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Re(V)–oxo–dppf and Re(V)–imido–dppf complexes: synthesis, structure, and properties of $Re(X)Cl_3(dppf)$ ($X = O$, NPh, N-C_6H_3-2,6-i-Pr_2; dppf $= Fe(\eta^5\text{-}C_5H_4PPh_2)_2$)

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Abstract

Re(V)–imido and Re(V)–oxo complexes containing 1,1′-bis(diphenylphosphino)ferrocene ($Fe(\eta^5\text{-}C_5H_4PPh_2)_2$, dppf) were prepared from *mer,trans*-$Re(O)Cl_3(PPh_3)_2$ (**1**), *mer,trans*-$Re(NPh)Cl_3(PPh_3)_2$ (**2**), or *mer,cis*-$Re(N\text{-}C_6H_3\text{-}2,6\text{-}i\text{-}Pr_2)_2Cl_3(py)$ (**3**). Compounds **1**–**3** reacted with dppf to give *fac*-$Re(O)Cl_3(dppf)$ (**4**), *fac*-$Re(NPh)Cl_3(dppf)$ (**5**), and *mer*-$Re(N\text{-}C_6H_3\text{-}2,6\text{-}i\text{-}Pr_2)Cl_3(dppf)$ (**6**), respectively. Electrochemical studies performed on Re–oxo–dppf complexes (**4**) and Re–imido–dppf complexes (**5** and **6**) showed different redox behavior depending on the type of ligand coordinated to the Re metal. The structure of compound **4** was determined by X-ray diffraction. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Re(V)–imido complexes; Re(V)–oxo complexes; Electrochemical studies

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1. Introduction

Transition-metal–imido (or nitrene, $L_nM{=}NR$) complexes, which have a multiple bonding character between the metal and the imido ligand, have attracted continuous interest [1–8]. Transition-metal–oxide (M=O) complexes have frequently been used to prepare the imido complexes by reactions with primary amines (RNH_2) or organic isocyanates (RNCO) (Eqs. (1) and (2)) [6].

$$L_nM{=}O + RNH_2 \rightarrow L_nM{=}NR + H_2O \qquad (1)$$

$$L_nM{=}O + RNCO \rightarrow L_nM{=}NR + CO_2 \qquad (2)$$

We are interested in Re–imido complexes (Re=NR). For instance, we recently prepared several Re–imido complexes of the type $Re(NAr)(PR_3)_2Cl_3$ ($PR_3 = PMe_3$, PEt_3, $P(OMe)_3$; $Ar = C_6H_5$, 2,6-i-Pr_2-C_6H_3) from the reactions of $Re(N\text{-}C_6H_3\text{-}2,6\text{-}i\text{-}Pr_2)_2Cl_3(py)$ with small phosphines or phosphites [9].

Various redox-active ligands have been reported to control the reactivities of transition-metal complexes [10]. The dppf (1,1′-bis(diphenylphosphino)ferrocene) ligand is a well known redox-active ligand, and its complexes are expected to exhibit a ferrocene-centered oxidation process, together with additional redox processes at other metal centers in the molecule. Because there have been no reports on high-oxidation-state Re-oxo and Re–imido complexes containing the dppf ligand, we set out to prepare Re–oxo–dppf and Re–imido–dppf complexes. Herein we report the preparation and some properties of *fac*-$Re(O)Cl_3(dppf)$ (**4**), *fac*-$Re(NPh)Cl_3(dppf)$ (**5**), and *mer*-$Re(N\text{-}C_6H_3\text{-}2,6\text{-}i\text{-}Pr_2)Cl_3(dppf)$ (**6**), including the structure of compound **4**.

2. Experimental

Unless otherwise stated, all reactions have been performed with standard Schlenk line and cannula techniques under argon. Air-sensitive solids were manipulated in a glove box filled with argon. Glassware was soaked in KOH-saturated 2-propanol for ca. 24 h and washed with distilled water and acetone before use.

