

Syntheses and characterization of novel ruthenium complexes based on 1,3-dicyanobenzene

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Abstract

The syntheses and full characterization of novel ruthenium complexes based on 1,3-dicyanobenzene are described. Crystal structures are reported for both [1,3-(*cis*-RuCl(P(CH₃)₃)₄N≡C)₂C₆H₄][PF₆]₂ (**1cis**) and [1,3-(*trans*-RuCl(dppe)₂N≡C)₂C₆H₄][H₂PO₄]₂ (**3'**). Ligand substitution in the homobimetallic complex (**3**) leads easily to the monometallic analogue, [1,3-(*trans*-RuCl(dppe)₂N≡C)-C₆H₄(C≡N)][PF₆] (**4**). A heterobimetallic complex, [1,3-(*trans*-RuCl(dppe)₂N≡C)C₆H₄(C≡N-FeCp(dppe))][PF₆]₂ (**5**), of satisfactory purity is also obtained.

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1. Introduction

Organonitriles represent a class of sterically undemanding, neutral monodentate ligands; they form stable complexes with transition metals and may stabilize the metal in different oxidation states, thereby providing convenient precursors [1–3]. Nitrile complexes can be readily prepared from other nitrile complexes by nitrile exchange reaction [1]. The coordination chemistry of ruthenium(II) with tertiary phosphines [4,5] and chelating diphosphine ligands [6–9] received much attention in the last decades because of their potential application in the field of homogeneous catalysis [10]. The chemistry of ruthenium(II) phosphines with simple, monodentate nitriles (i.e. acetonitrile) has been thoroughly investigated [11–15] and also a series of ruthenium(II) dihydrogen complexes have been prepared [16,17]. Garcia et al. synthesised a series of iron(II) and ruthenium(II) nitrile complexes [18–21], as model donor–

acceptor systems, to probe the effects of structural variation on non-linear optical (NLO) properties [22,23]. However, relatively few papers are reported on transition metal-coordinated polynitriles [24–26] including those [27,28] developed into metallodendrimers [29–31].

As a part of our research program on the field [27,28], we wished to prepare a series of ruthenium(phosphine) complexes based on 1,3-dicyanobenzene (1,3-DCB or *m*-DCB) that can theoretically behave as mono- and/or bidentate ligands. Janczak and Kubiak determined and compared the crystal structures of all isomers (*o*- [32], *m*- [33], and *p*- [34]) of dicyanobenzene. The ring distortions occurring within each structure were analyzed in terms of the distribution of the charge density caused by the two highly polar nitrile groups. We intended to utilize 1,3-DCB as a bifunctional model compound and its ruthenium complexes as potential building blocks for nitrile-based metallodendrimer synthesis. During the course of this work, Fillaut et al. reported the synthesis of wire-like mono- and poly-nuclear molecules based on the core *trans*-[Ru(alkynyl)(nitrile)(dppe)₂][PF₆] using 1,4-DCB as

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a bridging ligand [35]. Cordiner et al. have recently described a series of Group 8 benzonitrile complexes including homobimetallic ruthenium and iron complexes of 1,4-DCB [36].

2. Results and discussion

1,3-DCB was reacted overnight with different ruthenium precursors (2.5 molar ratio) in refluxing 1,2-dichloroethylene (DCE), TlPF₆ was used as a chloride abstracting agent (Chart 1). As a standard work-up procedure, after filtration of TlCl and evaporation of the solvent under vacuum, the residue was washed with diethyl ether, and reprecipitated from concentrated dichloromethane solution by addition of diethyl ether. ³¹P NMR was used to determine the composition of the yielded microcrystalline powders (Table 1). ¹H and ¹³C NMR assignments were also made when pure compounds were successfully isolated.

The reaction of 1,3-DCB with *trans*-RuCl₂(P(CH₃)₃)₄ gave a mixture of different components, making full ¹H NMR assignment impossible. However, the formation of the expected dicationic complex, [1,3-(*cis*-RuCl(P(CH₃)₃)₄N≡C)₂C₆H₄][PF₆]₂ (**1cis**), as the main product (68–70%), was confirmed based on ³¹P NMR analysis and from the integration ratio between the aromatic and methyl protons in the ¹H NMR spectrum. The formation of a well-known, undesired binuclear side product, resulting from a rearrangement into this halide-bridged dimer, [Ru(PMe₃)₃]₂[μ-Cl]₃[PF₆]₃ (8–10%) can also be detected from both the ³¹P NMR (21.5 ppm) [37] and TOF-MS analysis (*m/z* = 765.1 Da). Despite failed purification efforts, single crystals of **1cis** suitable for X-ray analysis were obtained at micro-scale levels. This was achieved by

the slow diffusion of diethyl ether into its dichloromethane solution. The X-ray structure of **1cis** was thus successfully determined (see Section 4.8).

The reaction of 1,3-DCB with *trans*-RuCl₂(dppm)₂ (dppm = bis(diphenylphosphino)methane) yielded highly complicated ¹H and ³¹P NMR spectra. The ³¹P NMR spectrum showed four multiplets, which were assigned to [1,3-(*cis*-RuCl(dppm)₂N≡C)₂C₆H₄][PF₆]₂ (**2**, 85–87%). The pair of triplets (13–15%) observed in the spectrum at 0.59 and –25.04 ppm (with *J*(³¹P–³¹P) = 36.6 Hz) was attributed to the previously characterised ruthenium(II) complex, *cis*-RuCl₂(dppm)₂ [38]. The formation of this complex can be explained by the thermal isomerization of the starting *trans*-RuCl₂(dppm)₂ complex [6]. The presence of four multiplets in **2** suggests the non-equivalency of the phosphorus donor atoms when the chelating dppm ligand is used for complexation. Similar ³¹P NMR patterns were observed for the previously described, related acetonitrile complexes, *cis*-[RuCl(CH₃CN)(dppm)₂]₂X, (X = BF₄ [12], X = PF₆ [11]). The bis-(acetonitrile) complexes, *cis*-[Ru(CH₃CN)₂(dppm)₂]₂X₂ (X = OTf [13], X = PF₆ [11]), also retained this stereochemistry with the four-membered ring diphosphine. However, the Higgins' group observed that the stereochemical outcome of ligand substitution reactions in related complexes can often be controlled simply by the order of addition of the reagents [12,39]. The low symmetry of the molecule, originating from the *cis* stereochemistry of **2**, explains the highly complex ¹H NMR spectrum in the aromatic region. The presence of **2** was also confirmed by TOF-MS, which shows the proper distribution of peaks around *m/z* = 2083.39 [M⁺–(PF₆)] and 1938.41 Da equivalent to [M⁺–(PF₆)₂].

