Inorganica Chimica Acta 363 (2010) 1701–1706

Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

Cyclo-ruthenated and -platinated complexes bearing phosphonate substituents

Sipke H. Wadman [a], Duncan M. Tooke [b], Anthony L. Spek [b], Gerard P.M. van Klink [a,1], Gerard van Koten [a,*]

[a] Chemical Biology and Organic Chemistry, Faculty of Science, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands
[b] Crystal and Structural Chemistry, Faculty of Science, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands

ARTICLE INFO

Article history:
Received 17 July 2009
Accepted 4 December 2009
Available online 6 January 2010

Keywords:
Cyclometalated
Ruthenium
Spectroscopy
Phosphonate

ABSTRACT

Two new, potentially cyclometalating terdentate ligands bearing phosphonate substituents, Et_2O_3P-N^C(H)^N (**5**) and Et_2O_3P-C(H)^N^N (**7**), have been prepared. The corresponding ruthenium complexes, $[\mathbf{1}]^+$ and $[\mathbf{2}]^+$, respectively, were obtained by reaction with $[RuCl_3(tpy)]$. Complexes $[\mathbf{1}]^+$ and $[\mathbf{2}]^+$ display electronic properties characteristic for cyclometalated ruthenium complexes. The platinum complex [**3**], of N^C(H)^N ligand **5**, was also prepared and is highly phosphorescent in solution. In general, the phosphonate group electronically behaves equivalent to a carboxylate moiety.

1. Introduction

Polypyridine complexes of ruthenium have been the focus of spectroscopic studies for decades [1–4]. The combination of a metal based oxidation in combination with ligand based reductions results in diverse and interesting properties such as emission from a charge transfer triplet state. These complexes are widely applied as pigments for dye sensitized solar cells (DSSCs) [5,6]. Replacing one of the coordinating nitrogen atoms for a carbon atom results in the corresponding cyclometalated [7] complex and this change has a tremendous effect on the electronic properties of the complex [8,9]. Recently we demonstrated that cycloruthenated complexes, anchored *via* carboxylate groups to TiO_2, can act as efficient sensitizers for DSSCs [10], and more recently this has been confirmed by others [11]. We then became interested in the corresponding phosphonate functionalized complexes for two reasons. Firstly, although the Hammett [12] parameter for the phosphonate moiety is close to that of the carboxylate group ($\sigma_{p(PO_3Et_2)} = 0.60$, $\sigma_{p(CO_2Et)} = 0.45$) the free phosphonate acts as a stronger anchoring moiety for attachment to solid inorganic substrates such as TiO_2 [13–15]. Secondly, organometallic phosphonates can also be used to produce irreversible inhibited *semi*-synthetic metallo-enzymes [16].

We have prepared ligands with either *N,C,N′*- or *C,N,N′*-binding motif bearing a diethylphosphonate moiety on the central ring. The cycloruthenated complexes were prepared and spectroscopically investigated. Because cycloplatinated complexes with *N,C,N′*-[17] and *C,N,N′*-bonding [18,19] motif are known to be very efficient emitters, we also prepared the platinum complex of the N^C(H)^N ligand.

