

Synthesis of Tricarbonyl Re(I) Complexes of N and P Donor Ligands

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Abstract

Reaction of 1,10-phenanthroline-5,6-dione **V** with 1,3-diphenyl propan-2-one afforded the keto-alcohol **VI**. Treatment of **VI** with alkynes, di(3-thienyl) acetylene and di(4-*tert*-butylphenyl) acetylene yielded 5,8-diphenyl-6,7-di(3-thienyl)-1,12-diaza-triphenylene **L¹** and 6,7-di(4-*tert*-butylphenyl)-5,8-diphenyl-1,12-diazatriphenylene **L²**, respectively. [ReCl(CO)₅] reacted with N[^]N-donor ligands **L¹**-**L⁶** to produce *fac*-tricarbonylrhenium(I) complexes (**20**)-(**25**) in good yields as coloured solids. Treatment of [ReCl(CO)₅] with the bulky P[^]N ligand **L⁷** formed the neutral complex *fac*-[ReCl(CO)₃(**L⁷**)] (**26**) whilst with the azine diphosphine *Z,Z*-**L⁸** afforded the cationic complex *fac*-[Re(CO)₃(*E,Z*-**L⁸**)]Cl (**27a**), where **L⁸** is a tridentate ligand. The chloride anion of the complex (**27a**) was replaced by treating it with NH₄PF₆ into *fac*-[Re(CO)₃(*E,Z*-**L⁸**)]PF₆ (**27b**). Above complexes were characterized by a combination of elemental analysis, IR, Mass and NMR spectroscopy.

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Introduction

All carbon polyphenylenes (*e.g.*, hexaarylbenzene derivatives) are the building blocks for polyaromatic hydrocarbons (*e.g.*, hexabenzocoronenes or superbenzene derivatives **I**), which exhibit interesting physical and electrochemical properties (Wu et al., 2007). Cyclodehydrogenation of tetraaryldipyrimidyl benzene (Draper et al., 2002) and triaryltripyrimidyl benzene (Wijesinghe et al., 2014) containing four or six nitrogen atoms at the periphery lead to the preparation of fully-cyclised N-heterosuperbenzenes **II–IV** (Draper et al., 2002; Wijesinghe et al., 2014). Ru(II) complexes of the N-heterosuperbenzene derivative **II** showed unique optical and electrochemical properties (Draper et al., 2004; Gregg et al., 2005, 2006). The incorporation of heteroatoms into the carbon frameworks provides a number of new opportunities to fine-tune the molecular properties as discussed in the review of Mullen and coworkers (Wang et al., 2019).

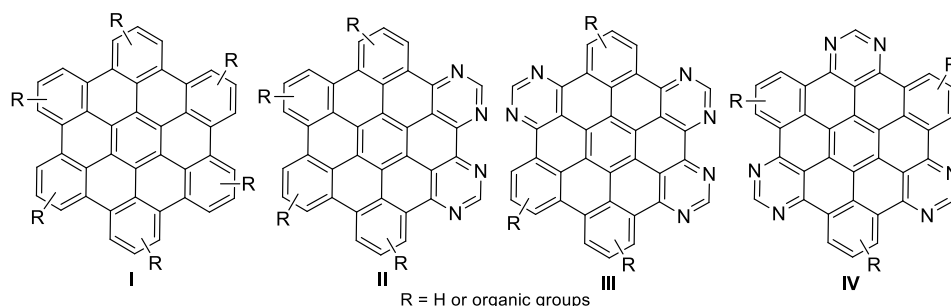


Figure 1. Molecular representation of superbenzenes and N-heterosuperbenzene derivatives

With the intention of finding more examples containing nitrogen and sulphur doped polycyclic aromatic hydrocarbons it was decided to synthesise polyphenylene derivatives such as 5,8-diphenyl-6,7-di(3-thienyl)-1,12-diaza-triphenylene **L¹**, 6,7-di(4-*tert*-butylphenyl)-5,8-diphenyl-1,12-diazatriphenylene **L²** and 3,4,5,6-tetraphenyl-2,2'-bipyridine **L³** (Figure 2). Rhenium(I) tricarbonyl complexes containing pyridine and phosphine-based ligands showed a wide variety of applications in supramolecular chemistry, catalysis, and in biology as fluorescence imaging agents (Amoroso et al., 2007; B.-Rodríguez et al, 2009; Gupta & Sathiyendiran, 2018; Tan et al., 2021; C.-Lopez et al., 2021; Acosta et al., 2021).

Thus, it is important to explore the chemistry of these bulky bipyridine ligands with rhenium(I) centres. In this publication, coordination modes of **L**¹–**L**³, half-cyclised N-heterosuperbenzene **L**⁴, 4-bromophenyl terpyridine **L**⁵, 4-phenyl-3,6-di(2-pyridyl)pyridazine **L**⁶ with Re(I) centres are reported. **L**¹–**L**⁴ can act as bidentate (N^N) ligands; **L**⁵ has three N-donors and it can act as either a bidentate (N^N) or a tridentate (N^N^N) ligand; **L**⁶ is an unsymmetrical ligand with four N-donors and it can show two different (N^N) bidentate modes.

This work was further extended to investigate the coordination modes of bulky P,N donor ligands *Z*-3-diphenylphosphino-(1*R*)-(+)-camphor dimethylhydrazone **L**⁷ and diphosphine *Z,Z*-PPh₂CH₂C(Bu^t)=N=N=C(Bu^t)CH₂PPh₂ **L**⁸. The ligand **L**⁷ has one P-donor and two N-donors and it can show two different (P^N) bidentate modes due to *Z* ↔ *E* isomerization around the C=N bond. The ligand **L**⁸ has two N-donors and two P-donors; it can show (P^P) and (P^N) bidentate modes, and one (P^N^P) tridentate mode because the energy barrier to the rotation around a C=N bond is quite low.

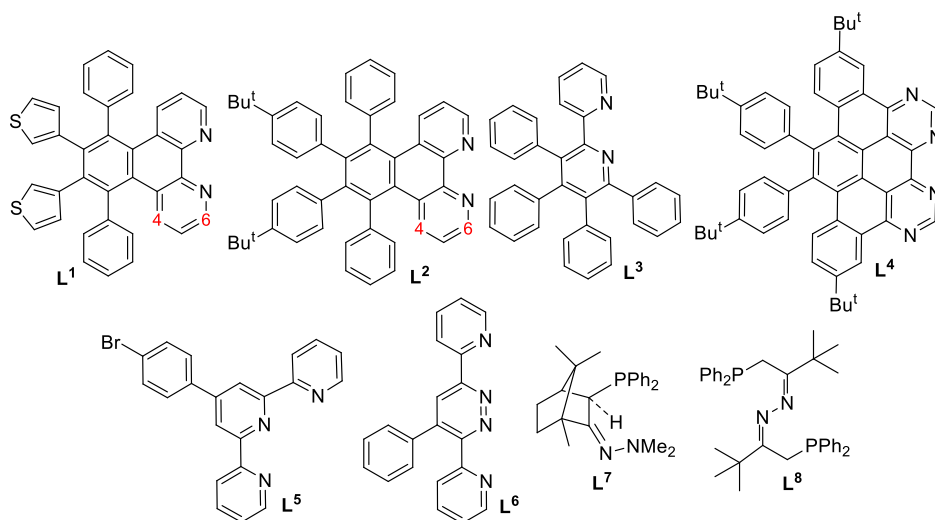


Figure 2. Molecular structures of N- and P-donor ligands depicting atom labelling used for the assignment of NMR data.

