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Nitrile ligands for controlled synthesis of alkynyl-ruthenium based homo and hetero bimetallic systems

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Abstract

Wire like mono- and poly-nuclear molecules based on alkynyl ruthenium complexes whose core unit is *trans*-[Ru(C≡C-R)(R′C≡N)(dppe)$_2$][PF$_6$] are readily formed in soft conditions. The electronic dual character of the metallic unit, donor through the acetylide moiety, acceptor versus the nitrile ligand is exemplified through electrochemical studies of a series of ethynylferrocene and cyanoferrocene derivatives. A single crystal X-ray diffraction analysis of the [(dppe)$_2$(PhC≡C)Ru(N≡C-C$_6$H$_4$-C≡N)Ru(C≡CPh)-(dppe)$_2$][2PF$_6$] bimetallic complex **5** shows that the global structure of such complexes consists of wire type dimetallic units. With the availability of this versatile, direct, and simple route, a new class of extended rigid rod systems of nanometric size with multilevel electron transfers is readily accessed.

Keywords: Ruthenium; Electron transfer; Alkynyl complexes; N ligands; Donor–acceptor systems

1. Introduction

Tailored carbon-rich organometallic have found a broad range of applications as electronic and optoelectronic materials [1,2], as NLO chromophores [3–5], building blocks for luminescent metal-based materials [6], and prototypes of molecular electronic wires and molecular devices [2,7–15]. Alkynylmetal complexes constitute a particularly important class of organometallic complexes with π-conjugated bridges both on account of their intrinsic interest and, more recently, their potential as components or models of nanoscale electronic [16–18] and optical devices [19–25], related to the fact that the metal atom lies in the same plane as the π-system and can participate to the extension of the π-conjugated path. From a design perspective, the metal acetylide linkage is appealing because of the rigid nature of the alkyne ligands and the defined directionality in the case of *trans* substituted metal centers [26–29]. Moreover, various acetylide-functionalised ligands can be easily synthesized and the alkynyl ligands can be readily incorporated into metal-containing polymers [30]. Within this framework, the geometry of *trans*-[RuCl(C≡C-R)(diphos)$_2$] systems [20,26,29,31], combined with appropriate bridging ligands, allows access to fully controlled architectures. In particular, the adapted use of coordination chemistry, already efficient for directing the rapid and easy formation of supramolecular architectures via self-assembly [32–34], provides a competitive synthetic strategy to increase the delocalization possibilities (e.g. progressing from small molecules to π-conjugated oligomers and polymers), controlling chain orientation, and the introduction of strong donor and acceptor functional groups [35]. The work presented here seeks to explore this strategy using the chemistry of *trans*-[Ru(C≡C-R)(L)(dppe)$_2$]$^+$ (L = benzonitrile, cyanoferrocene, 1,4-dicyanobenzene, etc.) (dppe = Ph$_2$PC$_2$H$_4$PPh$_2$)

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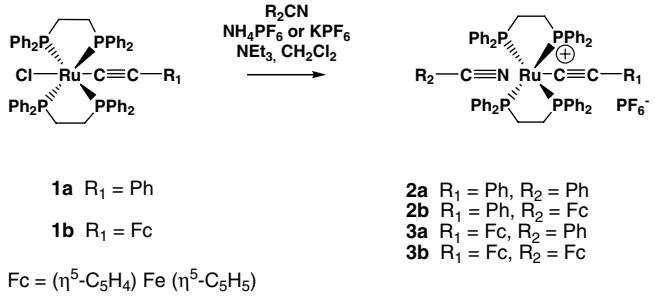
complexes as potential "building blocks" for large oligomeric complexes.

2. Results and discussion

Nitriles constitute an important class of ligands that form stable complexes with a wide variety of transition metals and may stabilise the metal in various oxidation states [33,36–40]. However, nitrile substituted *bis* diphosphine ruthenium derivatives $[RuX(NCR)(diphos)_2]^+$ (X = anionic ligand) have received recent attention [41–43]. Isomerically pure *cis*-$[RuCl(NCR)(dppe)_2]^+$ (R = Me, Ph, etc.) are formed upon addition of the respective nitrile to the five-coordinate *cis*-$[RuCl(dppe)_2]^+$ in dichloromethane solution at room temperature [43]. In contrast, we observed that the reaction of *trans*-$[RuCl(C{\equiv}C\text{-}R)(dppe)_2]$ complexes **1a** (R = Ph) and **1b** ($R = (\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)$) with nitriles $R_1C{\equiv}N$ (R_1 = Ph, $R_1 = (\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)$) in both the presence of NH_4PF_6 and NEt_3 in methylene chloride, led to the rapid formation (less than 1 h at room temperature) of isomerically pure *trans*-$[Ru(C{\equiv}C\text{-}(R_1C{\equiv}N)(dppe)_2][PF_6]$ complexes **2a**,**b** and **3a**,**b** (Scheme 1). In parallel, Fehlner and co-workers published on the design of molecular quantum-dot cells based on functionalized *trans*-$[Ru(NCCH_2CH_2NHR)(C{\equiv}C\text{–}Fc)(dppm)_2]$ ($Fc = (\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)$) complexes for surface binding, using $TlPF_6$ to accomplish the substitution of chloride in *trans*-$[RuCl(C{\equiv}C\text{-}R)(dppm)_2]$ complexes [16,18,44,45]. Thus, a major interest of our procedure lies in its simplicity and rapidity using mild conditions that can be adapted for specific examples.

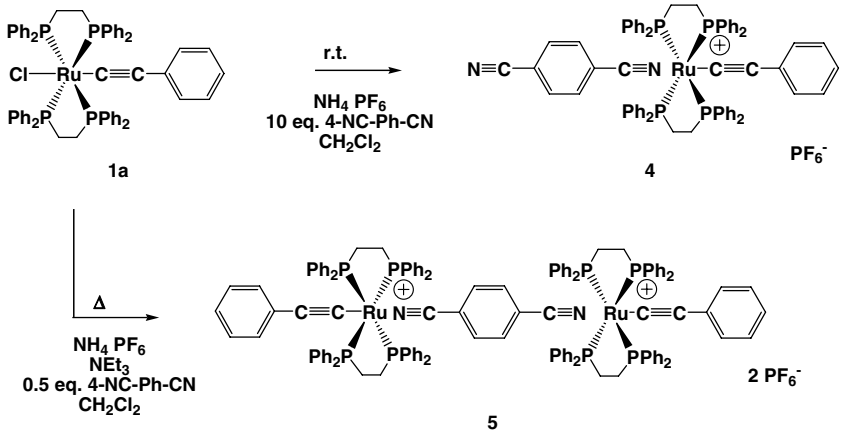


Scheme 1. General access to *trans*-$[Ru(C{\equiv}C\text{-}R)(R_1C{\equiv}N)(dppe)_2][PF_6]$ complexes.

The *trans*-$[Ru(C{\equiv}C\text{-}R)(R_1C{\equiv}N)(dppe)_2][PF_6]$ complexes were fully characterized by elemental analysis, IR and NMR spectroscopy. Their infrared spectra displayed characteristic C≡C stretching frequencies at approximately 2080 cm^{-1} and a broad PF_6^- band masked the 800–900 cm^{-1} region. A nitrile stretching band at approximately 2230 cm^{-1} were close to those observed for the free ligands. These values are consistent with a weak π-back donation from the metal to the nitrile ligands. The *trans* position of the nitrile and acetylide ligands was ascertained by the equivalence of the phosphorus nuclei (**2a** $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 49.98$ ppm) and by the ^{13}C NMR spectrum (**2a**) that showed one quintet at $\delta = 114.7$ ppm for the Ru–*C*≡ carbon atom and one singlet at $\delta = 117.5$ ppm for the ≡*C*–Ph carbon nuclei.

