4), $\text{O}(211)\text{--C}(21)$ 1.336(19), $\text{O}(212)\text{--C}(21)$ 1.224(19), $\text{O}(611)\text{--C}(61)$ 1.304(17), $\text{O}(612)\text{--C}(61)$ 1.250(18); $\text{O}(211)\text{--Re}(1)\text{--O}(611)$ 145.5(4), $\text{P}(1)\text{--Re}(1)\text{--P}(3)$ 177.77(15), $\text{Cl}(21)\text{--Re}(2)\text{--Cl}(22)$ 136.69(15), $\text{P}(2)\text{--Re}(2)\text{--P}(4)$ 173.85(14), $\text{N}(1)\text{--Re}(1)\text{--Re}(2)$ 179.1(3).

confirmed by a single-crystal X-ray structure determination (see Figure 6), which shows that it is an isomer of **5**. Its clean conversion to **6** implies that it is a kinetic product isolable with the use of mild reaction conditions. In the structure of **6**, the Re–Re bond is a little longer than that present in **5** (2.2750(10) Å versus 2.2512(3) Å) and it has a staggered rotational geometry with a χ_{av} value of 45.8°. It differs from **5** in having an axially bound pyridine N atom rather than an axial carboxylate O atom and has the pyridine-2,6-dicarboxylate ligand bound in a O,N,O tridentate fashion to only one Re atom, thereby giving a more symmetrical structure. Furthermore, there are two pairs of trans Re–P bonds rather than a trans and a cis pair as in **5**. These differences are also reflected by differences in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra and cyclic voltammetric properties of **5** and **6** (see Table 2). Like most $[\text{Re}_2]^{4+}$ complexes, **5** and **6** show two metal-based oxidations, but in both cases only the first approaches reversibility and is much more accessible in **6** (by almost 0.4 V), implying that the different coordination modes of the dipic ligand in these two compounds induces significant differences in the metal–metal bond orbital energies of **5** and **6** which is in accord with the changes in the ligand atom sets that are bound to the two Re centers in these complexes.

Any mechanism for the conversion of **6** to the more thermodynamically stable isomeric form **5** must, among other things, account for the change from two sets of trans Re–P bonds in **6** to a trans and cis pair in **5**. We believe that this conversion is readily explainable by the pathway represented in Scheme 2a, in which a *partial* “merry-go-round” process, of a type that is well documented for other dirhenium(II) complexes which contain the $[\text{Re}_2(\mu\text{-dppm})_2]^{4+}$ unit,^{8,18,19} can account for the following:

(1) the transfer of a chloride ligand from one metal atom to the other; (2) the change in coordination mode of the dipic

Scheme 2. Possible Partial “Merry-Go-Round” Processes in Which an Intermediate That Contains a *trans,trans*- $[\text{Re}_2(\mu\text{-dppm})_2]$ Structure Converts to Compound **1**, **3**, **4**, or **5** in Which This Unit Has a *Trans*, *Cis* Stereochemistry^a



^a Key: (a) conversion of **6** to **5**; (b) conversion of an intermediate (not isolated) in the case of **1**, **3**, and **4**. Note: (1) If a pair of P atoms is *trans*, then these atoms are not shown in the representations. (2) Chlorine atom(s) that transfer from one Re atom to the other are designated as an encircled Cl.

ligand; (3) the switch from a *trans*- to a *cis*- ReP_2 geometry at the coordinatively unsaturated Re center. A similar intramolecular mechanism could also explain why compounds **1**, **3**, and **4**, all of which involve N,O chelation by a pyridine-2-carboxylate ligand, have the same type of *trans,cis*- $[\text{Re}_2(\mu\text{-dppm})_2]$ structure (see Scheme 2b).

Concluding Remarks

In this study, we find that $\text{Re}_2\text{Cl}_4(\mu\text{-dppm})_2$ reacts with various pyridine-2-carboxylate ligands (either as the free acids or their $[\text{PPN}]^+$ salts) to give complexes **1**, **3**, and **4** (Scheme 1) in which the products contain the expected N,O chelation by the ligand but an unexpected switch in the coordination of the two dppm ligands from a *trans, trans* to a *trans, cis* stereochemistry. In the case of the reaction of $\text{Re}_2\text{Cl}_4(\mu\text{-dppm})_2$ with the pyridine-2,6-dicarboxylate ligand, both the kinetic product **6** and thermodynamic product **5** have been isolated and fully characterized. The quantitative conversion of **6** to **5** provides an explanation of how the *trans, trans* coordination of dppm ligands in $\text{Re}_2\text{Cl}_4(\mu\text{-dppm})_2$ and $\text{Re}_2[\eta^3(\text{O},\text{N},\text{O})\text{-dipic}]\text{Cl}_2(\mu\text{-dppm})_2$ (**6**) can convert to the *trans,cis* arrangement in $\text{Re}_2[\eta^3(\text{O},\text{N},\text{O})\text{-dipic}]\text{Cl}_2(\mu\text{-dppm})_2$ (**5**) and, by implication, how **1**, **3**, and **4** come to have structures similar to that of **5** (see Scheme 2).

The reaction of **1** with $[\text{PPN}]\text{O}_2\text{CCH}_3$ results in the complete replacement of picolinate by acetate and the formation of the well-known compound *cis*- $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{-Cl}_2(\mu\text{-dppm})_2$ ⁷ in high yield (see Experimental Section). We have not yet been able to prepare mixed acetate/pyridine carboxylate complexes such as $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)(\mu\text{-O}_2\text{C}-2\text{-C}_5\text{H}_4\text{N})\text{Cl}_2(\mu\text{-dppm})_2$ by this strategy.

We also note that attempts to prepare dirhenium(II) compounds that contain the 3,4- and 3,5-pyridinecarboxylate ligands were unsuccessful. The reactions of $\text{Re}_2\text{Cl}_4(\mu\text{-dppm})_2$ with these acids and their $[\text{PPN}]^+$ salts in refluxing ethanol

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Reactions of $\text{Re}_2\text{Cl}_4(\mu\text{-dppm})_2$

led to almost complete recovery of the unreacted starting material. In contrast, pyridine-3-carboxylate (as its $[\text{PPN}]^+$ salt) reacts to give *trans*- $\text{Re}_2[\mu:\eta^2(\text{O},\text{O})\text{-O}_2\text{C-3-C}_5\text{H}_4\text{N}]_2\text{Cl}_2(\mu\text{-dppm})_2$ (**2**), which is similar to the isonicotinate complex *trans*- $\text{Re}_2[\mu:\eta^2(\text{O},\text{O})\text{-O}_2\text{C-4-C}_5\text{H}_4\text{N}]_2\text{Cl}_2(\mu\text{-dppm})_2$ and to the *trans* isomer of the related acetate complex that have been isolated previously.³ Like the isonicotinate complex *cis*- $\text{Re}_2(\mu\text{-O}_2\text{C-4-C}_5\text{H}_4)_2\text{Cl}_2(\mu\text{-dppm})_2$,² and other transition metal complexes that contain isonicotinate or nicotinate ligands and which can be used to make mixed-metal assemblies (e.g. those of dirhodium(II)²⁰ and platinum(II)²¹), compound **2** and its isonicotinate analogue³ should be capable of fulfilling a

similar role. Attempts to use **2** to prepare small mixed-metal assemblies or polymers are now underway.

Acknowledgment. R.A.W. thanks the John A. Leighty Endowment Fund for support of this work.

Supporting Information Available: X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

IC030153Y

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