Precursors such as [ReX(CO)₅] (X = Cl, Br, OTf), [Re(CO)₃(OH₂)₃]⁺, [Re(CO)₃(NCMe)₃]⁺, [Re(CO)₃(dimethylsulphoxide)₃]⁺ & [Re(CO)₃Br₃]²⁻ have been used to prepare many different rhenium complexes including 2D and 3D metallacycles (Gupta & Sathiyendiran, 2018; Canadas *et al.*, 2019; Blanco-Rodríguez *et al.*, 2009; Coogan *et al.*, 2009). [ReX(CO)₅] (X = Cl, Br) has been used to polymerize 4-vinyl-

1-cyclohexene diepoxide photochemically and thermally without cocatalysts (Abu-Abdoun, 2019).

Rhenium(I) carbonyl complexes of the type *fac*-[ReX(N[^]N)(CO)₃] (**1**) (Figure 3) containing bidentate nitrogen donors are easy to prepare (Canadas et al., 2019; Deeba et al., 2021). These complexes are quite stable at room temperature, and photophysical properties can be tuned by using different types of ligands and by varying the R group. The rhenium(I) complex *fac*-[ReCl(2,2'-bipyridine)(CO)₃] selectively catalyses deoxygenation of nitrous oxide (N₂O) to dinitrogen in organic media in the presence of water (Deeba et al., 2021).

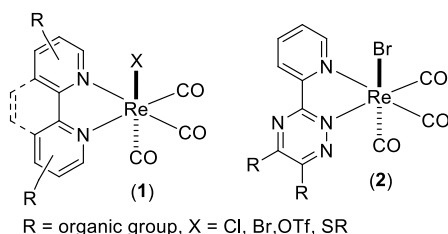


Figure 3. [ReX(N[^]N)(CO)₃] complexes with N[^]N donor ligands

Bipyridine-based mononuclear and binuclear Re(I) carbonyl complexes were successfully used in photocatalytic reduction of carbon dioxide to carbon monoxide (Bruckmeier et al., 2012). Rhenium(I) tricarbonyl complexes (**2**) containing the pyridyl triazine core have been synthesized using the precursors [Re(CO)₅Br] and [Re(CO)₃(H₂O)₃]OTf in an organic solvent mixture and water (Ranasinghe et al., 2016).

The reaction of the tridentate ligand (**3**) with [ReCl(CO)₅] formed the *fac*-tricarbonyl complex (**4**) (Coogan et al., 2009) with one uncoordinated pyridine ring, and the central ring has tautomerized to the 4-hydroxypyridine form (Figure 4). Similarly, with [ReCl(CO)₅] tridentate ligands 2,2':6',2''-terpyridine and tris(2-pyridyl)amine produced *fac*-tricarbonyl complexes (**5**) and (**6**), respectively (Anderson et al., 1990).

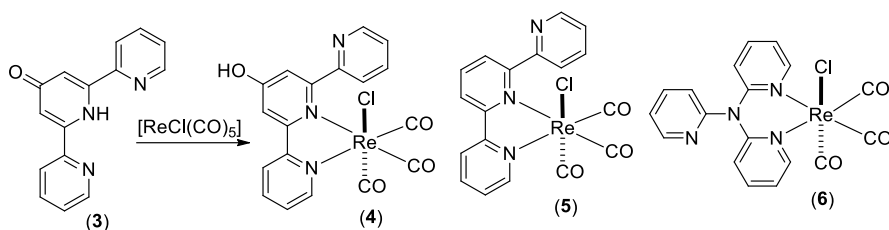


Figure 4. Structures of tricarbonyl Re(I) complexes with potential tridentate ligands

Various cationic complexes of the type $fac-[Re(L)(N^{\wedge}N)(CO)_3]^+$ (**7**) and (**8**) exhibited attractive photophysical properties with lifetimes up to microseconds (Fernández-Moreira et al., 2010) (Figure 5). These cationic complexes can be prepared by using the labile complex $fac-[Re(NCMe)(N^{\wedge}N)(CO)_3]^+$ or replacing the coordinating anion X from $[ReX(N^{\wedge}N)(CO)_3]$, in the presence of the ligand L and a non-coordinating anion.

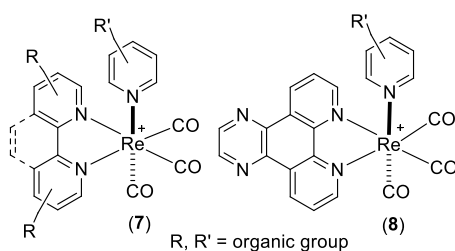


Figure 5. Cationic *fac*-complexes with bidentate ($N^{\wedge}N$) and monodentate (L) ligands

fac-Re(I) tricarbonyl bisimine complexes $[Re(bisimine)L(CO)_3]^+$ have the ability to retain their fluorescence in biological systems, thus, making them promising cell imaging agents (Amoroso et al., 2007). The cationic derivatives $[Re(bipy)(CO)_3(L)]^+$ have attracted the most attention in the imaging field, particularly those with axial pyridine ligands (Fernández-Moreira et al., 2010).

Methanol was added on to the bound-MeCN in the cationic complex $fac-[Re(CO)_3(Me_2bipy)(NCMe)]BF_4$ to form Re(I)(iminoether) complexes, $fac-[Re(CO)_3(Me_2bipy)\{HN=C(Me)OMe\}]BF_4$ (**9**) (Perera et al., 2012). Similarly, amines (HNR'_2) were added on to MeCN to give amidine-complexes, $fac-[Re(CO)_3(Me_2bipy)\{HN=C(Me)NR'_2\}]BF_4$ (**10**) (Abhayawardhana et al., 2012). Perera and co-workers studied the photophysical properties and the capability of cationic Re(I)

complexes (**11**) containing tridentate ligands as anti-inflammatory drug leads (Darshani et al., 2020).