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Glassware was either flame or oven dried. Hydrocarbon solvents were stirred over concentrated H_2SO_4 for ca. 48 h, neutralized with K_2CO_3, stirred over sodium metal, and distilled by vacuum transfer. Tetrahydrofuran (THF) was stirred over sodium metal and distilled by vacuum transfer. Benzene and diethyl ether were distilled over sodium metal under argon. Dichloromethane was stirred over CaH_2 and distilled by vacuum transfer. NMR solvent ($CDCl_3$) was degassed by freeze-pump-thaw cycles before use and stored over molecular sieves under argon. Re metal, rhenium(VII) oxide (Re_2O_7), triphenylphosphine (PPh_3), methyl lithium (MeLi, 1.4 M in diethyl ether), lithium ethoxide (LiOEt, 1 M in THF), methylmagnesium bromide (MeMgBr, 3 M in diethyl ether), hydrogen chloride (HCl, 1 M in diethyl ether), and *tert*-butyl isocyanate (*t*-BuNCO) were purchased from Aldrich and used as received. 2,6-Diisopropylphenyl isocyanate (2,6-*i*-Pr_2-C_6H_3NCO) was purchased from Fluka. *mer*,*trans*-Re(O)$Cl_3(PPh_3)_2$ (**1**) [11], *mer*,*trans*-Re(NPh)$Cl_3(PPh_3)_2$ (**2**) [12], PhN=PPh_3 [12], Fe(η^5-$C_5H_4PPh_2)_2$ (dppf) [13], Re(*N*-C_6H_3-2,6-*i*-$Pr_2)_2$(py)Cl_3 (**3**) [14,15], and Re(NPh)(dppe)Cl_3 (dppe = 1,2-bis-(diphenylphosphino)ethane) [16] were prepared by literature methods. The electrolyte tetrabutylammonium hexafluorophophate ([*n*-Bu_4N][PF_6]) and ferrocene ($FeCp_2$) were recrystallized from ethanol before use.

Electrochemical measurements were performed with a model 263A EG&G potentiostat. A standard three-electrode system was employed with a platinum disk as working electrode. A Pt wire was the counter electrode, and Ag wire served as a reference electrode. Measurements were carried out in CH_2Cl_2 containing 0.1 M [*n*-Bu_4N][PF_6] as a supporting electrolyte and ca. 1 mM metal complex. Instrumental *iR* compensation was applied in all measurements. The ferrocene/ferrocenium couple was 0.632 V at 300 mV s^{-1} in this cell. All the experiments were carried out under nitrogen.

^{1}H- and ^{13}C{^{1}H}-NMR spectra were recorded with a Bruker AMX 500 MHz spectrometer with reference to internal solvent resonances and are reported relative to tetramethylsilane. ^{31}P{^{1}H}-NMR spectra were also recorded with a Bruker AMX 500 MHz spectrometer with reference to 85% H_3PO_4. IR spectra were recorded with a Nicolet 205 FTIR spectrophotometer. Melting points were measured with a Thomas Hoover capillary melting point apparatus without calibration. Elemental analyses were performed by the Korea Basic Science Center.

2.1. Preparation of *fac*-Re(O)Cl_3(dppf) (4)

A mixture of yellow–green *mer*,*trans*-Re(O)$Cl_3(PPh_3)_2$ (**1**) (0.63 g, 0.756 mmol) and yellow dppf (0.63 g, 1.136 mmol) in benzene (60 ml) was stirred at room temperature (r.t.). The resulting solution became orange–brown, and deep green precipitates gradually formed during 5 min. The solution was allowed to stir for an additional 2 h at r.t. The resulting deep green solid was collected by filtration, washed with benzene (20 ml) and diethyl ether (2 × 30 ml), and then dried under vacuum to obtain 0.55 g (0.637 mmol, 84% yield) of *fac*-Re(O)Cl_3(dppf) (**4**). This product was recrystallized from CH_2Cl_2–hexane. ^{1}H-NMR ($CDCl_3$): δ 7.92 (4H, t, $J = 8.5$ Hz, phenyl), 7.75 (4H, t, $J = 8.5$ Hz, phenyl), 7.46–7.33 (12H, m, phenyl), 5.31 (2H, s, br, Cp), 4.72 (2H, s, br, Cp), 4.47 (2H, s, br, Cp), 4.43 (2H, s, br, Cp). ^{13}C{^{1}H}-NMR ($CDCl_3$): δ 135.80, 135.55, 132.04, 131.43, 129.02, 127.99 (phenyl), 81.41, 80.95, 76.96, 75.93, 74.33, 73.81 (Cp). ^{31}P{^{1}H}-NMR ($CDCl_3$): δ -26.00 (s). Anal. Calc. for $C_{34}H_{28}OP_2Cl_3FeRe$: C, 47.32; H, 3.27. Found: C, 47.34; H, 3.55%. mp (decom.): 233–235°C. IR (KBr): 3105, 3057, 1482, 1434, 1195, 1169, 1092, 1035, 967 (Re=O), 829, 743, 691, 548, 517, 491, 473, 443 cm^{-1}.

