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Heterobimetallic rhenium nitrido complexes containing the Kläui tripodal ligand $[Co(\eta^5\text{-}C_5H_5)\{P(O)(OEt)_2\}_3]^-$

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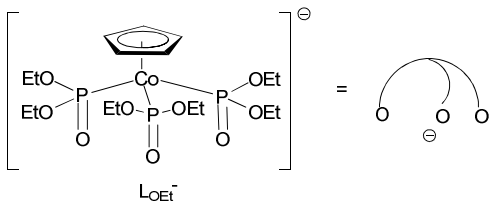
Rhenium nitrido complexes containing the Kläui tripodal ligand $[Co(\eta^5\text{-}C_5H_5)\{P(O)(OEt)_2\}_3]^-$ (L_{OEt}^-) have been synthesised and their reactions with $[Ir^I(cod)Cl]_2$ (cod = 1,5-cyclooctadiene) and $[Rh^{II}_2(OAc)_4]$ (OAc^- = acetate) have been studied. Treatment of $[Bu^n_4N][Re^{VI}(N)Cl_4]$ with NaL_{OEt} in methanol afforded the Re^{VI} nitride $[Re^{VI}(L_{OEt})(N)Cl(OMe)]$ (**1**). Reactions of **1** with $[Ir^I(cod)Cl]_2$ and $[Rh^{II}_2(OAc)_4]$ gave the μ-nitrido complexes $[(L_{OEt})(OMe)ClRe^{VI}(\mu\text{-}N)Ir^I(cod)Cl]$ (**2**) and $[Rh^{II}_2(OAc)_4\{(\mu\text{-}N)Re^{VI}(L_{OEt})(OMe)Cl\}_2]$ (**4**), respectively. $[(L_{OEt})Cl(PPh_3)Re^V(\mu\text{-}N)Ir^I(cod)Cl]$ (**3**) and $[(L_{OEt})Cl(PPh_3)Re^{VI}(\mu\text{-}N)Ir^I(cod)Cl][PF_6]$ (**3**·PF_6) have been synthesised from the reactions of $[Ir^I(cod)Cl]_2$ with $[Re^VL_{OEt}(N)Cl(PPh_3)]$ and $[Re^{VI}L_{OEt}(N)Cl(PPh_3)](PF_6)$, respectively. Similarly, the redox pair $[Rh^{II}_2(OAc)_4\{(\mu\text{-}N)Re^V(L_{OEt})(PPh_3)Cl\}_2]$ (**5**) and $[Rh^{II}_2(OAc)_4\{(\mu\text{-}N)Re^{VI}(L_{OEt})(PPh_3)Cl\}_2](PF_6)_2$ (**5**·$(PF_6)_2$) have been synthesised from the reactions of $[Rh_2(OAc)_4]$ with $[Re^VL_{OEt}(N)Cl(PPh_3)]$ and $[Re^{VI}L_{OEt}(N)Cl(PPh_3)](PF_6)$, respectively. While $[(L_{OEt})Cl_2Ru^{VI}(\mu\text{-}N)Ir^I(cod)]$ (**6**) was obtained from $[Ru^{VI}(L_{OEt})(N)Cl_2]$ and $[Ir^I(cod)Cl]_2$, the interaction between $[Ru^{VI}(L_{OEt})(N)Cl_2]$ and $[Rh^{II}_2(OAc)_4]$ in CH_2Cl_2 is reversible. The crystal structures of complexes **2**, **3**, **3**·PF_6, **5**, **5**·$(PF_6)_2$ and **6** have been determined. X-ray crystallography indicates that the nitrido bridges in **2**, **3**, **3**·PF_6 and **6** can be described as M≡N—Ir (M = Re, Ru) showing Ir-N multiple bond character, whereas the interaction between Re≡N and Rh in **5** and **5**·$(PF_6)_2$ is mostly of donor-acceptor type. The electrochemistry of the Re nitrido complexes has been investigated by cyclic voltammetry.

Introduction

Transition-metal nitrido complexes are of interest due to their potential applications in nitrogen atom transfer reactions.[1] Recently, Schneider and co-workers reported that in the presence of a reducing agent, a Re complex with a PNP pincer ligand is capable of splitting the dinitrogen N-N triple bond to afford a Re^V nitride that can be further functionalised through C-N bond formation.[2] This result prompted us to explore the reactivity of high-valent Re nitrido complexes that may be involved in Re-based functionalisation of N_2.

Although Re^V nitrido complexes are well documented, the paramagnetic Re^{VI} analogues have received less attention.[3,4] This may be due, in part, to the fact that Re^{VI} nitrido starting materials are less easily available than the Re^V congeners such as $[Re^V(N)Cl_2(PPh_3)_2]$.[5] In addition, Re^{VI} nitrides are generally more reactive than the Re^V analogues. For example, the metathesis reactions of $[Re^{VI}(N)Cl_4]^-$ with chelating ligands such as $Na(Et_2dtc)$ (Et_2dtc = *N*,*N*-diethyldithiocarbamate) and $Na_2(mnt)$ (mnt^{2-} = maleonitriledithiolate) resulted in formation of Re^V nitrides.[4a]

The Kläui tripodal ligand $[CoCp\{P(O)(OEt)_2\}_3]^-$ (Cp = η^5-C_5H_5; denoted as L_{OEt}^- hereafter) (Scheme 1) is known to be capable of stabilising metal ions in high oxidation states.[6] Stable Re^V, Os^{VI}, and Ru^{VI} nitrido and imido complexes with L_{OEt}^- have been isolated,[7,8] indicating that the $\{ML_{OEt}\}$ cores can serve as good platforms for the study of metal-nitrogen multiple bonds.



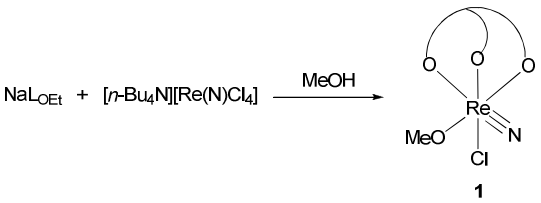
Scheme 1 Structure of the Kläui tripodal ligand L_{OEt}^-

We are particularly interested in heterobimetallic nitrido complexes derived from terminal metal nitrides. Previously, heterometallic nitrido complexes have been synthesised by reactions of Re^V and Os^{VI} nitrides with low-valent organometallic complexes.[9] We have also prepared dimetallic Ru^{IV}-N-Ru^{IV} and Ru^{VI}-N-Ru^{II} complexes featuring Ru-N multiple bonds from the Ru^{VI} nitride $[Ru^{VI}(N)L_{OEt}Cl_2]$ and organoruthenium(II) complexes.[10] As our continuous effort to explore the organometallic chemistry of nitrido complexes, we sought to synthesise bridged nitrido complexes containing the $\{Ir^I(cod)Cl\}$ (cod = 1,5-cyclooctadiene) and $\{Rh^{II}_2(OAc)_4\}$ (OAc^- = acetate) fragments. Whereas dirhodium(II) complexes containing amine and nitrile ligands are well known, to our knowledge, dirhodium nitrido complexes have not been reported.[11] In this paper, we report the synthesis and crystal structures of heterometallic Re/Ir and Re/Rh nitrido complexes derived from the Re nitrido complexes **1** and $[Re(N)(L_{OEt})Cl(PPh_3)]^n$ (n = 0 or +1). The success in isolation of both Re^V-N-M and Re^{VI}-N-M complexes offers us an opportunity to investigate the influence of the Re oxidation state on the Re-N-M bridge.

