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Dirhenium complexes that contain the ligand 1,1-bis(diphenylphosphino)ethene (dppE). Synthesis, characterization and reactivity of $\text{Re}_2\text{Cl}_4(\mu\text{-dppE})_2$

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Abstract

The dirhenium(II) compound $\text{Re}_2\text{Cl}_4(\mu\text{-dppE})_2$ (1), where dppE = $(\text{Ph}_2\text{P})_2\text{C}=\text{CH}_2$, which contains an electron-rich triple bond, has been prepared by the reaction of $(n-\text{Bu}_4\text{N})_2\text{Re}_2\text{Cl}_8$ with $\text{CH}_3\text{CO}_2\text{Na}$ and dppE in refluxing ethanol. Its reactivity towards CO alone, and CO in combination with XylNC and 2,5-Me₂–C₆H₃CN has been explored. The complexes $\text{Re}_2\text{Cl}_4(\mu\text{-dppE})_2(\text{CO})_2$ (2) and $[\text{Re}_2\text{Cl}_3(\mu\text{-dppE})_2(\text{CO})_2(\text{L})]\text{O}_3\text{SCF}_3$, where L = CO (3), XylNC (4) or 2,5-Me₂–C₆H₃CN (5) have been isolated and characterized by IR and NMR spectroscopy, cyclic voltammetry and X-ray crystallography. The complex *trans*-Re₂(μ -O₂CCH₃)₂Cl₂(μ -dppE)_2 (6) has been obtained by the reaction of $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_4\text{Cl}_2$ with dppE. Crystal structure determinations on 1, 2, 4 and 6 reveal that the Re–Re distances are 2.2448(5), 2.5748(5), 2.5767(5) and 2.2861(6) Å, which are in accordance with Re–Re bond orders of 3, 2, 2 and 3, respectively. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

The complex Re₂Cl₄(μ -dppm)₂, where dppm = Ph₂PCH₂PPh₂, is the prototypical dirhenium(II) compound with an electron-rich triple bond [1–3]. The exploration of its reactivity towards reagents as varied as O₂ [4], H₂S [5], CS₂ [6], organic nitriles [7] and carboxylates [8] has provided valuable insight into the nature of the $\sigma^2 \pi^4 \delta^2 \delta^{*2}$ ground state electronic configuration. Of additional interest is the large number of structural isomers of mixed carbonyl–isocyanide species of the types [Re₂Cl₃(μ -dppm)₂(CO)(CNXyl)₂]⁺ and [Re₂Cl₂(μ -dppm)₂(CO)(CNXyl)₃]²⁺ that have been prepared by various synthetic strategies starting from Re₂Cl₄(μ -dppm)₂ [9,10].

In order to examine the effects of varying the bridging group X and the R groups in the bidentate phosphines R_2PXPR_2 (where X represents CH_2 in the case of dppm) upon the reactivity of compounds of the type $\text{Re}_2\text{Cl}_4(\mu-\text{R}_2\text{PXPR}_2)_2$, we have been developing procedures for the synthesis of dirhenium(II) compounds with phosphines other than Ph₂PCH₂PPh₂. We have previously prepared and structurally characterized the compound $\text{Re}_2\text{Cl}_4(\mu\text{-dppa})_2$, where $dppa = Ph_2PNHPPh_2$, and examined a few aspects of its reactivity [11-13]. More recently, we isolated and characterized the compound $\text{Re}_2\text{Cl}_4(\mu\text{-dcpm})_2$, where $dcpm = Cy_2PCH_2PCy_2$ [14]. In the present report we describe the synthesis and structural characterization of another compound of the type Re2- $Cl_4(\mu-R_2PXPR_2)_2$, viz., $Re_2Cl_4(\mu-dppE)_2$, where dppE $= 1,1-(Ph_2P)_2C=CH_2$, and examine its reactivity towards carbon monoxide in combination with xylyl (XyINC) and 2,5-dimethylbenzonitrile isocyanide $(Me_2C_6H_3CN)$. The isolation and structural characterization of trans-Re₂(μ -O₂CCH₃)₂Cl₂(μ -dppE)₂ is also described.

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2. Experimental

2.1. Starting materials and reaction procedures

Standard literature procedures were used to prepare $(n-Bu_4N)_2Re_2Cl_8$ [15], *cis*-Re₂(O₂CCH₃)₂Cl₄(H₂O)₂ [16] and Re₂(O₂CCH₃)₄Cl₂ [17]. The ligand 1,1-bis(-diphenylphosphino)ethene (abbreviated dppE) was synthesized through the method described by Colquhoun and McFarlane [18]. All other reagents and organic solvents were purchased from commercial sources. Solvents were deoxygenated by purging with N₂(g) prior to use and all reactions were carried out under an atmosphere of N₂. Infrared spectra, NMR spectra and cyclic voltammetric measurements were determined as previously described [19]. Elemental microanalyses were performed by Dr Lee of the Purdue University Microanalytical Laboratory.

2.2. Synthesis of $Re_2Cl_4(\mu$ -dppE)₂ (1)

A mixture of $(n-Bu_4N)_2Re_2Cl_8$ (1000 mg, 0.88 mmol), CH₃CO₂Na (144 mg, 1.76 mmol), and dppE (770 mg, 1.94 mmol) in 40 ml of ethanol was refluxed for 48 h. The brown precipitate that formed was filtered off, washed with 15 ml of ethanol and dried under a vacuum. The complex was recrystallized from dichloromethane-diethyl ether to afford brown microcrystals; yield 720 mg (63%). *Anal.* Calc. for C₅₃H₄₆Cl₆P₄Re₂ (i.e. Re₂Cl₄(µ-dppE)₂·CH₂Cl₂): C, 45.73; H, 3.33. Found: C, 46.12; H, 3.16%.