2.2. Preparation of *fac*-Re(NPh)Cl_3(dppf) (5)

A benzene solution (60 ml) containing *mer*,*trans*-ReCl_3(NPh)$(PPh_3)_2$ (**2**) (0.29 g, 0.32 mmol) and dppf (0.183 g, 0.33 mmol) was refluxed for 1 h. The resulting green precipitates were filtered off and then washed with benzene (2 × 30 ml), diethyl ether (2 × 30 ml), and pentane (1 × 30 ml), and then dried under vacuum to obtain 0.26 g (0.28 mmol, 85% yield) of *fac*-Re(NPh)Cl_3(dppf) (**5**). Recrystallization was from CH_2Cl_2–hexane to give a CH_2Cl_2-solvated product. ^{1}H-NMR ($CDCl_3$): δ 6.67–8.02 (25H, m, Ph), 5.27 (2H, s, br, Cp), 4.68 (2H, s, br, Cp), 4.64 (2H, s, br, Cp), 4.58 (2H, s, br, Cp). ^{13}C{^{1}H}-NMR ($CDCl_3$): δ 155.13 (s, Ph), 136.02 (t, $J = 4.15$ Hz, Ph), 135.69 (s, Ph), 134.79 (d, $J = 4.65$ Hz, Ph), 134.36 (s, Ph), 133.90 (s, Ph), 130.90 (d, $J = 13.58$ Hz, Ph), 129.56 (s, Ph), 129.02 (s, Ph), 128.45 (d, $J = 5.16$ Hz, Ph), 127.97 (t, $J = 5.16$ Hz, Ph), 122.50 (s, Ph), 84.62 (s, Cp), 84.15 (s, Cp), 76.84 (s, Cp), 75.49 (s, Cp), 73.72 (s, Cp), 73.20 (s, Cp). ^{31}P{^{1}H}-NMR ($CDCl_3$): δ -17.19 (s). Anal. Calc. for $C_{40}H_{33}NP_2Cl_3FeRe$: C, 51.21; H, 3.54; N, 1.49. Found: C, 51.61; H, 3.32; N, 1.28%. mp (decom.): 239–241°C. IR (KBr): 3060, 1577, 1480, 1434, 1387, 1309, 1192, 1163, 1091, 1031, 995, 832, 750, 693, 634, 547, 512, 492, 473, 445 cm^{-1}.

2.3. Preparation of *mer*-Re(*N*-C_6H_3-2,6-*i*-Pr_2)Cl_3(dppf) (6)

An opaque green solution of *mer*,*cis*-Re(*N*-C_6H_3-2,6-*i*-$Pr_2)_2$(py)Cl_3 (**3**) (0.25 g, 0.346 mmol) and dppf (0.38 g, 0.685 mmol) in CH_2Cl_2 (30 ml) was stirred for 48 h at r.t. The solution gradually became transparent red–brown. The solvent was removed under vacuum to give a red–brown residue, which was extracted with benzene

Table 1
X-ray data collection and structure refinement for **4**

Formula	$C_{34}H_{28}OP_2Cl_3FeRe$
Fw	862.90
Temperature (K)	297(2)
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Unit cell dimensions	
a (Å)	11.519(1)
b (Å)	15.834(4)
c (Å)	17.460(2)
V (Å^3)	3184.5(9)
Z	4
D_{calc} (g cm^{-3})	1.800
μ (mm^{-1})	4.633
T_{min}	0.0748
T_{max}	0.5230
F(000)	1688
R_{int}	0.0934
Reflections measured	3227
Unique reflections	3208
Reflections with $I > 2\sigma(I)$	3120
Parameters refined	380
2θ range (°)	3.5–51.0
Scan type	ω
Scan speed	Variable
GOF (goodness-of-fit on F^2)	1.033
Maximum, minimum in $\Delta\rho$ (e Å^{-3})	1.613, −1.484
R	0.0369
wR_2 [a]	0.0969

[a] $wR_2 = \Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]^{1/2}$.