Results and discussion

Re^{VI} nitrido complex

Treatment of $(Bu^n_4N)[Re^{VI}(N)Cl_4]$ with NaL_{OEt} in CH_2Cl_2 gave a brown oily material that did not crystallise. However, when the reaction was carried out in methanol, a red crystalline solid characterised as the methoxy complex $[Re^{VI}(L_{OEt})(N)(OMe)Cl]$ (**1**) was isolated (Scheme 2). The methoxide ligand in **1** apparently came from the methanol solvent. Complex **1** is stable in both the solid state and solution. It is soluble in common organic solvents except hexanes. The measured magnetic moment (Evans method) of ca. 1.8 μ_B is close to the spin-only value for 1 unpaired electron. The X-band EPR spectrum of **1** in tetrahydrofuran at 4 K (Fig. 1) showed an anisotropic signal with $g_x \approx g_y = 1.89$ and $g_z = 1.84$ (with hyperfine coupling constants $A_{xx} \approx A_{yy} = 474 \times 10^{-4}$ cm^{-1} and $A_{zz} = 860 \times 10^{-4}$ cm^{-1}), consistent with the d^1 Re^{VI} formulation. Similar EPR spectral parameters have been reported for other Re^{VI} nitrido complexes.[4] Hyperfine couplings due to N and P atoms were not resolved due to the large linewidth of the signal. A preliminary X-ray diffraction study confirmed the identity of **1**. Unfortunately, owing to the disorder found for the chloride, nitrido and methoxo ligands, the metal-ligand bond distances have not been analysed.



Scheme 2 Synthesis of the Re^{VI} nitrido complex **1**.

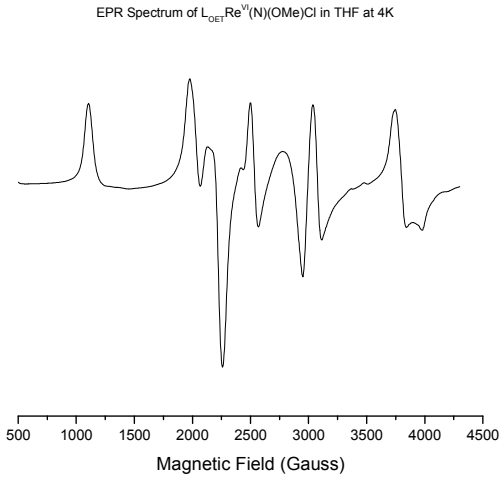
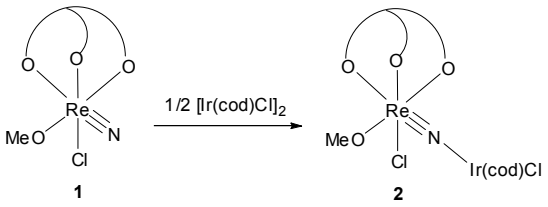


Fig. 1 X-Band EPR spectrum of **1** in tetrahydrofuran at 4 K. Microwave frequency, 9.399 GHz; microwave power, 10 mW; modulation frequency, 100 kHz; modulation amplitude, 3 Gauss; time constant, 1.28 ms; conversion time, 84 s.

Heterometallic Re/Ir nitrido complexes

Treatment of **1** with $[Ir^I(cod)Cl]_2$ afforded the μ-nitrido complex $[L_{OEt}(OMe)(Cl)Re^{VI}(\mu\text{-}N)Ir^I(cod)Cl]$ (**2**) (Scheme 3). The measured μ_{eff} for **2** of ca. 1.8 μ_B is consistent with the Re^{VI}-Ir^I formulation. The molecular structure of **2** is shown in Fig. 2. The geometry around Re in **2** is *pseudo* octahedral whereas that around Ir is roughly square pyramidal with the nitride at the apical position. The Re-N-Ir unit is essentially linear [175.5(3)°]. The Re-N distance of 1.690(4) Å is longer than that in $(Bu^n_4N)[Re^{VI}(N)Cl_4]$ [1.612(8) Å].[5] The Ir-N distance [1.942(4) Å] is shorter than typical Ir-N single bond distances [e.g. 2.123(5) Å in $[\{Ir(cod)Cl\}_2(\mu\text{-dpnapy})]$ where dpnapy is 7-diphenylphosphino-2,4-dimethyl-1,8-naphthyridine],[12] indicative of Ir-N multiple bond character. The observed Ir-N and Re-N bond distances in **2** suggest that the nitrido bridge is best described as Re≡N—Ir.[13] A similar bonding picture has been found for a related Re^V-Ir^I complex, $[Cl_2(PMe_2Ph)_3Re^V(\mu\text{-}N)Ir^I(cod)Cl]$ [Re-N 1.704(8) Å, Ir-N 1.962(8) Å].[9] The Ir-C bonds *trans* to nitride [2.176(5) and 2.161(5) Å] are longer that those *trans* to chloride [2.103(6) and 2.118(6) Å], showing that the μ-nitride has stronger *trans*-influence than chloride.



Scheme 3. Synthesis of **2**.

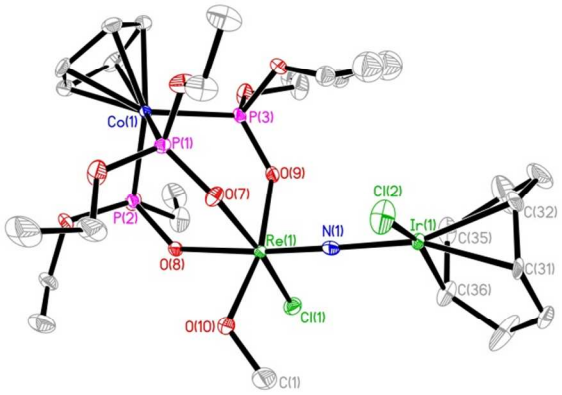
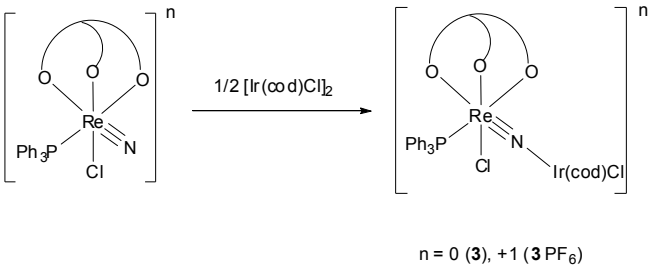


Fig. 2 Molecular structure of **2**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at 30 % probability.

Table 1 Selected bond lengths (Å) and angle (°) for **2**.