This reaction corresponds to the displacement of the chlorine atom from the *trans*-$[RuCl(C{\equiv}C\text{-}R)(dppe)_2]$ complexes by NH_4PF_6 and leads to the formation of a transient $[Ru(C{\equiv}C\text{-}R)(dppe)_2][PF_6]$ 16 electron species, which coordinates the nitrile. Interestingly, the presence of triethylamine makes this process fast at room temperature, whereas it needs a long time (more than 24 h) to proceed in its absence.

This synthetic route was then applied to 1,4-dicyanobenzene (Scheme 2). Interest in this ancillary ligand concerns the presence of two independent binding sites, which raises the possibility of formation of mono- and binuclear complexes [33,40]. Indeed, the reaction was successfully directed toward the formation of the monometallic complex **4**, or the bimetallic complex **5**. Complex **4** was obtained by addition at ambient temperature of *trans*-$[RuCl(C{\equiv}C\text{–}Ph)(dppe)_2]$ (**1a**) to a methylene chloride solution containing a large excess of 1,4-dicyanobenzene (10 equiv.) by using KPF_6 as the Cl^- extractor. This complex was trapped after 16 h as a yellow crystalline powder by addition of heptane. Infrared stretching frequencies of the nitrile ends



Scheme 2. Synthetic procedures to complexes **4** and **5**.

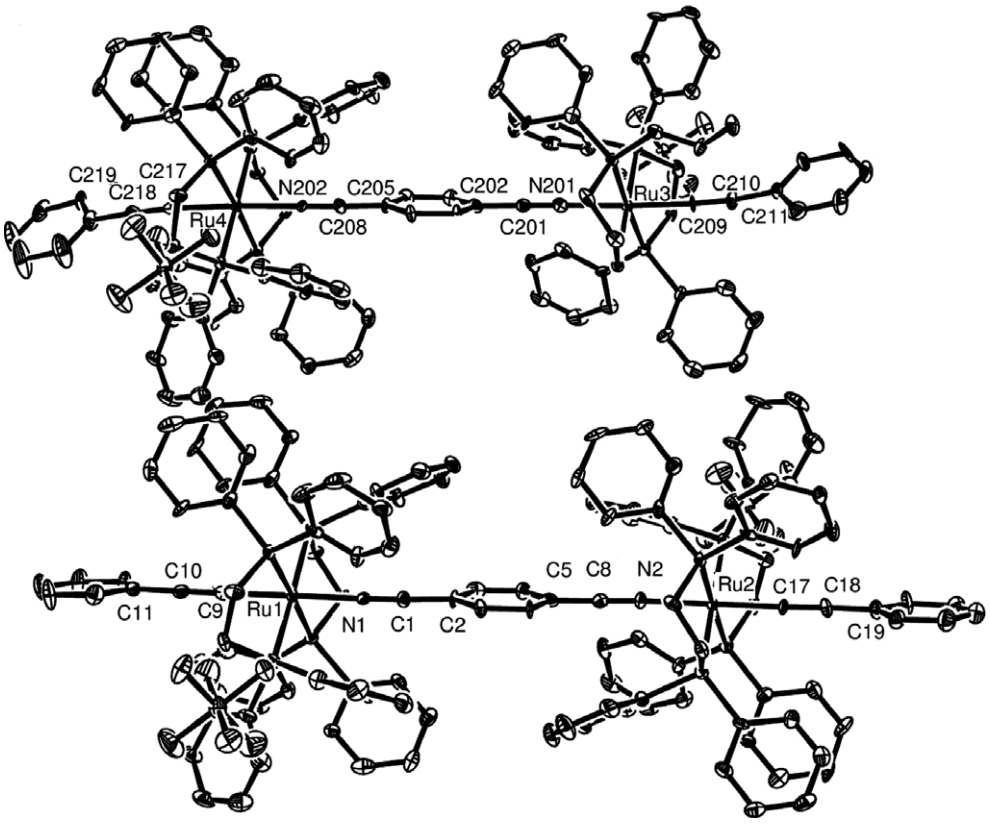


Fig. 1. Fragment of crystal packing of **5**, showing the two crystallographically independent bicationic units with atom labelling scheme. Thermal ellipsoids are drawn at the 50% probability level. Solvent molecules and hydrogen atoms have been omitted for clarity.

show up at 2225 cm^{-1} and 2233 cm^{-1}, the latter not significantly different from that of the free ligand (2231 cm^{-1}) [46,47]. Bimetallic complex **5** was obtained in presence of triethylamine by reversing the proportions of 1,4-dicyanobenzene (0.5 equiv.) and complex **1a** (Scheme 2). The solution became rapidly red-orange but the reaction required to be prolonged for 24 h at reflux in dichloromethane before completion. Compound **5** was isolated as orange-red crystals from a heptane-methylene chloride biphasic system. A single infrared band was observed for the nitrile ends at 2226 cm^{-1}, consistent with ruthenium (II) coordination of both nitrile functions of the dicyanobenzene moiety. Both complexes **4** and **5** exhibited a single C≡C stretching band at 2076 cm^{-1}. The symmetry of complex **5** was also established by the equivalence of the eight phosphorus atoms in this complex ($^{31}P\{^1H\}$ NMR (CD_2Cl_2: $\delta = 49.86$)). Complexes **4** and **5** are easily distinguished by their ^1H NMR spectra. The signals specific to the aromatic protons of the 1,4-dicyanobenzene appear in the form of two doublets at $\delta = 7.6$ and 6.5 ppm for **4**. These signals are compatible with a non-symmetrical system. In the dinuclear complex **5**, on the contrary, one observes a singlet at $\delta = 6.6$ ppm, that is consistent with a perfectly symmetrical system. The values of the chemical shifts of the ^{13}CN in **4** and **5** were assigned by means of HMBC and HMQC sequences. They confirm the perfect equivalence of these two carbon atoms in **5** ($\delta = 121.2$ ppm), whereas in **4**, two signals are observed at $\delta = 121.4$ ppm (complexed C≡N), and $\delta = 117.2$ ppm (uncomplexed C≡N), for the two nitrile groups of the 1,4-dicyanobenzene.

3. Description of the structure of 5

A single crystal X-ray analysis was carried out on crystals of **5** obtained from a methylene chloride–toluene biphasic mixture (Fig. 1).[1] Experimental crystallographic

[1] Crystal and refinement for **5**: Crystals were grown at room temperature in a biphasic dichloromethane/toluene system. $2(Ru_2P_8C_{128}N_2N_6H_{110})$, $4PF_6$, $6(C_7H_8)$: Mr = 5384.84, triclinic, P1, $a = 14.2476(1)$, $b = 20.0129(2)$, $c = 24.3521(2)$ Å, $\alpha = 112.8637(4)$, $\beta = 92.2422(4)$, $\gamma = 91.1401(5)°$, $V = 6388.54(9)$ $Å^{-3}$, $Z = 1$, $D_x = 1.391$ $Mg \cdot m^{-3}$, λ(Mo Kα) = 0.71073Å, $\mu = 4.33$ cm^{-1}, $F(000) = 2756$, $T = 110$ K. The sample (0.42*0.32*0.32 mm) was studied on a NONIUS Kappa CCD [65] with graphite-monochromatized Mo Kα radiation. The cell parameters were obtained with Denzo and Scalepack [66] with 10 frames (psi rotation: 1° per frame). The data collection ($2\theta_{max} = 60°$, 508 frames via 1.3° ω rotation and 18 s per frame, range *hkl*: *h* 0–20, *k* −28–28, *l* −34–34) gave 113043 reflections. The data reduction with Denzo and Scalepack [66] led to 36759 independent reflections from which 24543 with $I > 2.0\sigma(I)$. The structure was solved with SIR-97 [67], which revealed the non-hydrogen atoms of structure. After anisotropic refinement, many hydrogen atoms were found with a Fourier Difference. The whole structure was refined with SHELXH [68] by the full-matrix least-square techniques (use of F square magnitude; x, y, z, β_{ij} for Ru, P, F, N and C atoms, x, y, z in riding mode for H atoms; 3012 variables and 24543 observations with $I > 2.0\sigma(I)$; calc $w = 1/[\sigma^2(Fo^2) + (0.065P)^2 + 10.84P]$ where $P = (Fo^2 + 2Fc^2)/3$ with the resulting $R = 0.049$, $R_w = 0.125$ and $S_w = 1.027$, $\Delta\rho < 1.57$ e $Å^{-3}$.