(40 ml). The solvent (benzene) was removed under vacuum to a give a yellow–brown solid. The resulting solid was washed with diethyl ether (3 × 20 ml) and pentane (1 × 20 ml), and then dried under vacuum to obtain 0.11 g (31% yield) of *mer*-Re(N-C_6H_3-2,6-*i*-Pr_2)Cl_3(dppf) (**6**). ^{1}H-NMR ($CDCl_3$): δ 8.00–6.88 (23H, m, phenyl), 4.98 (2H, s, br, Cp), 4.75 (2H, s, br, Cp), 4.33 (2H, s, br, Cp), 4.31 (2H, s, br, Cp), 3.78 (2H, sept, $^3J_{H-H} = 6.5$ Hz, C*H*Me$_2$), 1.09 (6H, d, $^3J_{H-H} = 6.5$ Hz, CH*Me*$_2$), 0.40 (6H, d, $^3J_{H-H} = 6.5$ Hz, CH*Me*$_2$). ^{13}C{^{1}H}-NMR ($CDCl_3$): δ 155.69–124.98 (phenyl), 76.52–69.55 (Cp), 28.78 (*C*HMe$_2$), 26.48 (*C*HMe$_2$), 23.05 (CH*Me*$_2$). ^{31}P{^{1}H}-NMR ($CDCl_3$): δ 40.05 (1P, s), −32.69 (1P, s). Anal. Calc. for $C_{46}H_{45}NP_2Cl_3FeRe$: C, 54.05; H, 4.44; N, 1.37. Found: C, 54.16; H, 4.52; N, 0.97%. mp (decom.): 219–221°C. IR (KBr): 3054, 2961, 2924, 2864, 1479, 1463, 1435, 1385, 1364, 1310, 1143, 1093, 1031, 1000, 751, 726, 696, 565, 531, 496 cm^{-1}.

2.4. X-ray structure determination of 4

All X-ray data were collected using a Siemens P4 diffractometer equipped with a Mo X-ray tube and a graphite-crystal monochromator. Details on crystal data and intensity data are given in Table 1. The orientation matrix and unit-cell parameters were determined by least-squares analyses of the setting angles of 37 for compound **4** in the range $15.0 < 2\theta < 25.0°$. Three check-reflections were measured every 100 reflections throughout data collection and showed no significant variations in intensity. Intensity data were corrected for Lorenz and polarization effects. Decay corrections were also made. The intensity data were empirically corrected with ψ-scan data. All calculations were carried out with use of the SHELXTL programs [17].

A green crystal of **4** of approximate dimensions $0.80 \times 0.68 \times 0.60$ mm^3, shaped as a block, was used for crystal and intensity data collection. The unit-cell parameters and systematic absences, $h00$ ($h = 2n + 1$), $0k0$ ($k = 2n + 1$), and $00l$ ($l = 2n + 1$), unambiguously indicated $P2_12_12_1$ as a space group. The structure was solved by the direct method. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were generated in idealized positions and refined in a riding model. Selected bond distances and bond angles are shown in Table 2.

Table 2
Selected bond distances (Å) and bond angles (°) in **4**

Re1–O1	1.719(7)	Re1–Cl1	2.349(3)	Re1–Cl2	2.385(3)
Re1–Cl3	2.373(3)	Re1–P1	2.496(3)	Re1–P2	2.491(2)
Fe1–C1	2.01(1)	Fe1–C2	2.05(1)	Fe1–C3	2.06(1)
Fe1–C4	2.05(1)	Fe1–C5	2.03(1)	Fe1–C6	2.01(1)
Fe1–C7	2.04(1)	Fe1–C8	2.08(1)	Fe1–C9	2.05(1)
Fe1–C10	2.03(1)	P1–C1	1.798(11)	P2–C6	1.791(9)
O1–Re1–Cl1	103.2(3)	O1–Re1–Cl3	163.9(3)		
Cl1–Re1–Cl3	90.8(1)	O1–Re1–Cl2	98.9(2)		
Cl1–Re1–Cl2	85.4(1)	Cl3–Re1–Cl2	89.9(1)		
O1–Re1–P2	88.9(2)	Cl1–Re1–P2	80.9(1)		
Cl3–Re1–P2	85.56(9)	Cl2–Re1–P2	165.5(1)		
O1–Re1–P1	85.3(2)	Cl1–Re1–P1	170.7(1)		
Cl3–Re1–P1	81.2(1)	Cl2–Re1–P1	89.8(1)		
P2–Re1–P1	103.01(8)	P1–C1–Fe1	132.9(6)		
P2–C6–Fe1	128.7(5)				