Re(1)-Cl(1)	2.3366(13)	Re(1)-O(7)	2.042(3)
Re(1)-O(8)	2.150(3)	Re(1)-O(9)	2.093(3)
Re(1)-O(10)	1.929(4)	Re(1)-N(1)	1.690(4)
Ir(1)-Cl(2)	2.3567(15)	Ir(1)-N(1)	1.942(4)
Ir(1)-C(31)	2.176(5)	Ir(1)-C(32)	2.161(5)
Ir(1)-C(35)	2.103(6)	Ir(1)-C(36)	2.118(6)
Re(1)-N(1)-Ir(1)	175.5(3)		

To investigate the influence of the Re oxidation state on the Ir-N-Re bridge, heterometallic Re/Ir nitrido complexes derived from $[Ir(cod)Cl]_2$ and $[ReL_{OEt}(N)(PPh_3)Cl]^n$ (n = 0 or +1) have been prepared. Treatment of $[Ir^I(cod)Cl]_2$ with $[Re^V(L_{OEt})(N)(PPh_3)Cl]$ and $[Re^{VI}(N)(L_{OEt})(PPh_3)Cl](PF_6)$ afforded the redox pair $[L_{OEt}(PPh_3)(Cl)Re^V(\mu\text{-}N)Ir^I(cod)Cl]$ (**3**) and $[L_{OEt}(PPh_3)(Cl)Re^{VI}(\mu\text{-}N)Ir^I(cod)Cl](PF_6)$ (**3**·PF_6), respectively (Scheme 4). Whereas **3** is diamagnetic showing sharp ^1H NMR signals, **3**·PF_6 is paramagnetic with μ_{eff} of ca. 1.8 μ_B, which is consistent with the Re^{VI}-Ir^I formulation.



Scheme 4. Syntheses of heterometallic Re/Ir nitrido complexes **3** and **3**·PF_6.

The molecular structures of **3** and **3**·PF_6 have been determined (Fig 3); selected bond lengths and angles are summarised in Scheme 5. The Ir-N distance in $\mathbf{3}^+$ [1.883(5) Å] is significantly shorter than that in **3** [1.966(3) Å], showing that the Re^{VI} nitride is a stronger donor than the Re^V counterpart with respect to Ir^I. It seems likely that an increase in Re oxidation state enhances the Ir-N(Re) π interaction and thus shortens the Ir-N bond. In addition, the Re-N distance in $\mathbf{3}^+$ [1.710(5) Å] is slightly longer than **3** [1.697 (3) Å]. It may also be noted that the Re-N-Ir angle in $\mathbf{3}^+$ [173.6(3)°] is more linear than that in **3** [166.1(2)°].

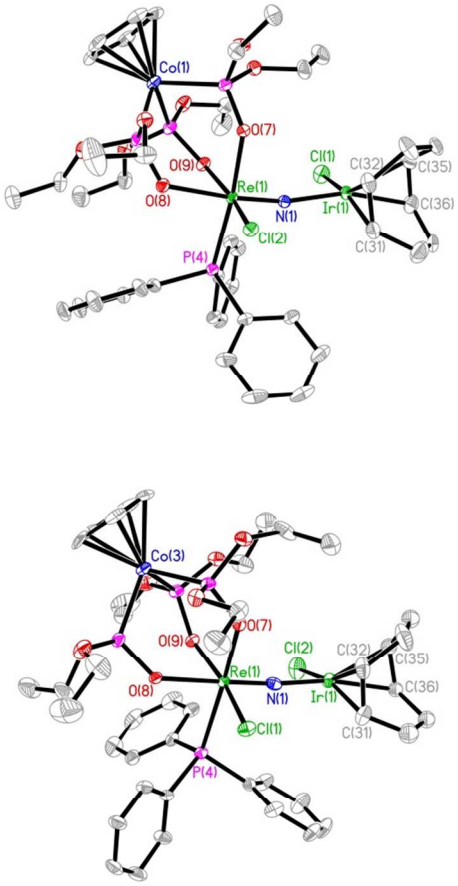
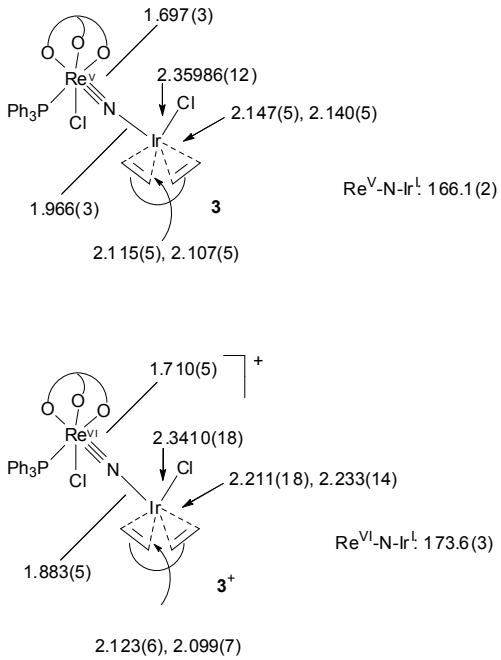


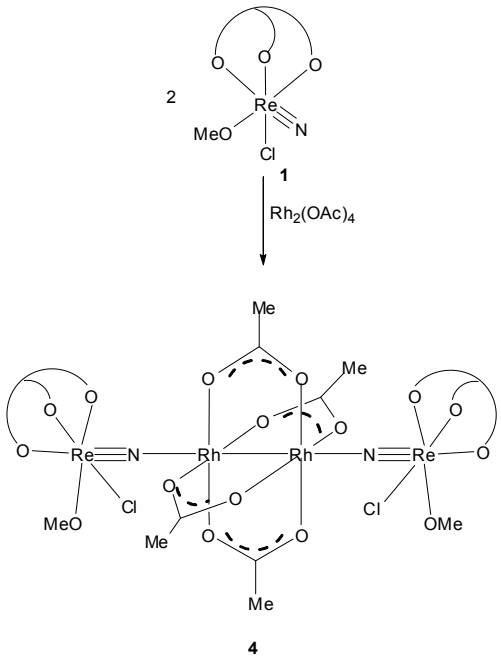
Fig. 3 Molecular structures of **3** (top) and the complex cation **3**$^{+}$ (bottom). Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at 30 % probability.



Scheme 5. Selected bond lengths (Å) and angles (°) in **3** (top) and **3**$^{+}$ (bottom).

Heterometallic Re/Rh nitrido complexes

Treatment of $[Rh^{II}_2(OAc)_4]$ with **1** resulted in a dark red solution. Recrystallisation of the crude product from CH_2Cl_2-hexanes led to isolation of air-stable dark red single crystals, characterised as $[Rh^{II}_2(OAc)_4\{(\mu\text{-}N)Re^{VI}(L_{OEt})(OMe)Cl\}_2]$ (**4**) (Scheme 6). Although dirhodium(II) complexes containing axial nitrogen ligands such as amines and nitriles are well documented, to our knowledge, **4** is the first heterometallic μ-nitrido complex of $[Rh^{II}_2(OAc)_4]$.