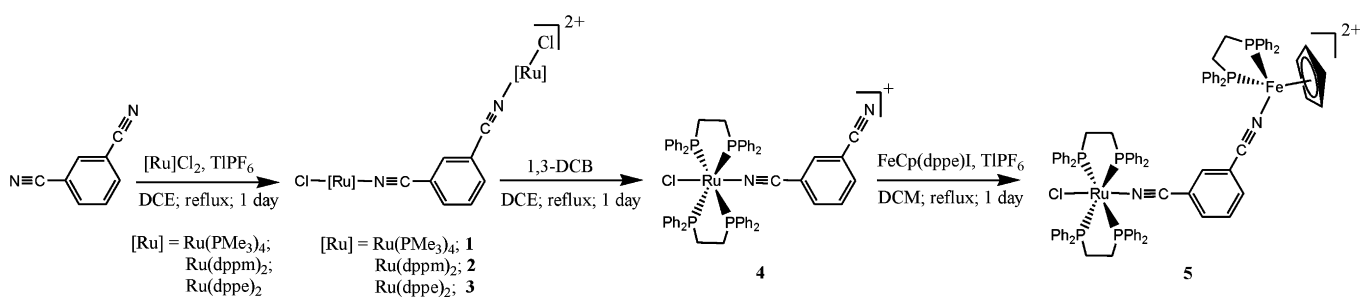


Chart 1. Reaction scheme (PF₆[−] counter ion(s) omitted).

Table 1
The composition of the reaction mixtures as analyzed by ³¹P NMR

Ru-precursor	Composition
<i>trans</i> -RuCl ₂ (P(CH ₃) ₃) ₄	[1,3-(<i>cis</i> -RuCl(P(CH ₃) ₃) ₄ N≡C) ₂ C ₆ H ₄][PF ₆] ₂ (1cis , 68–70%) [1,3-(<i>trans</i> -RuCl(P(CH ₃) ₃) ₄ N≡C) ₂ C ₆ H ₄][PF ₆] ₂ (1trans , 21–23%) [Ru(P(CH ₃) ₃) ₃] ₂ [μ-Cl] ₃ [PF ₆] ₃ (8–10%)
<i>trans</i> -RuCl ₂ (dppm) ₂	[1,3-(<i>cis</i> -RuCl(dppm) ₂ N≡C) ₂ C ₆ H ₄][PF ₆] ₂ (2 , 85–87%) <i>cis</i> -RuCl ₂ (dppm) ₂ (13–15%)
<i>cis</i> -RuCl ₂ (dppe) ₂	[1,3-(<i>trans</i> -RuCl(dppe) ₂ N≡C) ₂ C ₆ H ₄][PF ₆] ₂ (3 , 100%)

The reaction of 1,3-DCB with either *cis*- or *trans*- $\text{RuCl}_2(\text{dppe})_2$ (dppe = bis(diphenylphosphino)ethane) gave the bis-ruthenium complex, $[\text{1,3-}(trans\text{-RuCl}(\text{dppe})_2\text{N}\equiv\text{C})_2\text{-C}_6\text{H}_4][\text{PF}_6]_2$ (**3**), as the main product. However, the analogue monometallic complex, $[\text{1,3-}(trans\text{-RuCl}(\text{dppe})_2\text{N}\equiv\text{C})\text{C}_6\text{H}_4(\text{C}\equiv\text{N})][\text{PF}_6]$ (**4**), was always present (up to 20%) in the crude reaction mixture. Here, the protons of the 1,3-DCB core appeared as broad signals due to an equilibrium reaction between the two components. Basallote et al. investigated the kinetics and substitution reactions in *cis*- $[\text{RuCl}(\text{RCN})(\text{dppe})_2]^+$ complexes and equilibrium was found in solution with the formation of the pentacoordinated cation, $[\text{RuCl}(\text{dppe})_2]^+$ [14]. It is worth noting that the red colour of the reaction mixture is due to the formation of this stable, coordinatively unsaturated ionic complex, $[\text{RuCl}(\text{dppe})_2][\text{PF}_6]$, which was previously reported by Chin et al. [17]. In our reaction, *trans*- $\text{RuCl}_2(\text{dppe})_2$ proved to be equally useful, despite the fact that it has been described as a less reactive transition metal complex [7].

After reprecipitation, it was possible to isolate **3** as analytically pure material. As a result, the protons of the 1,3-DCB core became sharp and well-resolved, making full NMR assignment possible. Both the ^1H (see Fig. 1) and the ^{13}C NMR spectra of **3** indicated two types of dppe phenyl rings (axial, equatorial). All the protons of the core molecule are shifted *upfield* upon coordination. The H_4

and H_6 protons appear as a doublet at 4.54 ppm. This assignment was confirmed by ^1H - ^1H COSY measurements, as cross peaks between H_4 (H_6) and H_5 , as well as between H_4 (H_6) and H_2 . This is indicative of an unexpectedly large change in the chemical shift ($\Delta\delta = -3.37$ ppm) upon coordination, which can be explained by the unusually strong field shielding effect of the diphenylphosphino moieties. The ^{31}P NMR spectrum of **3** indicated the expected septet at -143.8 ppm with $J(^{31}\text{P}-^{19}\text{F}) = 711$ Hz for the PF_6^- counter ions, and only one singlet (at 42.5 ppm), corresponding to the *trans* arrangement of phosphorus atoms around ruthenium. This is in good agreement with the literature, where the similar bis-(acetonitrile) complex, *trans*- $[\text{Ru}(\text{CH}_3\text{CN})_2(\text{dppe})_2][\text{OTf}]_2$, also adopted the *trans* isomer [13]. Bickley et al. suggested that the slightly greater steric demand for the five-membered chelate rings favours attainment of the *trans* geometry with the dppe ligand. In addition to the singlet, a new peak at 43.4 ppm appeared after 1.5 h, the intensity of which increased with time and an elevation in temperature. This peak was later shown to be the thermodynamically more favourable ruthenium species (**4**), thus confirming the equilibrium (Eq. (1)) in solution described above.