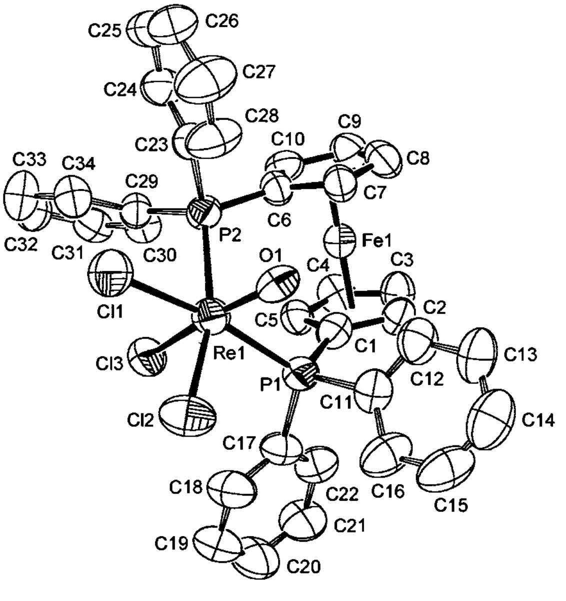
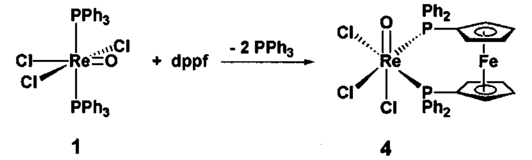


Fig. 1. ORTEP drawing of **4**, showing the atom-labeling scheme and 50% probability thermal ellipsoids.

3. Results and discussion

3.1. Preparation

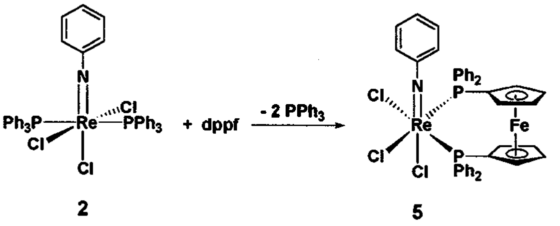
Compound **1** reacts with dppf in benzene at room temperature to give a Re–oxo–dppf compound, *fac*-Re(O)Cl_3(dppf) (**4**), in 84% yield (Eq. (3)). Compound **4** is air- and moisture-stable both in solution and in the solid state, and it is slightly soluble in dichloromethane, tetrahydrofuran, and acetone. The two monodentate PPh_3 ligands have been replaced by the bidentate dppf ligand during the reaction.



(3)

Compound **4** is a bimetallic complex that contains Re and Fe metals. The orientation of three chloro ligands has been changed from *meridional* (in **1**) to *facial* (in **4**) during the reaction. $^{31}P\{^1H\}$-NMR spectra of **4** exhibit a singlet at δ −26.00 ppm, which indicates *cis*-orientated phosphorus nuclei of the dppf ligand to be equivalent. In ^1H-NMR spectra of the free dppf, the cyclopentadienyl (Cp) protons show two triplets at δ 4.25 and 3.98 ppm. However, upon coordination of this ligand to the Re metal in **4**, these signals are split into the four broad singlets at δ 5.31, 4.72, 4.47, and 4.43 ppm, consistent with the lowered molecular symmetry. The strong IR band at 967 cm^{-1}, assigned to the Re=O bond, is consistent with those found for mononuclear terminal monooxo Re complexes [5].

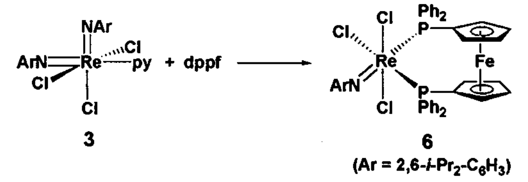
Compound **2** reacts with dppf in refluxing benzene for 1 h to give a Re–imido–dppf compound, *fac*-Re(NPh)Cl_3(dppf) (**5**) (Eq. (4)), which is air- and moisture-stable both in solution and in the solid state and is slightly soluble in dichloromethane. Compound **5** is also a bimetallic (Re–Fe) complex containing three *facial* chloro ligands. As expected, compound **5** exhibits a singlet at δ −17.19 ppm in its $^{31}P\{^1H\}$-NMR spectra and four broad singlets (Cp protons) at δ 5.27, 4.68, 4.64, and 4.58 ppm in its ^1H-NMR spectra.



(4)

Compound *mer,cis*-Re(N-C_6H_3-2,6-i-Pr_2)$_2$(py)Cl_3 (**3**) reacts with the dppf ligand in benzene at room temperature to give a Re–imido–dppf compound, *mer*-Re(N-C_6H_3-2,6-i-Pr_2)Cl_3(dppf) (**6**), in 31% yield (Eq. (5)). In this reaction, the Re metal has been formally reduced from +7 to +5. It is worth noting that one of the strongly bound aryl imido ligands (N-C_6H_3-2,6-i-Pr_2) has been replaced during the reaction. Unfortunately, we cannot give an explanation for the unusual stoichiometry and reactivities (the imido group abstraction and the Re metal reduction). However, these phenomena have been previously observed in the reaction between compound **3** and trimethylphosphine (PMe_3) that gives *mer,trans*-Re(N-C_6H_3-2,6-i-Pr_2)(PMe_3)$_2Cl_3$ [9].