Scheme 6. Synthesis of $\{(L_{OEt})(OMe)ClRe(\mu\text{-}N)\}_2[Rh_2(OAc)_4]$ (**4**).

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Table 2. Crystallographic data and experimental details for **2**, **3**·PF_6, **3**, **5**·PF_6, **5** and **6**.

	2	**3**·PF_6·CH_2Cl_2	**3**·C_7H_8	**5**·$(PF_6)_2$·$4CH_2Cl_2$	**5**·$2CH_2Cl_2$	**6**·C_4H_8O
Formula	$C_{26}H_{50}Cl_2CoIrNO_{10}P_3Re$	$C_{44}H_{64}Cl_4CoF_6IrNO_9P_5Re$	$C_{50}H_{70}Cl_2CoIrNO_9P_4Re$	$[C_{41}H_{60}Cl_5CoF_6NO_{13}P_5ReRh]_2$	$C_{80}H_{116}Cl_6Co_2N_2O_{26}P_8Re_2Rh_2$	$C_{29}H_{55}Cl_3CoIrNO_{10}P_3Ru$
Fw	1137.81	1598.94	1461.18	3138.08	2678.29	1129.20
a (Å)	14.7743(10)	16.2567(2)	13.2940(4)	12.1611(2)	12.4445(9)	9.2573(17)
b (Å)	13.7892(10)	15.5814(2)	13.3589(6)	14.3726(3)	12.5644(8)	12.638(2)
c (Å)	18.2139(10)	22.6734(3)	16.5754(7)	32.8546(6)	17.9581(11)	17.985(3)
α (°)	90	90	76.440(4)	90	81.475(5)	85.953(2)
β (°)	90.506(10)	90	78.948(3)	97.1682(18)	86.215(5)	75.562(2)
γ (°)	90	90	83.055(3)	90	64.836(7)	75.848(2)
V (Å^3)	3710.5(4)	5743.22(13)	2799.63(19)	5697.70(18)	2513.3(3)	1975.7(6)
Z	4	4	2	4	1	2
Cryst system	monoclinic	orthorhombic	triclinic	monoclinic	triclinic	triclinic
Space group	$P2_1/c$	$Pna2_1$	P-1	$P2_1/n$	P-1	P-1
ρ_{calcd} (g·cm^{-3})	2.037	1.849	1.733	1.829	1.770	1.898
T (K)	173	173	173	100	100	100
μ (mm^{-1})	19.480	5.094	13.320	12.801	12.963	4.528
F(000)	2204	3132	1444	3112	1334	1120
No. of reflns	20667	33721	16990	24314	14070	21648
No. of indep reflns	6613	9919	9914	10113	8876	8404
R_{int}	0.0439	0.0330	0.0513	0.0673	0.0466	0.0686
$R1$[a], $wR2$[b] ($I > 2\sigma(I)$)	0.0370, 0.0965	0.0279, 0.0572	0.0384, 0.1056	0.0505, 0.1116	0.0546, 0.1229	0.0583, 0.1095
$R1$, $wR2$ (all data)	0.0383, 0.0978	0.0301, 0.0581	0.0395, 0.1070	0.0726, 0.1214	0.0620, 0.1256	0.0764, 0.1154
GoF[c]	1.026	1.014	1.024	1.002	1.001	1.016

[a] $R1 = \Sigma \left| |F_o| - |F_c| \right| / \Sigma |F_o|$. [b] $wR2 = [\Sigma w(|F_o^2| - |F_c^2|)^2 / \Sigma w |F_o^2|^2]^{1/2}$.

[c] $GoF = [\Sigma w(|F_o| - |F_c|)^2 / (N_{obs} - N_{param})]^{1/2}$.

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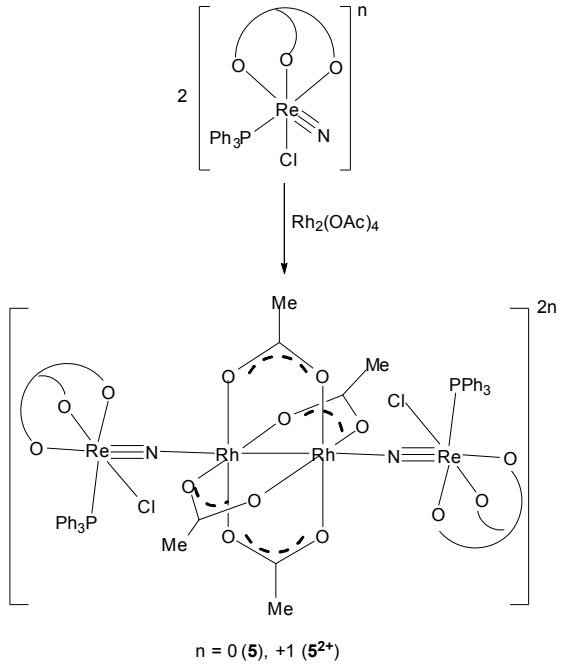
An attempt to synthesise a trinuclear $ReRh_2$ complex, $[\{Rh^{II}_2(OAc)_4\}\{(\mu\text{-}N)Re^{VI}(L_{OEt})(OMe)Cl)\}]$, by reacting **1** with one equivalent of $[Rh^{II}_2(OAc)_4]$ failed; only **4** along with unreacted $[Rh^{II}_2(OAc)_4]$ were isolated from the reaction mixture. A preliminary X-ray diffraction study confirmed that **4** is a tetranuclear Re/Rh complex containing Re-N-Rh bridges. Unfortunately, the crystal structure has not been refined satisfactorily due to disorder of the methoxo and chloride ligands.

Similarly, treatment of $[Rh^{II}_2(OAc)_4]$ with 2 equivalents of $[Re^{V}(N)L_{OEt}Cl(PPh_3)]$ and $[Re^{VI}(N)L_{OEt}Cl(PPh_3)](PF_6)$, which was prepared by oxidation of $[Re^{V}(N)L_{OEt}Cl(PPh_3)]$ with $[FeCp_2](PF_6)$,[7] afforded the redox pair $[Rh^{II}_2(OAc)_4\{(\mu\text{-}N)Re^{V}(L_{OEt})(PPh_3)Cl\}_2]$ (**5**) and $[Rh^{II}_2(OAc)_4\{(\mu\text{-}N)Re^{VI}(L_{OEt})(PPh_3)Cl\}_2](PF_6)_2$ (**5**·$(PF_6)_2$), respectively (Scheme 7).



Scheme 7. Syntheses of heterometallic Re/Rh nitrido complexes **5** and **5**·$(PF_6)_2$.