Table 1
Structure determination summary of **5**

Empirical formula	$2(Ru_2P_8C_{128}N_2N_6H_{110}) \cdot 4PF_6 \cdot 6(C_7H_8)$
Molecular weight	5384.84
T (K)	110(1)
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	14.2476(1)
b (Å)	20.0129(2)
c (Å)	24.3521(2)
α (°)	112.8637(4)
β (°)	92.2422(4)
γ (°)	91.1401(5)
V (Å^3)	6388.6 (1)
Z	1
Color	Red
Crystal size (mm)	$0.42 \times 0.32 \times 0.32$
ρ_{calc} (Mg m^{-3})	1.391
$F(000)$	2756
μ (Mo Kα) (cm^{-1})	4.35
λ (Å)	0.71073
Diffractometer	NONIUS Kappa CCD
$h/k/l$ Limits	0–20/−28–28/−34–34
Scan range (θ) (°)	1.72/30.07
Reflections collected	36759
R_{int}	0.0000
Data with $[I > 2\sigma(I)]$	24543
Data/restrains/parameters	36759/3/3000
Goodness-of-fot on F^2	1.027
Final R indices $[I > 2\sigma(I)]$ $R1/wR_2$	0.0494/0.1255
R indices (all data) $R1/wR_2$	0.0860/0.1499
Absolute structure parameter	−0.08(3)
Largest difference in peak and hole (e Å^{-3})	1.579 and −0.945

Table 2
Selected bond lengths d (Å) and angles ω (°) in **5**

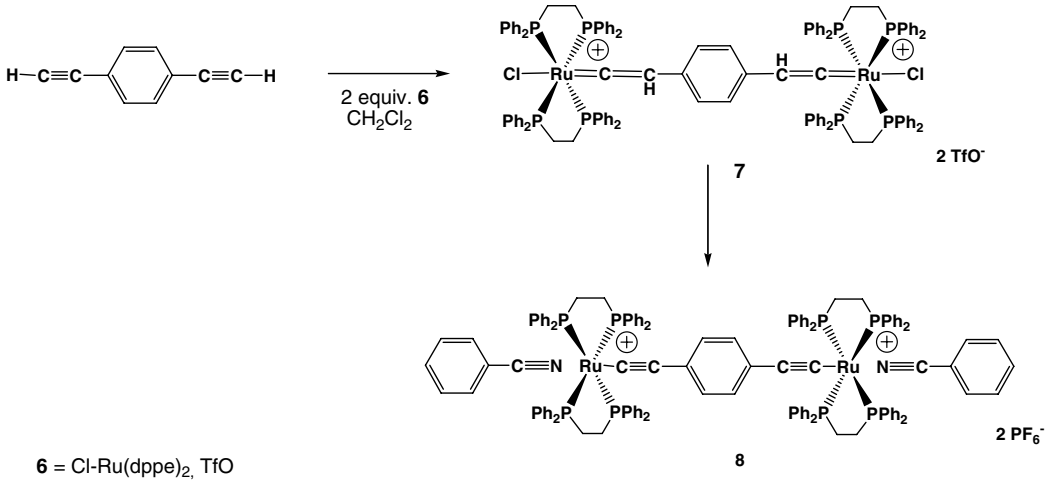
Bond	d	Bond	d
Ru(1)–C(9)	2.011(10)	Ru(1)–N(1)	2.044(8)
Ru(2)–C(17)	2.029(10)	Ru(2)–N(2)	2.056(8)
Ru(3)–C(209)	2.035(11)	Ru(3)–N(201)	2.044(7)
Ru(4)–C(217)	2.005(8)	Ru(4)–N(202)	2.053(9)
C(9)–C(10)	1.223(14)	N(1)–C(1)	1.147(12)
C(17)–C(18)	1.213(15)	N(2)–C(8)	1.141(13)
C(209)–C(210)	1.197(14)	N(201)–C(201)	1.172(13)
C(217)–C(218)	1.230(12)	N(202)–C(208)	1.133(14)
Angle	**ω**	**Angle**	**ω**
C(9)–Ru(1)–N(1)	176.3(4)	C(1)–N(1)–Ru(1)	173.7(9)
C(17)–Ru(2)–N(2)	178.5(4)	C(8)–N(2)–Ru(2)	170.8(9)
C(209)–Ru(3)–N(201)	176.7(4)	C(201)–N(201)–Ru(3)	171.6(9)
C(217)–Ru(4)–N(202)	176.8(4)	C(208)–N(202)–Ru(4)	173.7(9)
C(10)–C(9)–Ru(1)	176.7(9)	N(1)–C(1)–C(2)	179.4(14)
C(18)–C(17)–Ru(2)	179.5(12)	N(2)–C(8)–C(5)	177.4(12)
C(210)–C(209)–Ru(3)	176.3(9)	N(201)–C(201)–C(202)	174.8(11)
C(218)–C(217)–Ru(4)	176.1(10)	N(202)–C(208)–C(205)	179.5(13)
C(9)–C(10)–C(11)	172.0(10)		
C(17)–C(18)–C(19)	173.5(12)		
C(209)–C(210)–C(211)	170.0(11)		
C(217)–C(218)–C(219)	166.2(11)		

data are given in Table 1 and a selection of bond distances and angles is given in Table 2.

The global structure of **5** consists of two crystallographically independent bicationic units, four PF_6 anions, and six toluene molecules as inclusion solvent. The two bicationic moieties differ by the conformation of the central chain: very linear in form 1 and s-conformation in form 2. The main differences in these two units concern the orientation of the terminal phenyl groups of the molecules versus the plane formed by the central dicyanobenzene ring. In one molecule of **5** (form 1), the phenyl groups of the alkynyl ligands perfectly lie within this plane. In contrast, for the other molecule (form 2), the corresponding phenyl groups have rotated about the Ru–C bond, and lie out of the plane of the dicyanobenzene ring. These differences can neither be attributed to interaction with solvent molecules or counteranion nor to packing effects. On the other hand, we observed that crystals obtained with acetone as crystallisation solvent lead to a statistically disordered structure (random distribution of the two forms with 8 acetone molecules).

All bond lengths and angles lie in the same range for the two units. The intermetallic, through space distances are estimated to be ca. 12 Å. The ruthenium atoms adopt a distorted octahedral ligand environment. The nitrile ligands are σ-coordinated via the nitrogen atom and occupy apical position *trans* to the alkynyl groups. The C–Ru–N angles range from 176.3(4)° to 178.0(4)° and are close to linearity. Bond lengths and angles are typical of benzonitrile ligands when compared with related structures [47–50]. The Ru–N bond distances in **5** (in the range from 2.044(8) Å to 2.056(8) Å) are shorter than that observed in *trans*-$[Ru(C{\equiv}C–Ph)(NH_3)(dppe)_2][PF_6]$ (2.215(5) Å) [51,52]. The average values for the σ-alkynyl Ru–C bond distances are similar in these two complexes (**5**: 2.011(10) and 2.029(10) Å in form 1, 2.005(8) and 2.035(11) Å in form 2; *trans*-$[Ru(C{\equiv}C–Ph)(NH_3)(dppe)_2][PF_6]$: Ru–C = 2.014(5) Å). The average Ru–C≡C– and Ru–N≡C– bond angles are 177.1° and 172.4° which indicates that the complex remains close to linearity from one alkynyl-ruthenium moiety to the other.

