

## Synthesis of dirhenium species with benzamidate ligands via hydrolysis of benzonitrile †

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Benzonitrile co-ordinated to a metal–metal bonded dirhenium core has been shown to undergo hydrolysis in ethanol solvent systems to form benzamidate and remains co-ordinated to the dirhenium core as a bridging ligand. The compounds  $[\text{NBu}_4][\text{Re}_2\text{Cl}_6\{\mu\text{-PhC(O)NH}\}]\cdot 0.5\text{CH}_2\text{Cl}_2$  **1** and  $[\text{Re}_2\text{Cl}_4(\mu\text{-dppm})_2\{\mu\text{-PhC(O)NH}\}]$  **2**, where dppm is bis(diphenylphosphino)methane, were synthesized from the reaction of  $[\text{NBu}_4]_2[\text{Re}_2\text{Cl}_8]$  in an ethanol solvent system with benzonitrile containing 3% water. While compound **1** is the hydrolysis product of the reaction of  $[\text{NBu}_4]_2[\text{Re}_2\text{Cl}_8]$  with benzonitrile, **2** arises from the reduction of **1** upon co-ordination of the bidentate phosphine ligand dppm. The structures of **1** and **2** were determined by X-ray crystallography and the compounds characterized by a variety of spectroscopic methods.

The hydrolysis or partial hydrolysis of nitriles to carboxylates or amides under milder reaction conditions is a process that has been studied for many years, demonstrating the importance of this reaction in organic chemistry.<sup>1,2</sup> In most syntheses, the reaction mixture is first made very basic via the addition of KOH and subsequently neutralized by the addition of a concentrated acid.<sup>3–6</sup> However, these harsh conditions are not always viable in the presence of other functional groups and researchers have been examining new methods to synthesize amides for their use in the fine chemical and pharmaceutical industry.<sup>7</sup> With the potential to limit the hydrolysis of nitriles to the formation of amides by co-ordination of the nitrogen atom, complexes with a number of transition metal centers such as Pt,<sup>7–15</sup> Pd,<sup>9,16</sup> Rh,<sup>17</sup> Ir,<sup>17</sup> Cu,<sup>18</sup> Ni,<sup>19</sup> W<sup>20</sup> and Co<sup>21</sup> are currently under investigation. In addition to the relevance of this research to organic synthesis, the enzymatic hydrolysis mechanisms of nitriles are under investigation to understand the chemo-, regio- and stereo-selectivity of the reactions which are performed under mild conditions.<sup>22–25</sup>

For example, cobalt complexes as artificial enzymes have been widely studied for their ability to form amides from co-ordinated nitriles under neutral pH conditions.<sup>3–6,26,27</sup> For  $[\text{Co}(\text{cyclen})(\text{CO})_3][\text{ClO}_4]$ , where cyclen is 1,4,7,11-tetraazacyclododecane, studies have shown a diaqua complex  $[\text{Co}(\text{cyclen})(\text{OH}_2)_2]^{3+}$  is formed prior to the co-ordination of benzonitrile and the subsequent hydrolysis of the nitrile results in the formation of a benzamidate intermediate.<sup>21</sup> The resultant benzamidate intermediate in the cobalt complex is chelated to the metal center, as in the case of the dirhenium core of  $[\text{NBu}_4][\text{Re}_2\text{Cl}_6\{\mu\text{-PhC(O)NH}\}]\cdot 0.5\text{CH}_2\text{Cl}_2$  **1** and  $[\text{Re}_2\text{Cl}_4(\mu\text{-dppm})_2\{\mu\text{-PhC(O)NH}\}]$  **2** where dppm is bis(diphenylphosphino)methane.<sup>27</sup>

Bimetallic or polymetallic cores are often found in the active site of hydrolytic enzymes, such as urease, phosphatases and esterases.<sup>22–25</sup> The commonly accepted rationale, termed ‘two-metal mechanism’ by Steitz and Steitz,<sup>28</sup> is that the transfer of positive charge from one metal center enhances the electrophilicity of the bound substrate, and the second metal ion facilitates the deprotonation of the co-ordinated water to yield a

bound hydroxide that serves as an intramolecular nucleophile. Co-operativity between two metal centers is not limited to enzymes and has also been proposed as the key of dirhodium-based hydroformylation catalysts.<sup>29,30</sup> Especially interesting in the synthesis of  $[\text{NBu}_4][\text{Re}_2\text{Cl}_6\{\mu\text{-PhC(O)NH}\}]\cdot 0.5\text{CH}_2\text{Cl}_2$  **1** is the retention of a Re–Re quadruple bond in the product and the ability to study a potential two-metal mechanism for the hydrolysis of nitriles.