Both **5** and **5**·$(PF_6)_2$ are stable in solution and have been characterised by X-ray diffraction (Fig 4). Selected bond lengths and angles are summarised in Scheme 8. The two tripodal ligands in both **5** and $\mathbf{5}^{2+}$ are in an *anti* arrangement. The Re-N distance in $\mathbf{5}^{2+}$ [1.681(6) Å] is slightly shorter than that in **5** [1.703(6) Å]. The Rh-N(Re) distances in **5** [2.156(6) Å] and $\mathbf{5}^{2+}$ [2.126(6) Å] are rather long, but shorter than those in the adducts $[Rh^{II}_2(OAc)_4(L)_2]$ [L = MeCN (av. 2.254 Å),[14] pyridine (av. 2.227 Å)[15]]. Upon coordination to the Re nitrides, the Rh-Rh bond in the $[Rh_2(OAc)_4]$ moiety is slightly lengthened from 2.3855(5) Å[16] to 2.4255(10) (**5**) and 2.4091(10) ($\mathbf{5}^{2+}$) Å, respectively. The Re-N-Rh angle in $\mathbf{5}^{2+}$ [173.4(3)°] is more linear than that in **5** [169.4(4)°]. The rather long observed Rh-N distances together with the electrochemical data (see later section) suggest that there is no significant π interaction between Rh and the Re nitrides in **5** and $\mathbf{5}^{2+}$. It seems likely that the interaction between Re≡N and Rh is mostly of donor-acceptor type [i.e. Re≡N:→Rh].

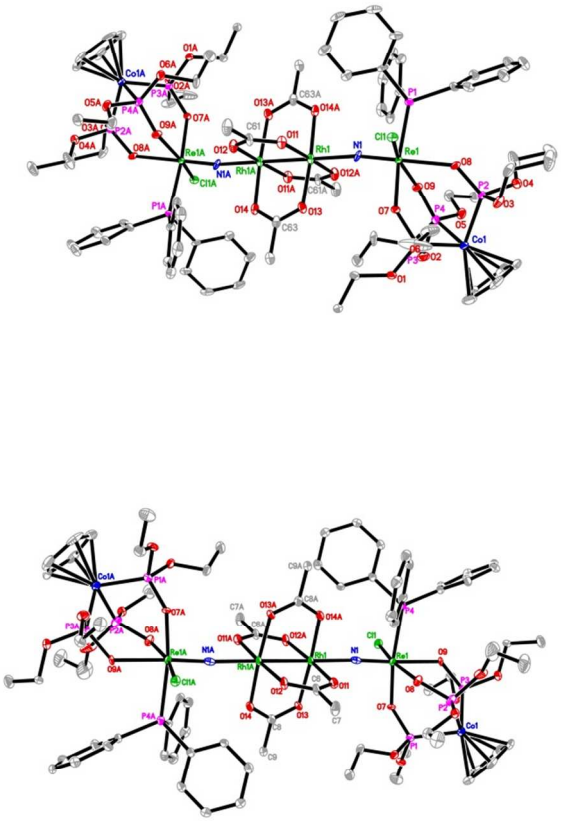
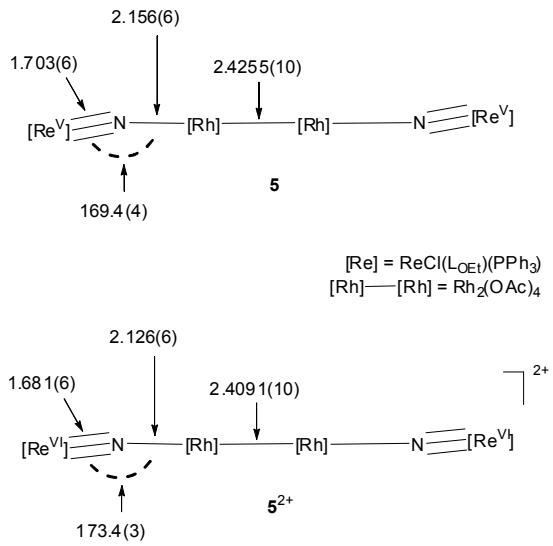


Fig. 4 Molecular structures of **5** (top) and the complex cation $\mathbf{5}^{2+}$ (bottom). Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at 30 % probability.



Scheme 8. Selected bond lengths (Å) and angles (°) in **5** and $\mathbf{5}^{2+}$.

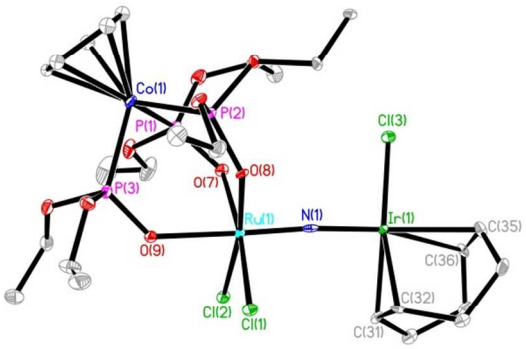


Fig. 5 Molecular structure of **6**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at 30 % probability. Selected bond lengths (Å) and angles (°): Ru(1)–N(1) 1.696(7), Ir(1)–N(1) 1.793(7), Ir(1)-Cl(3) 2.3322(19), Ir(1)-C(31) 2.139(8), Ir(1)-C(32) 2.165(7), Ir-C(35) 2.289(8), Ir(1)-C(36) 2.318(8); Ru(1)–N(1)–Ir(1) 175.3(4).

Heterometallic Ru nitrido complexes

An attempt has been made to prepare a Ru/Rh analogue of **5** starting from $[Ru^{VI}(N)(L_{OEt})Cl_2]$.[8] Addition of 2 equivalents of $[Ru^{VI}(N)L_{OEt}Cl_2]$ to a suspension of $[Rh^{II}_2(OAc)_4]$ in CH_2Cl_2 resulted in a homogeneous dark red solution, indicating that a reaction (presumably coordination of the Ru nitride to Rh) occurred. However, upon precipitation of the product with Et_2O, the starting materials $[Rh^{II}_2(OAc)_4]$ and $[Ru^{VI}(N)(L_{OEt})Cl_2]$ were recovered in good yield, indicating that the interaction between $[Rh^{II}_2(OAc)_4]$ and the Ru nitride is reversible. This is understandable as the Ru^{VI} nitride is a weaker Lewis base than the Re analogue and expected to form a weaker dative bond with Rh. In fact, $[Ru^{VI}(N)(L_{OEt})Cl_2]$ has been shown to exhibit electrophilic behaviour and reacts with nucleophiles instead of electrophiles.[8] Indeed, $[Ru^{VI}(N)(L_{OEt})Cl_2]$ reacted with electron-rich $[Ir^{I}(cod)Cl]_2$ irreversibly to give $[(L_{OEt})Cl_2Ru^{VI}(\mu\text{-}N)Ir^{I}(cod)Cl]$ (**6**), which has been characterised by X-ray diffraction (Fig. 5). The Ru-N distance in **6** of 1.696(7) Å is longer than that in $[Ru^{VI}(N)(L_{OEt})Cl_2]$ [1.573(6) Å][8] but shorter than that in the dinuclear Ru^{IV}=N=Ru^{IV} complex $[\{Ru^{IV}(L_{OEt})Cl_2\}_2(\mu\text{-}N)]^-$ [1.7325(4) Å],[10] suggestive of a Ru-N bond order between 3 and 2. The Ir-N distances in **6** of 1.793(7) Å is significantly shorter than those in the Re/Ir analogues **3** [1.966(3) Å] and $\mathbf{3}^+$ [1.883(5) Å]. The strong Ir-N multiple bond character for **6** can be attributed to the π-accepting capability of the electrophilic Ru^{VI} nitride.[17] The Ru-N-Ir unit is essentially linear [175.3(4)°]. The above structural data indicates that the bonding in **6** can be represented by two resonance forms, Ru^{VI}≡N-Ir^{I} and Ru^{IV}=N=Ir^{III}.