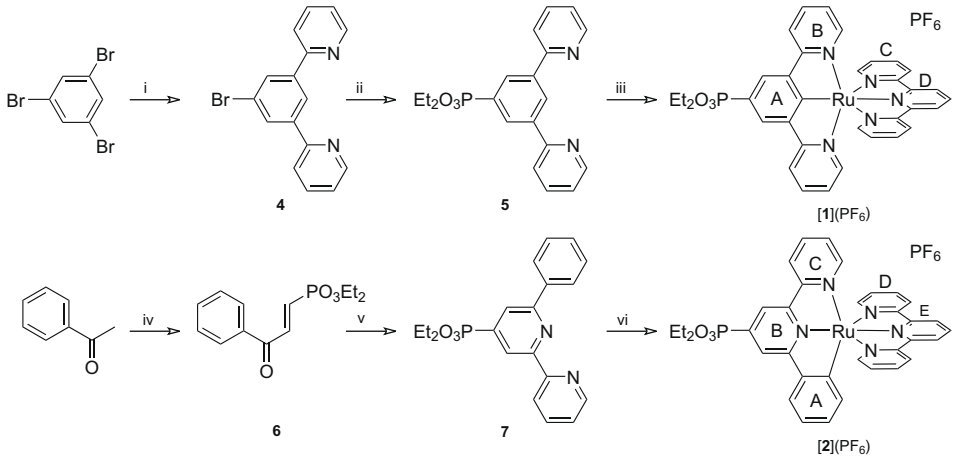
2. Results and discussion

2.1. Synthesis

For the preparation of the phosphonate bearing complexes $[\mathbf{1}](PF_6)$ and $[\mathbf{2}](PF_6)$ the synthetic procedure as depicted in Scheme 1 was followed. The C_{2v}-symmetrical cyclometalated complex $[\mathbf{1}]^+$ was prepared by reaction of $[RuCl_3(tpy)]$, activated with $AgBF_4$ in acetone, with ligand **5** in *n*-BuOH, and isolated as the PF_6^- salt by anion exchange. Ligand **5** was obtained from bromo compound **4** by applying palladium mediated coupling with diethyl phosphite. Compound **4** was obtained from 1,3,5-tribromobenzene using Suzuki C–C coupling methodology. Compound **4** has previously been prepared utilizing Stille [20] or Negishi [21] methodology, however, the procedure described here is higher yielding and circumvents the use of toxic stannane intermediates. In this procedure, CuI is added to prevent coordination of the product, a potential ligand, to the palladium catalyst [22]. Complex $[\mathbf{2}]^+$ was prepared by reacting $[RuCl_3(tpy)]$ with ligand **7** in aqueous MeOH in the presence of *N*-methylmorpholine as sacrificial reductant. Ligand **7** was obtained using Kröhnke's method for pyridine condensation [23]. Chalcone **6** was reacted with (2-pyridinylcarbonyl)pyridinium iodide in the presence of NH_4OAc as nitrogen source. Compound **6** was prepared from acetophenone by condensation with ethyl formate, chlorination using $SOCl_2$, followed by Michaelis–Arbuzov condensation with triethylphosphite. Complexes $[\mathbf{1}]^+$ and $[\mathbf{2}]^+$ were obtained as dark red and purple

* Corresponding author.
E-mail address: g.vankoten@uu.nl (G. van Koten).
[1] Present address: DelftChemTech, Faculty of Applied Sciences, Delft University of Technology, Julianalaan 136, 2628 BL Delft, The Netherlands.

0020-1693/$ - see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.ica.2009.12.008



Scheme 1. Synthesis of $[\mathbf{1}]^+$ and $[\mathbf{2}]^+$, and NMR numbering scheme. (i) Dimethylpyridin-2-boronate, CuI, $Pd(PPh_3)_4$, KOH, DME, reflux 20 h, (ii) HPO_3Et_2, $Pd(PPh_3)_4$, NEt_3, reflux 5 h, (iii) $[RuCl_3(tpy)]$, $AgBF_4$, acetone, *n*-BuOH, (iv) (1) NaH, ethyl formate, 3 h, (2) aqueous H_2SO_4, C_6H_6, (3) $SOCl_2$, C_6H_6, reflux, 12 h, (4) $(EtO)_3P$, 145 °C, 0.5 h, (v) (2-pyridinylcarbonyl)pyridinium iodide, NH_4OAc, MeOH, reflux, 3 h, (vi) $[RuCl_3(tpy)]$, *N*-methylmorpholine, aqueous MeOH, reflux, 18 h.

microcrystalline solids, respectively. Deprotection of the phosphonate ester to the phosphoric acid was attempted with refluxing hydrochloric acid, treatment with bromotrimethylsilane, or boron tribromide, all of which resulted in fast decomposition of the complexes. The complexes are stable in refluxing strongly alkaline solutions, but even with extended reaction times only partial saponification could be achieved, which unfortunately prohibited solar cell testing of these compounds.

The platinum complex [PtCl(Et_2O_3P-N^C^N)], [**3**], could be prepared by heating a solution of **5** with K_2PtCl_6 in aqueous MeCN. Additionally, the ester-functionalized ruthenium complexes [Ru(MeO_2C-N^C^N)(tpy)], and [Ru(EtO_2C-C^N^N)(tpy)], were available from previous studies [9,10], and selected parameters are presented here for comparative purposes.