The presence of triethylamine not only allows the fast removal of the chlorine atom of *trans*-$[RuCl(C{\equiv}C\text{-}R)(dppe)_2]$ complexes but is widely used as a base to perform the deprotonation of *trans*-$[RuCl(=C=C(H)\text{-}R)(dppe)_2][X]$ cationic vinylidene species into alkynyl systems. Thus, we combined these two steps as a one pot procedure for the synthesis of the bimetallic complex **8**starting from the bis vinylidene species **7** (Scheme 3). Compound **7** results from the reaction of two equivalents of *cis*-$[RuCl(dppe)_2][TfO]$ (**6**) with 1,4-diethynylbenzene in dichloromethane. This complex, the formation of which was monitored by $^{31}P\ \{^1H\}$ NMR, was directly used in the next step, and this avoids the tedious purification of the corresponding bis alkynyl complex [53]. Similarly to **2a**, the complex **8** is obtained by addition at ambient temperature of a methylene chloride solution containing a



Scheme 3.

large excess of benzonitrile (10 equiv.) by using KPF_6 as the Cl^- extractor, in the presence of triethylamine. This complex was trapped after 16 h as a yellow crystalline powder by addition of heptane.

4. Electrochemical studies

Table 3 summarizes the oxidation potentials observed for these complexes, and related derivatives that are pertinent to this study. Complex **2** exhibit one perfectly reversible wave ($\Delta E_p = 70$–80 mV; $i_a/i_c \cong 1$) in the range of 500–600 mV versus $FeCp_2$, corresponding to the oxidation of the cationic ruthenium center. The complexes containing the ethynylferrocene fragment **3** show irreversible oxidation waves in the range of 1000 mV versus $FeCp_2$ for this ruthenium center. This suggests that the ferrocene fragments in both **3a** and **3b** already being oxidized, appear unable to stabilize the species resulting from the ruthenium centred oxidation.

The ruthenium oxidation appears less sensitive to the presence of the cyanoferrocene instead of benzonitrile as a ligand. Indeed, the oxidation occurs at slightly higher potentials ($\Delta E_p \sim 70$ mV) in the cyclic voltammogram (CV) of **2b** than that of **2a**. Moreover, comparison of the voltammograms of complexes **2b** and **3a** with that of the free ferrocene ligands (**2b** versus cyanoferrocene; **3a** versus ethynylferrocene) indicates that the $[Ru(C{\equiv}C\text{-}R)(dppe)_2^+]$ moiety enhances the electron withdrawing effect of the nitrile moiety ($\Delta E_p \sim +55$ mV), and behaves as an efficient donor head towards the ethynylferrocene ($\Delta E_p \sim -130$ mV).

The CV of the complex **3b** contains three waves. The first two waves occur at -175 mV and $+405$ mV versus $FeCp_2$ corresponding to the oxidation of the two ferrocenyl centers, while an irreversible wave at $+930$ mV is assigned to the $Ru^{II/III}$ oxidation. The first $Fe^{II/III}$ oxidation wave, at -175 mV versus $FeCp_2$, was assigned to oxidation of the ethynyl ferrocene moiety. This oxidation occurs at a slightly more negative potential than the corresponding

Table 3
Cyclic voltammetry data

Complex	$Fe^{II/III}$	$Fe^{II/III}$	$Ru^{II/III}$
	$E_{1/2}$ [a,c]	$E_{1/2}$ [a,d]	$E_{1/2}$ or E_p [a,b]
trans-[RuCl(-C≡C-Ph)(dppe)$_2$] (**1a**)			−60
trans-[RuCl(-C≡C-Fc)(dppe)$_2$] (**1b**) [51]	−344		377
Fc-C≡CH [51]	130		
trans-[Ru(-C≡C-Ph)(Ph-C≡N)(dppe)$_2$][PF_6] (**2a**)			515
trans-[Ru(-C≡C-Ph)(Fc-C≡N)(dppe)$_2$][PF_6] (**2b**)		385	590
Fc-C≡N		330	
trans-[Ru(-C≡C-Fc)(Ph-C≡N)(dppe)$_2$][PF_6] (**3a**)	−160		870[b]
trans-[Ru(-C≡C-Fc)(Fc-C≡N)(dppe)$_2$][PF_6] (**3b**)	−175	405	930[b]
trans-[Ru(-C≡C-Ph)(1,4-NC–C_6H_4-CN)(dppe)$_2$][PF_6] (**4**)			520
trans-[(dppe)$_2$(-C≡C-Ph)Ru(1,4-NC–C_6H_4-CN)–Ru(-C≡C-Ph)(dppe)$_2$][2PF_6] (**5**)			520
trans-[(dppe)$_2$ Ph-C≡N)Ru(1,4-C≡C–C_6H_4-C≡C)Ru(Ph-C≡N)(dppe)$_2$][2PF_6] (**8**)			205 and 495

[a] mV vs. ferrocene, Pt working electrode, CH_2Cl_2 containing 0.1 M [n-Bu_4N][PF_6], 20 °C, scan rate 200 mV s^{-1}.
[b] E_p (irreversible wave).
[c] Ethylnylferrocene part.
[d] Cyanoferrocene part.

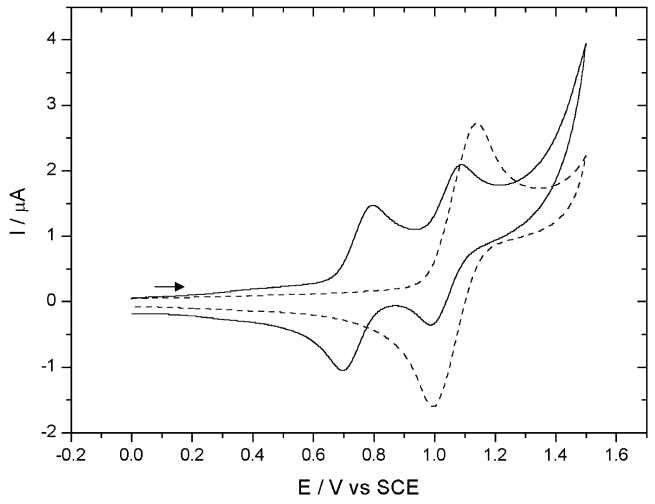


Fig. 2. Cyclic voltamogram of **5** (dashed) and **8** (full) at a scan rate of 100 mV S^{-1}, using dichloromethane, Pt electrodes with reference to SCE, n-Bu_4NPF_6 (10^{-3} M) as the electrolyte.

one in the CV of complex **3a** at −160 mV and is consistent with a weakening of the electron-accepting abilities of the nitrile ligand. Conversely, the oxidation of the complexed cyanoferrocene moiety is observed at a higher potential in **3b** than in the CV of **2b** (**3b**: 405 mV versus $FeCp_2$; **2b**: 385 mV). These values highlight the influence of the electron donating effect of the ethynyl ligands towards the *trans*-nitrile groups through the ruthenium centre.