Dirhenium-(III) and -(II) species have a diverse reactivity due to their high electron density,  $\sigma^2\pi^4\delta^2$  and  $\sigma^2\pi^4\delta^2\delta^{*2}$  respectively, which allows them to co-ordinate and activate a variety of unsaturated organic substrates.<sup>31–33</sup> For instance, reductive coupling of co-ordinated acetonitrile solvent molecules at the Re<sub>2</sub> core leads to the formation of the  $\text{HN}_2\text{C}_2\text{Me}_2$  fragment.<sup>33–35</sup>

Our research combines the activation of unsaturated organic molecules with the study of the hydrolysis of benzonitrile and demonstrates that bridging benzamidate,  $\mu\text{-PhC(O)NH}^-$ , results from the hydrolysis of a nitrile co-ordinated to  $\text{Re}_2\text{Cl}_8^{2-}$  without oxidation of the transition metal core. The structural and spectroscopic characterization of two different species, a  $\text{Re}^{\text{III}}_2$  and a  $\text{Re}^{\text{III}}\text{Re}^{\text{II}}$  core, from the dinuclear starting material  $[\text{NBu}_4]_2[\text{Re}_2\text{Cl}_8]$  are presented.

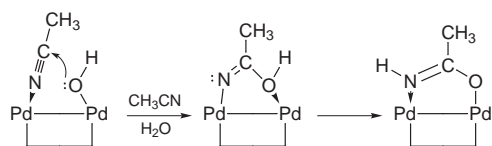
## Results and Discussion

### Synthesis and reaction mechanism

As demonstrated by related studies with mononuclear transition metal complexes, the synthesis of amides from the hydrolysis by water<sup>27,36,37</sup> or nucleophilic attack by base<sup>3–6,26</sup> on a nitrile co-ordinated to a single transition metal center is a well established synthetic strategy. However, a bimetallic pathway is proposed as the mechanism for the hydration of nitriles to amides in dipalladium(II) complexes with thiolate-hinged ligands.<sup>16,38</sup> Co-ordination of the nitrile to a single palladium center with co-ordination of  $\text{OH}^-$  on the adjacent metal center leads to a concerted formation of the amide, as shown in Scheme 1. Unlike the mononuclear platinum systems,<sup>7,9,11,13–15</sup> the reaction of the dipalladium(II) complex is performed in water–MeCN mixtures and is acid catalyzed.<sup>16</sup>

Compound **1**,  $[\text{NBu}_4][\text{Re}_2\text{Cl}_6\{\mu\text{-PhC(O)NH}\}]\cdot 0.5\text{CH}_2\text{Cl}_2$ , a  $\text{Re}^{\text{III}}_2$  system, is synthesized in the reaction between  $[\text{NBu}_4]_2$

† Non-SI unit employed:  $\mu_{\text{B}} \approx 9.27 \times 10^{-24} \text{ J T}^{-1}$ .



**Scheme 1** Proposed mechanism of the formation of co-ordinated benzamide at a dipalladium core

$[\text{Re}_2\text{Cl}_8]$  and benzonitrile in ethanol solvent mixtures. Without the addition of acid or base the reaction medium is slightly acidic based on the character of ethanol as a weak acid, similar to water.<sup>39</sup> In order to determine the oxygen source in our studies of benzonitrile,  $^1\text{H}$  NMR spectra were obtained for the PhCN and the ethanol solvent used in the reactions. The spectrum of the benzonitrile indicates 3% water is present and, since the reactions were performed under an argon atmosphere,  $\text{O}_2$  is eliminated as the source of the oxygen in the resultant benzamidate. Therefore, hydrolysis of the nitrile occurs due to the presence of water in the reaction mixture, similar to the water-MeCN solvent mixtures in the dipalladium systems.<sup>16</sup>