The NMR spectroscopic data obtained for the NMR active nuclei agreed with the structures proposed for the complexes. All resonances in the ^1H and $^{13}C\{^1H\}$ spectra were unequivocally assigned using two-dimensional correlation experiments. *J*-coupling to the ^{31}P nucleus was observed for the adjacent ^1H nuclei, as well as to all ^{13}C nuclei in the central ring, except for the formally anionic $^{13}C_{ipso}$ in $[\mathbf{1}]^+$. The *J*-coupling constant in $[\mathbf{1}]^+$ and $[\mathbf{2}]^+$ for the A4 and B4 ^{13}C nucleus, respectively, agreed with the observed coupling between the carbon satellites in the ^{31}P NMR spectra, corroborating the assignment. In the platinum complex, [**3**], ^{195}Pt satellites are observed for the proximal B6 proton nuclei. Again, the ^{13}C resonances assigned to the central ring are split by *J*-coupling to the phosphorus nucleus, and the coupling constant of A4 agrees with the observed satellites in the ^{31}P NMR spectrum.

2.2. Crystal structure determination of [1](PF6)

Single crystals of [Ru(Et_2O_3P-N^C^N)(tpy)](PF_6), $[\mathbf{1}](PF_6)$ suitable for X-ray diffraction analyses were obtained by slow evaporation of an MeCN solution. The tpy and *N,C,N′*-binding ligands adopt a rather flat geometry and are mutual perpendicularly coordinated to the ruthenium center in $[\mathbf{1}]^+$, see Fig. 1 and Table 1 for the molecular geometry and relevant data of the cation $[\mathbf{1}]^+$. The constrained geometry of the ligands results in an overall distorted octahedral geometry, as is usually observed in comparable crystal structures [24,25]. As can be expected for the non-uniform donor set, the bond lengths span a wide range from 1.93 Å for the carbon-to-ruthenium bond to 2.09 Å for the peripheral pyridine nitrogen-to-ruthenium bonds on the same ligand. As a matter of fact,

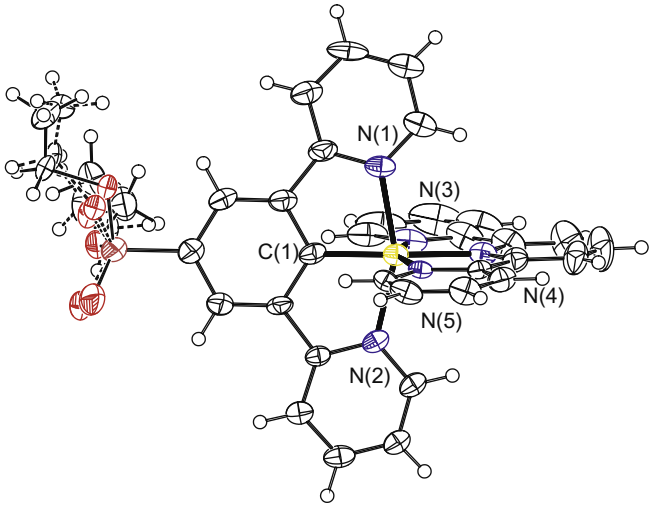


Fig. 1. View of the molecular structure of [Ru(Et_2O_3P-N^C^N)(tpy)](PF_6) ($[\mathbf{1}](PF_6)$). Displacement ellipsoids are drawn at the 50% probability level. The PF_6 anion has been omitted for clarity.

Table 1
Selected bond lengths (Å), angles (°) for $[\mathbf{1}]^+$.

C1–Ru	1.931 (4)	N3–Ru	2.073 (4)
N1–Ru	2.093 (4)	N4–Ru	2.029 (4)
N2–Ru	2.079 (4)	N5–Ru	2.069 (4)
N1–Ru–N2	157.2 (2)	C1–Ru–N4	178.4 (2)
N3–Ru–N5	155.7 (2)		

$[\mathbf{1}]^+$ and the ester-functionalized analogue, [Ru(MeO_2C-N^C^N)(tpy)], are virtually isostructural.