$^{31}P\{^1H\}$-NMR spectra of **6** exhibit two singlets at δ 40.05 and −32.69 ppm, which clearly indicates the phosphorus nuclei of the dppf ligand to be inequivalent. The only structure that can explain these spectra is the one shown in Eq. (5), in which one phosphorus atom is *trans* to the chloro ligand and the other to the imido ligand. As is the case for **4** and **5**, the Cp protons in **6** appear separately as four broad singlets at δ 4.98, 4.75, 4.33, and 4.31 ppm.



(Ar = 2,6-i-Pr_2-C_6H_3)

(5)

3.2. Structure of **4**

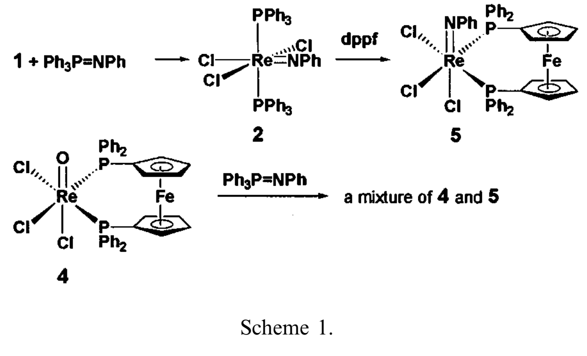
The molecular structure of **4** with the atom-numbering scheme is shown in Fig. 1. The molecular structure of **5** has recently been reported by our group [18]. Compound **4** has three *fac*-chloro ligands, one oxo ligand, and one bidentate dppf ligand. The coordination sphere of the Re metal can be described as a distorted octahedron. The equatorial plane, defined by Cl1, Cl2, P1, and P2, is relatively planar with an average atomic displacement of 0.0256 Å. The Re metal lies above the equatorial plane by 0.147(2) Å.

The bond distance (1.719(7) Å) of Re–O1 is fairly typical of the oxo ligand in a monoxo Re (d^2) complex in a +5 oxidation state, in which the Re–O bond distance ranges from 1.63(7) to 1.76(1) Å [3]. Nugent and Mayer have suggested that monoxo complexes are best thought of as having a triple bond, *cis*-dioxo complexes a bond order of 2.5, and *trans*-dioxo and *fac*-trioxo complexes a bond order of 2 [5]. Therefore, the Re–O1 bond seems to be a Re≡O triple bond, and the oxo ligand can be regarded as a six-electron donor. On the basis of these arguments, **4** can be regarded as an 18-electron complex.

The two Cp rings are not perfectly parallel but are twisted from each other with a dihedral angle of 3.2(9)°. The torsion angle of P1–C7–C12–P2 is 26.9(5)°, indicating that the two Cp rings adopt a gauche (or staggered) conformation. For comparison, the ideal torsion angle for the gauche conformation is 36°. The Fe–Ct (Ct: a centroid of the Cp ring) distances are 1.647 and 1.649 Å, and the angle Ct1–Fe–Ct2 (Ct1: C1–C5; Ct2: C6–C10) is 178.28°. The bite angle P1···Fe···P2 is 68.64(6)°, and the distance P1···P2 is 3.903(4) Å. The above bonding parameters within a ferrocene moiety are consistent with those found in octahedral rhenium complexes in which the dppf group acts as a ligand [10]. The distance Re···Fe is 4.391(2) Å, which clearly rules out direct bonding interaction between the two metals.