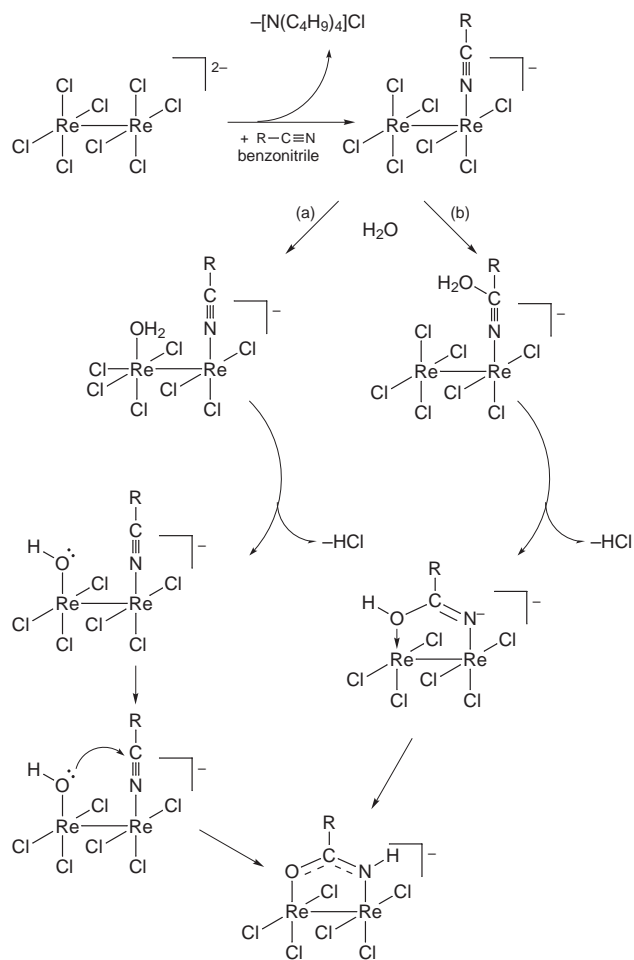
One potential reaction mechanism, analogous to the dipalladium system,<sup>16</sup> is the co-ordination of either water or base to an open co-ordination site of the dirhenium core followed by hydrolysis of the nitrile *via* an intramolecular reaction. However, the intermolecular reaction resulting from direct attack of water on the carbon of the nitrile is also a viable reaction mechanism. Co-ordination of the nitrile in the first step of Scheme 2 results in a more electrophilic C–N bond of the nitrile from the positive charge of the  $\text{Re}^{3+}$  which facilitates the nucleophilic attack of the  $\text{OH}^-$  co-ordinated to the adjacent  $\text{Re}^{3+}$  center, illustrated in Scheme 2(a). Since  $\text{OH}^-$  is a stronger nucleophile than  $\text{H}_2\text{O}$ , the reaction is shown as the attack of the lone pair of electrons of a co-ordinated hydroxide. After the  $\text{HO}-\text{C}(\text{Me})\text{N}$  bond formation of the anionic ligand, proton rearrangement occurs to result in **1**.

Scheme 2(b) illustrates the other possible mechanism, the nucleophilic attack of an  $\text{H}_2\text{O}$  at the carbon on the co-ordinated nitrile. In related studies mononuclear rhenium nitrile compounds such as  $[\text{ReCl}_3(\text{PPh}_3)_2(\text{MeCN})]$ ,<sup>40</sup>  $[\text{NET}_4][\text{Re}(\text{NO})\text{Br}_4(\text{MeCN})]$ <sup>41</sup> and  $[\text{ReCl}_4(\text{MeCN})_2]$ <sup>42</sup> have been synthesized and show some interesting reactivity.<sup>43,44</sup> For example, the reaction of  $[\text{ReCl}_4(\text{MeCN})_2]$  with primary aromatic amines yields substituted amidines of the general formula  $[\text{ReCl}_4\{\text{MeC}(\text{NH})\text{NHR}\}_2]$ , as confirmed by IR analysis and the isolation of *N-p*-tolylacetamide formed from the reaction of *p*-toluidine with  $[\text{ReCl}_4(\text{MeCN})_2]$ .<sup>42</sup> Treatment of  $[\text{ReCl}_4(\text{MeCN})_2]$  with ethanol results in the formation of  $[\text{ReCl}_4\{\text{Me}(\text{NH})\text{OEt}\}_2]$  from the nucleophilic addition of alcohol at the nitrile carbon.<sup>42</sup> Note that both of these reactions result in a change in the oxidation state on the central rhenium atom, unlike the reaction between  $[\text{NBu}_4][\text{Re}_2\text{Cl}_8]$ , water and benzonitrile.<sup>42</sup> Direct attack of  $\text{OH}^-$  is unlikely since ethanol is slightly acidic and preliminary studies indicate that the direct attack of  $\text{OH}^-$  at the nitrile carbon is not probable because the reaction does not occur in a basic medium, instead a brown insoluble powder is formed. In contrast, the reaction proceeds under acidic conditions resulting from the addition of 0.5 mL of concentrated  $\text{HCl}(\text{aq})$  to the reaction mixture.