2.3. Electronic properties

The electrochemical data for the complexes are presented in Table 2. In general in polypyridine ruthenium complexes, the oxidation process is metal based, while the reduction processes are ligand based [1,2]. The cyclometalation results in a negative shift of 700 and 730 mV for $[\mathbf{1}]^+$ and $[\mathbf{2}]^+$, respectively, compared to the non-cyclometalated $[Ru(Et_2O_3P\text{-tpy})(tpy)]^{2+}$ ($E^{ox}_{1/2}$ = 0.94 V) [26]. Since it has been previously established that the level of the

Table 2
Cyclic voltammetry data.[a].

		Ru^{II}/Ru^{III}	L1L2/L1$^{\bullet-}$L2	L1$^{\bullet-}$L2/L1$^{\bullet-}$L2$^{\bullet-}$
	$E_{1/2}$ (V) (ΔE_p (mV))			
[**1**]$^+$	1.34[b]	0.24 (62)	−1.91 (67)	
[**2**]$^+$	0.94[b]	0.21 (59)	−1.85 (61)	−2.18 (87)
[**3**]$^+$[c]		0.58[b,d]	−2.03 (72)	

[a] Data collected in MeCN with n-Bu_4NPF_6 as supporting electrolyte at 100 mV/s; potentials reported relative vs. ferrocene/ferrocenium (Fc/Fc^+) used as internal standard.
[b] Irreversible, $E_{p,a}$ given.
[c] Data collected at 1 V/s.
[d] Pt based.

Table 3
Spectroscopic properties.

Complex	Absorption[a] λ_{max} (nm) ($\varepsilon(10^3\ M^{-1}\ cm^{-1})$)	Emission[b] λ_{max} (nm)	φ_{em}[c]
[**1**]$^+$	495 (14.6), 315 (40.5), 278 (69.4), 240 (47.5)	744	1.5×10^{-5}
[Ru(MeO_2C-N^C^N)-(tpy)](PF_6)	492 (13.8)	743	1.5×10^{-5}
[**2**]$^+$	517 (17.0), 318 (37.8), 276 (48.1), 237 (46.5)	783	1.1×10^{-5}
[Ru(EtO_2C-C^N^N)-(tpy)](PF_6)	523 (18.8)	780	1.3×10^{-5}
[**3**]$^+$ [d]	478 (0.15), 398 (5.8), 378 (7.6), 289 (19.2), 256 (41.2)	482	0.22

[a] In MeCN at rt.
[b] In argon deaerated MeCN solution at rt.
[c] Emission quantum yield, relative to [Ru(bpy)$_3$](PF_6)$_2$ as a standard in deaerated MeCN; φ_{em} = 0.062 [34].
[d] In argon deaerated CH_2Cl_2 solution at rt.

lowest unoccupied molecular orbital (LUMO) for the cyclometalated ligand is expected to be higher in energy than that of an isoelectronic but neutral polypyridine ligand [27,28]. It thus seems logical to assign the first reduction processes as tpy based, although in the case of [**2**]$^+$ it might well be associated with the cyclometalating ligand [9]. In [**2**]$^+$ one additional reduction process is observed in the available electrochemical window, assigned as based on the cyclometalated ligand. Due to the electron rich metal center, the ligand based reductions are also negatively shifted compared to [Ru(Et_2O_3P-tpy)(tpy)]$^{2+}$ ($E^{red}_{1/2}$ = −1.60 V) [26], but to a lesser extent as the oxidation process. The N^C(H)^N ligand in platinum complex [**3**] is reduced at increased negative potential, while the platinum based oxidation is observed as an irreversible wave, with a significant larger gap between the oxidation and reduction processes.

The absorption spectra of [**1**]$^+$ and [**2**]$^+$ see Fig. 2 and Table 3, display strong ligand-centered π–π* transitions in the UV part of the spectrum assigned to both ligands. The visible region is dominated by strong metal-to-ligand charge transfer (^{1}MLCT) transitions characteristic for ruthenium polypyridine complexes [1,2]. Compared to [Ru(Et_2O_3P-tpy)(tpy)]$^{2+}$ (λ_{max} = 482 nm) the ^{1}MLCT features are bathochromically shifted, in line with the decrease in the gap between the oxidation and reduction processes in [**1**]$^+$ and [**2**]$^+$. The strong σ-donating anionic carbon destabilizes the mostly metal based ground state more than the ^{1}MLCT excited state. The absorption spectra of complexes [**1**]$^+$ and [**2**]$^+$ are almost identical to that obtained for the carboxylate functionalized complexes [Ru(MeO_2C-N^C^N)(tpy)] and [Ru(EtO_2C-C^N^N)(tpy)]