As expected, the CV of **4** shows a single perfectly reversible wave at $E_{1/2} = 610$ mV versus $FeCp_2$ ($\Delta E_p = 80$ mV at 100 mV s^{-1}, $i_{pc}/i_{pa} \cong 1$), in the range of those observed for **2a** and **2b**. More surprisingly, the cyclic voltammogram of **5** (Fig. 2a) is almost identical, $E_{1/2} = 605$ mV ($\Delta E_p = 70$ mV at 100 mV s^{-1}, $i_{pc}/i_{pa} \cong 1$). As there is no other wave in the CV, and the oxidation potentials are close to the $Ru^{II/III}$ oxidation in **4**, this wave was assigned to the superimposed oxidations of the two ruthenium centers present in this complex. Thus, the 1,4-dicyanobenzene ligand acts as an insulator in this complex.

Conversely, 1,4-diethynylbezene is a well established π-conjugated spacer [1,26,54–58]. Thus, the bimetallic system **8** shows two successive reversible oxidation waves ($E^\circ = 205$ ($i_{p,a}/i_{p,c} = 1.06$) and 495 mV versus $FeCp_2$ ($i_{p,a}/i_{p,c} = 1.03$)) related to the formation of the Ru^{III}–Ru^{II} and Ru^{III}–Ru^{III} systems (Fig. 2b). The E° values for the two redox processes differ by 290 mV, clearly indicating a communication between the two ruthenium centers through the 1,4-diethynylbenzene bridge. The nature of the terminal metal centers also influences the electrochemical response of the bimetallic system **8** as compared with the binuclear parent complex *trans*-[$(dppe)_2$Cl-Ru(1,4-C≡C-C_6H_4-C≡C)Ru-Cl$(dppe)_2$] with the same conjugated bridge. A greater difference is observed between the oxidation waves of the two chloro ruthenium-centerd redox systems in *trans*-[$(dppe)_2$Cl-Ru(1,4-C≡C-C_6H_4-C≡C)Ru-Cl$(dppe)_2$] [59], as compared to **8** ($\Delta E^\circ = 360$ mV instead of 230 mV). These variations could be due to the relative contributions of the bridging ligand to the HOMO (target orbital for the oxidation) in the ruthenium systems **8** and *trans*-[$(dppe)_2$Cl-Ru(1,4-C≡C-C_6H_4-C≡C)Ru-Cl$(dppe)_2$] [26].

On the other side, the first oxidation of compound **8** is easier ($E^\circ = 205$ mV versus $FeCp_2$) than that of the corresponding monometallic complex **2a** ($E^\circ = 595$). This difference confirms the electron-donating capability of the ruthenium (II) moiety *trans*-[PhCNRu$(dppe)_2$] through alkynyl bridges and, in particular, a –C≡C–C_6H_4≡C– bridge.

5. Conclusion

An effective strategy has been developed to obtain *trans*-[Ru(C≡C-R)(R_1C≡N)$(dppe)_2$][PF_6] complexes. The *trans* geometry of the σ-alkynyl ruthenium monomers, combined with appropriate bridging ligands, offer potentially valuable models with wire like arrangements. As a preliminary example, the ruthenium binuclear complex **5** bearing a 1,4-dicyanobenzene bridge was obtained. X-ray determination for this complex exhibits well-defined, linear geometries of nearly 30 Å. The dual character of the metal center, donor through the acetylide moiety, acceptor towards the nitrile ligand as exemplified through electrochemical studies of typical complexes, appears of interest in order to build polynuclear complexes that display subsequent multilevel electron transfers, as exemplified by the bimetallic complex **8**. Work to combine different organometallic subunits in which donor–acceptor units are attached through the coordination of the nitrile end is also currently under way in our laboratory.

6. Experimental

6.1. General information

All reactions were carried out in Schlenk flasks under nitrogen by using septum and syringe techniques. Solvents were dried and distilled according to standard procedures. The following were prepared by the literature procedures: 1,4-diethynylbenzene [60], 4-ethynylbenzonitrile [61], cyanoferrocene [62], ethynylferrocene [63]. The ruthenium derivatives *cis*-$RuCl_2(dppe)_2$ ($dppe = Ph_2PCH_2CH_2PPh_2$) [64], **1a** [29] and **6** [13] were prepared according to previously published protocols. Microanalyses were carried out at the Center for Microanalyses of the CNRS at Lyon-Solaise, France or at the Centre de Mesures Physiques de l'Ouest at Rennes, France. Secondary ion (SI) mass spectra were recorded on a VG ZAB 2SEQ spectrometer (30 kV Cs^+ ions, current 1 mA, accelerating potential 8 kV, matrix m-nitrobenzylic alcohol) at the Centre de Mesures Physiques de l'Ouest at Rennes, France. Peaks are reported as *m*/*z* (assignment, relative intensity). Routine NMR spectra were recorded using a Bruker DPX 200 spectrometer. HMBC and HMQC sequences for the determination of carbon shifts in complexes **4** and **5** were

recorded using a Bruker AV 500 spectrometer. Chemical shifts are given in parts per million relative to tetramethylsilane (TMS) for ^1H and ^{13}C NMR spectra and H_3PO_4 for ^{31}P $\{^1H\}$ NMR spectra. Transmittance-FTIR spectra were recorded between KBr plates using a Bruker IFS 28 spectrometer. UV–Vis spectra were recorded on a UVIKON XL spectrometer. Electrochemical data were acquired with a computer-controlled Autolab PG start 30 potentiostat utilizing the GPES program version 4.7. Electrochemical experiments were performed in a standard three-electrode system (platinum working/auxiliary electrode and SCE reference electrode) in the presence of internal decamethylferrocene. Bu_4NPF_6 was used as the supporting electrolyte. Scan rates were typically 100 mV s^{-1}.

6.2. Synthesis of complexes 2–3

Typical procedure: A mixture of complex **1a** (100 mg, 9.7×10^{-2} mmol), or **1b** (110 mg, 9.7×10^{-2} mmol), NEt_3 (0.16 mL, 0.11 mmol), NH_4PF_6 (40 mg, 0.24 mmol), and the desired nitrile (0.11 mmol) in CH_2Cl_2 (10 mL) was stirred at room temperature for 1 h. The solvent was then removed under reduced pressure and the solid washed with water (3×20 mL) and ether (3×20 mL) to afford a pale yellow solid, which was crystallized from CH_2Cl_2–heptane.

2a (102 mg, 85%). IR(nujol, KBr): ν(C≡N) 2233 cm^{-1}; ν(C≡C) 2077 cm^{-1}. ^1H NMR ($CDCl_3$): δ ppm: 7.87 (br. s, 8H, Ph dppe), 7.70–6.98 (m, Ph), 6.84 (br. s, 8H, Ph dppe), 7.66 (d, 2H, PhCN), 5.30 (CH_2Cl_2), 2.74 (br. m, 8H, CH_2 dppe); ^{13}C NMR ($CDCl_3$) δ ppm: 135.1–128.11 (Ph), 125.41 (C_{quat}–C), 124.11 (s, *C*N), 117.51 (s, Ru–C≡*C*–), 114.72 (quint, Ru–*C*≡C–, $^2J_{PC} = 17$ Hz), 110.92 (s, C_{quat}–CN), 53.50 (CH_2Cl_2), 30.35 (12 Hz); ^{31}P $\{^1H\}$ NMR ($CDCl_3$) δ ppm: 49.98. Anal. Calc. for $C_{67}H_{58}NF_6P_5Ru \cdot 1.5CH_2Cl_2$: C, 59.86; H, 4.47. Found: C, 59.41; H, 4.82%. Mass spectrum: *m/z* calc. for $C_{60}H_{53}P_4{}^{102}Ru$; $[M-PhCN]^+$: 999.2141; found: 999.2163.