Compound **1** undergoes a one-electron reduction upon addition of the bidentate phosphine ligand dppm to form **2**,  $[\text{Re}_2\text{Cl}_4(\mu\text{-dppm})_2\{\mu\text{-PhC}(\text{O})\text{NH}\}]$ , a  $\text{Re}^{\text{III}}\text{Re}^{\text{II}}$  system with the bridging phosphines in a *trans* geometry. The reduction of a  $\text{Re}^{\text{III}}_2$  core by a phosphine ligand is not unusual as demonstrated in the synthesis  $[\text{Re}_2\text{Cl}_4(\mu\text{-dppm})_2]$  from  $[\text{Re}_2\text{Cl}_6(\text{P}^n\text{Bu}_3)_2]$ , a two-electron reduction.<sup>45,46</sup>

### Confirmation of structure

Since one of the difficulties in the hydrolysis of nitriles is the tendency to form carboxylate species, a methodology to deter-



**Scheme 2** Proposed reaction mechanism of the formation of the co-ordinated benzamidate ligand

mine if the dirhenium reaction terminates at the formation of the benzamidate ligand,  $\mu\text{-PhC}(\text{O})\text{NH}^-$ , or reacts further to form the benzoate ligand,  $\mu\text{-PhCO}_2^-$ , has been established. The structure of compound **1** allowed the nitrogen and oxygen atoms to be distinguished in the benzamidate ligand, disorder in the oxygen and nitrogen atom positions in **2** required fitting the positions as 50% O and 50% N and the nature of the ligand could not be confirmed directly using NMR spectroscopy since the compound is paramagnetic,  $\sigma^2\pi^4\delta^2\delta^*1$ . Magnetic susceptibility studies performed on **2** confirmed the paramagnetic  $\text{Re}^{\text{III}}\text{Re}^{\text{II}}$  system. A  $\mu_{\text{eff}}$  value of 1.45  $\mu_{\text{B}}$  was obtained after performing a diamagnetic correction for **2** and the value compares well with the spin only  $\mu_{\text{eff}}$  value of 1.73  $\mu_{\text{B}}$  predicted for a system with one unpaired electron.<sup>47</sup>

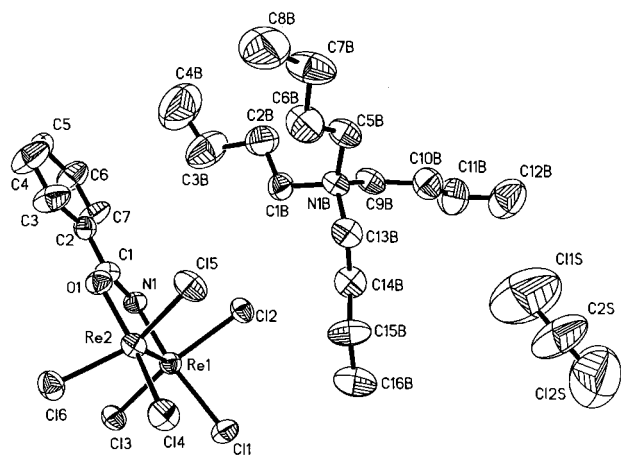
Using the oxidizing agent  $\text{AgBF}_4$ , a diamagnetic  $\text{Re}^{\text{II}}_2$  derivative of **2** was synthesized in order to perform NMR spectroscopy. Subsequent  $^{31}\text{P}\{-^1\text{H}\}$  NMR studies confirm that the benzamidate ligand is synthesized and not the benzoate ligand. As expected for a co-ordinated benzamidate ligand, the  $^{31}\text{P}\{-^1\text{H}\}$  NMR spectrum of the oxidized  $[\text{Re}_2\text{Cl}_4(\mu\text{-dppm})_2\{\mu\text{-PhC}(\text{O})\text{NH}\}]$  compound contains a complex pattern indicating inequivalent phosphorus magnetic environments with peaks centered at  $\delta -9.43$  and  $-17.69$ . A singlet in the  $^{31}\text{P}\{-^1\text{H}\}$  NMR spectrum is predicted if  $[\text{Re}_2\text{Cl}_4(\mu\text{-dppm})_2(\mu\text{-O}_2\text{CPh})]$  had been synthesized.