Electrochemistry

The electrochemistry of the Re nitrido complexes has been studied by cyclic voltammetry and the results are summarised in Table 3. The cyclic voltammogram (CV) of complex **1** in acetonitrile displayed a reversible couple at 0.35 V vs. $FeCp_2^{+/0}$, which is assigned as the Re^{VII}-Re^{VI} couple. By contrast, no Re^{VI}-Re^{VII} oxidation was found for $[Re^{VI}(N)L_{OEt}(PPh_3)Cl]^+$ or $[Re^{VI}(N)Cl_4]^-$. Attempts to synthesise a Re^{VII} nitride by oxidation of **1** with 1-electron oxidants failed. Reaction of **1** with NR_3SbF_6 (R = 4-bromophenyl) resulted in decomposition of the complex. Treatment of **1** with cerium(IV) ammonium nitrate gave a diamagnetic species, possibly a Re^{VII} complex, as evidenced by NMR spectroscopy. We have not been able to crystallise this diamagnetic species for further characterisation.

Unlike **1**, the Re^{VII}-Re^{VI} redox couple for the dinuclear Re/Ir complex **2** is irreversible. The Re^{VI}-Re^{VII} oxidation for **2** occurred at a slightly less positive potential (E_{pa} = 0.25 V) than that of **1**. By contrast, **3** exhibited a reversible Re^{VI}-Re^{V} couple at ca. -0.14 V that is more anodic than that of $[Re^{V}(N)L_{OEt}(PPh_3)Cl]$ (-0.22 V). In addition, there is an irreversible event at 0.87 V, which is probably an Ir-centred oxidation.

The CV of the trinuclear Re/Rh complex **5** in CH_2Cl_2 (Fig. 6) showed two reversible redox couples at 1.01 and -0.15 V. The latter couple is approximately twice as high as the former. These two couples are tentatively assigned as the 1-electron $Rh^{III}Rh^{II}$-$Rh^{II}Rh^{II}$ and 2-electron $Re^{VI}Re^{VI}$-$Re^{V}Re^{V}$ processes, respectively. Consistent with this assignment, the oxidation of **5** with 2 equivalents of $[FeCp_2](PF_6)$ afforded the Rh^{II}-Re^{VI} complex $\mathbf{5}^{2+}$ that has been synthesised from $[Rh_2(OAc)_4]$ with 2 equivalents of $[Re^{VI}(N)L_{OEt}(PPh_3)Cl](PF_6)$. Like **3**, the Re^{VI}-Re^{V} potential of **5** is more positive than that of $[Re^{V}(N)L_{OEt}(PPh_3)Cl]$. The observation of a single Re^{VI}-Re^{V} redox event for **5** indicates the lack of electronic

communication between two Re centres. Similarly, the CV of **4** displayed two redox couples at 0.98 and 0.29 V that are tentatively assigned to the $Rh^{III}Rh^{II}$-$Rh^{II}Rh^{II}$ and $Re^{VI}Re^{VI}$-$Re^{V}Re^{V}$ couples, respectively. Again, the observation of a single Re^{VII}-Re^{VI} couple indicates the absence of electronic communication between the Re^{VI} centres in **4**.

Table 3. Redox potentials (E^o) for Re nitrido complexes.[a]

Complex	E^o (V vs. $FeCp_2^{+/0}$)	
	Reduction	Oxidation
$[Re(L_{OEt})(N)(OMe)Cl]$ (**1**)		0.35
$[Re(L_{OEt})(N)(PPh_3)Cl]$	-0.22	
$[L_{OEt}(OMe)(Cl)Re(\mu\text{-}N)Ir(cod)Cl]$ (**2**)		0.25[b]
$[L_{OEt}(PPh_3)(Cl)Re(\mu\text{-}N)Ir(cod)Cl]$ (**3**)	-0.14	0.87[b]
$[Rh_2(OAc)_4\{(\mu\text{-}N)Re(L_{OEt})(OMe)Cl\}_2]$ (**4**)[c]		0.29[d], 0.98
$[Rh_2(OAc)_4\{(\mu\text{-}N)Re(L_{OEt})(PPh_3)Cl\}_2]$ (**5**)[c]	-0.15[d]	1.01

[a] Glassy carbon working electrode, Pt counter electrode, Ag-$AgNO_3$ in MeCN reference electrode, 0.1 mol·dm^{-3} $Bu^n_4NPF_6$ in MeCN as supporting electrolyte, scan rate = 100 mVs^{-1}. [b] Irreversible, E_{pa} value. [c] 0.1 mol·dm^{-3} $Bu^n_4NPF_6$ in CH_2Cl_2 as supporting electrolyte. [d] Redox peaks approximately two times higher.

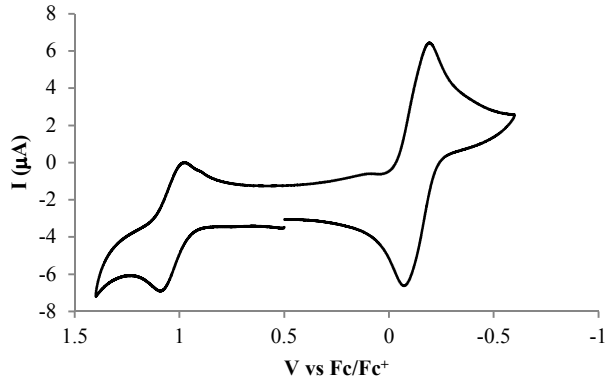


Fig. 6 Cyclic voltammogram of **5** in CH_2Cl_2.

Conclusion

In summary, we have synthesised and characterised a stable Re^{VI} nitrido complex, **1**, supported by the Kläui tripodal ligand L_{OEt}^-. Reactions of **1** and $[ReL_{OEt}(N)(PPh_3)Cl]^n$ (n = 0, +1) with $[Ir^I(cod)Cl]_2$ afforded heterometallic Re/Ir nitrido complexes. X-ray crystallography indicates that the nitrido bridge in these Re/Ir complexes is best described as Re$\equiv$N—Ir. Also, it appears that the Re^{VI} nitride forms a stronger bond with Ir^I than the Re^V analogue does. Reactions of Re^V and Re^{VI} with $[Rh^{II}_2(OAc)_4]$ yielded tetranuclear Re/Rh nitrido complexes, which are first examples of dirhodium(II) μ-nitrido complexes. X-ray crystallography indicates the absence of π interaction between the Re nitrides and the $[Rh_2(OAc)_4]$ moiety. No electronic communication was found between the Re centres in these Re/Rh nitrido complexes. The results of this work demonstrate that tripodal ligand L_{OEt}^- ligand is an excellent supporting ligand for high-valent Re nitrides. The $\{ReL_{OEt}\}$ core can serve as a good platform for the study of the catalytic chemistry of Re complexes featuring metal-nitrogen multiple bonds.