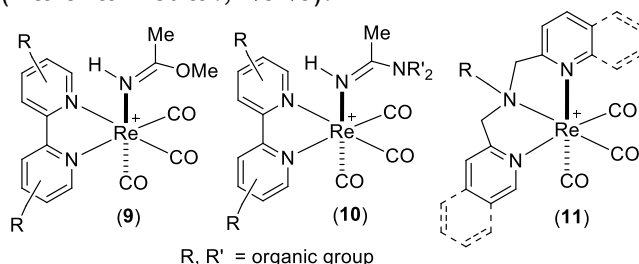


Figure 6: Cationic complexes: $fac\text{-[Re(CO)}_3\text{(N}^{\wedge}\text{N)}\{\text{HN}=\text{C}(\text{Me})\text{OMe}\}]^+$, $fac\text{-[Re(CO)}_3\text{(N}^{\wedge}\text{N)}\{\text{HN}=\text{C}(\text{Me})\text{NR}^{1_2}\}]^+$ and $fac\text{-[Re(CO)}_3\text{(N}^{\wedge}\text{N}^{\wedge}\text{N)}]^+$

Recently, the role of zero-field splitting (ZFS) and the geometric arrangement including π -stacking interactions present in complexes (**12**), (**13**), $[\text{Re}(\text{bpy})(\text{CO})_3(4\text{-phenyl-1-methyl-1H-1,2,3-triazole})]^+$ and $[\text{Re}(\text{bpy})(\text{CO})_3(4\text{-phenyl-1-propyl-1,2,3-triazole})]^+$ (bpy = 2,2'-bipyridine) were studied (C-Lopez et al., 2021).

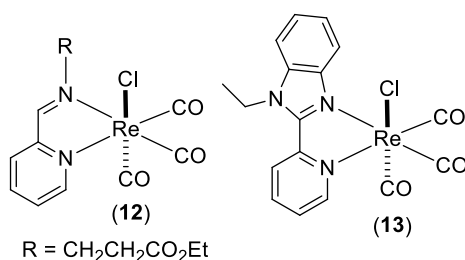


Figure 7. Molecular structures of $fac\text{-[ReCl(CO)}_3\text{(N}^{\wedge}\text{N)}]$ complexes

The synthesis of rhenium(I) tricarbonyl phosphine bromides and hydrides of the type $fac\text{-[ReX(CO)}_3\text{(P}^{\wedge}\text{P)}]$ (**14**)-(**16**) (Figure 8), where (X = Br or H), P[^]P = bis(diphenylphosphino)propane (dppp), 1,4-bis(diphenylphosphino)butane (dppb), and 1,10-bis(diphenylphosphino)ferrocene (dppf) has been reported (Beckett et al., 2003; Kimari et al., 2005).

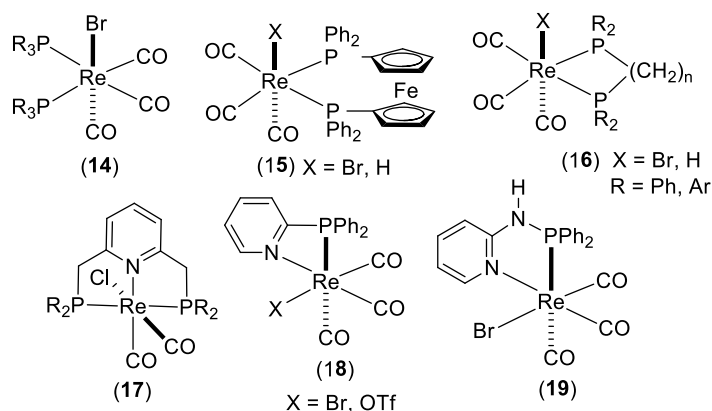


Figure 8. Molecular structures of tricarbonyl Re(I) complexes containing N- and P-donor ligands

Vogt et.al. (2014) reported the synthesis of the pincer complex *mer,cis*-[Re(P[^]N[^]P)(CO)₂Cl] (**17**) (Figure 8). Interestingly, the dearomatized five-coordinate complex [Re(P[^]N[^]P)(CO)₂] underwent a reversible 1,3-addition of CO₂ to form *cis*-[Re(P[^]N[^]P-COO)(CO)₂] via Re-O and C-C bond formation (Vogt et al., 2014). *fac*-Re(I)tricarbonyl complexes (**18**)-(**19**) exhibited photoisomerization upon irradiation at 365 nm and they are found to be promising antibacterial agents (Acosta et al., 2021).

Methodology

All experiments were carried out in an inert atmosphere (nitrogen or argon). Elemental analysis was carried out on a Carlo Erba 1006 automatic analyser. IR spectra were recorded on a Perkin-Elmer Spectrum One spectrometer fitted with a Universal-ATR sampling accessory. Mass spectral data were obtained using a micromass LCT electrospray mass spectrometer. MALDI-TOF mass spectra were recorded on a Waters Premier spectrometer using α-cyano-4-hydroxy cinnamic acid matrix. Accurate mass spectra were referenced against Leucine Enkephalin. NMR spectra were recorded on a DPX 400 spectrometer operating at 400.13 MHz for ¹H, and 100.62 MHz for ¹³C, and were standardized with respect to TMS. ³¹P NMR spectra were recorded at 161 MHz and were standardized with respect to phosphoric acid.

[ReCl(CO)₅] was purchased from Aldrich and 1,10-phenanthroline-5,6-dione (Rosa et al., 1996), **L**¹ (Perera et al., 2007), **L**² (Perera et al., 2011), **L**³ (Ollangnier et al., 2008), **L**⁴ (Gregg et al., 2005), **L**⁵

(Wang et al., 2005), **L**⁶ (Varughese et al., 2009), **L**⁷ (Perera et al., 1991) and **L**⁸ (Perera et al., 1992) were prepared according to literature procedures.

11b-Hydroxy-1,3-diphenyl-1,11b-dihydro-7,8-diaza-cyclopenta[l]phenanthren-2-one (VI)

1,10-Phenanthroline-5,6-dione (**V**) (Scheme 1) (1.32 g, 6.28 mmol), 1,3-diphenylpropan-2-one (2.0 g, 9.5 mmol) and potassium hydroxide (65 mg) were stirred at room temperature in dry methanol (12 mL) for 2h under nitrogen. The resulting solid was filtered and washed with little cold methanol. This solid was dissolved in dichloromethane (20 mL), filtered through celite and solvent was removed under reduced pressure. The residue (**VI**) was crystallised from methanol as a white crystalline solid. Yield (2.2 g, 87%). Found: C, 76.76; H, 4.71; N, 6.46; calcd. (%) for C₂₇H₁₈N₂O₂·1.25CH₃OH: C, 76.69; H, 5.24; N, 6.33. IR (neat) cm⁻¹: 3666 (O-H), 3223 (O-H), 1706 (C=O), 1575, 1415, 1342, 1090, 763, 740, 717 and 699. ESI-MS (m/z): found: 403.1459, calcd. 403.1447 for C₂₇H₁₉N₂O₂, [M+1]⁺. ¹H NMR (400 MHz, CDCl₃, δ in ppm): 8.74 (dd, 2H, ³J(HH) 4.5 Hz, ⁴J(HH) 1.5 Hz, H⁶), 8.71 (dd, 2H, ³J(HH) 4.5 Hz, ⁴J(HH) 1.5 Hz, H⁶), 8.03 (dd, 2H, ³J(HH) 8.0 Hz, ⁴J(HH) 1.5 Hz, H⁴), 7.60 (dd, 2H, ³J(HH) 8.0 Hz, ⁴J(HH) 1.5 Hz, H⁴), 7.6-7.4 (m, 8H, H_{Ph}), 7.36-7.33 (m, 3H, H_{Ph} and H⁵), 7.13 (dd, 2H, ³J(HH) 4.5, 8.5 Hz, H⁵), 4.49 (s, 1H, CHPh) and 3.19 (br, s, 1H, OH). ¹³C NMR (100 MHz, CDCl₃, δ in ppm): 202.3 (C=O), 158.3, 152.1 (C⁶), 150.4 (C⁶), 149.8, 149.7, 139.8, 136.1 (C⁴), 136.0, 134.4, 133.5 (C⁴), 131.5 (C_{Ph}), 129.4, 128.7, 128.6 (C_{Ph}), 128.5 (C_{Ph}), 127.8 (C_{Ph}), 124.8, 124.2 (C⁵), 123.2 (C⁵), 74.3 (C=) and 60.5 (CHPh).