2.3. Synthesis of $Re_2Cl_4(\mu-dppE)_2(CO)_2$ (2)

A quantity of $\text{Re}_2\text{Cl}_4(\mu\text{-dppE})_2$ (131 mg, 0.10 mmol) was dissolved in 30 ml of dichloromethane. Carbon monoxide was bubbled into this solution for 2 h, and the solution was then stirred under an atmosphere of carbon monoxide for 24 h at room temperature. The volume of the green-brown solution was reduced to about 3 ml, then 15 ml of diethyl ether were added to give a greenish-brown precipitate of **2** which was filtered off, washed with 20 ml of diethyl ether and dried under a vacuum; yield 118 mg (87%). *Anal.* Calc. for $C_{55}H_{46}Cl_6O_2P_4Re_2$ (i.e. $Re_2Cl_4(\mu\text{-dppE})_2(CO)_2$. CH_2Cl_2): C, 45.56; H, 3.34. Found: C, 45.22; H, 3.18%.

2.4. Synthesis of $[Re_2Cl_3(\mu-dppE)_2(CO)_3]SO_3CF_3$ (3)

A solution that contained the dicarbonyl complex 2 (136 mg, 0.10 mmol) and TIO_3SCF_3 (35.3 mg, 0.10 mmol) in 30 ml of dichloromethane was stirred under an atmosphere of CO at room temperature for 24 h. The resulting red-brown mixture was filtered to remove insoluble materials and the volume of the filtrate was reduced to about 3 ml. An excess of diethyl ether

(25 ml) was added to afford a red-brown precipitate, **3**, which was filtered off, washed with 20 ml of diethyl ether and dried under a vacuum; yield 75 mg (50%). *Anal.* Calc. for $C_{56}H_{44}Cl_3F_3O_6P_4Re_2S$: C, 44.70; H, 2.95. Found: C, 44.79; H, 2.97%.

2.5. Synthesis of $[Re_2Cl_3(\mu-dppE)_2(CO)_2(CNXyl)]$ -SO₃CF₃ (**4**)

A mixture of **2** (136 mg, 0.10 mmol), TlO₃SCF₃ (35.3 mg, 0.10 mmol) and XylNC (13 mg, 0.10 mmol) in 30 ml of dichloromethane was stirred at room temperature for 20 h. The yellow–brown mixture was filtered to remove insoluble materials, and the volume of the filtrate was reduced to about 3 ml. Diethyl ether (15 ml) was added to precipitate the yellow–brown complex **4** which was filtered off, washed with 20 ml of diethyl ether and dried under a vacuum; yield 102 mg (64%). *Anal.* Calc. for C₆₅H₅₅Cl₅F₃NO₅P₄Re₂S (i.e. [Re₂Cl₃(μ -dppE)₂(CO)₂(CNXyl)]O₃SCF₃·CH₂Cl₂): C, 46.12; H, 3.27. Found: C, 45.85; H, 3.18%.

2.6. Synthesis of $[Re_2Cl_3(\mu-dppE)_2(CO)_2(NCC_6H_3-2,5-Me_2)]O_3SCF_3$ (5)

The reaction between **2** (200 mg, 0.15 mmol), TlO₃SCF₃ (52.0 mg, 0.15 mmol) and 2,5-dimethylbenzonitrile (24 mg, 0.185 mmol) in 30 ml of dichloromethane was carried out as described in Section 2.5 to afford the yellow–brown product **5**; yield 123 mg (51%). *Anal.* Calc. for $C_{64}H_{53}Cl_3F_3NO_5P_4Re_2S$: C, 47.81; H, 3.32. Found: C, 47.39; H, 3.65%.

2.7. The reaction of $Re_2(\mu - O_2CCH_3)_4Cl_2$ with dppE

A mixture of $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_4\text{Cl}_2$ (100 mg, 0.15 mmol) and dppE (350 mg, 0.90 mmol) was refluxed in 25 ml of methanol for 3 days. The cooled reaction mixture was filtered and the insoluble brown crystals of *trans*-Re₂(μ -O₂CCH₃)₂Cl₂(μ -dppE)₂ (**6**) were washed with methanol (10 ml) and diethyl ether (10 ml) and dried under a vacuum; yield 53 mg (27%). *Anal.* Calc. forC₅₇H₅₄Cl₂O₅P₄Re₂(i.e. Re₂(μ -O₂CCH₃)₂Cl₂(μ -dppE)₂[.] MeOH): C, 49.39; H, 3.93. Found: C, 49.59; H, 3.88%.

2.8. The reaction of $cis-Re_2(\mu-O_2CCH_3)_2Cl_4(H_2O)_2$ with dppE

A mixture of $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_2\text{Cl}_4(\text{H}_2\text{O})_2$ (100 mg, 0.15 mmol) and dppE (131 mg, 0.33 mmol) was refluxed in 25 ml of ethanol for 3 h. The brown crystalline product, $\text{Re}_2\text{Cl}_4(\mu\text{-dppE})_2$ (1) was filtered off, washed with fresh ethanol (10 ml), and dried under vacuum; yield 87 mg (45%). The identity of this product

was confirmed by comparison of its spectroscopic and electrochemical properties with those of an authentic sample (see Section 2.2).

2.9. X-ray crystallography

Single crystals of 1 and 4 were grown by the vapor diffusion of diethyl ether into dichloromethane solutions of the complexes, while crystals of 2 were grown at room temperature by the slow evaporation of a solution of the complex in dichloromethane. In the case of 6, crystals were harvested directly from the reaction mixture.

The data collections were performed at 193 ± 1 K on a Nonius KappaCCD diffractometer. Lorentz and polarization corrections were applied to the data sets. The crystallographic data for the compounds are given in Table 1.