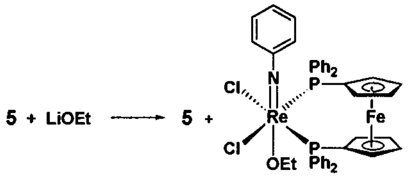
3.3. Properties

Compound **1** is known to react with PhN=PPh$_3$ to give *mer*-Re(NPh)Cl$_3$(PPh$_3$)$_2$ (**2**) [12], which has been treated with dppf to give *fac*-Re(NPh)Cl$_3$(dppf) (**5**) in our study (Scheme 1). As shown in Eq. (3), compound **1** reacts with dppf to give *fac*-Re(O)Cl$_3$(dppf) (**4**). Compound **4** was treated with PhN=PPh$_3$ in refluxing benzene for 2 h in order to check whether compound **5** can be prepared directly from compound **4**. This reaction gives a mixture of **4** (63%) and **5** (37%), as shown in Scheme 1. When the reaction time is increased, the ratio of **4** to **5** becomes 22:78 (6 h) and 13:87 (24 h), respectively. However, the reaction never goes to completion even after extremely long reaction times (120 h). The attempt to separate **4** and **5** was not successful because of their similar solubility in various organic solvents. This reaction was monitored by $^{31}P\{^1H\}$-NMR spectroscopy which exhibits two singlets with different intensities corresponding to **4** and **5**. Compound **4** was treated with organic isocyanates such as *t*-BuNCO and 2,6-*i*-Pr$_2$-C$_6$H$_3$NCO in order to prepare its imido analogs, but no sign of reaction was observed even under vigorous conditions (refluxing THF or benzene).



Scheme 1.

When **4** and **5** are treated with MeLi, we can only isolate the free dppf ligand. In addition, they react with MeMgBr to give too many intractable species. Surprisingly, compound **5** is robust toward HCl and H$_2$O; in other words, they do not decompose in their presence. Compound **5** reacts with an oxygen nucleophile (LiOEt) under refluxing ethanol for 3 h to give a mixture of **5** (26%) and Re(NPh)(OEt)Cl$_2$(dppf) (74%). In $^{31}P\{^1H\}$-NMR spectra of this mixture, phosphorous nuclei of Re(NPh)(OEt)Cl$_2$(dppf) exhibit a singlet at δ −8.81 ppm, indicating the phosphorous nuclei of the dppf ligand to be equivalent. The only structure that can explain these $^{31}P\{^1H\}$-NMR spectra is the one shown in Eq. (6), in which the ethoxy ligand is *trans* to the imido ligand. In ^1H-NMR spectra, the OEt protons in *fac*,*trans*-Re(NPh)(OEt)Cl$_2$(dppf) exhibit a quartet at δ 3.95 (CH$_2$, $^3J_{H-H} = 7$ Hz) ppm and a triplet at δ 0.94 (CH$_3$, $^3J_{H-H} = 7$ Hz) ppm.



(6)

As shown in Table 3 and Fig. 2, compound **4** containing the Re–oxo fragment exhibits one reversible oxidation, and compounds **5** and **6** containing the Re–imido fragment exhibit two reversible oxidations. The free dppf ligand in dichloromethane exhibits one irreversible, ferrocene-centered oxidation [19]. Compound Re(NPh)(dppe)Cl$_3$, which has a chelating bisphosphine ligand (dppe = bis(diphenylphosphino)ethane) instead of the dppf ligand, exhibits one re-

Table 3
Electrochemical data from cyclic voltammetry studies

Compound	Scan rate (mV s^{-1})	$E°$ (V)	I_{pc}/I_{pa}	E_{pa} (V)	E_{pc} (V)
4	100	1.223	0.933	1.274	1.173
	200	1.222	0.908	1.276	1.168
	300	1.217	0.877	1.272	1.163
	500	1.220	1.035	1.28	1.158
	1000	1.225	1.073	1.296	1.153
5	100	0.871	0.91	0.924	0.818
		1.423	1.063	1.476	1.370
	200	0.891	0.937	0.949	0.834
		1.445	1.031	1.505	1.384
	300	0.876	0.953	0.939	0.812
		1.434	0.973	1.498	1.370
	500	0.883	0.989	0.952	0.815
		1.442	1.016	1.514	1.370
	1000	0.880	0.988	0.968	0.792
		1.447	1.091	1.533	1.361
6	100	0.655	0.936	0.705	0.605
		1.224	0.935	1.280	1.167
	200	0.653	0.956	0.705	0.600
		1.217	0.956	1.276	1.158
	300	0.649	0.965	0.705	0.593
		1.219	0.982	1.280	1.158
	500	0.649	0.933	0.708	0.590
		1.219	1.023	1.286	1.151
	1000	0.649	0.913	0.718	0.580
		1.220	1.045	1.295	1.145
Re(NPh)(dppe)Cl_3	100	1.261	1.043	1.308	1.214
	200	1.259	1.036	1.308	1.211
	300	1.263	1.073	1.314	1.211
	500	1.261	1.046	1.317	1.204
	1000	1.263	1.012	1.327	1.198

versible oxidation wave at 1.263 V at the scan rate of 300 mV s^{-1} (Fig. 3). The oxidation potential of Re(NPh)(dppe)Cl_3 is included to show that the Re–imido center is not oxidized at potentials where the ferrocene-centered oxidation occurs. On the basis of the oxidation potential values of the free dppf and Re(NPh)(dppe)Cl_3, the second oxidation in the oxidation of compounds **5** and **6** probably results from the presence of the Re–imido fragment. Therefore, it can be inferred that the coordinated dppf ligand in **4**–**6** displays a reversible oxidation process.