5,8-diphenyl-6,7-di(3-thienyl)-1,12-diazatriphenylene (L¹)

Di(3-thienyl) acetylene (350 mg, 1.83 mmol), 11b-hydroxy-1,3-diphenyl-1,11b-dihydro-7,8-diaza-cyclopenta[l]phenanthren-2-one (**VI**) (600 mg, 1.49 mmol) and benzophenone (2.5 g) were heated at 330 °C under argon for 75 min. The product was purified by column chromatography on silica using 5%MeOH in dichloromethane as the eluent, to yield a pale-yellow solid (470 mg, 58%). Found: C, 76.42; H, 3.99; N, 4.84; calcd. (%) for C₃₆H₂₂N₂S₂·0.25CH₂Cl₂: C, 76.72; H, 3.99; N, 4.93. IR (neat) cm⁻¹: 1566, 1426, 1276, 1260, 764, 744, 718 and 703. ESI-MS (m/z): found: 547.1301, calcd. 547.1303 for C₃₆H₂₃N₂S₂, [M+1]⁺. ¹H-NMR (400 MHz, CDCl₃, δ in ppm): 8.93 (d, 2H, ³J(HH) 4.5 Hz, H⁶), 7.83 (d, 2H, ³J(HH) 8.5, Hz, H⁴), 7.25-7.20 (m, 6H, H_{Ph}), 7.10 (d, 4H, ³J(HH) 7.5 Hz, H_{Ph}), 7.06 (dd, 2H, ³J(HH) 4.5, 8.5, Hz, H⁵), 6.95 (dd, 2H, ³J(HH) 5.0, Hz, ⁴J(HH) 3.0 Hz, H_{Th}), 6.49 (d, 2H, ⁴J(HH) 3.0 Hz,

H_{Th}) and 6.43 (d, 2H, ³J(HH) 5.0 Hz, H_{Th}). ¹³C-NMR (100 MHz, CDCl₃, δ in ppm): 148.8 (C⁶), 137.2 (C⁴), 131.2 (C_{Ph}), 129.9 (C_{Th}), 128.7 (C_{Ph}), 127.1 (C_{Ph}), 124.3 (C_{Th}), 123.5 (C_{Th}) and 121.6 (C⁵).

6,7-di(4-*tert*-butylphenyl)-5,8-diphenyl-1,12-diazatriphenylene (L²)

Di(4-*tert*-butylphenyl) acetylene (210 mg, 0.723 mmol), (VI) (300 mg, 0.745 mmol) and benzophenone (1.2 g) were heated at 300 °C under argon for 1 h. Column chromatography on silica using 5% methanol in dichloromethane afforded **L²** as an off-white solid (255 mg, 55%). MA ESI-MS (m/z): found: 647.3431, calcd. 647.3426 for C₄₈H₄₃N₂, [M+]⁺. ¹H-NMR (400 MHz, CDCl₃, δ in ppm): 8.91 (dd, 2H, ³J(HH) 4.5 Hz, ⁴J(HH) 1.5 Hz, H⁶), 7.83 (dd, 1H, ³J(HH) 8.5 Hz, ⁴J(HH) 1.5 Hz, H⁴), 7.11-7.17 (m, 6H, H_{Ph}), 7.07 (m, 4H, H_{Ph}), 7.04 (dd, 2H, ³J(HH) 4.5, 8.5 Hz, H⁵), 6.88 (d, 2H, ³J(HH) 8.5 Hz, H_{Ar}), 6.57 (m, 2H, ³J(HH) 8.5 Hz, H_{Ar}) and 1.17 (s, 18H, CMe₃). ¹³C-NMR (100 MHz, CDCl₃, δ in ppm): 148.5 (C⁶), 147.7, 146.8, 141.5, 137.5, 136.4, 136.2 (C⁴), 131.4 (C_{Ph}), 130.4 (C_{Ar}), 128.8, 127.8, 127.4 (C_{Ph}), 126.2, 125.4 (C_{Ph}), 122.9 (C_{Ar}), 120.7 (C⁵), 33.7 (CMe₃) and 30.8 (CMe₃).

***fac*-[ReCl(CO)₃(L¹)] (20)**

A suspension containing [ReCl(CO)₅] (10 mg, 0.027 mmol) and 5,8-diphenyl-6,7-di(3-thienyl)-1,12-diazatriphenylene **L¹** (15 mg, 0.027 mmol) in degassed benzene (2.5 mL) was heated under reflux for 3 h to give a yellow solution. It was allowed to cool and then concentrated to a low volume and triturated with hexane to yield (**20**) as a yellow solid (21 mg, 89%). Found: C, 55.05; H, 2.65; N 3.30, calcd. (%) for C₃₉H₂₂ClN₂O₃S₂Re: C, 54.95; H, 2.60; N 3.29. ESI-MS (THF, m/z): found: 852.0358, calcd. 852.0318 for C₃₉H₂₂N₂O₃S₂ClRe, [M]⁺. IR (neat, cm⁻¹): 2926, 2017, 1912, 1878, 1575, 1438, 1377, 1019, 773, 699 and 680. ¹H NMR (400 MHz, CDCl₃, δ): 9.11 (d, 2H, ³J(HH) 5.1 Hz, H_{Py}), 8.01 (d, 2H, ³J(HH) 8.0 Hz, H_{Py}), 7.39 (s, C₆H₆), 7.34-7.29 (m, 6H, H_{Ph}), 7.22 (dd, 2H, ³J(HH) 5.1, 8.0 Hz, H_{Py}), 7.13 (d, 4H, ³J(HH) 7.3 Hz, H_{Ph}), 6.96 (m, 2H, H_{Th}), 6.52 (d, 2H, ⁴J(HH) 1.5 Hz, H_{Th}) and 6.43 (d, 2H, ³J(HH) 4.3 Hz, H_{Th}). ¹³C NMR (100 MHz, CDCl₃, δ): 197.2, 190.0, 151.4, 148.1, 140.9, 139.7, 139.6, 138.6, 138.4, 130.9, 130.7, 129.5, 129.3, 129.1, 128.3, 127.9, 127.8, 124.7, 123.9 and 123.6.