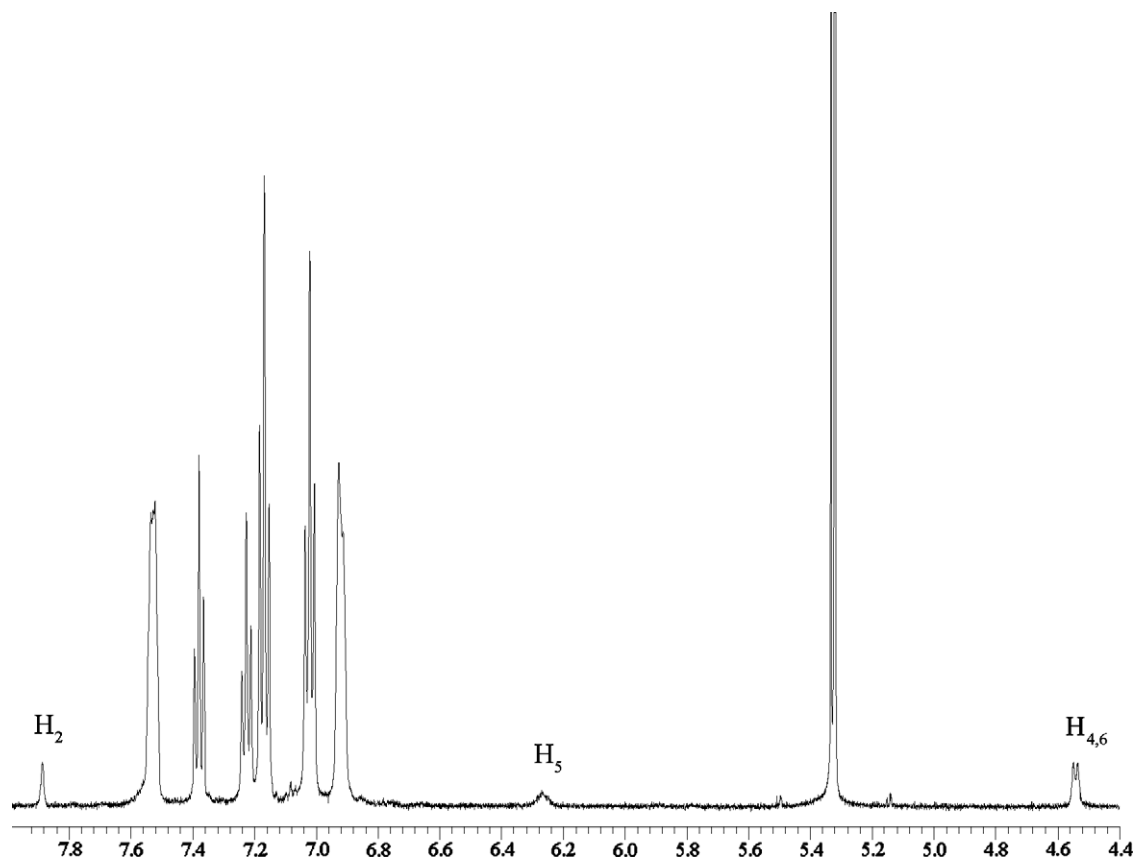
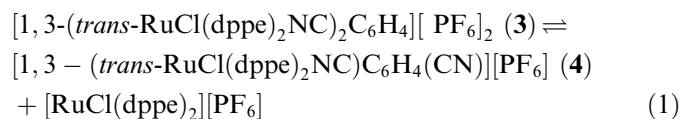


Fig. 1. The downfield part of the ^1H NMR spectrum of **3** in CD_2Cl_2 at 20 °C.

Virtual quintets (the A part of an $AX^1X^2X^3X^4$ system, where $A = {}^{13}\text{C}$ and $X^1 = X^2 = X^3 = X^4 = {}^{31}\text{P}$) appear for all the carbons connected directly to the phosphorous atoms (i.e. CH_2 and C_{ipso} of the Ph) in the ${}^{13}\text{C}$ NMR spectrum of **3**. Virtual couplings of the four phosphorus nuclei in bis(diphosphine)-bridged binuclear complexes is quite common [40,41]. Furthermore, the nitrile bands were shifted by -24 cm^{-1} upon coordination in the IR spectrum, possibly due to enhanced π -backdonation between the metal d orbitals and the π^* orbital of the nitrile group [18,42]. However, the nature of the M–N coordinate bond has been recently described as a predominantly σ -interaction [36]. The formation of **3** was also confirmed by TOF-MS analysis ($m/z = 2139.72$ [$\text{M}^+ - (\text{PF}_6)$]). The nature of the cation was unequivocally established by the X-ray analysis of a single crystal of the $[1,3\text{-}(trans\text{-RuCl}(\text{dppe})_2\text{N}\equiv\text{C})_2\text{C}_6\text{H}_4][\text{H}_2\text{PO}_4]_2 \cdot (\text{H}_3\text{PO}_4) \cdot (\text{CH}_2\text{Cl}_2)$ (**3'**) analogue (see Section 4.8). This was obtained by the anionic exchange of the two PF_6^- anions of **3** in an NMR tube following ${}^{31}\text{P}$ NMR measurements.

In order to extend the structures, 2.5 mol of 1,3-DCB was added to the DCE solution of **2** and **3** under similar reaction conditions as those used for the first synthetic step. In the case of **2**, a substantial amount of white precipitate was observed at the end of the reaction, probably due to an oligomerization reaction. If methanol was used as solvent, a mixture of components, including **2**, was observed in the ${}^{31}\text{P}$ NMR spectrum after work-up. The low symmetry of the *cis* complex renders identification of other components in the ${}^1\text{H}$ and ${}^{13}\text{C}$ NMR spectra impossible.