The structures were solved using the structure solution program PATTY in DIRDIF-92 [20]. 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 $U(H) = 1.3U_{eq}(C)$. They were included in the refinement but constrained to ride on the atom to which they are bonded. An empirical absorption correction using SCALEPACK [21] was applied. The final refinements were performed by the use of the program SHELXL-97 [22].

During the course of the structure analysis of 1, one dichloromethane molecule from the crystallization sol-

vents was found crystallized with the dirhenium molecule in the asymmetric unit. It was included in the analysis and refined satisfactorily with anisotropic thermal parameters. The largest remaining peak in the final difference Fourier was 3.79 e Å⁻³.

In the case of 2, the dirhenium unit lies on a crystallographic inversion center. Consequently, the bridging carbonyl group atoms C(11) and O(11) were disordered with the bridging chlorine Cl(11), while the terminal carbonyl group atoms C(2) and O(2) were found to be disordered with the terminal chlorine Cl(2). In the final refinement, the bridging group atoms C(11), O(11) and Cl(11), and the terminal group atoms C(2), O(2) and Cl(2) were each given fixed site-occupancy factors of 0.5. A common isotropic thermal parameter was refined for atoms C(11), O(11), C(2), and O(2). Two dichloromethane molecules from the crystallization solvents were found crystallized with 2 in the asymmetric unit. These were included in the analysis and refined satisfactorily with anisotropic thermal parameters. The largest remaining peak in the final difference Fourier was 1.44 $e Å^{-3}$.

The crystal of compound **4** had two sites of partial dichloromethane molecules from the crystallization solvents in the asymmetric unit; their C and Cl atoms were located and refined satisfactorily with anisotropic thermal parameters. Refinement of these two solvent molecules gave occupancies of 0.797 and 0.736. The largest remaining peak in the final difference Fourier was 1.09 e Å⁻³.

Table 1

 $Crystallographic data for Re_2Cl_4(\mu-dppE)_2 \cdot CH_2Cl_2 (1), Re_2Cl_4(\mu-dppE)_2(CO)_2 \cdot 2CH_2Cl_2 (2), [Re_2Cl_3(\mu-dppE)_2(CO)_2(CNXyl)]O_3SCF_3 \cdot 1.533 \\ CH_2Cl_2 (4) and \textit{trans-Re}_2(\mu-O_2CCH_3)_2Cl_2(\mu-dppE)_2 \cdot MeOH (6)$

	1	2	4	6
Chemical formula	$C_{53}H_{46}Cl_6P_4Re_2$	$C_{56}H_{48}Cl_8O_2P_4Re_2$	C _{65,53} H _{56,07} Cl _{6,07} F ₃ NO ₅ P ₄ Re ₂ S	C ₅₇ H ₅₄ Cl ₂ O ₅ P ₄ Re ₂
Formula weight	1391.97	1532.93	1738.06	1386.27
Space group	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)	$P2_12_12_1$ (no. 19)	<i>C</i> 2/ <i>c</i> (no. 15)
Unit cell dimensions				
a (Å)	12.7450(4)	8.8964(2)	12.2601(2)	15.0451(9)
b (Å)	18.4561(6)	22.3308(6)	15.2336(3)	22.1142(14)
c (Å)	21.7440(7)	14.1592(3)	35.6102(9)	16.2959(7)
α (°)	90	90	90	90
β (°)	96.6764(18)	96.0002(15)	90	107.701(4)
γ (°)	90	90	90	90
$V(Å^3)$	5080.0(5)	2797.5(2)	6650.8(4)	5165.1(10)
Z	4	2	4	4
$D_{\rm calc} (\rm g \ cm^{-3})$	1.820	1.820	1.736	1.783
μ (Mo K α) (mm ⁻¹)	5.306	4.922	4.114	5.022
Transmission factors (min./max.)	0.40, 0.88	0.50, 0.61	0.42, 0.66	0.44, 0.69
$R(F_{\rm o})^{\rm a}$	0.049	0.049	0.057	0.044
$R_{\rm w}(F_{\rm o}^2)^{\rm b}$	0.109	0.135	0.087	0.083
GOF	1.019	1.084	1.019	0.957

^a $R = \Sigma ||F_{o}| - |F_{c}|| / \Sigma |F_{o}|$ with $F_{o}^{2} > 2\sigma(F_{o}^{2})$.

^b $R_{\rm w} = [\Sigma w (|F_{\rm o}^2| - |F_{\rm c}^2|)^2 / \Sigma w |F_{\rm o}^2|^2]^{1/2}.$

Table 2 Important bond distances (Å) and angles (°) for the complex $Re_2Cl_4(\mu$ -dppE)₂·CH₂Cl₂ (1) ^a

Re(1)–Re(2)	2.2448(5)	Re(2)-Cl(22)	2.367(2)
Re(1)-Cl(12)	2.360(2)	$\operatorname{Re}(2) - \operatorname{P}(2)$	2.443(2)
Re(1)-Cl(11)	2.369(2)	$\operatorname{Re}(2)-\operatorname{P}(4)$	2.460(2)
Re(1) - P(3)	2.417(2)	C(11)–C(12)	1.334(13)
Re(1) - P(1)	2.450(2)	C(21)-C(22)	1.305(12)
Re(2)-Cl(21)	2.356(2)		
Re(2)-Re(1)-Cl(12)	118.59(6)	Re(1)-Re(2)-Cl(21)	115.90(6)
Re(2)-Re(1)-Cl(11)	116.34(6)	Re(1)-Re(2)-Cl(22)	120.06(6)
Cl(12)-Re(1)-Cl(11)	124.99(8)	Cl(21)-Re(2)-Cl(22)	124.02(8)
Re(2)-Re(1)-P(3)	90.90(6)	Re(1)-Re(2)-P(2)	89.18(5)
Cl(12)-Re(1)-P(3)	88.32(8)	Cl(21)-Re(2)-P(2)	88.70(8)
Cl(11)-Re(1)-P(3)	88.08(8)	Cl(22)-Re(2)-P(2)	90.68(8)
Re(2)-Re(1)-P(1)	94.44(6)	Re(1)-Re(2)-P(4)	93.77(6)
Cl(12)-Re(1)-P(1)	88.53(8)	Cl(21)-Re(2)-P(4)	91.47(8)
Cl(11)-Re(1)-P(1)	90.15(8)	Cl(22)-Re(2)-P(4)	86.43(8)
P(3)-Re(1)-P(1)	174.61(8)	P(2)-Re(2)-P(4)	176.62(8)

^a Numbers in parentheses are estimated S.D.s in the least significant digits.