### Crystal structures

The Re–Re bond length of 2.2209(5) Å for compound **1** (Fig. 1, Table 1), a  $\text{Re}^{\text{III}}_2$  system, falls within the range observed for both the starting material  $[\text{NBu}_4][\text{Re}_2\text{Cl}_8]$  [2.222(2) Å]<sup>49</sup> and other quadruply bonded dirhenium species.<sup>50</sup> In contrast, the Re–Re bond length of 2.3129(7) Å for compound **2** (Fig. 2,

**Table 1** Selected bond lengths (Å) and angles (°) for compounds **1** and **2** when the numbering scheme differs from **1** to **2** superscripts were attached to denote the respective compounds

	<b>1</b>	<b>2</b>
Re(1)–Re(2)	2.2209(5)	2.3129(7)
Re(1)–N(1) <sup>1</sup> and Re(1)–ONX(2) <sup>2</sup>	2.044(7)	2.06(2)
Re(2)–O(1) <sup>1</sup> and Re(1)–ONX(1) <sup>2</sup>	2.009(6)	2.096(14)
Re(1)–Cl(1)	2.334(2)	2.618(3)
Re(1)–Cl(2)	2.375(2)	2.375(3)
Re(1)–Cl(3)	2.332(2)	
Re(2)–Cl(4) <sup>1</sup> and Re(2)–Cl(3) <sup>2</sup>	2.322(3)	2.589(3)
Re(2)–Cl(5) <sup>1</sup> and Re(2)–Cl(4) <sup>2</sup>	2.310(3)	2.389(3)
Re(2)–Cl(6)	2.306(3)	
N(1)–C(1) <sup>1</sup> and ONX(1)–C(51) <sup>2</sup>	1.315(11)	1.28(2)
O(1)–C(1) <sup>1</sup> and ONX(2)–C(51) <sup>2</sup>	1.302(11)	1.34(2)
Re(1)–Re(2)–O(1) <sup>1</sup> and Re(1)–Re(2)–ONX(1) <sup>2</sup>	92.7(2)	90.1(5)
Re(2)–Re(1)–N(1) <sup>1</sup> and Re(2)–Re(1)–ONX(2) <sup>2</sup>	88.1(2)	88.5(5)
Re(2)–Re(1)–Cl(1)	105.37(7)	162.40(8)
Re(2)–Re(1)–Cl(2)	100.07(6)	104.41(9)
Re(2)–Re(1)–Cl(3)	101.39(6)	
Re(1)–Re(2)–Cl(4) <sup>1</sup> and Re(1)–Re(2)–Cl(3) <sup>2</sup>	103.86(8)	167.95(8)
Re(1)–Re(2)–Cl(5) <sup>1</sup> and Re(1)–Re(2)–Cl(4) <sup>2</sup>	106.17(7)	99.89(8)
Re(1)–Re(2)–Cl(6)	106.61(7)	

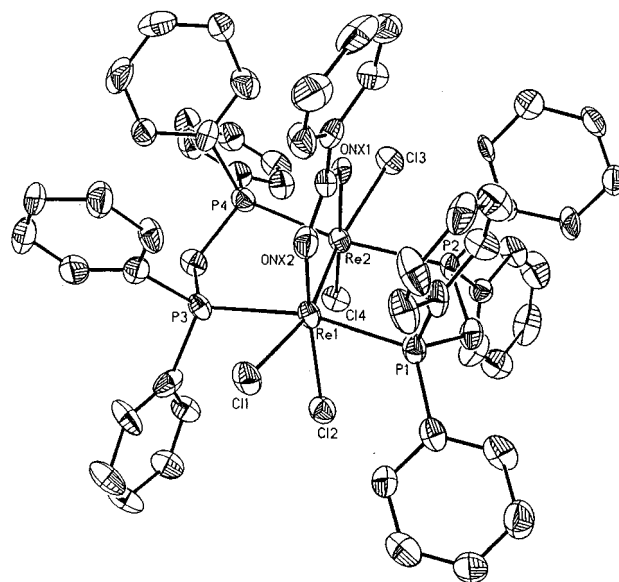


**Fig. 1** An ORTEP<sup>48</sup> drawing of the crystal structure of  $[\text{NBu}_4][\text{Re}_2\text{Cl}_6(\text{PhCONH})] \cdot 0.5\text{CH}_2\text{Cl}_2$  with thermal ellipsoids drawn at 50% probability. Hydrogen atoms were omitted for clarity