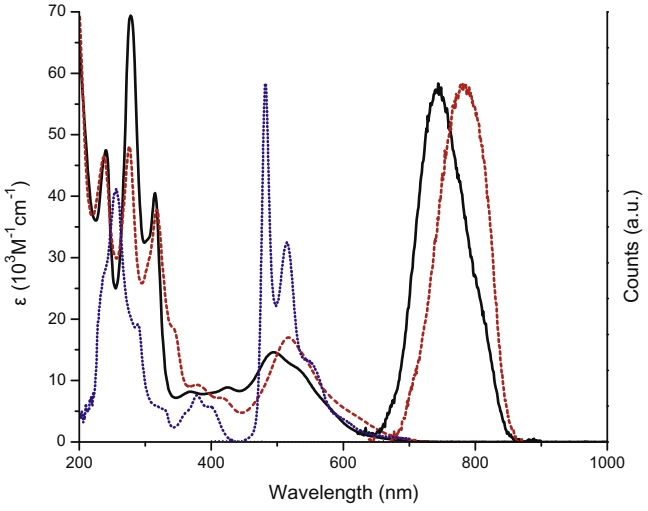


Fig. 2. Electronic absorption spectrum and normalized emission of [**1**]$^+$ (black, solid) and [**2**]$^+$ (red, dash) in MeCN and [**3**]$^+$ (blue, dot) in CH_2Cl_2 at rt. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

[10], while the Hammett parameter for the phosphonate moiety (σ_p = 0.60) is slightly larger than that of the carboxylate group ($\sigma_{p(CO_2Me)}$ = 0.45) [12]. The platinum complex [**3**] also displays intense bands below 300 nm, assigned as π–π* transitions. In addition, a low energy feature is observed, composed of several transitions, previously assigned to a mixture of π–π* and charge transfer transitions [17]. The very weak features around 475 nm are assigned to platinum assisted direct population of the ^{3}π–π* states [17,18].

As a result of the distorted octahedral geometry in [Ru(tpy)$_2$]$^{2+}$ type complexes a relatively weak ligand field is apparent [1–4]. As a consequence, the ^{3}MLCT state is provided with an efficient, non-radiative, decay path via low lying metal centered (^{3}MC) states, and the complexes are non-emissive at room temperature. Introduction of electron accepting moieties on one of the ligands is a feasible way to stabilize the ^{3}MLCT compared to the ^{3}MC as well as the GS and hence promote room temperature emission [29]. Indeed, room temperature phosphorescence is observed for [Ru(Et_2O_3P-tpy)(tpy)]$^{2+}$ (λ_{max} = 650 nm) [26] and [Ru(EtO_2C-tpy)-(tpy)]$^{2+}$ (λ_{max} = 667, $\phi_{em} = 2.7 \times 10^{-4}$) [30]. Cyclometalation has been established as another effective way to increase room temperature emission by destabilizing the ^{3}MC state [27,28,31]. As also the metal based GS is affected, the increase in room temperature efficiency comes at the expense of the emission energy. Indeed, emission is observed for [**1**]$^+$ and [**2**]$^+$, see Table 3, at longer wavelengths compared to that of the non-cyclometalated complex, and, in line with the energy gap law [2,32], with lower efficiency. The platinum complex [**3**] is a much more efficient emitter with a quantum yield of 22%. The emission profile is highly structured, with a vibronic progression of 1300 cm^{-1}, typical for coupling with aromatic C=C vibrations and characteristic of π–π* ligand-centered emission with little involvement of the metal [33]. Compared to the native complex [PtCl(N^C^N)] (λ_{max} = 491, ϕ_{em} = 0.60) and the ester-functionalized [PtCl(EtO_2C-N^C^N)] (λ_{max} = 481, ϕ_{em} = 0.58) the quantum efficiency of **3** is somewhat decreased [17].