The atoms Re(1), Re(2), Cl(1) and Cl(2) of the dirhenium unit in compound **6** are located on a twofold crystallographic rotational axis. One molecule of methanol from the crystallization solvents was found in the asymmetric unit during the course of the structure determination. It was included in the analysis and refined satisfactorily with anisotropic thermal parameters. The largest remaining peak in the final difference Fourier was 0.80 e Å⁻³.

The important intramolecular bond distances and angles for the structures of 1, 2, 4 and 6 are given in Tables 2-5.

3. Results and discussion

3.1. The synthesis and characterization of $Re_2Cl_4(\mu-dppE)_2$

The synthesis of Re₂Cl₄(μ -dppE)₂ utilized the reaction between (n-Bu₄N)₂Re₂Cl₈, NaO₂CCH₃ and dppE in refluxing ethanol and is similar to the procedure we used to obtain Re₂Cl₄(μ -dppm)₂ [2]. This reaction almost certainly proceeds through the intermediacy of the paramagnetic [Re₂]⁵⁺ complex Re₂(μ -O₂CCH₃)Cl₄(μ dppE)₂. This procedure is a convenient alternative to the one whereby a bisphosphine ligand is reacted with *cis*-Re₂(O₂CCH₃)₂Cl₄(H₂O)₂ [2a,11a]. The cyclic voltammetric (CV) properties of **1**, recorded on solutions in 0.1 M n-Bu₄NPF₆-CH₂Cl₂ with the use of a Pt-bead electrode, consist of two reversible one-electron oxidations with *E*_{1/2}(ox) = + 0.92 and + 0.37 V versus Ag/ AgCl and *E*_p values of 60 mV. These data can be contrasted with data reported for Re₂Cl₄(μ -dppm)₂, which has $E_{1/2}(ox) = +0.87$ and +0.29 V versus Ag/AgCl, and Re₂Cl₄(μ -dppa)₂, with $E_{1/2}(ox) = +0.94$ and +0.40 V [12]. The ¹H NMR spectrum of **1** (recorded in CD₂Cl₂) shows a pentet at δ + 6.17 due to the bridge-head >C=CH₂ group, while the ³¹P{¹H} NMR spectrum consists of a singlet at δ + 14.6.

The crystal structure of $\text{Re}_2\text{Cl}_4(\mu\text{-dppE})_2$ confirms its close structural relationship to $\text{Re}_2\text{Cl}_4(\mu\text{-dppm})_2$ [3] and $\text{Re}_2\text{Cl}_4(\mu\text{-dppa})_2$ [12]. An ORTEP representation [23] of the structure is given in Fig. 1 and key structural parameters are listed in Table 2. The Re–Re distance of 2.2448(5) Å is close to the values reported for $\text{Re}_2\text{Cl}_4(\mu\text{-dppm})_2$ (2.234(3) Å) and $\text{Re}_2\text{Cl}_4(\mu\text{-dppa})_2$ (2.2417(5) Å), and the expected fully staggered rotational geometry is confirmed by values for the torsion angles Cl(11)-Re(1)-Re(2)-Cl(21), Cl(12)-Re(1)-Re(2)-Cl(22), P(1)-Re(1)-Re(2)-P(2) and P(3)-Re(1)-Re(2)-P(4) of 48.5, 43.8, 44.3 and 43.3°, respectively.

3.2. Reactions of $Re_2Cl_4(\mu$ -dppE)₂ (1)

Several reactions of the title complex 1 were carried out in order to compare its reactivity patterns with those of $\text{Re}_2\text{Cl}_4(\mu\text{-dppm})_2$. The results are summarized in Eqs. (1)–(4).

$$Re_{2}Cl_{4}(\mu-dppE)_{2} \xrightarrow{CO} Re_{2}Cl_{4}(\mu-dppE)_{2}(CO)$$
$$\xrightarrow{CO} \rightarrow Re_{2}Cl_{4}(\mu-dppE)_{2}(CO)_{2} \quad (1)$$

 $Re_2Cl_4(\mu$ -dppE)₂(CO)₂

$$\xrightarrow{\text{TIO}_3\text{SCF}_3} [\text{Re}_2\text{Cl}_3(\mu\text{-dppE})_2(\text{CO})_3]\text{O}_3\text{SCF}_3 \quad (2)$$

Table 3

Important bond distances (Å) and angles (°) for the complex $Re_2Cl_4(\mu$ -dppE)₂(CO)₂·2CH₂Cl₂ (**2**)^a