Table 1) marks one of the longest distances observed for a  $\text{Re}^{\text{III}}\text{Re}^{\text{II}}$  species where  $\text{Re}\text{--}\text{Re}$  bond distances of 2.20 to 2.30 Å are typical.<sup>50</sup> However, two axially co-ordinated chlorides are present and the  $\text{Re}\text{--}\text{Re}$  bond lengths in systems with axial halides are usually longer than those in  $\text{Re}^{\text{III}}\text{Re}^{\text{II}}$  systems with no axial halides. Weakening of the  $\text{Re}\text{--}\text{Re}$   $\sigma$  bond results from the axially co-ordinated ligand, as in the case of the  $\text{Re}^{\text{III}}_2$  system  $[\text{Re}_2(\mu\text{-dfm})_4(\text{OMe})_2]$  (Hdfm is di-*p*-tolylformamidine) with a  $\text{Re}\text{--}\text{Re}$  bond distance of 2.3047 Å.<sup>50,51</sup>

The  $\text{Re}\text{--}\text{O}$  and  $\text{Re}\text{--}\text{N}$  bond distances for compound **1** of 2.009(6) and 2.044(7) Å are only slightly shorter than those observed for the respective  $\text{Re}\text{--}\text{O}$  and  $\text{Re}\text{--}\text{N}$  bond distances in dirhenium(III) carboxylato {2.025(4) Å for  $[\text{Re}_2\text{Cl}_2(\mu\text{-O}_2\text{-CMe})_4]$  and amidinato complexes (2.055(9) Å for  $[\text{Re}_2\text{Cl}_2\text{--}\{(\text{MeN})_2\text{CPh}\}_4\text{--}\text{CCl}_4]$  with axial chlorides.<sup>52,53</sup> The  $\text{Re}\text{--}\text{ONX}$  bond distance of 2.078 Å (average) for **2** is similar to the 2.07 Å (average)  $\text{Re}\text{--}\text{N}$  bond distance for the amidinato complex without axial halides  $[\text{Re}_2\text{Cl}_4\{(\text{PhN})_2\text{CMe}\}_2]$  but a direct comparison of this 'average'  $\text{Re}\text{--}\text{ONX}$  bond distance to those of other systems holds significant error.<sup>53</sup>

The  $\text{C}\text{--}\text{O}$  and  $\text{C}\text{--}\text{N}$  bond distances for unco-ordinated neutral benzamide are 1.24 and 1.31 Å, respectively.<sup>54</sup> The co-



**Fig. 2** An ORTEP drawing of the crystal structure of  $[\text{Re}_2\text{Cl}_4(\mu\text{-dppm})_2(\text{PhCONH})]$ . Details as in Fig. 1

ordinated benzamido ligand in compound **1** has bond distances of 1.302(11) and 1.315(11) Å for  $\text{C}\text{--}\text{O}$  and  $\text{C}\text{--}\text{N}$ , while **2** has a distance of 1.31 Å (average) for the disordered  $\text{ONX}\text{--}\text{C}$  positions, distances that are within the range expected for the anionic ligand. In both compounds the benzamido ligand retains an  $\text{sp}^2$  hybridization so little deviation in the  $\text{N}\text{--}\text{C}\text{--}\text{O}$  bond angle from  $120^\circ$  is predicted. As expected, **1** has an  $\text{N}\text{--}\text{C}\text{--}\text{O}$  bond angle of  $118.3(8)^\circ$  and **2** an  $\text{ONX}\text{--}\text{C}\text{--}\text{ONX}$  angle of  $118.2(12)^\circ$ .

## Conclusion

This study marks the first use of a multiply bonded dirhenium species to synthesize co-ordinated benzamido ligands from benzonitrile. It is currently being expanded to include other substituted nitriles to determine if these species will undergo an analogous selective hydrolysis process. Experiments are being carried out fully to characterize the diamagnetic product of the oxidation of  $[\text{Re}_2\text{Cl}_4(\mu\text{-dppm})_2\{\mu\text{-PhC}(\text{O})\text{NH}\}]$ , including elucidation of the coupling constants observed in the  $^{31}\text{P}\text{--}\{^1\text{H}\}$  NMR spectra.