3. Conclusions

We have prepared two new, phosphonate functionalized, cyclometalating terdentate ligands with *N,C,N′*- and *C,N,N′*-binding mode, and the corresponding ruthenium complexes. The single crystal X-ray structure displayed the expected mutual perpendicular coordination of the ligands. Cations [**1**]$^+$ and [**2**]$^+$ displayed electronic properties characteristic for cyclometalated ruthenium complexes. All NMR resonances could be unequivocally assigned

using two-dimensional correlation experiments and *J*-coupling considerations. The oxidation and reduction processes are negatively shifted as a result of the increased electron density at the metal center. The ^{1}MLCT absorption features are significantly bathochromically shifted. As a result of the destabilization of the ^{3}MC states, room temperature emission is observed. The emission energy is rather low, and as a consequence the efficiency is decreased. The platinum complex [**3**] displays electronic properties very similar to its unsubstituted and ester-functionalized analogues. Its intense room temperature emission is highly structured, but somewhat decreased in quantum yield. The strong binding of phosphonates to semiconductor surfaces renders these complexes interesting candidates as pigments for dye sensitized solar cells.

4. Experimental

4.1. General

All air-sensitive reactions were performed under a dry nitrogen atmosphere using standard Schlenk techniques. Absolute solvents were dried over appropriate drying agents and distilled before use. All other solvents and reagents were purchased and used as received. ^{1}H, ^{13}C{^{1}H}, ^{31}P, and ^{195}Pt NMR spectra were recorded at 298 K on a Varian 300 MHz Inova spectrometer and/or on a Varian 400 MHz NMR system. NMR spectra were referenced to the solvent residual signal [35], except for the ^{195}Pt spectra, which were externally referenced to a 1 M solution of Na_2PtCl_6 in D_2O [36]. ^{1}H spectral assignments were based on chemical shift and integral considerations as well as COSY and NOESY two-dimensional experiments. The ^{13}C{^{1}H} resonances are assigned on the basis of gHSQC, gHMBC experiments and *J*-coupling considerations. Solution UV–Vis spectra were recorded on a Cary 50 Scan UV–Vis spectrophotometer. Steady-state emission spectra were obtained on a SPEX fluorolog spectrometer. The emission quantum yield was measured by the method of Crosby and Demas [37] with $[Ru(bpy)_3](PF_6)_2$ in argon deaerated MeCN as standard ($\phi_r = 0.062$) and calculated by $\phi_s = \phi_r(B_r/B_s)(n_s/n_r)^2(D_s/D_r)$, in which n is the refractive index of the solvents, D is the integrated intensity and the subscripts s and r refer to sample and reference standard solution, respectively. The quantity B is calculated by $B = 1–10^{-AL}$, where A is the absorbance and L is the optical path length. Cyclic voltammograms were recorded in a single compartment cell under a dry nitrogen atmosphere. The cell was equipped with a Pt microdisk working electrode, Pt wire auxiliary electrode and a Ag/AgCl wire reference electrode. The working electrode was polished with Alumina nano powder between scans. All redox potentials are reported against the ferrocene–ferrocenium (Fc/Fc^+) redox couple used as an internal standard [38,39]. The potential control was achieved with a PAR Model 263A potentiostat. All electrochemical samples were 10^{-1} M in Bu_4NPF_6 as the supporting electrolyte in CH_3CN distilled over $KMnO_4$ and Na_2CO_3. Elemental analyses were carried out by Kolbe Mikroanalytisches Laboratorium (Mülheim an der Ruhr, Germany). (2-Pyridinylcarbonyl)pyridinium iodide [40] and $[RuCl_3(tpy)]$ [41] were prepared following literature procedure.

4.2. Bromo-3,5-di(2-pyridyl)benzene (4)

Freshly prepared dimethylboropyridine [22] (starting from 2-bromopyridine (3.7 mL, 38 mmol) was dissolved in DME and added to 1,3,5-tribromobenzene (3.5 g, 11 mmol), CuI (2.5 g, 13 mmol), $Pd(PPh_3)_4$ (0.7 g, 0.6 mmol), and crushed KOH (3.6 g, 64 mmol). The resulting mixture was heated under reflux for 20 h. After cooling down to rt, H_2O (100 mL) was added, the phases separated and the aqueous phase extracted with Et_2O (3 × 200 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated *in vacuo*. The product was purified by column chromatography on SiO_2 (ethyl acetate:pentane:NEt_3 = 1:1:3%, v/v) yielding **4** as a off-white solid (2.76 g, 70%).