***fac*-[ReCl(CO)₃(L²)] (21)**

A suspension containing [ReCl(CO)₅] (8.4 mg, 0.023 mmol) and 6,7-di(4-*tert*-butylphenyl)-5,8-diphenyl-1,12-diazatriphenylene **L²** (15 mg, 0.023 mmol) in degassed benzene (2.5 mL) was heated under reflux for 3 h to give a yellowish brown solution. It was allowed to cool, then concentrated to a low volume, and hexane was added to

yield (**21**) as a yellow solid (20 mg, 91%). Analytical sample was crystallised from dichloromethane/methanol. Found: C, 62.35; H, 4.05; N 2.60, calcd. (%) for $C_{51}H_{42}ClN_2O_3Re \cdot 0.5CH_2Cl_2$: C, 62.16; H, 4.36; N 2.82. ESI-MS (THF, m/z): found: 952.2477, calcd. 952.2442 for $C_{51}H_{42}N_2O_3ClRe$, $[M]^+$. IR (neat, cm^{-1}): 2962, 2017, 1910, 1898, 1866, 1600, 1437, 1024, 808, 699 and 678. 1H NMR (400 MHz, $CDCl_3$, δ): 9.10 (d, 2H, $^3J(HH)$ 5.0 Hz, H_{Py}), 8.01 (d, 2H, $^3J(HH)$ 9.0 Hz, H_{Py}), 7.39 (s, C_6H_6), 7.25-7.16 (m, 8H, H_{Py} & H_{Ph}), 7.10 (d, 4H, $^3J(HH)$ 7.0 Hz, H_{Ph}), 6.89 (d, 4H, $^3J(HH)$ 8.5 Hz, H_{Ar}), 6.57 (m, 4H, H_{Ar}) and 1.17 (s, 18H, CMe_3).

fac-[ReCl(CO)₃(L³)] (22)

A suspension containing $[ReCl(CO)_5]$ (16 mg, 0.044 mmol) and 3,4,5,6-tetraphenyl-2,2'-bipyridine **L³** (22 mg, 0.047 mmol) in degassed benzene (6 mL) was heated under reflux for 3 h to result a yellow solution. It was allowed to cool and then concentrated to yield (**22**) as a yellow solid (33 mg, 97%). Found: C, 59.80; H, 3.35; N 3.30, calcd. (%) for $C_{37}H_{24}ClN_2O_3Re \cdot 0.5C_6H_6$: C, 59.66; H, 3.38; N 3.48. ESI-MS (THF, m/z): found: 789.0924, calcd. 789.0931 for $C_{37}H_{24}N_2O_3ReClNa$, $[M+Na]^+$. IR (neat, cm^{-1}): 3031, 2015, 1908, 1872, 1602, 1551, 1478, 1448, 768, 698 and 682. 1H NMR (400 MHz, $CDCl_3$, δ): 9.06 (d, 1H, $^3J(HH)$ 5.0 Hz, H_{Py}), 7.60 (d, 2H, $^3J(HH)$ 7.5 Hz, H_{Py}), 7.52-7.40 (m, 3H, H_{Py} & H_{Ph}), 7.39 (s, C_6H_6), 7.25-7.16 (m, 8H, H_{Py} & H_{Ph}), 6.75 (d, 1H, $^3J(HH)$ 8.0 Hz, H_{Ar}), 6.69 (d, 2H, $^3J(HH)$ 8.0 Hz, H_{Ar}) and 6.65 (d, 1H, $^3J(HH)$ 6.5 Hz, H_{Ph}). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 197.3 (CO), 196.8 (CO), 191.5 (CO), 161.7, 159.0, 154.6, 152.9, 152.7, 140.5, 138.3, 137.2, 136.9, 136.4, 135.7, 131.7, 131.2, 130.8, 130.5, 130.2, 130.0, 129.9, 129.6, 129.3, 129.1, 129.0, 128.3, 128.2, 127.9, 127.6, 127.3, 127.2, 126.7, 127.1, 127.0, 126.6 and 124.8.

fac-[ReCl(CO)₃(L⁴)] (23)

A suspension containing $[ReCl(CO)_5]$ (3 mg, 0.0083 mmol) and **L⁴** (4.5 mg, 0.0059 mmol) in chloroform (2 mL) was heated under reflux for 6 h to give a cherry red solution. It was concentrated to a low volume and triturated with methanol to yield (**23**) as a dark brown solid (5 mg, 79%). Maldi (THF, m/z): found: 1027.3564, calcd. 1027.3597 for $C_{54}H_{52}N_4O_3Re$, $[M-Cl]^+$. IR (neat, cm^{-1}): 2962, 2018, 1921, 1885, 1609, 1556, 1535, 1464, 1397, 1362, 1259, 1024 and 835. 1H NMR (600 MHz, $CDCl_3$, δ): 10.28 (s, 2H, H^1), 9.65 (d, 2H, $^4J(HH)$ 2.3 Hz, H^2), 7.88 (d, 2H, $^3J(HH)$ 9.0 Hz, H^4), 7.50 (dd, 2H, $^3J(HH)$ 9.0 Hz, $^4J(HH)$ 2.3 Hz, H^3), 7.33 (m, 4H, H^6), 7.07 (d, 4H, H^5), 1.51 (s, 18H, CMe_3) and 1.38 (s, 18H, CMe_3). ^{13}C NMR (161 MHz, $CDCl_3$, δ): 196.2 (CO *trans* to N), 187.5 (CO *trans* to Cl), 156.6, 155.3, 151.9, 151.2, 150.5, 144.9, 138.9, 132.9, 130.4,

130.3, 129.5, 129.3, 128.4, 125.1, 124.9, 123.0, 120.0, 118.6, 35.0 (CMe₃), 34.5 (CMe₃), 31.2 (CMe₃) and 31.0 (CMe₃).

[ReCl(CO)₃(L⁵)] (24)

A suspension containing [ReCl(CO)₅] (15 mg, 0.041 mmol) and 4-bromophenyl-terpyridine **L⁵** (17 mg, 0.043 mmol) in chloroform (5 mL) was heated under reflux for 4 h to give a yellowish brown solution. It was allowed to cool and then concentrated to a low volume to yield (**24**) as a yellow solid (28 mg, 96%). Found: C, 37.20; H, 1.70; N 5.10, calcd. (%) for C₂₄H₁₄BrClN₃O₃Re·1.0CHCl₃: C, 36.92; H, 1.86; N 5.17. IR (neat, cm⁻¹): 2983, 2016, 1912, 1873, 1708, 1613, 1482, 1386, 1080, 1008, 829, 788 and 745. ESI-MS (DCM, m/z): found: 657.9783, calcd. 657.9776 for C₂₄H₁₄BrN₃O₃Re, [M-Cl]⁺. ¹H NMR (400 MHz, CDCl₃, δ): 9.15 (d, 1H, ³J(HH) 5.5 Hz, H⁶), 8.87 (d, 1H, ³J(HH) 4.5 Hz, H⁶), 8.40-8.36 (m, 3H, H³, H⁷ and H⁷), 8.11 (t, 1H, ³J(HH) 8.5 Hz, H⁴ or H⁴'), 7.97 (m, 2H, ³J(HH) 8.5 Hz, H⁴ or H⁴'), 7.92 (d, 1H, ⁴J(HH) 1.5 Hz, H³), 7.73 (d, 2H, ³J(HH) 8.5 Hz, H_{Ar}), 7.65 (d, 2H, ³J(HH) 8.5 Hz, H_{Ar}) and 7.56 (m, 2H, H⁵ and H⁵).