## Experimental

### Starting materials

Reagent ethanol was dried over magnesium turnings, methylene chloride over  $\text{P}_2\text{O}_5$ , and hexanes over potassium/sodium-benzophenone. All solvents were freshly distilled under an atmosphere of argon prior to use. The starting material,  $[\text{NBu}_4]_2[\text{Re}_2\text{Cl}_8]$ , was synthesized as previously reported.<sup>55</sup> Bis(diphenylphosphino)methane (dppm) from Aldrich Chemical Co. was evacuated overnight under dynamic vacuum to remove any residual oxygen or moisture. Benzonitrile in a Sure-Seal bottle from Aldrich Chemical Co. was used without further purification. All reagent transfers were performed using standard Schlenk, vacuum line and dry-box techniques under an inert atmosphere of argon.

### Syntheses

**$[\text{NBu}_4][\text{Re}_2\text{Cl}_6\{\mu\text{-PhC}(\text{O})\text{NH}\}] \cdot 0.5\text{CH}_2\text{Cl}_2$  1.** The complex  $[\text{NBu}_4]_2[\text{Re}_2\text{Cl}_8]$  (0.25 g, 2.19 mmol) was suspended in ethanol (30  $\text{cm}^3$ ) and PhCN (1  $\text{cm}^3$ , 9.77 mmol) added. The solution was stirred for 3 d at room temperature and a deep blue-green solution formed. All solvent was removed under dynamic vacuum overnight to yield a blue product (0.168 g, 85%) (Found: C,

28.70; H, 4.40; N, 2.91. Calc. for  $C_{23.50}H_{42}Cl_7N_2ORe_2$ : C, 28.54; H, 4.28; N, 2.83%.  $\lambda_{max}/nm$  ( $CH_2Cl_2$ ): 614.  $\tilde{\nu}_{max}/cm^{-1}$  2955, 2930 and 2873 (NH and CH) and 1530, 1469 and 1379 (CO and CN).  $\delta_H$ (400 MHz; solvent  $CDCl_3$ ; standard  $SiMe_4$ ) 1.05 (t,  $J$  6.6), 1.54 (s, broad), 1.77 (s, broad), 3.31 (s, broad), 7.46 (d,  $J$  7.3), 7.54 (t,  $J$  7), 7.94 (d,  $J$  7.3 Hz) and 11.34 (s).

**[ $Re_2Cl_4(\mu-dppm)_2\{\mu-PhC(O)NH\}$ ] 2.** Compound **1** (0.216 g, 2.19 mmol) dissolved in ethanol (30  $cm^3$ ) was transferred *via* cannula to a Schlenk flask containing dppm (0.17 g, 4.38 mmol) and heated at reflux for 45 min. The brown product precipitated and was washed three times with 30  $cm^3$  aliquots of ethanol and dried under dynamic vacuum (0.174 g, 59%). Compound **2** can also be synthesized from **1** prepared *in situ* by the addition of dppm (Found: C, 48.55; H, 3.99; N, 1.18. Calc. for  $C_{57}H_{49}Cl_4NOP_4Re_2$ : C, 48.82; H, 3.53; N, 1.00%).  $\lambda_{max}/nm$  ( $CH_2Cl_2$ ): 482 (sh), 722, 1066.  $\tilde{\nu}_{max}/cm^{-1}$  2949, 2926 and 2872 (NH and CH) and 1466 and 1378 (CO and CN).

### Instrumentation

The UV/VIS spectra were recorded on a Hewlett-Packard model 8453 diode array spectrophotometer from 400 to 1100 nm,  $^{31}P\{-^1H\}$  (162 MHz) and  $^1H$  NMR spectra (400 MHz) of compounds **1** and **2** in  $CH_2Cl_2$  on a General Electric Omega spectrometer with a 10 mm variable temperature broad band probe referenced to  $H_3PO_4$  ( $\delta$  0.00) and  $SiMe_4$  ( $\delta$  0.00), respectively. The  $^1H$  NMR spectra (300 MHz) of neat benzonitrile and ethanol were recorded on a General Electric QE NMR spectrometer. Magnetic susceptibility measurements were performed on a Johnson Matthey magnetic susceptibility balance and diamagnetic corrections were applied.<sup>47</sup> Infrared measurements were recorded on a MIDAC FT-IR spectrometer as liquid samples in CsI cells using  $CH_2Cl_2$  as the solvent. Elemental analyses were performed on compound **1** by Exeter Analytical, Inc. and on **2** by Oneida Research Services.