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.72 (d, 2H, ^3J = 5.1 Hz, $Ar^{6'}H$), 8.56 (s, 1H, Ar^4H), 8.23 (s, 2H, $Ar^{2,6}H$), 7.86–7.74 (m, 4H, ^3J = 5.6 Hz, $Ar^{3'}H + Ar^{4'}H$), 7.29 (d, 2H, ^3J = 6.9 Hz, ^3J = 5.1 Hz, $Ar^{5'}H$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.9, 150.0, 141.9, 137.1, 130.5, 124.3, 123.8, 123.0, 121.0.

4.3. Diethyl 3,5-di(2-pyridyl)phenylphosphonate (5)

A solution of **4** (0.6 g, 2 mmol), HPO_3Et_2 (0.60 mL, 4.6 mmol), and $Pd(PPh_3)_4$ (0.11 g, 0.1 mmol) in NEt_3 (5 mL) was heated under reflux for 5 h. The volatiles were removed *in vacuo*, and the residue taken up in MeOH and filtered over SiO_2 with MeOH and CH_2Cl_2. The product was purified by column chromatography on SiO_2 (ethylacetate:NEt_3 = 95:5, v/v), yielding Et_2O_3P-N^C^N as a colorless oil (0.175 g, 25%).

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.90–8.88 (m, 1H, A4), 8.70 (d, ^3J = 4.5 Hz, 2H, B6), 8.72 (dd, $^2J_{31P-1H}$ = 13.5 Hz, ^4J = 1.5 Hz, 2H, A2,6), 7.86 (d, ^3J = 7.8 Hz, 2H, B3), 7.76 (dd, ^3J = 7.8 Hz, ^3J = 7.5 Hz, 2H, B4), 7.25 (dd, ^3J = 7.5 Hz, ^3J = 4.5 Hz, 2H, B5), 4.2–4.1 (m, 4H, CH_2CH_3), 1.4–1.3 (m, 6H, CH_2CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.0, 149.8, 140.2 ($^2J_{31P-13C}$ = 15 Hz), 137.0, 130.4 ($^1J_{31P-13C}$ = 11 Hz), 129.5 ($^3J_{31P-13C}$ = 188 Hz), 129.4, 122.8, 120.9, 62.3 ($^2J_{31P-13C}$ = 5 Hz), 16.4. ^{31}P NMR (162 MHz, CD_3CN): δ 14.2 ($^1J_{31P-13C}$ = 188 Hz). *Anal.* Calc. for $C_{20}H_{21}N_2O_3P$: C, 65.21; H, 5.75; N, 7.60. Found: C, 65.00; H, 5.65; N, 7.43%.

4.4. Diethyl 3-oxo-3-phenylpropenylphosphonate (6)

Compound **6** was prepared following adapted literature procedures [42–44]. To a suspension of NaH (5.25 g, 220 mmol) in THF (200 mL) was added at 0 °C ethyl formate (18.0 mL, 220 mmol) and acetophenone (17.0 mL, 146 mmol). The cooling bath was removed and the resulting mixture was stirred for 3 h. The formed precipitate was isolated by centrifugation and washed with Et_2O (2 × 80 mL), suspended in benzene (80 mL), and decomposed with H_2O (40 mL) and 10% aqueous H_2SO_4 (40 mL). The benzene layer was separated and dried over $CaCl_2$. To this solution $SOCl_2$ (12.0 mL, 166 mmol) was added, and the mixture heated under reflux for 12 h. The compound was isolated by distillation, yielding phenyl-2-chlorovinylketone as colorless oil. A mixture of phenyl-2-chlorovinylketone (1.87 g, 11 mmol) and triethylphosphite (2.0 mL, 11 mmol) was placed in a oil bath heated to 100 °C, and gradually heated to 145 °C during which the evolution of gas was observed. The product was isolated by column chromatography on SiO_2 (ethylacetate:CH_2Cl_2 = 1:1, v/v), yielding the product as a colorless oil (0.738 g, 27%).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.98 (d, 2H, ^3J = 8.0 Hz, Ar^2H), 7.79 (dd, 1H, ^3J = 17.0 Hz, $^2J_{31P-1H}$ = 21.3 Hz, $CHCHPO_3Et_2$), 7.60 (t, 1H, ^3J = 7.0 Hz, Ar^4H), 7.49 (dd, 2H, ^3J = 8.0 Hz, ^3J = 7.0 Hz, Ar^3H), 6.91 (dd, 1H, ^3J = 17.0 Hz, $^3J_{31P-1H}$ = 19.2 Hz, $CHCHPO_3Et_2$), 4.2–4.1 (m, 4H, CH_2CH_3), 1.3–1.4 (m, 6H, CH_2CH_3).