In the analogue reaction with sample **3**, the mono-ruthenium complex (**4**) was *quantitatively* formed. This time we were able to fully characterise **4**. It was clear from the

${}^1\text{H}$ - ${}^1\text{H}$ COSY experiment (see Fig. 2.) that the 1,3-DCB lost its symmetry due to only “mono-coordination” to the ruthenium, resulting in the non-equivalency of the H_4 and H_6 protons. Weak cross peaks can be seen between H_2 and H_4/H_6 due to *meta* coupling, while there are stronger cross peaks between H_5 and H_4/H_6 due to *ortho* coupling. The characteristic features of the ${}^1\text{H}$ and ${}^{13}\text{C}$ NMR spectra, namely the two types of phenyl ring, as well as the virtual quintets for carbons adjacent to phosphorus atoms, remained the same. In addition to the characteristic septet of the PF_6^- counter ion, the ${}^{31}\text{P}$ NMR of **4** shows a singlet at 43.4 ppm ($\Delta\delta = 0.9$ ppm with respect to **3**), suggesting that the compound retained the *trans* geometry. This complex proved to be stable in solution (in contrast to **3**), as no new components in the ${}^{31}\text{P}$ NMR spectra were detected, even after 3 days. Only one broad nitrile band was observed in the IR spectrum at 2229 cm^{-1} , between the free ligand (2235 cm^{-1}) and the homobimetallic complex (**3**, 2211 cm^{-1}). As expected for this unsymmetrical structure, two well-resolved signals (113.14 ppm for the uncomplexed $\text{C}\equiv\text{N}$ and 113.79 for the complexed $\text{C}\equiv\text{N}$) were present in the nitrile region of the ${}^{13}\text{C}$ NMR spectrum. TOF-MS showed the proper distribution of peaks around $m/z = 1061.02$ [$\text{M}^+ - (\text{PF}_6)$].

Isolation of the intermediate complex from **3** (abstraction of the chlorides) was attempted by reacting **3** with 2.5 mol of TIPF_6 at $90\text{ }^\circ\text{C}$ for 2 days. No new components were observed in the ${}^{31}\text{P}$ NMR spectrum at this stage. After filtration, 1,3-DCB was slowly added to this solution in DCE ($\sim 10^{-3}\text{ M}$). After 1 day reaction at room temperature, the quantity of **3** substantially decreased in the ${}^{31}\text{P}$ NMR spectrum. This was accompanied by the appearance of **4**, along with other unidentified complexes. However, by elevating the temperature up to $90\text{ }^\circ\text{C}$, the reaction was complete after another day, resulting in pure **4**. Analytically pure **4** can also be obtained by simply mixing **3** with 1,3-DCB in DCE at $90\text{ }^\circ\text{C}$ overnight.

Ligand substitution occurs easily because of the lability of the nitrile ligands bound to ruthenium. Furthermore, addition of 1,3-DCB to the solution of **3** will shift the equilibrium in (Eq. (1)) to the right, with the exquisite formation of **4**. It is worth noting that similar observations were made for another polynitrile, (1,3,5-tris(4-ethynylbenzotrile)benzene), which will be reported in the near future [43]. In the literature, there are some examples of nitrogen-containing bidentate ligands (i.e. $\text{C}_5\text{H}_4\text{N}-4-\text{C}\equiv\text{N}$), which surprisingly gave mononuclear species, in spite of the stoichiometric excess of the organometallic precursor [44]. Even in the case of dicyanobenzene isomers, only one of the two $\text{C}\equiv\text{N}$ groups was successfully transformed in organic reactions [45–47]. However, these phenomena are normally explained by steric hindrance.

In view of the use of compound **4** as a terminal building block for convergent syntheses of metallodendrimers, an attempt was made to terminate **4** with the electron rich organometallic fragment $\text{FeCp}(\text{dppe})$ (Chart 1). Following the standard work-up procedure, the targeted heterobime-

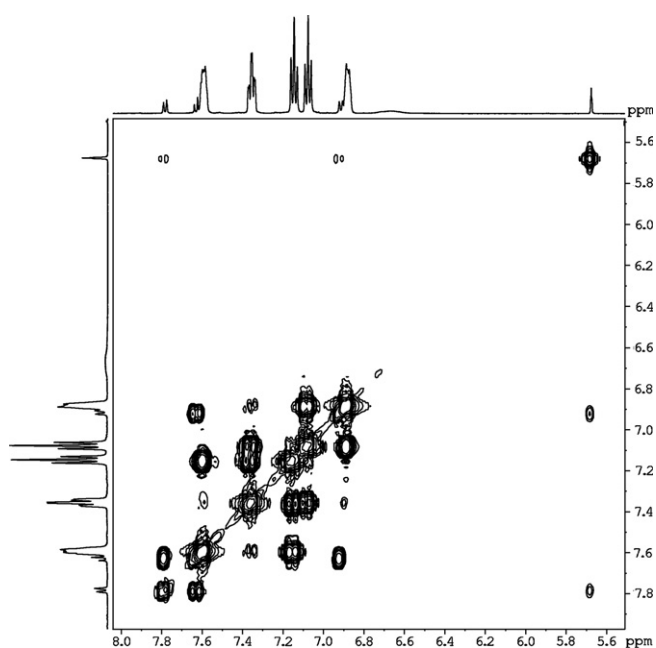


Fig. 2. ${}^1\text{H}$ - ${}^1\text{H}$ COSY spectrum of **4** in CD_2Cl_2 at $20\text{ }^\circ\text{C}$.

tallic compound, $[1,3\text{-}(trans\text{-RuCl}(\text{dppe})_2\text{N}\equiv\text{C})\text{C}_6\text{H}_4\text{-}(\text{C}\equiv\text{N}\text{-FeCp}(\text{dppe}))][\text{PF}_6]_2$ (**5**), was evidenced by peaks at 97.5 and 43.4 ppm (at a ratio of 1:2) in the ^{31}P NMR spectrum. The formation of **5** (~80%) was normally accompanied by other unidentified components (~20%). However, after several crystallization attempts, red needles from the dichloromethane/*n*-hexane system were obtained, displaying up to 95% enhanced purity. Due to the lack of complete purity, only partial spectroscopic data (IR, ^1H NMR, ^{31}P NMR) have been given for this complex (see Section 4). TOF-MS analysis ($m/z = 1725.45 [\text{M}^+ - (\text{PF}_6)]$) also supports the suggested structure of **5**.

Compounds **3** and **4** were studied by cyclic voltammetry at several scan rates in the potential range of 0.0–2.0 V. Only one quasi-reversible redox process was observed for both compounds **3** (1507 mV half-wave potential and 142 mV peaks potential separation) and **4** (1501 mV half-wave potential and 133 mV peaks potential difference) at $v = 100$ mV/s scan rate, which can be attributed to the redox pair $\text{Ru}^{\text{II/III}}$ (see the Supporting Information). The charges involved in the redox process are slightly different, which means that only one ruthenium

redox centre is electrochemically converted in **3**. Both compounds oxidize at very high positive potential values, as evidenced by their half-wave potentials, which suggests that the 1,3-DCB core behaves as a strong electronic acceptor.