$\mathbf{D}_{2}(1) = \mathbf{D}_{2}(1)^{1}$	2 5749(5)	$\mathbf{P}_{a}(1)/(C!(11))$	2 462(5)
Re(1) - Re(1)	2.3746(3)	Re(1) = CI(11)	2.402(3)
$\operatorname{Re}(1)$ – $\operatorname{C}(2)$	1.864(17)	$\operatorname{Re}(1)' - \operatorname{Cl}(2)$	2.466(4)
Re(1)'-C(11)	1.83(3)	$\operatorname{Re}(1) - \operatorname{P}(1)$	2.4713(18)
Re(1)-C(11)	2.38(2)	O(11)-C(11)	1.22(3)
Re(1)-Cl(1)	2.399(2)	O(2)–C(2)	1.15(2)
Re(1)-Cl(11)	2.425(4)	C(311)-C(312)	1.308(11)
Re(1)–P(2)	2.4560(18)		
C(2)-Re(1)-C(11)	73.9(8)	C(2)-Re(1)-Re(1)'	117.1(5)
C(2)-Re(1)-Cl(1)	97.6(5)	C(11)-Re(1)-Re(1)'	43.3(6)
C(11)-Re(1)-Cl(1)	170.4(6)	Cl(1)-Re(1)-Re(1)	145.06(8)
C(2)-Re(1)-Cl(11)	173.5(5)	Cl(11)-Re(1)-Re(1)'	58.91(11)
C(11)-Re(1)-Cl(11)	100.7(6)	P(2)-Re(1)-Re(1)'	95.00(4)
Cl(1)-Re(1)-Cl(11)	88.08(12)	Cl(11)-Re(1)'-Re(1)	57.51(9)
C(11)-Re(1)'-Cl(11)	121.4(6)	Cl(2)-Re(1)'-Re(1)	141.41(11)
C(11)-Re(1)-Cl(1)	82.7(7)	P(1)-Re(1)-Re(1)'	95.13(5)
C(11)-Re(1)'-Cl(2)	155.4(7)	Re(1)-Cl(11)-Re(1)'	63.58(11)
Cl(1)-Re(1)'-Cl(2)	73.53(14)	Re(1)-C(11)-Re(1)'	74.2(7)
Cl(11)-Re(1)'-Cl(2)	83.03(16)	O(2)-C(2)-Re(1)	179.4(17)
P(2)-Re(1)-P(1)	169.10(6)	O(11)-C(11)-Re(1)'	159.8(18)
C(11)-Re(1)'-Re(1)	62.6(7)	O(11)-C(11)-Re(1)	125.0(17)

^a Numbers in parentheses are e.s.d.s in the least significant digits.

Table 4

Important bond distances (Å) and angles (°) for the complex $[Re_2Cl_3(\mu\text{-}dppE)_2(CO)_2(CNXyl)]O_3SCF_3\cdot 1.533CH_2Cl_2$ (4) a

$Re(1)-Re(2) \\ Re(1)-C(100) \\ Re(1)-C(12) \\ Re(1)-C(1) \\ Re(1)-P(1) \\ Re(1)-P(1) \\ Re(2)-C(201) \\ Re(2)-C(201) \\ Re(2)-C(12) \\ C(100)-Re(1)-C(12) \\ C(100)-Re(1)-C(1) \\ C(10)-Re(1)-C(1) \\ C(10)-Re(1)-P(3) \\ C(12)-Re(1)-P(3) \\ C(10)-Re(1)-P(3) \\ C(10)-Re(1)-P(1) \\ C(10)-Re(1)-P(1) \\ C(12)-Re(1)-P(1) \\ C(12)-Re(1)-P(1) \\ C(12)-Re(1)-C(12) \\ C(10)-Re(1)-C(12) \\ C(10)-Re(1)-C(12) \\ C(10)-Re(1)-C(12) \\ P(3)-Re(1)-C(12) \\ P(3)-Re(1)-C(12) \\ P(3)-Re(1)-C(12) \\ P(1)-Re(1)-C(12) \\ C(10)-Re(1)-Re(2) \\ C(12)-Re(1)-Re(2) \\ C(12)-Re(1)-Re(2) \\ P(3)-Re(1)-Re(2) \\ P(3)-Re(1)-Re(1)-Re(2) \\ P(3)-Re(1)-Re(1)-Re(1) \\ P(3)-Re(1)-Re(1) \\ P(3)-Re(1)-Re(1) \\ P(3)-Re(1)-Re(1$	$\begin{array}{c} 2.5767(5)\\ 2.013(11)\\ 2.033(11)\\ 2.417(2)\\ 2.475(3)\\ 2.475(3)\\ 2.475(3)\\ 2.477(3)\\ 2.484(2)\\ 1.910(10)\\ 2.114(10)\\ 76.1(4)\\ 82.1(3)\\ 158.2(3)\\ 87.6(3)\\ 93.0(3)\\ 85.29(9)\\ 85.2(3)\\ 93.0(3)\\ 85.29(9)\\ 85.2(3)\\ 93.0(3)\\ 85.29(9)\\ 85.2(3)\\ 93.0(3)\\ 85.29(9)\\ 85.2(3)\\ 93.0(3)\\ 85.29(9)\\ 85.2(3)\\ 93.0(3)\\ 85.29(9)\\ 85.2(3)\\ 93.0(3)\\ 85.29(9)\\ 85.2(3)\\ 93.0(3)\\ 85.29(9)\\ 85.2(3)\\ 93.0(3)\\ 112.2(3)\\ 90.54(8)\\ 92.19(8)\\ 93.57(9)\\ 129.0(3)\\ 53.0(3)\\ 148.77(7)\\ 96.44(6)\\ 91.2000000000000000000000000000000000000$	$\begin{array}{l} Re(2)-Cl(2)\\ Re(2)-P(4)\\ Re(2)-P(4)\\ Re(2)-P(2)\\ O(12)-C(12)\\ O(202)-C(201)\\ N(100)-C(100)\\ C(1)-C(2)\\ C(3)-C(4)\\ \hline\\ C(12)-Re(2)-Cl(12)\\ C(20)-Re(2)-P(4)\\ C(12)-Re(2)-P(4)\\ Cl(2)-Re(2)-P(4)\\ Cl(2)-Re(2)-P(4)\\ Cl(2)-Re(2)-P(4)\\ C(12)-Re(2)-P(4)\\ C(12)-Re(2)-P(2)\\ C(12)-Re(2)-P(2)\\ C(12)-Re(2)-P(2)\\ C(12)-Re(2)-P(2)\\ C(12)-Re(2)-P(2)\\ C(12)-Re(2)-P(2)\\ C(12)-Re(2)-P(2)\\ C(12)-Re(2)-Re(1)\\ C(12)-Re(2)-Re(1)\\ C(12)-Re(2)-Re(1)\\ C(12)-Re(2)-Re(1)\\ C(12)-Re(2)-Re(1)\\ C(12)-Re(2)-Re(1)\\ P(4)-Re(2)-Re(1)\\ P(4)-Re(2)-Re(1)\\ P(2)-Re(2)-Re(1)\\ Re(2)-Cl(12)-Re(1)\\ Re(1)-C(12)-Re(2)\\ \end{array}$	$\begin{array}{c} 2.417(3)\\ 2.465(2)\\ 2.488(3)\\ 2.496(3)\\ 1.176(11)\\ 1.135(11)\\ 1.151(12)\\ 1.314(13)\\ 1.331(13)\\ 109.1(3)\\ 93.39(9)\\ 89.6(3)\\ 94.7(3)\\ 84.40(9)\\ 88.82(8)\\ 90.5(3)\\ 90.5($
P(1)-Re(1)-Cl(12) C(100)-Re(1)-Re(2) C(12)-Re(1)-Re(2) C(12)-Re(1)-Re(2)	93.57(9) 129.0(3) 53.0(3)	C(12)-Re(2)-Re(1) P(4)-Re(2)-Re(1) P(2)-Re(2)-Re(1) P(2)-Re(2)-Re(1) P(2)-Re(2)-Re(1)	58.98(6) 95.01(6) 94.55(6)
P(3)-Re(1)-Re(2) P(1)-Re(1)-Re(2) Cl(12)-Re(1)-Re(2) C(201)-Re(2)-Cl(2) C(201)-Re(2)-Cl(2) C(12)-Re(2)-Cl(2) C(12)-Re(1)-Re(2)-Cl(2) C(12)-Re(2)-Cl(2) C(12)-Re(2)-Re(2)-Cl(2) C(12)-Re(2)-	96.44(6) 96.45(6) 58.27(5) 71.9(4) 85.5(3) 157.4(3)	Re(1)-C(12)-Re(1) Re(1)-C(12)-Re(2) O(12)-C(12)-Re(1) O(12)-C(12)-Re(2) O(202)-C(201)-Re(2) N(100)-C(10)-Re(1) C(100)-N(100)-C(101)	76.8(4) 143.1(8) 140.0(9) 178.6(9) 179.5(10) 169.9(10)
C(201)–Re(2)–Cl(12)	178.1(3)		