Experimental

General considerations

All manipulations were carried out under nitrogen by standard Schlenk techniques. Solvents were dried, distilled and degassed before use. NMR spectra were recorded on a Bruker AV 400 MHz NMR spectrometer operating at 400, 376.5 and 162.0 MHz for ^1H, ^{19}F and ^{31}P, respectively. Chemical shifts (δ, ppm) were reported with reference to $SiMe_4$ (^1H and ^{13}C), $CF_3C_6H_5$ (^{19}F), and H_3PO_4 (^{31}P). The X-band EPR spectrum was recorded on a Bruker EMX EPR spectrometer equipped with a variable temperature helium flow cryostat system (Oxford Instruments). Cyclic voltammetry was performed with a CH Instrument model 600D potentiostat. The working and reference electrodes were glassy carbon and Ag-$AgNO_3$ (0.1 mol dm^{-3} in acetonitrile) electrodes, respectively. Potentials were reported with reference to the ferrocenium-ferrocene couple. Elemental analyses were performed by Medac Ltd, Surrey, UK.

The compounds $[Bu^n_4N][Re^{VI}(N)Cl_4]$,[5] $[Re^V(L_{OEt})(N)Cl(PPh_3)]$,[7] $[Ir^I(cod)Cl]_2$[18] and $[Rh^{II}_2(OAc)_4]$[19] were prepared according to literature methods. $[Re^{VI}(L_{OEt})(N)Cl(PPh_3)](PF_6)$ was synthesised by oxidation of $[Re^V(L_{OEt})(N)Cl(PPh_3)]$ with $[FeCp_2](PF_6)$ as described elsewhere.[7]

Syntheses

$[Re^{VI}L_{OEt}(N)(OMe)Cl]$ (1). To a solution of NaL_{OEt} (100 mg, 0.18 mmol) in methanol (3 mL) was added $[Bu^n_4N][Re^{VI}(N)Cl_4]$ (105 mg, 0.18 mmol). The yellowish orange solution turned brown gradually. The solvent was removed in vacuo, and the brown residue was extracted with Et_2O and purified by column chromatography (silica) using ethyl acetate-hexane (1:1, v/v) as eluant. The product was isolated as an orange band. Recrystallisation from Et_2O-hexane afforded orange crystals. Yield: 36 mg (25%). μ_{eff} = 1.8 μ_B. Anal. Calc. for $C_{18}H_{38}ClCoNO_{10}P_3Re$: C, 26.96; H, 4.78; N, 1.75; Cl, 4.42. Found: C, 26.68; H, 4.58; N, 1.76; Cl, 4.74%.

$[L_{OEt}(OMe)(Cl)Re^{VI}(\mu\text{-}N)Ir^I(cod)Cl]$ (2). To a solution of **1** (30 mg, 0.037 mmol) in Et_2O (5 mL) was added $[Ir^I(cod)Cl]_2$ (13 mg, 0.019 mmol). The reaction mixture was stirred at room temperature overnight. The solvent was removed and the residue was washed with hexane. Recrystallisation from Et_2O-hexanes afforded dark red crystals. Yield: 33 mg (79%). Anal. Calc. for $C_{26}H_{50}Cl_2CoIrNO_{10}P_3Re$: C, 27.44; H, 4.43; N, 1.23. Found: C, 27.28; H, 4.35; N, 1.33%.

$[L_{OEt}(PPh_3)(Cl)Re^V(\mu\text{-}N)Ir^I(cod)Cl]$ (3). To a solution of $[Re^VL_{OEt}(N)Cl(PPh_3)]$ (30 mg, 0.029 mmol) in CH_2Cl_2 (5 mL)

was added $[Ir^{I}(cod)Cl]_2$ (10 mg, 0.015 mmol). The reaction mixture was stirred at room temperature overnight. The solvent was removed and the residue was washed with hexane. Recrystallisation from CH_2Cl_2-hexanes afforded red crystals. Yield: 28 mg (70%). ^{1}H NMR ($CDCl_3$): δ 0.76 (t, 3H, CH_3), 0.88 (t, 3H, CH_3), 1.24 (t, 3H, CH_3), 1.31 (t, 3H, CH_3), 1.53 (t, 6H, CH_3), 2.20-2.27 (m, 2H, CH_2), 2.31-2.38 (m, 2H, CH_2), 2.45-2.53 (m, 2H, CH_2), 2.60-2.68 (m, 2H, CH_2), 2.88-3.09 (m, 2H, OCH_2), 3.27-3.43 (m, 2H, OCH_2), 4.07-4.10 (m, 2H, OCH_2), 4.30-4.39 (m, 2H, OCH_2), 4.63-4.74 (m, 4H, OCH_2), 4.97 (s, 5H, Cp), 5.27-5.31 (m, 2H, CH), 5.33-5.37 (m, 2H, CH), 7.17 (m, 3H, PPh_3), 7.38 (m, 6H, PPh_3), 7.93 (m, 6H, PPh_3). ^{31}P {^{1}H} NMR ($CDCl_3$): δ110.63 (m), 117.21 (m), 118.28 (m), 4.40 (s, PPh_3). Anal. Calc. for $C_{43}H_{62}Cl_2CoIrNO_9P_4Re{\cdot}C_7H_8$: C, 41.10; H, 4.83; N, 0.96. Found: C, 40.74; H, 5.18; N, 1.00%.

$[L_{OEt}(PPh_3)(Cl)Re^{VI}(\mu\text{-}N)Ir^{I}(cod)Cl](PF_6)$ (3·PF_6). To a solution of $[Re^{VI}L_{OEt}(N)Cl(PPh_3)](PF_6)$ (53 mg, 0.045 mmol) in CH_2Cl_2 (5 mL) was added $[Ir^{I}(cod)Cl]_2$ (15 mg, 0.022 mmol). The reaction mixture was stirred at room temperature overnight. The solvent was removed and the residue was washed with hexane. Recrystallisation from CH_2Cl_2-hexanes afforded brown crystals. Yield: 50 mg (73%). Anal. Calc. for $C_{43}H_{62}Cl_2CoF_6IrNO_9P_5Re{\cdot}CH_2Cl_2$: C, 33.05; H, 4.03; N, 0.88. Found: C, 33.10; H, 4.05; N, 0.90%.

$[Rh^{II}_2(OAc)_4\{(\mu\text{-}N)Re^{VI}(L_{OEt})(OMe)Cl\}_2]$ (4). To a solution of **1** (30 mg, 0.037 mmol) in CH_2Cl_2 (5 mL) was added $[Rh^{II}_2(OAc)_4]$ (8 mg, 0.019 mmol). The orange solution turned red and the reaction mixture was stirred at room temperature overnight. The solvent was removed and the residue was washed with hexane. Recrystallisation from CH_2Cl_2-hexanes afforded dark red crystals. Yield: 21 mg (54%). Anal. Calc. for $C_{44}H_{88}Cl_2Co_2N_2O_{28}P_6Re_2Rh_2{\cdot}CH_2Cl_2$: C, 25.36; H, 4.26; N, 1.31. Found: C, 25.10; H, 4.07; N, 1.45%.