Single crystals of **1cis** suitable for X-ray analysis were obtained by the slow diffusion of diethyl ether into its dichloromethane solution. Single crystals of **3'** were obtained by the anionic exchange of the two PF_6^- counter ions of **3** with H_2PO_4^- anions following the ^{31}P NMR measurements. The asymmetric unit of **1cis** contains one dication, two PF_6^- anions and two CH_2Cl_2 solvent inclusion molecules. The asymmetric unit of **3'** contains one dication, two H_2PO_4^- anions, one H_3PO_4 and one CH_2Cl_2 inclusion solvent molecules. The molecular structures of **1cis** and **3'** cations are shown in Figs. 3 and 4, respectively. The experimental crystallographic data for each structure is reported in Table 2. In both compounds a bimetallic complex cation is formed, with 1,3-dicyanobenzene acting as a bidentate ligand. Only a few structures involving such non linear, strongly angulated bridging ligands are reported in the literature [48,49].

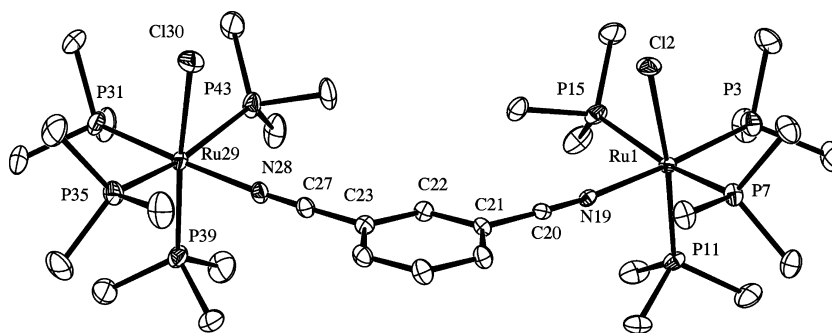


Fig. 3. Ortep view of the cation from **1cis**. Thermal ellipsoids are drawn at 30% probability level. H atoms, the PF_6^- counter ions and solvent molecules are omitted for clarity.

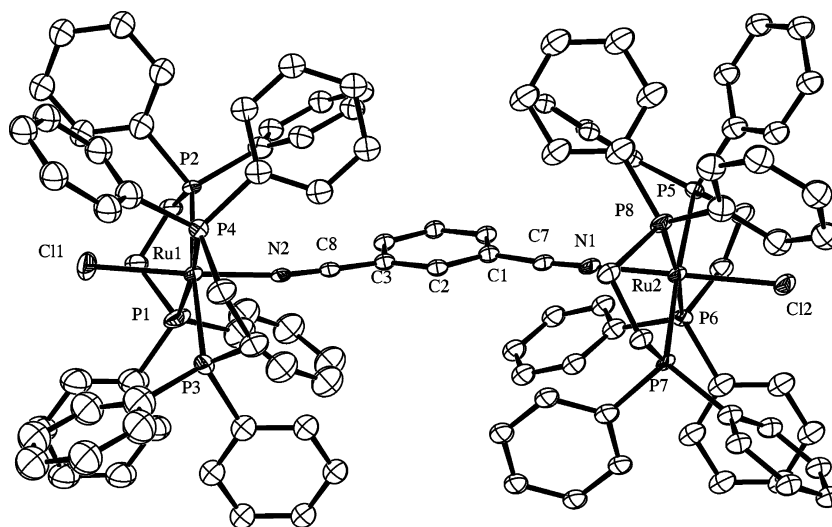


Fig. 4. Ortep view of the cation from **3'**. Thermal ellipsoids are drawn at 30% probability level. H atoms, the H_2PO_4^- counter ions and solvent molecules are omitted for clarity.

Table 2
The experimental crystallographic data for **1cis** and **3'**

	1cis	3'
Formula	C ₃₂ H ₈₀ Cl ₂ N ₂ P ₈ Ru ₂ , 2(PF ₆) 2(CH ₂ Cl ₂)	C ₁₁₂ H ₁₀₀ Cl ₂ N ₂ P ₈ Ru ₂ 2(H ₂ PO ₄) H ₃ PO ₄ , CH ₂ Cl ₂
F _w	1469.54	2371.63
T (K)	173	173
Cryst. system	Monoclinic	Orthorhombic
Space group	P2 ₁ /a	Pbca
a (Å)	9.709(2)	24.035(8)
b (Å)	31.833(4)	23.479(5)
c (Å)	20.432(4)	39.849(7)
α (°)	90	90
β (°)	96.29(2)	90
γ (°)	90	90
V (Å ³)	6277(2)	22488(10)
Z, D _c (g cm ⁻³)	4, 1.555	8, 1.401
μ (mm ⁻¹)	1.054	0.580
Size (mm), color	0.5 × 0.15 × 0.10, yellow	0.20 × 0.15 × 0.04, yellow
θ range (°)	3.01–24.71	3.02–20.0
Reflections collected/unique	17,365/10,591 [R _{int} = 0.0371]	56,018/9668 [R _{int} = 0.142]
Observed reflections [I > 2σ(I)]	7443	5648
Parameters/restraints	596/0	1069/1640
R ₁ (obs) [I > 2σ(I)]	0.0438	0.1458
wR ₂ (all data)	0.0940	0.3474
Δρ _{max} ; Δρ _{min} (e Å ⁻³)	0.761; -0.662	1.739; -1.739

Each ruthenium atom in **1cis** adopts a distorted octahedral geometry, with the nitrogen atom *cis* to the chlorine atom. As a result of a local mirror symmetry of the cation, the Cl atoms are on the same side with respect to the plane of the ligand. A slight bent shape of the cation is also observed. This is a consequence of a small deviation from collinearity of each Ru–N≡C–C group (Ru–N≡C bond angles are 174.2(6)° and 176.7(4)°). The recorded bond lengths and angles of the cation are in good agreement with those reported for *m*-dicyanobenzene and other analogous compounds. Also, the bond distances around the Ru atom are comparable to those observed in similar complexes [11,33,35]. Selected bond distances (Å) and angles (°) with e.s.d.'s in parentheses: Ru1–Cl2 2.469(1), Ru29–Cl30 2.470(2), Ru1–N19 2.075(4), Ru29–N28 2.074(4), N19–C20 1.141(5), N28–C27 1.139(5), C20–C21 1.440(6), C23–C27 1.439(6), Cl2–Ru1–N19 82.6(1), Cl30–Ru29–N28 84.6(1), Ru1–N19–C20 174.2(6), Ru29–N28–C27 176.7(4), N19–C20–C21 178.4(5), N28–C27–C23 178.6(5), C20–C21–C22 118.6(4), C22–C23–C27 119.0(4).