^a Numbers in parentheses are estimated S.D.s in the least significant digits.

Re₂Cl₄(µ-dppE)₂(CO)₂

$$\xrightarrow[XyINC]{\text{HO}_3\text{SCF}_3} [\text{Re}_2\text{Cl}_3(\mu\text{-dppE})_2(\text{CO})_2(\text{CNXyl})]O_3\text{SCF}_3 \quad (3)$$

 $Re_2Cl_4(\mu$ -dppE)₂(CO)₂

 $\xrightarrow{\text{TIO}_3\text{SCF}_3}_{2,5\text{-Me}_2\text{C}_6\text{H}_3\text{CN}} [\text{Re}_2\text{Cl}_3(\mu\text{-dppE})_2(\text{CO})_2(\text{NCC}_6\text{H}_3\text{-}2,5\text{-Me}_2)]$

$$O_3SCF_3$$
 (4)

The reaction of $\text{Re}_2\text{Cl}_4(\mu\text{-dppE})_2$ with CO proceeds through the intermediacy of $\text{Re}_2\text{Cl}_4(\mu\text{-dppE})_2(\text{CO})$ to afford the edge-sharing bioctahedral complex $\text{Re}_2\text{Cl}_4(\mu\text{-dppE})_2(\text{CO})_2$ (2), which shows a close structural relationship to $\text{Re}_2\text{Cl}_4(\mu\text{-dppm})_2(\text{CO})_2$ [24]. The IR spectrum of 2 (KBr pellet) shows $\nu(\text{CO})_t$ and $\nu(\text{CO})_b$ modes at 1953(vs) and 1736(m) cm⁻¹, respectively, while the presence of a singlet at δ + 9.0 in the ³¹P{¹H} NMR spectrum and an apparent pentet at δ + 6.21 for the bridgehead >C=CH₂ group in the ¹H NMR spectrum (spectra recorded in CD₂Cl₂ at 25°C) accords with this molecule being fluxional, as is the case for Re₂Cl₄(μ -dppm)₂(CO)₂ [24]. Further confirmation of the close relationship between **2** and Re₂Cl₄(μ -dppm)₂(CO)₂ is the similarity between their CV properties, which for solutions of **2** in 0.1 M n-Bu₄NPF₆-CH₂Cl₂ consists of a one-electron oxidation at $E_{1/2} =$ + 1.01 V ($E_p = 60$ mV) and a one-electron reduction at $E_{1/2} =$ - 0.58V ($E_p = 65$ mV) versus Ag/AgCl.