2b (100 mg, 76%). IR(nujol, KBr): ν(C≡N) 2225 cm^{-1}; ν(C≡C) 2086 cm^{-1}. ^1H NMR ($CDCl_3$): δ ppm: 7.78 (br. s, 8H, Ph dppe), 7.47–7.10 (m, Ph), 6.94 (br. s, 8H, Ph dppe), 5.30 (CH_2Cl_2), 4.49 and 3.99 (m, 2×2H, C_5H_4), 4.14 (s, 5H, C_5H_5), 2.76 (br. m, 8H, CH_2 dppe); ^{13}C $\{^1H\}$ NMR ($CDCl_3$) δ ppm: 134.6–134.0 (Ph), 130.24 (C_{quat}–C), 127.21 (s, *C*N), 117.13 (s, Ru–C≡*C*–), 114.95 (quint, Ru–*C*≡C–, $^2J_{PC} = 17$ Hz), 110.92 (s, C_{quat}–CN), 72.33 and 72.04 (C_5H_4), 70.65 (C_5H_5), 53.50 (CH_2Cl_2), 30.36 (12 Hz); ^{31}P $\{^1H\}$ NMR ($CDCl_3$) δ ppm: 49.83. Anal. Calc. for $C_{71}H_{62}NF_6FeP_5Ru \cdot 0.5CH_2Cl_2$: C, 61.49; H, 4.47. Found: C, 61.33; H, 4.76%.

3a (105 mg, 80%). IR(nujol, KBr): ν(C≡N) 2230 cm^{-1}; ν(C≡C) 2082 cm^{-1}. ^1H NMR ($CDCl_3$): δ ppm: 7.84 (br. s, 8H, Ph dppe), 7.48–7.05 (m, Ph), 6.91 (br. s, 8H, Ph dppe), 6.35 (d, 2H, dppe), 5.30 (CH_2Cl_2), 4.21 and 4.18 (m, 2×2H, C_5H_4), 3.99 (s, 5H, C_5H_5), 2.74 (br. m, 8H, CH_2 dppe); ^{13}C $\{^1H\}$ NMR (CD_2Cl_2) δ ppm: 134.61–128.41 (Ph), 123.69 (s, *C*≡N), 111.21 (s, Ru–C≡*C*–), 105.60 (quint, Ru–*C*≡C, $^2J_{PC} = 17$ Hz), 112.83 (s, C_{quat}–C≡N), 74.16 (C_{quat}–C≡C); 69.28 and 67.47 (C_5H_4), 68.99 (C_5H_5), 30.28 ($J_{PC} = 12$ Hz); ^{31}P $\{^1H\}$ NMR ($CDCl_3$): δ ppm: 49.59. Anal. Calc. for $C_{71}H_{62}NF_6FeP_5Ru \cdot 1.5CH_2Cl_2$: C, 58.76; H, 4.42. Found: C, 58.87; H, 4.24%.

3b (110 mg, 76%). IR(nujol, KBr): ν(C≡N) 2226 cm^{-1}; ν(C≡C) 2088 cm^{-1}. ^1H NMR ($CDCl_3$): δ ppm: 7.92 (br. s, 8H, Ph dppe), 7.49–7.19 (m, Ph), 6.98 (br. s, 8H, Ph dppe), 5.30 (CH_2Cl_2), 4.55 and 4.10 (m, 2×2H, C_5H_4), 4.15 and 4.13 (m, 2×2H, C_5H_4), 4.24 and 3.94 (s, 2×5H, C_5H_5), 2.74 (br. m, 8H, CH_2 dppe); ^{13}C $\{^1H\}$ NMR (CD_2Cl_2) δ ppm: 134.95–128.37 (Ph), 126.68 (s, *C*≡C), 117.72 (s, Ru–C≡*C*–), 112.75 (quint, Ru–*C*≡C–, $^2J_{PC} = 17$ Hz), 72.29, 71.94, 71.25 and 70.48 (C_5H_4), 70.06 and 69.25 (C_5H_5), 30.30 ($J_{PC} = 12$ 12 Hz); ^{31}P $\{^1H\}$ NMR ($CDCl_3$) δ ppm: 49.31. Anal. Calc. for $C_{75}H_{66}F_6Fe_2NP_5Ru \cdot 1.5CH_2Cl_2$: C, 59.25; H, 4.46. Found: C, 59.46; H, 4.69%.

6.3. Synthesis of complex 4

A mixture of complex **1a** (100 mg, 9.7×10^{-2} mmol), KPF_6 (45 mg, 0.24 mmol), and 1,4-dicyanobenzene (128 mg, 1 mmol) in CH_2Cl_2 (10 mL) was stirred at room temperature for 16 h. The resulting mixture was then washed with water (3×20 mL) and dried (Na_2SO_4). The solvent was then removed under reduced pressure and the solid washed with ether (5×30 mL) and water to afford a pale yellow solid, which was crystallized from CH_2Cl_2–heptane.

4 (85 mg, 80%). IR(nujol, KBr): ν(C≡N) 2233 and 2228 cm^{-1}; ν(C≡C) 2078 cm^{-1}. ^1H NMR: δ ppm: 7.90 (br. s, 8H, Ph dppe), 7.59 (d, 2H, Ph), 7.36–6.92 (m, Ph), 6.79 (br. s, 8H, Ph dppe), 6.52 (d, 2H, Ph), 5.30 (CH_2Cl_2), 2.80 (br. m, 8H, CH_2 dppe); ^{13}C NMR 125.75 MHz (HMBC and HMQC sequences) ([D_6] acetone): δ ppm: 137.75–128.10 (Ph), 133.14 and 132.50 (CH, 1,4-dicyanobenzene), 121.40 (s, complexed *C*≡N), 117.18 (s, uncomplexed *C*≡N), 115.04 (s, C_{ipso}-complexed C≡N), 116.39 (s, C_{ipso}-free C≡N) 117.70 (s, Ru–C≡*C*), Ru–*C*≡ not observed, 55.0 (CH_2Cl_2), 29.09 (CH_2, $J_{PC} = 12$ Hz); ^{31}P $\{^1H\}$ NMR (CD_2Cl_2) δ ppm: 50.10; ($CDCl_3$) δ ppm: 50.14. Anal. Calc. for $C_{68}H_{57}N_2F_6P_5Ru \cdot 1.5CH_2Cl_2$: C, 61.07; H, 4.38. Found: C, 61.15; H, 4.18%.

6.4. Synthesis of complex 5

A mixture of complex **1a** (110 mg, 1.06×10^{-1} mmol), NEt_3 (0.16 mL, 0.11 mmol), NH_4PF_6 (40 mg, 0.24 mmol), and 1,4-dicyanobenzene (6.4 mg, 0.05 mmol) in 1,2 dichloroethane (10 mL) was stirred at reflux for 48h. The resulting mixture was then washed with water (3×20 mL) and dried (Na_2SO_4). The solvent was then removed under reduced pressure and the solid washed with ether (3×20 mL) to afford a red-orange solid, which was crystallized from CH_2Cl_2–heptane (suitable crystals for X-ray analysis were obtained in a methylene chloride–toluene biphasic mixture).