In **3'** a distorted octahedral geometry around each Ru atom is observed, with the N atom *trans* to the Cl atom. A local binary symmetry of the cation can also be seen. However, the poor quality of the **3'** crystals prevents a more detailed description of the geometric molecular parameters of the complex.

3. Conclusion

A convenient synthetic approach combined with simple work-up procedure provides the homobinuclear complex 1,3-(*trans*-RuCl(dppe)₂N≡C)₂C₆H₄][PF₆]₂ (**3**) in high

yield. The instability of this transition metal complex in solution may be one of the factors for the observed ligand substitution chemistry leading to the analogous monometallic complex, [1,3-(*trans*-RuCl(dppe)₂N≡C)C₆H₄(C≡N)]-[PF₆] (**4**). The heterobinuclear complex [1,3-(*trans*-RuCl(dppe)₂N≡C)C₆H₄(C≡N–FeCp(dppe))][PF₆]₂ (**5**) was also obtained after recrystallization. These compounds are presently under study in view of their use as building blocks for convergent metallodendrimer synthesis.

4. Experimental

4.1. General procedures and materials

All experiments were carried out under nitrogen atmosphere by using standard Schlenk-techniques. Solvents were dried by conventional methods [50], distilled and kept under an inert atmosphere. *trans*-RuCl₂(P(CH₃)₃)₄ [5], *trans*-RuCl₂(dppm)₂ [51], *cis*-RuCl₂(dppe)₂ [52], *trans*-RuCl₂(dppe)₂ [8] and FeCp(dppe)I [20] were synthesised as described previously. 1,3-DCB (98%) was purchased from Avocado Research Chemicals Ltd., NaPF₆ (99+%) was an Alfa Aesar product.

Melting points were obtained on Leica Gallen equipment, and were not corrected. The IR spectra were recorded on a Nicolet Avatar 360 FTIR spectrometer in KBr pellets, calibrated with polystyrene. Only significant bands are cited in the text. The ¹H, ¹³C and ³¹P NMR spectra were recorded at 293 K in CD₂Cl₂ (or CDCl₃) on a Bruker AM 500 spectrometer at 500.13 MHz (¹H NMR measurements), 125.77 MHz (¹³C NMR measurements) and at 202.45 MHz (³¹P NMR measurements), respec-

tively. The ^1H chemical shifts (δ), reported in parts per million (ppm) downfield, are referenced to residual CD_2Cl_2 (5.32 ppm) or CDCl_3 (7.24 ppm), respectively. The $^{13}\text{C}\{^1\text{H}\}$ chemical shifts were reported in ppm relative to the carbon resonance of the deuterated NMR solvent: CDCl_3 (77.00 ppm) or CD_2Cl_2 (54.00 ppm), respectively. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra are reported in ppm downfield, from external standard 85% H_3PO_4 at 0.0 ppm. Abbreviations in the NMR descriptions are as follows: b.s. = broad signal; b.d. = broad doublet; b.m. = broad multiplet; t.d. = triplets of a doublet; v.q. = virtual quintet, quat. = quaternary carbon.

TOF-MS spectra were obtained on a Micromass LCT spectrometer; peaks are reported as m/z . Elemental analyses were performed at Instituto Superior Técnico, using a Fisons Instruments EA1108 system; data acquisition, integration and handling were performed using a PC with software package *Eager 200* (*Carlo Erba Instruments*). UV–Vis spectra were recorded at 293 K with a GBC-Cintra 40 spectrometer using 1 cm optical path quartz cells with freshly prepared solutions of approximately 10^{-4} M concentration. The spectrum is presented as λ_{max} or shoulder (*sh*) [nm], (ϵ_{max} [$\text{M}^{-1}\text{cm}^{-1}$]). Conductivity measurements were made at 293 K on freshly made 2×10^{-4} M nitromethane solutions of the complexes using a Hanna EC215 bench conductivity meter. Molar conductivities (A_m) are given in units of $\Omega^{-1}\text{mol}^{-1}\text{cm}^2$; the accepted range for 2:1 electrolytes under these conditions is 115–250 [53]. Cyclic voltammetric measurements were performed on a PARSTAT 2263 with the Advanced Electrochemistry Software PowerSuite (v. 2.35.2.), using a single compartment three electrode cell (PAR polarographic cell) with a 1.5 mm diameter Pt disk as a working electrode, a Pt foil as a counter electrode and a Ag, AgCl/KCl saturated reference electrode or a KCl saturated calomel reference electrode, at room temperature in nitrogen atmosphere. Solutions (purged with N_2 for 15 min) were 10^{-3} M and 10^{-1} M in the supporting electrolyte (*n*-tetrabutylammonium hexafluorophosphate). All potential values are referenced to the Ag, AgCl/KCl saturated reference electrode; ferrocene/ferrocenium complex ($E_{1/2} = 0.48$ V versus Ag/AgCl) was used as an internal standard under the same experimental conditions.

4.2. 1,3-DCB

IR (KBr, cm^{-1}): 2235 (ν_{CN}); ^1H NMR (CD_2Cl_2): 7.67 (t, $J = 7.8$ Hz, 1 H, H_5); 7.91 (d, 7.8 Hz, 2H, $\text{H}_{4,6}$); 7.97 (s, 1H, H_2); ^{13}C NMR (CDCl_3): 114.00 ($\text{C}\equiv\text{N}$); aromatic carbons: 116.48; 130.23; 135.29; 135.89. UV–Vis: 234; 280; 288 (CH_2Cl_2).

4.3. Attempted preparation of [1,3-(*cis*- $\text{RuCl}(\text{P}(\text{CH}_3)_3)_4\text{N}\equiv\text{C})_2\text{C}_6\text{H}_4][\text{PF}_6]_2$ (1)

1,2-Dichloroethane solution (25 ml) containing 250 mg (0.52 mmol) *trans*- $\text{RuCl}_2(\text{PMe}_3)_4$ and 26 mg (0.2 mmol) 1,3-DCB was slowly added to 175 mg (0.5 mmol) TIPF_6

and was left stirring at 90 °C overnight. The colour of the reaction mixture changed to yellow and some precipitate (TlCl) formed which was filtered off. After evaporation of the solvent, the residue was washed with diethyl ether. Reprecipitation from the dichloromethane solution with diethyl ether yielded a yellow powder. NMR analysis of the powder indicated a mixture of components. Some selected data.