The crystal structure of 2 was solved using a disorder model in which the bridging and terminal CO ligands are disordered with two of the Cl ligands through a crystallographic inversion center. In this model the terminal CO ligand (C(2)O(2)) is disordered only with atom Cl(2) and not Cl(1), while the bridging CO ligand (C(11)O(11)) is disordered with Cl(11). A disorder was also encountered in solving the structure of $\text{Re}_2\text{Cl}_4(\mu$ $dppm)_2(CO)_2$, but in this case it involved all four equatorial terminal metal-ligand sites as well as a disorder between the two bridging ligands [24]. The ORTEP representation [23] of the structure of 2 in Fig. 2 shows one half of the disorder, in which we assume the CO ligands are cis to one another. This is substantiated by the structure of the xylyl isocyanide complex 4 (vide infra), which is a derivative of 2. Important structural parameters are given in Table 3. The structure of 2 shows that the bridging CO ligand is unsymmetrically bound to the two Re centers in the solid state, the Re-C distances being 1.83(3) and 2.38(2) Å (see Table 3). The Re-Re bond distance of 2.5748(5) Å is close to that reported for $\text{Re}_2\text{Cl}_4(\mu\text{-dppm})_2(\text{CO})_2$ (2.584(1) Å) [24]. The eightmembered [Re(µ-P-C-P)₂Re] ring exists in a chair conformation in accordance with the crystallographically imposed center of symmetry.

The derivatization of 2 in the presence of TlO₃SCF₃ and CO, XylNC or 2,5-Me₂– C_6H_3CN (see Eqs. (2)–(4)) affords complexes of the type [Re₂Cl₃(µ-dppE)₂- $(CO)_2(L)]O_3SCF_3$, where L = CO (3), XylNC (4) or 2,5-Me₂– C_6H_3CN (5). On the basis of the similarity of their spectroscopic and cyclic voltammetric properties, and a crystal structure determination of 4, these complexes are assigned an all-cis structure of the type $[(CO)ClRe(\mu-Cl)(\mu-CO)(\mu-dppE)_2ReCl(L)]^+$, with the two CO ligands and ligand L being cis to one another on one side of the molecule. The ORTEP representation [23] of 4 is given in Fig. 3 and important structural parameters are listed in Table 4. The Re-Re distance of 2.5767(5) Å is essentially identical to that of 2(2.5748(5) Å). While the dppm complex, which is analogous to 4, has been isolated [25], it has not yet been crystallographically characterized. However, strucdeterminations ture on $[\text{Re}_2\text{Cl}_3(\mu\text{-dppm})_2(\text{CO})_2\text{-}$ (NCEt)]PF₆ [26] and [Re₂Cl₃(µ-dppm)₂(CO)₃]PF₆ [27] reveal the same type of structure as that for 4 (Fig. 3), with Re-Re distances of 2.586(1) and 2.582(1) Å, respectively.

Complexes 3–5 show an intense band for the triflate anion at ca. 1270 cm⁻¹ in their IR spectra (KBr pellets), along with characteristic v(CO) and v(CN)modes for the CO, XyINC and 2,5-Me₂–C₆H₃CN ligands; for 3 at 2014(vs), 1897(m), and 1717(m-s) cm⁻¹, for 4 at 2156(vs), 2005(vs) and 1719(m) cm⁻¹, and for 5 at 2258(w), 1995(vs), ~1940sh, and 1719(m) cm⁻¹. The bands at 2156 and 2258 cm⁻¹ in the IR spectra of 4 and 5, respectively, are assigned to v(CN) modes, while the $v(CO)_b$ mode for each of the three complexes is at approximately 1720 cm⁻¹.

The symmetrical nature of **3** is shown by a singlet at δ +9.9 in the ³¹P{¹H} NMR spectrum (recorded in CD₂Cl₂), while the related spectra of **4** and **5** are

Table 5

Important bond distances (Å) and angles (°) for the complex 'trans-Re₂(μ -O₂CCH₃)₂Cl₂(μ -dppE)₂·MeOH (6) ^a

Re(1)-Re(2)	2.2861(6)	Re(2)-Cl(2)	2.634(3)
Re(1)-O(1)	2.122(5)	O(1)–C(1)	1.287(8)
Re(1) - P(2)	2.439(2)	O(2)–C(1)	1.253(8)
Re(1)-Cl(1)	2.608(3)	C(1)–C(2)	1.481(10)
Re(2)-O(2)	2.128(5)	C(11)-C(12)	1.356(10)
Re(2)–P(1)	2.431(2)		
O(1)-Re(1)-O(1)'	179.4(3)	O(2)-Re(2)-O(2)'	176.4(3)
O(1)-Re(1)-Re(2)	89.70(14)	O(2)-Re(2)-Re(1)	88.20(13)
O(1)-Re(1)-P(2)	87.30(15)	O(2)-Re(2)-P(1)	89.53(16)
O(1)' - Re(1) - P(2)	92.76(15)	Re(1)-Re(2)-P(1)	101.67(5)
Re(2)-Re(1)-P(2)	95.65(5)	O(2)'-Re(2)-P(1)	91.20(16)
P(2)-Re(1)-P(2)'	168.71(10)	P(1)-Re(2)-P(1)'	156.66(10)
O(1)-Re(1)-Cl(1)	90.30(14)	O(2)-Re(2)-Cl(2)	91.80(13)
Re(2)-Re(1)-Cl(1)	180.00(14)	Re(1)-Re(2)-Cl(2)	180.00(13)
P(2)-Re(1)-Cl(1)	84.35(5)	P(1)-Re(2)-Cl(2)	78.33(5)

^a Numbers in parentheses are estimated standard deviations in the least significant digits. Primed atoms are related to the unprimed ones by a twofold rotation axis Cl(1)-Re(2)-Cl(2).



Fig. 1. ORTEP [23] representation of the structure of the molecule of $\text{Re}_2\text{Cl}_4(\mu\text{-}dppE)_2$ as present in 1. The thermal ellipsoids are drawn at the 50% probability level except for the phenyl group atoms of the dppE ligands which are circles of arbitrary radius.