### X-Ray crystallography

Suitable crystals for X-ray crystallography were grown by layering  $CH_2Cl_2$  solutions of the respective compounds with hexanes. Crystals of **1** and **2** were mounted on glass fibers with grease. A summary of data collection parameters is provided in Table 2.

Data were collected using a Siemens SMART CCD (charge coupled device) based diffractometer equipped with a LT-2 low-temperature apparatus operating at 213 K for compound **1** and 173 K for **2**. Omega scans of  $0.3^\circ$  per frame for 30 s were used, such that a hemisphere was collected. A total of 1271 frames were collected with a final resolution of 0.85 Å. The first 50 frames were recollected at the end of data collection to monitor for decay. Cell parameters were retrieved using SMART<sup>56</sup> software and refined using SAINT<sup>57</sup> on all observed reflections. Data reduction was performed using the SAINT software, which corrects for Lorentz polarization and decay. Absorption corrections were applied using SADABS<sup>58</sup> supplied by George Sheldrick. The structures were solved by the direct method using the SHELXS 90<sup>59</sup> program and refined by least squares on  $F^2$  using SHELXL 97,<sup>60</sup> incorporated in SHELXTL-PC V 5.03.<sup>61</sup> Neither of the crystals showed decomposition during data collection.

Compound **1** crystallized in the triclinic crystal system. The space group  $P\bar{1}$  was assumed and confirmed by the successful solution refinement of the structure. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were found by Fourier-difference methods and refined isotropically.

The structure of compound **2** was solved in the monoclinic crystal system. The space group  $P2_1/n$  was assumed and confirmed by the successful solution and refinement of the structure. Although the majority of the structure was readily apparent, the co-ordinated O and N atoms of the benzamidate

**Table 2** Crystallographic and experimental details of the X-ray studies for compounds **1** and **2**

	<b>1</b>	<b>2</b>
Formula	$C_{23.50}H_{42}Cl_7N_2ORe_2$	$C_{57}H_{49}Cl_4NOP_4Re_2$
$M$	989.14	1402.05
$\lambda/\text{\AA}$	0.710 73	0.710 73
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$
$a/\text{\AA}$	11.9970(7)	17.9845(2)
$b/\text{\AA}$	12.2518(7)	14.4872(1)
$c/\text{\AA}$	12.9875(7)	21.2250(2)
$\alpha/^\circ$	79.379(1)	
$\beta/^\circ$	73.206(1)	105.937(1)
$\gamma/^\circ$	79.478(1)	
$U/\text{\AA}^3$	1779.2(2)	5317.52(9)
$Z$	2	4
$D_c/g\text{ cm}^{-3}$	1.846	1.751
$\mu/\text{mm}^{-1}$	7.342	4.911
Crystal size/mm	$0.05 \times 0.15 \times 0.15$	$0.05 \times 0.10 \times 0.10$
$\theta$ Range for data collection/ $^\circ$	1.65 to 24.72	1.32 to 23.20
Index ranges	$-14 \leq h \leq 14$ , $-11 \leq k \leq 14$ , $-12 \leq l \leq 15$	$-19 \leq h \leq 19$ , $-15 \leq k \leq 15$ , $-23 \leq l \leq 13$
Reflections collected	9289	19 872
Independent reflections ( $R_{int}$ )	5980 (0.0372)	7438 (0.1509)
Data/restraints/parameters	5980/0/334	7436/0/618
$R1 [I > 2\sigma(I)]$	0.0419	0.0656
$wR2 [I > 2\sigma(I)]$	0.0887	0.1606

ligand could not be distinguished. The two positions, ONX1 and ONX2, were each refined as 50% oxygen and 50% nitrogen. The geometrically constrained hydrogen atoms were placed in calculated positions with isotropic vibrational factors equal to 120% of the atom to which they were bonded. Refinement of non-hydrogen atoms was carried out with anisotropic thermal parameters except for C20, a carbon on one of the phenyl rings of the dppm ligand.

CCDC reference number 186/1053.

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