5 (90 mg, 74%) IR(nujol, KBr): ν(C≡N) 2227 cm^{-1}; ν(C≡C) 2077 cm^{-1}. ^1H NMR ([D_6] acetone): δ ppm: 8.02

(br. s, 8H, Ph dppe), 7.52–7.15 (m, Ph), 7.02 (br. s, 8H, Ph dppe), 6.63 (s, 2H, Ph), 5.65 (CH_2Cl_2), 2.92 and 3.09 (br. m, 8H, CH_2dppe); ^{13}C NMR 125.75 MHz (HMBC and HMQC sequences) ([D_6] acetone) δ ppm: 137.6–128.11 (Ph), 132.32 (CH, 1,4-dicyanobenzene), 121.22 (s, *C*≡N), 115.26 (s, C_{ipso}–C≡N), 117.70 (s, Ru–C≡*C*), Ru–*C*≡ not observed, 54.95 (CH_2Cl_2) 29.09 (CH_2, $J_{PC} = 12$ Hz); ^{31}P {^1H} NMR (CD_2Cl_2) δ ppm: 49.86; ($CDCl_3$) δ ppm: 50.38. Anal. Calc. for $C_{128}H_{110}N_2$- $F_{12}P_{10}Ru_2 \cdot 1.5CH_2Cl_2$: C, 61.15; H, 4.48. Found: C, 61.33; H, 4.76%.

6.5. Synthesis of complex **8**

In a typical procedure, a mixture of **6** (330 mg, 0.20 mmol), and 1,4-diethynylbenzene (19 mg, 0.15 mmol) in CH_2Cl_2 (10 mL) was stirred at room temperature for 16 h. The solvent was then removed under reduced pressure and the solid washed with ether (3 × 20 mL) to afford [(*trans*-RuCl)$_2$(=C=CH-*p*-C_6H_4-CH=C=)(dppe)$_4$][2TfO] (**7**) as a red solid, which can be used without further purification in the next step. NEt_3 (0.96 mL, 0.66 mmol), KPF_6 (2790 mg, 1.44 mmol), and benzonitrile (0.36 mmol) in CH_2Cl_2 (20 mL) were then added and the resulting mixture was stirred at room temperature for 16 h. The solvent was then removed under reduced pressure and the solid washed with water (3 × 20 mL) and ether (3 × 20 mL) to afford a pale yellow solid, which was crystallized from CH_2Cl_2–heptane.

[(*trans*-RuCl)$_2$(=C=CH-*p*-C_6H_4-CH=C=)(dppe)$_4$][2TfO] (**7**) ^1H NMR (200.133 MHz, $CDCl_3$, 297 K, δ ppm): 7.64–6.92 (45H, Ph), 6.83 (app. d., 2H, $^3J_{HH} = 8.2$ Hz, C_6H_5), 6.43 (app. d., 2H, $^3J_{HH} = 8.4$ Hz, C_6H_4I) 2.64 (m, 8H, PCH_2CH_2P). $^{31}P\{^1H\}$ NMR (121.50 MHz, $CDCl_3$, 297 K, δ ppm): 55.0 (s, PPh_2).

trans-[(dppe)$_2$Ph-C≡N)Ru(1,4-C≡C–C_6H_4-C≡C)Ru-(PhC≡N)(dppe)$_2$][2PF_6] (**8**) (245 mg, 68%). ν(C≡N) 2225 cm^{-1}; ν(C≡C) 2075 cm^{-1}. ^1H NMR ([D_6] acetone): δ ppm: 8.0 (br. m, 18H, Ph dppe), 7.7 (app. t., 2H, C_6H_5CN), 7.6–7.05 (m, Ph), 7.0 (br. m, 16H, Ph dppe), (d, 4H, Ph), 5.62 (CH_2Cl_2), 3.0 (br. m, 8H, CH_2dppe); ^{13}C NMR 125.75 MHz (HMBC and HMQC sequences) ([D_6] acetone): δ ppm: 137.65–127.55 (Ph), 121.30 (s, *C*≡N), 115.25 (s, C_{ipso}–C≡N), 117.50 (s, Ru–C≡*C*), Ru–*C*≡ not observed, 54.95 (CH_2Cl_2) 29.10 (CH_2, $J_{PC} = 12$ Hz); ^{31}P {^1H} NMR ([D_6] acetone): δ ppm: 49.62; −143.0 (sept., PF_6). *Anal.* Calc. for $C_{128}H_{110}N_2$-$F_{12}P_{10}Ru_2 \cdot 1.5CH_2Cl_2$: C, 61.15; H, 4.48, found: C, 61.33; H, 4.76.

Atomic scattering factors from International Tables for X-ray Crystallography (1992) [69]. Ortep views realized with PLATON-98 [70].

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Appendix A. Supplementary material

CCDC 211235 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic 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.2006.09.008.

References

[1] B.J. Coe, N.R.M. Curati, Comments Inorg. Chem. 25 (2004) 147.
[2] N.J. Long, C.K. Williams, Angew. Chem., Int. Ed. 42 (2003) 2586.
[3] S. Di Bella, Chem. Soc. Rev. 30 (2001) 355.
[4] C.E. Powell, M.G. Humphrey, Coord. Chem. Rev. 248 (2004) 725.
[5] I.R. Whittall, A.M. McDonagh, M.G. Humphrey, M. Samoc, Adv. Organomet. Chem. 42 (1998) 291.
[6] V.W.W. Yam, Acc. Chem. Res. 35 (2002) 555.
[7] A.S. Abd-El-Aziz, E.K. Todd, Coord. Chem. Rev. 246 (2003) 3.
[8] R. Dembinski, T. Bartik, B. Bartik, M. Jaeger, J.A. Gladysz, J. Am. Chem. Soc. 122 (2000) 810.
[9] M. Mayor, H.B. Weber, J. Reichert, M. Elbing, C. von Hanisch, D. Beckmann, M. Fischer, Angew. Chem., Int. Ed. 42 (2003) 5834.
[10] F. Paul, C. Lapinte, Coord. Chem. Rev. 180 (1998) 431.
[11] F. Paul, W.E. Meyer, L. Toupet, H.J. Jiao, J.A. Gladysz, C. Lapinte, J. Am. Chem. Soc. 122 (2000) 9405.
[12] T. Ren, Organometallics 24 (2005) 4854.
[13] S. Rigaut, J. Massue, D. Touchard, J.-L. Fillaut, S. Golhen, P.H. Dixneuf, Angew. Chem., Int. Ed. 41 (2002) 4513.
[14] S. Rigaut, J. Perruchon, S. Guesmi, C. Fave, D. Touchard, P.H. Dixneuf, Eur. J. Inorg. Chem. (2005) 447.
[15] C.-Y. Wong, C.-M. Che, M.C.W. Chan, J. Han, K.-H. Leung, D.L. Phillips, K.-Y. Wong, N. Zhu, J. Am. Chem. Soc. 127 (2005) 13997.
[16] J. Jiao, G.J. Long, F. Grandjean, A.M. Beatty, T.P. Fehlner, J. Am. Chem. Soc. 125 (2003) 7522.
[17] Z. Li, A.M. Beatty, T.P. Fehlner, Inorg. Chem. 42 (2003) 5707.
[18] H. Qi, S. Sharma, Z. Li, G.L. Snider, A.O. Orlov, C.S. Lent, T.P. Fehlner, J. Am. Chem. Soc. 125 (2003) 15250.
[19] M.P. Cifuentes, C.E. Powell, M.G. Humphrey, G.A. Heath, M. Samoc, B. Luther-Davies, J. Phys. Chem. A 105 (2001) 9625.
[20] J.-L. Fillaut, J. Perruchon, P. Blanchard, J. Roncali, S. Golhen, M. Allain, A. Migalsaka-Zalas, I.V. Kityk, B. Sahraoui, Organometallics 24 (2005) 687.
[21] M. Samoc, A. Samoc, B. Luther-Davies, M.G. Humphrey, M.S. Wong, Opt. Mater. 21 (2003) 485.
[22] T. Weyland, I. Ledoux, S. Brasselet, J. Zyss, C. Lapinte, Organometallics 19 (2000) 5235.
[23] K.M.C. Wong, S.C.F. Lam, C.C. Ko, N.Y. Zhu, V.W.W. Yam, S. Roue, C. Lapinte, S. Fathallah, K. Costuas, S. Kahlal, J.F. Halet, Inorg. Chem. 42 (2003) 7086.
[24] I.Y. Wu, J.T. Lin, Y.S. Wen, Organometallics 18 (1999) 320.
[25] V.W.W. Yam, Pure Appl. Chem. 73 (2001) 543.
[26] A. Klein, O. Lavastre, J. Fiedler, Organometallics 25 (2006) 635.
[27] H. Lang, D.S.A. George, G. Rheinwald, Coord. Chem. Rev. 206 (2000) 101.
[28] S. Rigaut, J. Perruchon, L. Le Pichon, D. Touchard, P.H. Dixneuf, J. Organomet. Chem. 670 (2003) 37.
[29] D. Touchard, P. Haquette, S. Guesmi, L. LePichon, A. Daridor, L. Toupet, P.H. Dixneuf, Organometallics 16 (1997) 3640.
[30] W.-Y. Wong, J. Inorg. Organomet. Polym. Mater. 15 (2005) 197.
[31] C.E. Powell, M.P. Cifuentes, J.P. Morrall, R. Stranger, M.G. Humphrey, M. Samoc, B. Luther-Davies, G.A. Heath, J. Am. Chem. Soc. 125 (2003) 602.