1cis: ^{31}P NMR (CD_2Cl_2): 6.9 (t, $J(^{31}\text{P}-^{31}\text{P}) = 32$ Hz, PMe_3); -11.9 (t, $J(^{31}\text{P}-^{31}\text{P}) = 32$ Hz, PMe_3); -143.8 (sept., $J(^{31}\text{P}-^{19}\text{F}) = 711$ Hz, PF_6^-). **1trans:** ^{31}P NMR (CD_2Cl_2): -8.0 (s, PMe_3); -143.8 (sept., $J(^{31}\text{P}-^{19}\text{F}) = 711$ Hz, PF_6^-).

4.4. Attempted preparation of [1,3-(*cis*- $\text{RuCl}(\text{dppm})_2\text{N}\equiv\text{C})_2\text{C}_6\text{H}_4][\text{PF}_6]_2$ (2)

1,2-Dichloroethane solution (40 ml) containing 493 mg (0.52 mmol) *trans*- $\text{RuCl}_2(\text{dppm})_2$ and 26 mg (0.2 mmol) 1,3-DCB was slowly added to 175 mg (0.5 mmol) TIPF_6 and was left stirring at 90 °C overnight. The colour of the reaction mixture changed to light yellow and some precipitate (TlCl) formed which was filtered off. After evaporation of the solvent, the residue was washed with diethyl ether. Reprecipitation from dichloromethane solution with diethyl ether gave a light yellow powder. NMR analysis of the powder indicated a mixture of components. Some selected data.

^{31}P NMR (CD_2Cl_2): -0.6 (m, PPh_2); -6.8 (m, PPh_2); -19.5 (m, PPh_2); -24.5 (m, PPh_2); -143.8 (sept., $J(^{31}\text{P}-^{19}\text{F}) = 711$ Hz, PF_6^-); TOF-MS: $m/z = 2083.39$ ($\text{M}^+ - (\text{PF}_6)$); 1938.41: ($\text{M}^+ - (\text{PF}_6)_2$); 1033.28 [$\text{C}_6\text{H}_4(\text{C}\equiv\text{N})_2\text{Ru}(\text{dppm})_2\text{Cl}]^+$; 905.18 [$\text{Ru}(\text{dppm})_2\text{Cl}]^+$; 869.24 [$\text{Ru}(\text{dppm})_2$] $^+$.

4.5. Preparation of [1,3-(*trans*- $\text{RuCl}(\text{dppe})_2\text{N}\equiv\text{C})_2\text{C}_6\text{H}_4][\text{PF}_6]_2$ (3)

In a typical experiment, 1,2-dichloroethane solution (90 ml) containing 968 mg (1 mmol) *cis*- $\text{RuCl}_2(\text{dppe})_2$ and 51 mg (0.4 mmol) 1,3-DCB was slowly added to 350 mg (1 mmol) TIPF_6 and was left stirring at 90 °C overnight. The colour of the reaction mixture changed to red and some precipitate (TlCl) formed which was filtered off. After evaporation of the solvent, the residue was washed with diethyl ether. Reprecipitation from dichloromethane solution with diethyl ether gave a yellow powder as a pure product (yield: 79%).

M.p.: 208–210 °C; IR (KBr, cm^{-1}): 2211 (ν_{CN}); 839 and 529 (ν_{PF}); ^1H NMR (CD_2Cl_2): 2.98 (b.s., 8H, CH_2); 3.07 (b.s., 8H, CH_2); 4.54 (d, $J = 7$ Hz, 2H, $\text{H}_{4,6}$); 6.27 (b.s., 1H, H_5); 6.92 (b.m., 16H, H_{meta} of Ph_1); 7.02 (t, $J = 7.6$ Hz, 16H, H_{ortho} of Ph_1); 7.17 (t, $J = 7.6$ Hz, 16H, H_{ortho} of Ph_2); 7.23 (t, $J = 7.3$ Hz, 8H, H_{para} of Ph_1); 7.38 (t, $J = 7.3$ Hz, 8H, H_{para} of Ph_2); 7.53 (b.m., 16H, H_{meta} of Ph_2); 7.88 (s, 1H, H_2); ^{13}C NMR (CD_2Cl_2): 29.83 (v.q., CH_2); 113.37 ($\text{C}\equiv\text{N}$); aromatic carbons: 124.12 (core); 128.59 (Ph); 129.41 (core); 129.50 (Ph); 130.13

(core); 130.88 (Ph); 131.08 (Ph); 133.11 (v.q., C_{ipso} of the Ph) overlapped with 133.28 (Ph); 134.26 (v.q., C_{ipso} of the Ph); 134.69 (Ph); 139.03 (core); ^{31}P NMR (CD_2Cl_2): 42.5 (s, PPh_2); -143.8 (sept., $J(^{31}\text{P}-^{19}\text{F}) = 711$ Hz, PF_6^-); TOF-MS (ES^+): $m/z = 2139.72$ ($\text{M}^+ - \text{PF}_6$); 1061.39 [$\text{C}_6\text{H}_4(\text{C}\equiv\text{N})_2\text{Ru}(\text{dppe})_2\text{Cl}$] $^+$; 933.36 [$\text{Ru}(\text{dppe})_2\text{Cl}$] $^+$. Anal. Calc.: C, 58.88; H, 4.41; N, 1.23. Found: C, 58.02; H, 4.56; N, 1.17%. UV-Vis [nm]: $\lambda_{\text{max}} = 368$ (CH_2Cl_2); 362 (acetone); molar conductance [$\Omega^{-1}\text{mol}^{-1}\text{cm}^2$]: $A_M = 218$.

4.6. Preparation of [1,3-(trans- $\text{RuCl}(\text{dppe})_2\text{N}\equiv\text{C})\text{C}_6\text{H}_4(\text{C}\equiv\text{N})$][PF_6] (4)

To the 1,2-dichloroethane solution (10 ml) containing 100 mg (0.044 mmol) of **3**, 14 mg (0.11 mmol) of 1,3-DCB was added. The red colour changed to yellow immediately. The reaction mixture was left stirring at 90 °C overnight. After filtration of TiCl_4 and evaporation of the solvent, the residue was reprecipitated twice from dichloromethane solution with diethyl ether. This yielded a light yellow powder (yield: 83%).