[ReCl(CO)₃(L⁶)] (25)

A suspension containing [ReCl(CO)₅] (34 mg, 0.091 mmol) and 4-phenyl-3,6-di(2-pyridyl)-pyridazine **L⁶** (30 mg, 0.096 mmol) in degassed benzene (4 mL) was heated under reflux for 2 h to give a red solution. The solvent was removed and the residue was crystallized from dichloromethane/methanol to yield (**25**) as an orange solid (49 mg, 88%). Found: C, 44.55; H, 2.20; N 8.65, calcd. (%) for C₂₃H₁₄ClN₄O₃Re·0.25CH₂Cl₂: C, 43.82; H, 2.29; N 8.80. IR (neat, cm⁻¹): 2010, 1907, 1880, 1862, 1603, 1561, 1478, 1443, 1396, 1229, 1152, 994, 798, 757 and 699. MS (m/z-MALDI-TOF, CH₂Cl₂): found: 581.0614; calcd. 581.0624 for C₂₃H₁₄N₄O₃Re, [M-Cl]⁺. ¹H NMR (400 MHz, CDCl₃, δ): 9.16 (d, 1H, ³J(HH) 5.2 Hz, H_{Py}), 8.83 (d, 1H, ³J(HH) 7.9 Hz, H_{Py}), 8.75 (s, 1H, H_{PyT}), 8.74 (d, 1H, H_{Py}, overlaps with the singlet), 8.01 (dt, 1H, ³J(HH) 7.8 Hz, ⁴J(HH) 1.4 Hz, H_{Py}), 7.73-7.45 (m, 8H, H_{Ph} & H_{Py}) and 7.34 (d, 1H, ³J(HH) 8.3 Hz, H_{Py}). ¹³C NMR (100 MHz, CDCl₃, δ): 198.2 (CO), 196.6 (CO), 189.3 (CO), 158.2, 156.8, 154.4, 153.7, 150.7, 149.7, 144.8, 137.7, 137.6, 135.8, 130.5, 130.0, 128.2, 128.0, 127.1, 126.2 and 123.0.

[ReCl(CO)₃(L⁷)] (26)

A suspension containing [ReCl(CO)₅] (16 mg, 0.044 mmol) and **L⁷** (18 mg, 0.047 mmol) in degassed benzene (3 mL) was heated at 65 °C for 3.5 h to give a colourless solution. It was concentrated to a low volume and hexane was added to yield (**26**) as a white solid (21 mg, 70%). Found: C, 47.05; H, 5.00, N, 4.25. calcd. (%) for

$C_{27}H_{31}N_2O_3ClPRe$: C, 47.40; H, 4.57, N, 4.09. IR (neat, cm^{-1}): 2022 (CO), 1925 (CO), 1880 (CO), 1642, 1478, 1435, 1090, 745, 693 and 679. MS (m/z -MALDI-TOF, CH_2Cl_2): found: 621.1682; calcd. 621.1680 for $C_{26}H_{31}N_2O_2PRe$, $[M-CO-Cl]^+$. 1H NMR (400 MHz, $CDCl_3$, δ): 7.71-7.61 (m, 2H), 7.52-7.36 (m, 8H), 3.68 (s, 3H, NMe), 2.76 (d, 1H, $^2J(PH)$ 12.6 Hz), 2.64 (m, 1H), 2.57 (s, 3H, NMe), 2.15 (m, 1H), 1.84 (m, 1H), 1.64 (m, 1H), 1.47 (m, 1H), 1.01 (s, 3H, Me), 0.74 (s, 3H, Me) and -0.18 (s, 3H, Me). ^{13}C NMR (100 MHz, $CDCl_3$): 193.4 (d, $^2J(PC)$ 5.8 Hz), 191.6 (d, $J(PC)$ 74.3 Hz, CO *trans* to P), 191.0 (d, $J(PC)$ 7.8 Hz), 179.4 (C=N), 137.2 (d, $J(PC)$ 10.8 Hz), 132.7, 131.5 (d, $J(PC)$ 46.0 Hz), 130.4, 130.1 (d, $J(PC)$ 43.0 Hz), 128.6 (d, $J(PC)$ 9.8 Hz), 128.4, 128.3 (d, $J(PC)$ 6.0 Hz), 66.9, 55.7, 50.7, 47.9 (d, $J(PC)$ 47.9 Hz), 46.6, 37.0 (d, $J(PC)$ 11.7 Hz), 33.2, 30.2 (d, $J(PC)$ 5.9 Hz), 22.2, 19.0 and 11.2. ^{31}P NMR (161 MHz, $CDCl_3$): 45.9 (s).

fac-[Re(CO)₃(E,Z-**L**⁸)]Cl (27a)

A suspension containing $[ReCl(CO)_5]$ (14 mg, 0.0376 mmol) and azine diphosphine **L**⁸ (23 mg, 0.04 mmol) in degassed benzene (3 mL) was heated under reflux for 6 h to give a white precipitate. The reaction mixture was concentrated to a low volume, and hexane was added to yield (**27a**) as a white solid (29 mg, 88%). Found: C, 55.85; H, 5.20, N, 3.35. calcd. (%) for $C_{39}H_{42}N_2O_3ClP_2Re \cdot 0.5C_6H_6$: C, 55.47; H, 4.99, N, 3.08. IR (neat, cm^{-1}): 2966, 2028, 1960, 1915, 1618, 1478, 1382, 1198, 1098, 1080, 833, 739 and 693. MS (m/z -MALDI-TOF, CH_2Cl_2): found: 835.2223; calcd. 835.2228 for $C_{39}H_{42}N_2O_3P_2Re$, $[M-Cl]^+$. 1H NMR (400 MHz, $CDCl_3$): 7.91-7.76 (m, 2H), 7.76-7.56 (m, 5H), 7.51-7.35 (m, 5H), 7.21-7.08 (m, 3H), 7.08-6.97 (m, 3H), 6.72-6.59 (m, 2H), 4.70 (dd, 1H, $^3J(HH)$ = 18.6 Hz, $^2J(PH)$ 11.5 Hz, CH_2), 4.40 (t, 1H, $^3J(HH)$ = $^2J(PH)$ 13.1 Hz, CH_2), 3.57 (dd, 1H, $^3J(HH)$ = 18.6 Hz, $J(PH)$ 2.5 Hz, CH_2), 3.16 (t, 1H, $^3J(HH)$ = $^2J(PH)$ 13.1 Hz, CH_2), 1.59 (s, 9H, CMe_3) and 1.05 (s, 9H, CMe_3). ^{31}P NMR (161 MHz, $CDCl_3$): 31.9 (d) and 19.3 (d), $^2J(PP)$ = 24 Hz.