$[Rh^{II}_2(OAc)_4\{(\mu\text{-}N)Re^{V}(L_{OEt})(PPh_3)Cl\}_2]$ (5). A mixture of $[Rh^{II}_2(OAc)_4]$ (12 mg, 0.027 mmol) and 2 equivalents of $[Re^{V}L_{OEt}(N)Cl(PPh_3)]$ (56.1 mg, 0.054 mmol) was stirred at room temperature in CH_2Cl_2 (10 mL) for 2 h. The solvent was reduced volume to 5 mL and Et_2O-hexanes was added to the mixture. The mixture was allowed to stand overnight during which red crystalline was formed. The solvent was decanted and the residue was washed with hexane. Recrystallisation from CH_2Cl_2-Et_2O-hexanes afforded red crystals. Yield: 52 mg, 76%. ^{1}H NMR (C_6D_6): δ 0.87 (t, 6H, CH_3), 1.03 (t, 6H, CH_3), 1.23-1.32 (t, 24H, CH_3), 1.40 (s, 12H, CH_3), 2.72-2.88 (m, 4H, OCH_2), 3.83-3.93(m, 4H, OCH_2), 4.27-4.60 (m, 16H, OCH_2), 4.87 (s, 10H, Cp), 7.05-7.13 (m, 18H, PPh_3), 8.3 (m, 12H, PPh_3). ^{31}P {^{1}H} NMR (C_6D_6): δ 13.78 (s, PPh_3), 109.31-117.74 (m). Anal. Calc. for $C_{78}H_{112}Cl_2Co_2N_2O_{26}P_8Re_2Rh_2{\cdot}2CH_2Cl_2$: C, 35.87; H, 4.37; N, 1.05. Found: C, 35.74; H, 4.40; N, 1.11%.

$[Rh^{II}_2(OAc)_4\{(\mu\text{-}N)Re^{VI}(L_{OEt})(PPh_3)Cl\}_2](PF_6)_2$ (5·$(PF_6)_2$).
Method A: A mixture of **5** (50 mg, 0.02 mmol) and 2 equivalents of $[Cp_2Fe](PF_6)$ (13.2 mg, 0.04 mmol) was stirred at RT in CH_2Cl_2 (10 mL) overnight. The solvent was removed and the residue was washed with hexanes. Recrystallisation from CH_2Cl_2-Et_2O afforded dark red crystals. Yield: 51 mg, 91%. Anal. Calc. for $C_{78}H_{112}Cl_2Co_2F_{12}N_2O_{23}P_{10}Re_2Rh_2{\cdot}4CH_2Cl_2$: C, 32.09; H, 4.02; N, 0.90. Found: C, 32.54; H, 3.86; N, 0.74.
Method B: This complex was prepared similarly as for **5** using $[Re^{VI}L_{OEt}(N)Cl(PPh_3)](PF_6)$ in place of $[Re^{V}L_{OEt}(N)Cl(PPh_3)]$. Yield: 90%.

$[L_{OEt}Cl_2Ru^{VI}(\mu\text{-}N)Ir^{I}(cod)Cl]$ (6). A mixture of $[Ru^{VI}L_{OEt}(N)Cl_2]$ (72 mg, 0.1 mmol) and 1 equivalent of $[Ir^{I}(cod)Cl]_2$ (34 mg, 0.05 mmol) in CH_2Cl_2 (10 mL) was stirred at room temperature overnight during which the colour of solution changed to green. The solvent was removed in vacuo and the residual solid was washed by hexanes (10 mL). Recrystallisation in CH_2Cl_2-hexanes (10 mL, v/v = 1:1) afforded green blocks which were suitable for X-ray diffraction. Yield: 66 mg (62 %). ^{1}H NMR ($CDCl_3$): δ 1.21-1.25 (t, 6H, CH_3), 1.25-1.28 (t, 6H, CH_3), 1.35-1.39 (t, 6H, CH_3), 2.25-2.32 (m, 2H, CH_2), 2.35-2.43 (m, 2H, CH_2), 2.52-2.59 (m, 2H, CH_2), 2.76-2.84 (m, 2H, CH_2), 4.13-4.21 (m, 8H, OCH_2), 4.32-4.39 (m, 2H, OCH_2), 4.40-4.48 (m, 2H, OCH_2), 5.01 (s, 5H, Cp), 5.57-5.60 (m, 2H, CH), 5.62-5.65 (m, 2H, CH). ^{31}P {^{1}H} NMR ($CDCl_3$): δ 114.5 (m), 120.9 (m). Anal. Calc. for $C_{25}H_{47}Cl_3CoIrNO_9P_3Ru$: C, 28.40; H, 4.48, N, 1.32. Found: C, 28.65; H, 4.79; N, 1.48%.

X-ray crystallography

Complexes **2**, **3**, **3**·PF_6, **5**, **5**·$(PF_6)_2$ and **6** have been characterised by X-ray diffraction. The diffraction intensity data of **6** was collected on a Bruker APEX CCD diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). The diffraction intensity data of **2**, **3** and **5** were collected with an Agilent Technologies Gemini™ S Ultra X-ray Diffractometer with monochromatized Cu-Kα radiation (λ = 1.54178 Å) at 173 K. Whereas the data of **3**·PF_6 was collected with monochromatized Mo-Kα radiation (λ=0.71073 Å) at 173 K. The diffraction intensity data of **5**·$(PF_6)_2$ was collected with an Agilent Technologies SuperNova Atlas X-ray Diffractometer with monochromatized Cu-Kα radiation (λ = 1.54178 Å) at 100 K. Lattice determination and data collection of **6** was carried out using SMART v5.625 software (Bruker, 2001). Data reduction and absorption correction were performed using SAINT v7.34A (Bruker, 2002) and SADABS v 2.03.[20] Diffraction data of **2**, **3**, **3**·PF_6, **5**, **5**·$(PF_6)_2$ were collected and processed using the CrysAlisPro software (Agilent Tech., 2012). Empirical absorption corrections were performed using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm in the CrysAlisPro software suite. Structure solution and refinement for all complexes were performed using the Olex2 software package[21] (which embedded SHELXTL[22]). All the structures were solved by direct methods, expanded by difference Fourier syntheses and refined by full matrix least-squares on F^2. All non-hydrogen atoms were refined anisotropically with a riding model for the

hydrogen atoms except noted separately. All the pictures of molecules were made using XP implemented in SHELXTL.[22] CCDC 1010165, 1010167, 1010166, 1010169, 1010168 and 1035538 contain the supplementary crystallography data for complexes **2**, **3**, **3**·PF_6, **5**, **5**·$(PF_6)_2$ and **6** respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

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†Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

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Heterobimetallic rhenium nitrido complexes containing the Kläui tripodal ligand $[Co(\eta^5\text{-}C_5H_5)\{P(O)(OEt)_2\}_3]^-$

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