Fig. 2. ORTEP [23] representation of the structure of the molecule of $\text{Re}_2\text{Cl}_4(\mu\text{-}dpp\text{E})_2(\text{CO})_2$ as present in **2**. This representation shows half of the disorder involving the CO and Cl ligands which are related by a center of symmetry at the mid-point of the Re-Re bond. The unlabeled atoms are related to the labeled ones by the center of symmetry. The unlabeled Re atom is designated as Re(1)' in Table 3. The thermal ellipsoids are drawn at the 50% probability level except for the phenyl group atoms of the dppE ligands which are circles of arbitrary radius.

AA'BB' patterns with the centers of the two complex multiplets being at δ + 12.7 and δ + 3.6 (for 4), and δ + 13.5 and δ + 1.2 (for 5). The CVs of 3–5 (recorded in 0.1 M n-Bu₄NPF₆-CH₂Cl₂) are very similar, each showing two reversible one-electron reductions, with $E_{1/2}$ values of + 0.22/ - 0.80, -0.01/ - 0.96 and - 0.13/ - 1.11 V versus Ag/AgCl for 3, 4 and 5, respectively; the values of $E_{\rm p}$ (i.e. $E_{\rm p,a} - E_{\rm p,c}$) for each of the



Fig. 3. ORTEP [23] representation of the structure of the dirhenium cation $[\text{Re}_2\text{Cl}_3(\mu\text{-dppE})_2(\text{CO})_2(\text{CNXyl})]^+$ present in the structure of **4**. The thermal ellipsoids are drawn at the 50% probability level except for the phenyl group atoms of the dppE ligands and the xylyl group atoms of the XylNC ligand which are circles of arbitrary radius.



Fig. 4. ORTEP [23] representation of the structure of the molecule of *trans*-Re₂(μ -O₂CCH₃)₂Cl₂(μ -dppE)₂ as present in **6**. The thermal ellipsoids are drawn at the 50% probability level except for the phenyl group atoms of the dppE ligands which are circles of arbitrary radius. The unlabeled atoms are related to the labeled ones by a twofold rotational axis which contains atoms Re(1), Re(2), Cl(1) and Cl(2). In Table 5 they are labeled with a prime.

processes are in the range 60-70 mV. These data resemble those reported previously for dppm complexes of these types [25–27].

3.3. Isolation and characterization of trans- $Re_2(\mu - O_2CCH_3)_2Cl_2(\mu - dppE)_2$

We have previously shown that the *cis* and *trans* isomers of the dirhenium(II) complexes $Re_2(\mu-O_2CCH_3)_2$ - $Cl_2(\mu$ -dppm)₂ and $Re_2(\mu$ -O₂CCH₃)₂Cl₂(μ -dppa)₂ can be prepared through the reactions of $\text{Re}_2\text{Cl}_4(\mu\text{-dppm})_2$ with [(Ph₃P)₂N]O₂CCH₃, and of cis-Re₂(O₂CCH₃)₂-Cl₄(H₂O)₂ or Re₂(O₂CCH₃)₄Cl₂ with dppm or dppa [11,28]. In the present study we have used the reaction between $\text{Re}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}_2$ and dppE in refluxing methanol to form *trans*-Re(μ -O₂CCH₃)₂Cl₂(μ -dppE)₂ (6) and thereby further demonstrate the close relationship between dppm and dppE in their reactivity towards dirhenium complexes. Compound 6 shows a singlet at δ + 22.1 in its ³¹P{¹H} NMR spectrum (recorded in CD₂Cl₂), while its CV in 0.1 M n- $Bu_4NPF_6-CH_2Cl_2$ possesses a one-electron oxidation at $E_{1/2} = +0.97$ V versus Ag/AgCl (with $E_p = 60$ mV) and a one-electron reduction at $E_{1/2} = -0.27$ V versus Ag/ AgCl ($E_p = 60$ mV). The CV properties are characteristic of the trans isomer [11], and this was confirmed by X-ray crystallography. The ORTEP representation [23] of the structure is shown in Fig. 4 and the key structural parameters are provided in Table 5. The Re-Re distance of 2.2861(6) Å is essentially identical to the value of 2.2763(7) Å for trans-Re₂(O₂CCH₃)₂Cl₂(μ - dppm)₂ [28] and shorter by approximately 0.02 Å than the Re–Re distances for the *cis* isomers of both the dppm and dppa complexes [11].

4. Concluding remarks

In contrast to the behavior of the phosphine ligands Me₂PCH₂PMe₂ (dmpm) and Ph₂Ppy, which form the tris(bidentate phosphine) dirhenium(II) complexes $Re_2Cl_4(\mu-dmpm)_3$ [29] and $Re_2Cl_4(\mu-Ph_2Ppy)_3$ [30], the ligand $(Ph_2P)_2C=CH_2$ (dppE) gives the bis-complex $Re_2Cl_4(\mu$ -dppE)₂. This compound most closely resembles $\operatorname{Re}_2\operatorname{Cl}_4(\mu\text{-dppm})_2$ (dppm = $\operatorname{Ph}_2\operatorname{PCH}_2\operatorname{PPh}_2$) [1-3,7,8] and $\text{Re}_2\text{Cl}_4(\mu\text{-dppa})_2$ (dppa = Ph₂PNHPPh₂) [11–13] in terms of its structure and chemical reactivity. The present report serves as a prelude to a detailed comparison of the reactions of $Re_2Cl_4(\mu-dppE)_2$, $\text{Re}_2\text{Cl}_4(\mu\text{-dppm})_2$ $\text{Re}_2\text{Cl}_4(\mu\text{-dcpm})_2$ (dcpm = and Cy₂PCH₂PCy₂) with the isocyanide ligands t-BuNC and XylNC, the details of which will be communicated shortly.

5. Supplementary material

Tables giving full details for the crystal data and data collection parameters, atomic positional parameters, anisotropic thermal parameters, bond distances and bond angles for compounds 1, 2, 4 and 6 are available on request from the author (R.A.W.).

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