fac-[Re(CO)₃(E,Z-**L**⁸)]PF₆ (27b)

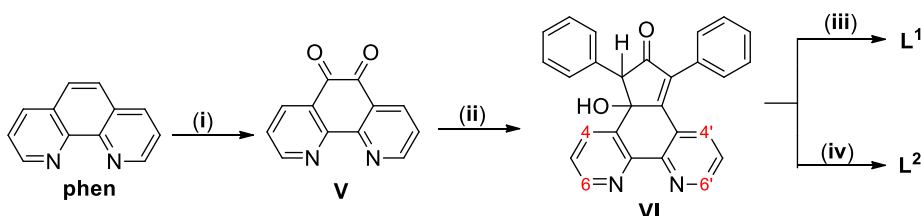
A solution of NH_4PF_6 (14 mg, 0.086 mmol) in methanol (0.5 mL) was added to a solution of (**27a**) (26 mg, 0.029 mmol) in methanol (0.5 mL). After 15 min, the solution was concentrated to a low volume to yield (**27b**) as a white solid (23 mg, 79%). Found: C, 47.65; H, 4.05, N, 2.55. calcd. (%) for $C_{39}H_{42}N_2O_3F_6P_3Re$: C, 47.80; H, 4.32, N, 2.86. IR (neat, cm^{-1}): 2041 (CO), 1960 (CO), 1914 (CO), 1642, 1578, 1478, 1436, 1097, 832, 740 and 697. MS (m/z -MALDI-TOF, CH_2Cl_2): found: 835.2211; calcd. 835.2228 for

$C_{39}H_{42}N_2O_3P_2Re$, $[M- PF_6]^+$. 1H NMR (400 MHz, $CDCl_3$): 7.96-7.56 (m, 7H), 7.49-7.38 (m, 3H), 7.27-7.12 (m, 3H), 7.11-6.69 (m, 5H), 6.61-6.49 (m, 2H), 4.58 (dd, 1H, $^3J(HH) = 18.6$ Hz, $^2J(PH) 11.5$ Hz, CH_2), 4.02 (t, 1H, $^3J(HH) = ^2J(PH) 13.1$ Hz, CH_2), 3.52 (ddd, 1H, $^3J(HH) = 18.6$ Hz, $J(PH) 2.5, 4.5$ Hz, CH_2), 2.81 (t, 1H, $^3J(HH) = ^2J(PH) 13.1$ Hz, CH_2), 1.54 (s, 9H, CMe_3) and 0.98 (s, 9H, CMe_3). ^{31}P NMR (161 MHz, $CDCl_3$): 30.5 (d) and 19.5 (d), $^2J(PP) = 24$ Hz.

Results and Discussion

Synthesis of ligands

Oxidation of 1,10-phenanthroline (phen) with bromine and conc. sulphuric acid yielded 1,10-phenanthroline-5,6-dione **V** as a yellow solid (Scheme 1). Base-catalysed condensation of 1,10-phenanthroline-5,6-dione **V** with 1,3-diphenylpropan-2-one afforded the keto-alcohol **VI** as a white solid in 89% yield. Characterising data for compound (**VI**) and other compounds are given under methodology and all new compounds were characterized by a combination of elemental analysis, IR, Mass and NMR spectroscopy.



Scheme 1. (i) Br_2 /conc. H_2SO_4 ; (ii) 1,3-diphenylpropan-2-one; (iii) di(3-thienyl) acetylene; (iv) di(4-*tert*-butylphenyl) acetylene

The IR spectrum of **VI** showed IR bands at 3666 and 3223 cm^{-1} for the OH group and a band at 1706 cm^{-1} for the carbonyl group. The proton resonances for the CHPh and OH appeared at 4.49 ppm (singlet) and 3.19 ppm (broad singlet), respectively. Diels-Alder cycloaddition reaction in benzophenone melts under argon between (**VI**) and di(3-thienyl) acetylene and di(4-*tert*-butylphenyl) acetylene afforded ligands **L¹** and **L²** (Figure 2), respectively, in moderate yields. Characterizing data of **L¹** and **L²** are in good agreement with the proposed structures. The 1H -NMR spectrum of **L¹** showed resonances at 6.95 (dd, $^3J(HH) 5.0$, $^4J(HH) 3.0$ Hz), 6.49 (d, $^4J(HH) 3.0$ Hz) and 6.43 (d, $^3J(HH) 5.0$ Hz) for thienyl protons. The 1H -NMR spectrum of **L²** showed peaks at 6.88 (d, $^3J(HH) 8.5$ Hz) and 6.57

(d, $^3J(\text{HH})$ 8.5 Hz) ppm for the aryl protons; and a singlet at 1.17 ppm for the *tertiary*-butyl groups.

Synthesis of rhenium(I) complexes containing N-donor ligands

Reaction of $[\text{ReCl}(\text{CO})_5]$ with several N-donor ligands was studied; as expected, bidentate ligands **L1-L4** afforded *fac*-chlorotricarbonyl rhenium(I) complexes, *fac*- $[\text{ReCl}(\text{CO})_3(\text{N}^{\wedge}\text{N})]$ (**20**)-(**23**) (Figure 9) in good yields as coloured solids. For example, mass spectral data of (**20**) indicated (m/z , 852.0358 for $\text{C}_{39}\text{H}_{22}\text{ClN}_2\text{O}_3\text{S}_2\text{Re}$) the presence of M^+ ion. The ^1H -NMR spectrum showed resonances at 6.96 (m), 6.52 (d, $^4J(\text{HH})$ 1.5 Hz) and 6.43 (d, $^3J(\text{HH})$ 4.3 Hz) for thienyl protons. In the ^{13}C NMR spectrum of (**20**), the carbon resonances for the three carbonyl ligands appeared at 197.2 and 190.0 ppm with the intensity ratio of (2:1), which were assigned to carbonyl ligands *trans* to nitrogen and chlorine, respectively. These values and assignments are in good agreement with the values reported in the literature (Canadas *et al*, 2019). The IR spectrum showed three strong IR bands at 2017, 1912 and 1878 cm^{-1} for carbonyl ligands. The complexes (**22**)-(**23**) (Figure 9) were characterized in a similar manner and their IR and NMR data suggest them to have the molecular formula *fac*- $[\text{ReCl}(\text{CO})_3(\text{N}^{\wedge}\text{N})]$, where $\text{N}^{\wedge}\text{N} = \text{L}^2\text{-L}^4$.