[32] F.A. Cotton, C. Lin, C.A. Murillo, Acc. Chem. Res. 34 (2001) 759.
[33] N.C. Gianneschi, M.S. Masar, C.A. Mirkin, Acc. Chem. Res. 38 (2005) 825.
[34] R.S. Seidel, P.J. Stang, Acc. Chem. Res. 35 (2002) 972.
[35] P. Nguyen, G. Lesley, T.B. Marder, I. Ledoux, J. Zyss, Chem. Mater. 9 (1997) 406.
[36] M.F.C. Guedes da Silva, J.J.R. Frausto da Silva, A.J.L. Pombeiro, C. Amatore, J.N. Verpeaux, Inorg. Chem. 37 (1998) 2344.
[37] C. Ornelas, J. Ruiz, J.C. Blais, J. Rodrigues, D. Astruc, Organometallics 23 (2004) 4271.
[38] C. Ornelas, V. Vertlib, J. Rodrigues, K. Rissanen, Eur. J. Inorg. Chem. (2006) 47.
[39] Y.K. Shin, D.J. Szalda, B.S. Brunschwig, C. Creutz, N. Sutin, Inorg. Chem. 36 (1997) 3190.
[40] B. Nohra, S. Graule, C. Lescop, R. Reau, J. Am. Chem. Soc. 128 (2006) 3520.
[41] M.G. Basallote, J. Durán, J. Fernández-Trujillo, M.A. Máñez, J. Chem. Soc., Dalton Trans. (1998) 3227.
[42] J.F. Bickley, S.J. Higgins, C.A. Stuart, A. Steiner, Inorg. Chem. Commun. 3 (2000) 211.
[43] R.F. Winter, T. Scheiring, Z. Anorg. Allg. Chem. 626 (2000) 1196.
[44] Z.H. Li, A.M. Beatty, T.P. Fehlner, Inorg. Chem. 42 (2003) 5707.
[45] Z.H. Li, T.P. Fehlner, Inorg. Chem. 42 (2003) 5715.
[46] These observations are consistent with that reported by Dowling and Henry, [47] for the monoruthenium binuclear complex $[(NH_3)_5RuN\text{-}CFcCN]^{2+}$, that displayed two nitrile stretching bands, one at approximately the free ligand value of 2226 cm^{-1} and the other at 2214 cm^{-1} at lower wavenumber characteristic of a ruthenium (II)-bound nitrile.
[47] N. Dowling, P.M. Henry, Inorg. Chem. 21 (1982) 4088.
[48] C.T. Eagle, D.G. Farrar, G.N. Holder, W.T. Pennington, R.D. Bailey, J. Organomet. Chem. 596 (2000) 90.
[49] M.H. Garcia, M.P. Robalo, A.R. Dias, M. Fatima, M.A. Galvao, W. Wenseleers, E. Goovaerts, J. Organomet. Chem. 619 (2001) 252.
[50] A. Singh, A.N. Sahay, D.S. Pandey, M.C. Puerta, P. Valerga, J. Organomet. Chem. 605 (2000) 74.
[51] D. Touchard, S. Guesmi, L. Le Pichon, A. Daridor, P.H. Dixneuf, Inorg. Chim. Acta 280 (1998) 118.
[52] D. Touchard, C. Morice, V. Cadierno, P. Haquette, L. Toupet, P.H. Dixneuf, J. Chem. Soc., Chem. Commun. (1994) 859.
[53] S.K. Hurst, M.P. Cifuentes, A.M. McDonagh, M.G. Humphrey, M. Samoc, B. Luther-Davies, I. Asselberghs, A. Persoons, J. Organomet. Chem. 642 (2002) 259.
[54] A.S. Abd-El-Azi, Macromol. Rapid Commun. 23 (2002) 995–1031.
[55] M.I. Bruce, B.C. Hall, P.J. Low, B.W. Skelton, A.H. White, J. Organomet. Chem. 592 (1999) 74.
[56] M.C.B. Colbert, J. Lewis, N.J. Long, P.R. Raithby, M. Younus, A.J.P. White, D.J. Williams, N.N. Payne, L. Yellowlees, D. Beljonne, N. Chawdhury, R.H. Friend, Organometallics 17 (1998) 3034.
[57] J. Lewis, M.S. Khan, A.K. Kakkar, B.F.G. Johnson, T.B. Marder, H.B. Fyfe, F. Wittmann, R.H. Friend, A.E. Dray, J. Organomet. Chem. 425 (1992) 165.
[58] D. Zargarian, N.J. Taylor, T.B. Marder, J. Chem. Soc., Chem. Commun. (1991) 188.
[59] O. Lavastre, J. Plass, P. Bachmann, S. Guesmi, C. Moinet, P.H. Dixneuf, Organometallics 16 (1997) 184.
[60] G.J. Bodwell, D.O. Miller, R.J. Vermeij, Org. Lett. 3 (2001) 2093.
[61] D.F. Dos Santos, M. Argentini, R. Weinreich, H.-J. Hansen, Helv. Chim. Acta 83 (2000) 2926.
[62] G.D. Broadhead, J.M. Osgerby, P.L. Pauson, J. Org. Chem. (1958) 650.
[63] M. Rosenblum, N. Brown, J. Papenmeiner, M. Applebaum, J. Organomet. Chem. 6 (1966) 173.
[64] B. Chaudret, G. Commenges, R.J. Poilblanc, Chem. Soc., Dalton Trans. (1984) 1635.
[65] Nonius, Kappa CCD Software, Nonius BV, Delft, The Netherlands, 1999.
[66] Z. Otwinowski, W. Minor, in: C.W. Carter, R.M. Sweet (Eds.), Processing of X-ray Diffraction Data Collected in Oscillation Mode in Methods in Enzymology, Macromolecular Crystallography, Part A, vol. 276, Academic Press, London, 1997, pp. 307–326.
[67] A. Altomare, M.C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, A.G.G. Moliterni, G. Polidori, R. Spagna, J. Appl. Crystallogr. 31 (1998) 74–77.
[68] G.M. Sheldrick, SHELX-97: Program for the Refinement of Crystal Structures, University of Göttingen, Göttingen, Germany, 1997.
[69] International Tables for X-ray Crystallography, vol. C. Ed A.J.C., Kluwer Academic Publishers, Dordrecht, 1992.
[70] A.L. Spek, PLATON: A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands, 1998.