M.p.: 180–184 °C; IR (KBr, cm^{-1}): 2229 (ν_{CN}); 836 and 529 (ν_{PF}); ^1H NMR (CD_2Cl_2): 2.82 (b.m., 4 H, CH_2); 2.88 (b.m., 4H, CH_2); 5.72 (t, $J_{\text{meta}} = 1.5$ Hz, 1H, H_2); 6.84 (t.d., $J_{\text{ortho}} = 7.8$ Hz, $J_{\text{meta}} = 1.5$ Hz, 1H, H_4); 6.89 (b.m., 8H, H_{meta} of Ph_1); 7.08 (t, $J = 7.7$ Hz, 8H, H_{ortho} of Ph_1); 7.15 (t, $J = 7.8$ Hz, 8 H, H_{ortho} of Ph_2); 7.36 (t, $J = 7.6$ Hz, 8H, H_{para} of $\text{Ph}_{1,2}$); 7.57 (b.m., 8H, H_{meta} of Ph_2) overlapped with 7.60 (1H, H_5); 7.78 (t.d., $J_{\text{ortho}} = 7.8$ Hz, $J_{\text{meta}} = 1.5$ Hz, 1H, H_6); ^{13}C NMR (CD_2Cl_2): 29.45 (v.q., CH_2); 113.14 ($\text{C}\equiv\text{N}$); 113.79 ($\text{C}\equiv\text{N}$); aromatic carbons: 116.80 (quat., core); 123.17 (quat., core); 128.67 (Ph); 129.65 (Ph); 131.13 (Ph); 131.27 (Ph); 131.34 (core); 132.02 (v.q., C_{ipso} of the Ph); 133.2 (Ph); 133.94 (v.q., C_{ipso} of the Ph); 134.67 (Ph); 135.89 (core); 136.18 (core); 136.9 (core); ^{31}P NMR (CD_2Cl_2): 43.4 (s, PPh_2); -143.8 (sept., $J(^{31}\text{P}-^{19}\text{F}) = 711$ Hz, PF_6^-); TOF-MS (ES^+): $m/z = 1061.02$ [$\text{M} - \text{PF}_6$] $^+$; 932.98 [$\text{Ru}(\text{dppe})_2\text{Cl}$] $^+$; 897.04 [$\text{Ru}(\text{dppe})_2$] $^+$. Anal. Calc. C, 59.73; H, 4.34; N, 2.32. Found: C, 59.45; H, 5.09; N, 2.68%. UV-Vis [nm]: $\lambda_{\text{max}} = 260$; 361 (CH_2Cl_2); 352 (acetone).

4.7. Preparation of [1,3-(trans- $\text{RuCl}(\text{dppe})_2\text{N}\equiv\text{C})\text{C}_6\text{H}_4(\text{C}\equiv\text{N}-\text{FeCp}(\text{dppe}))$][PF_6] $_2$ (5)

58.8 mg (0.09 mmol) $\text{FeCp}(\text{dppe})\text{I}$ was dissolved in 20 ml dichloromethane, then 32 mg (0.09 mmol) TIPF_6 and 100 mg (0.036 mmol) of **4** were added as solids. The reaction mixture was left stirring for 24 h at reflux temperature. By the end of the reaction time, a colour change to red was observed. Following the filtration of the yellow precipitate and evaporation of the solvent, the yielded orange powder was reprecipitated twice from dichloromethane solution by addition of diethyl ether (yield: 48%). Recrystallization from dichloromethane/hexane gave

red needles as a compound with 95% purity. Some selected data.

IR (KBr, cm^{-1}): 2219 (ν_{CN}); 840 and 530 (ν_{PF}); ^1H NMR (CDCl_3): 2.66 (b.s., CH_2 , 4H); 2.89 (b.s., CH_2 , 8H); 4.52 (s, 1H, H_2); 4.61 (s, 5H; Cp); 5.18 (d; $J = 7$ Hz, 1H, H_4); 6.35 (d; $J = 7$ Hz, 1H, H_6); 6.68 (b.s., 1H, H_5); 6.79–7.97 (b.m., 60H, Ph); ^{31}P NMR (CD_2Cl_2): 43.4 (s, 4P, PPh_2); 97.5 (s, 2P, PPh_2); -143.8 (sept., $J(^{31}\text{P}-^{19}\text{F}) = 711$ Hz, PF_6^-); TOF-MS (ES^+): $m/z = 1725.45$ [$\text{M} - \text{PF}_6$] $^+$; 1061.26 [$\text{C}_6\text{H}_4(\text{C}\equiv\text{N})_2\text{Ru}(\text{dpp e})_2\text{Cl}$] $^+$; 933.22 [$\text{Ru}(\text{dppe})_2\text{Cl}$] $^+$; 899.23 [$\text{Ru}(\text{dppe})_2$] $^+$; 647.20 [$\text{C}_6\text{H}_4(\text{C}\equiv\text{N})_2\text{Fe}(\text{dppe})\text{Cp}$] $^+$; 519.13 [$\text{Fe}(\text{dppe})\text{Cp}$] $^+$.

4.8. Crystallographic studies

Data collections for **1cis** and **3'** were performed on a Nonius KappaCCD single crystal diffractometer (graphite monochromated Mo $\text{K}\alpha$ ($\lambda = 0.71073$ Å) radiation) at 173 K. Data collections were made using Collect software [54]. Cell parameters and data reduction were obtained using HKL Denzo and Scalepack [55] for **1cis** and Eval-CCD [56] for **3'**. The structures were solved by direct methods and anisotropically refined by the full matrix least-squares method on F^2 against all independent measured reflections (SHELXS97 and SHELXL97 programs of the SHELX-97 package [57]). All H atoms were geometrically positioned and refined by a riding model with thermal parameters U_{iso} set to $1.2U_{\text{eq}}$ of the carrier atom. However, the H atoms of the H_2PO_4^- counter ions in **3'** were not included in the refinement as their location could not be evidenced from the difference Fourier maps. As a consequence of the poor quality of the **3'** crystals and the possible presence of a large fraction of disordered solvent molecules, constraints were applied to all light atoms in the refinement of **3'**. U_{ij} constraints were also used for all chemically similar atoms and rigid group constraints were applied to all phenyl groups. This accounts for the high value of the reported R_1 .

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Appendix A. Supplementary data

CCDC 647759 and 647760 contain the supplementary crystallographic data for **1cis** and **3'**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallo-

graphic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.08.012.

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