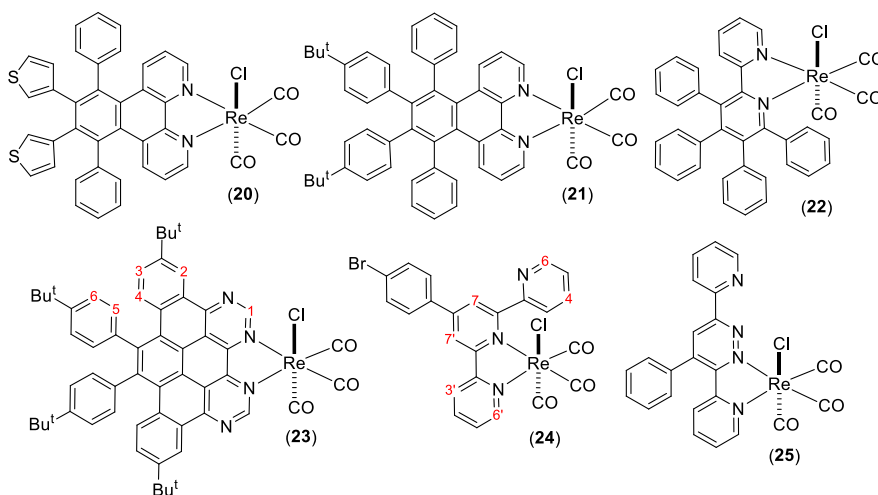


Figure 9. Molecular structures of (**20**)-(**25**) and atom labelling used for the assignment of NMR data

4-Bromophenyl terpyridine **L5** has three N-donors; it can be a bidentate ($\text{N}^{\wedge}\text{N}$) or tridentate ($\text{N}^{\wedge}\text{N}^{\wedge}\text{N}$) ligand depending on the

geometrical and electronic requirements of the metal centre, and the reaction conditions used. Reaction of $[\text{ReCl}(\text{CO})_5]$ with **L⁵** in refluxing chloroform resulted in the formation of *fac*- $[\text{ReCl}(\text{CO})_3(\text{L}^5\text{-N}^{\wedge}\text{N})]$ (**24**) (Figure 9) as a yellow solid in 96% yield where terpy ligand **L⁵** is a bidentate ligand as shown by its ^1H -NMR data for the H⁶ of the coordinated and uncoordinated pyridyl groups: 9.15 (d, 1H, $^3\text{J}(\text{HH})$ 5.5 Hz, coordinated-H⁶) and 8.87 (d, 1H, $^3\text{J}(\text{HH})$ 4.5 Hz, uncoordinated-H⁶).

4-Phenyl-3,6-di(2-pyridyl)-pyridazine **L⁶** is an unsymmetrical ligand with four N-donors and it has two different (N[^]N) bidentate sites for coordination to a metal centre. Treatment of $[\text{ReCl}(\text{CO})_5]$ with **L⁶** in boiling benzene afforded *fac*- $[\text{ReCl}(\text{CO})_3(\text{L}^6\text{-N,N})]$ (**25**) (Figure 9 & 10) as an orange solid in 88% yield. Accurate mass peak at m/z , 581.0601 corresponds to the $[\text{M-Cl}]^+$ ion. Strong IR bands observed at 2010, 1907 and 1880 cm^{-1} for carbonyls are in agreement with the *fac*- $\text{Re}(\text{CO})_3$ arrangement. The X-ray crystal structure of (**25**) (Figure 10) was determined to find out the exact coordination site of the pyridazine ligand **L⁶**, and it confirmed that the Re(I) centre is coordinated to the (N[^]N) bidentate site next to the phenyl group.

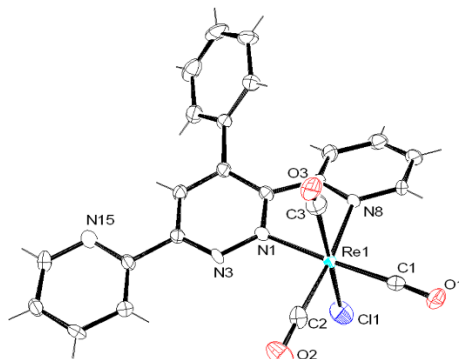


Figure 10. X-ray crystal structure of the complex (**25**)

Synthesis of Re(I) complexes containing P,N ligands

Coordination modes of two P,N ligands were studied. The camphor ligand **L⁷** has one P-donor and two N-donors and it has shown two different (P[^]N) coordination modes (Perera *et al.*, 1991). Treatment of **L⁷** with $[\text{ReCl}(\text{CO})_5]$ formed *fac*- $[\text{ReCl}(\text{CO})_3(\text{L}^7)]$ (**26**) (Figure 11) as indicated by its ^1H NMR spectral data: the presence of two singlets at 2.76 and 3.68 ppm for the two sets of methyl protons of the NMe_2 group clearly suggests the coordination of nitrogen of the NMe_2 group to the rhenium centre. The phosphorus-31 resonance of (**26**) is a singlet at 45.9 ppm.

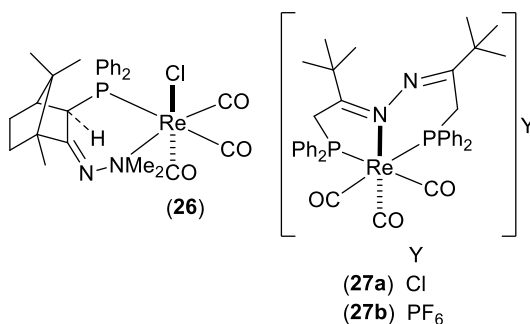


Figure 11. Molecular structures of **(26)** and **(27)** with P,N-donors

The ligand **L⁸** has two N-donors and two P-donors and it has shown the (P[^]P) coordination mode forming a 9-membered chelate ring and the tridentate (P[^]N[^]P) coordination mode forming 5- and 6-membered chelate rings (Perera et al., 1992). Reaction of [ReCl(CO)₅] with **L⁸** in boiling benzene precipitated the chloride salt *fac*-[Re(CO)₃(**L⁸**-P,N,P)]Cl (**27a**) (Figure 11) as a white solid in 88% yield. It was converted to the PF₆ salt *fac*-[Re(CO)₃(**L⁸**-P,N,P)]PF₆ (**27b**) by treating a methanolic solution of (**27a**) with NH₄PF₆ in methanol. The phosphorus-31 resonances of the two tricarbonyl rhenium(I) complexes (**27**) appeared as two doublets with a ²J(PP) of 24 Hz confirming the *facial*-arrangement of the ligand **L⁸**.

Conclusions

1,10-Phenanthroline was converted into two hexa-substituted benzene derivatives **L¹** and **L²**. Treatment of [ReCl(CO)₅] with N,N-donor ligands **L¹** - **L⁶** produced *facial* tricarbonyl rhenium(I) complexes *fac*-[ReCl(CO)₃(N[^]N)] (**20**)-(25) in good yields as coloured solids. Treatment of the P,N-donor ligand **L⁷** with [ReCl(CO)₅] formed *fac*-[ReCl(CO)₃(**L⁷**-P,N)] (**26**). The salts *fac*-[Re(CO)₃(**L⁸**-P,N,P)]Cl (**27a**) and *fac*-[Re(CO)₃(**L⁸**-P,N,P)]PF₆ (**27b**) were obtained by treating [ReCl(CO)₅] with the P[^]N[^]P-donor ligand **L⁸**.

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