The oxidation potential of the free dppf ligand (0.53 V) is shifted considerably to more positive values in the Re–oxo–dppf (**4**) and Re–imido–dppf (**5** and **6**) compounds, which suggests that the Re moieties might behave as electron-withdrawing groups as a whole. This type of a positive shift in $E°$ is also observed for Re(dppf)$(CO)_4$Cl which shows one reversible ferrocene-centered oxidation at 0.67 V at the scan rate of 100 mV s^{-1} [19]. As expected, compound **6**, which has a more electron-donating isopropyl substituent on the imido phenyl ring, is more easily oxidized than compound **5** (Table 3). At various scan rates (Table 3), the oxidation potentials of all compounds remain constant, which indicates that their oxidized forms are stable on the cyclovoltammetry time scale.

In summary, we have prepared Re(V)–oxo–dppf and Re(V)–imido–dppf compounds, one of which has been structurally characterized. These compounds exhibit interesting redox processes in which the oxidation behavior appears to be dependent on the type of ligand coordinated to the Re metal.

4. Supplementary material

Crystallographic data for structural analysis have been deposited at the Cambridge Crystallographic Data Center, CCDC No. 155394 for compound **4**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

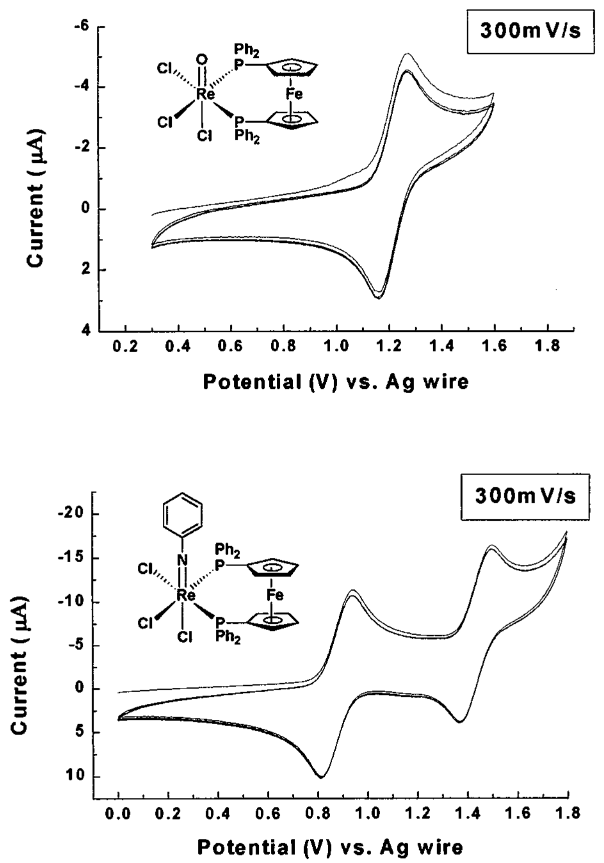


Fig. 2. Cyclic voltammograms (300 mV s^{-1}) in 0.1 M [*n*-Bu_4N][PF_6]–CH_2Cl_2 solutions of **4** (top) and **5** (bottom).

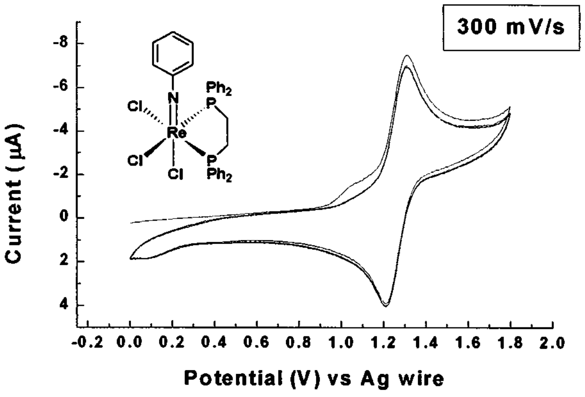


Fig. 3. Cyclic voltammograms (300 mV s^{-1}) in 0.1 M [*n*-Bu_4N][PF_6]–CH_2Cl_2 solutions of Re(NPh)(dppe)Cl_3.

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