4.5. Diethyl 6-phenyl-2,2′-bipyridin-4-ylphosphonate (7)

A suspension of **6** (0.74 g, 2.75 mmol), NH_4OAc (2.3 g, 30 mmol), and (2-pyridinylcarbonyl)pyridinium iodide (1.02 g, 3.1 mmol) in MeOH (20 mL) was heated under reflux for 3 h. The resulting suspension was filtered over SiO_2 (ethyl acetate + 2% NEt_3) and evaporated to dryness. The resulting oil was heated *in vacuo* to 75 °C for 2 h, and purified by column chromatography on SiO_2 (ethyl acetate:pentane = 1:1, v/v), yielding the product as a colorless oil (0.63 g, 63%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.66 (d, 1H, $^3J_{31P-1H}$ = 14.0 Hz, B5), 8.59 (d, 1H, ^3J = 4.4 Hz, C6), 8.51 (d, 1H, ^3J = 8.0 Hz, C3), 8.10 (d, 2H, ^3J = 7.6 Hz, A2), 8.09 (d, 1H, $^3J_{31P-1H}$ = 14.4 Hz, B3), 7.71 (dd, 1H, ^3J = 8.0 Hz, ^3J = 7.6 Hz, C4), 7.40 (dd, 2H, ^3J = 7.6 Hz, ^3J = 7.2 Hz, A3), 7.33 (t, 1H, ^3J = 7.2 Hz, A4), 7.20 (dd, 1H, ^3J = 7.2 Hz, ^3J = 4.4 Hz, C5), 4.12 (m, 4H, CH_2CH_3), 1.12 (m, 6H, CH_2CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.6 ($^2J_{31P-13C}$ = 13 Hz), 156.1 ($^2J_{31P-13C}$ = 13 Hz), 155.2, 149.0, 139.1 ($^1J_{31P-13C}$ = 185 Hz), 138.1, 136.7, 129.4, 128.6, 126.8, 124.0, 121.7 ($^3J_{31P-13C}$ = 10 Hz), 121.2, 120.5 ($^3J_{31P-13C}$ = 10 Hz), 62.5 ($^2J_{31P-13C}$ = 6 Hz), 16.2. ^{31}P NMR (162 MHz, $CDCl_3$): δ 16.5 ($^1J_{31P-13C}$ = 185 Hz). *Anal.* Calc. for $C_{20}H_{21}N_2O_3P$: C, 65.21; H, 5.75; N, 7.60. Found: C, 65.29; H, 5.81; N, 7.53%.

4.6. [Ru(Et$_2$O$_3$P-N^C^N)(tpy)](PF$_6$), [**1**]$^+$

A suspension of [$RuCl_3$(tpy)] (140 mg, 0.31 mmol) and $AgBF_4$ (195 mg, 0.99 mmol) in acetone (40 mL) was heated under reflux for 2 h. The resulting suspension was filtered, and the purple solution concentrated *in vacuo*. The solid was dissolved in *n*-BuOH (40 mL), **5** (175 mg, 0.47 mmol) was added, and the mixture heated under reflux for 20 h. After cooling down, the solution was filtered over Celite, the product precipitated by addition of an excess of aqueous KPF_6 solution, and collected by filtration. The product was collected through the filter with acetone, and purified by column chromatography on SiO_2 (MeCN:H_2O:1 M $NaNO_3$ = 18:1:1, v/v), yielding the product as a red solid (180 mg, 68%).

^{1}H NMR (400 MHz, CD_3CN): δ 8.77 (d, 2H, ^3J = 8.0 Hz, D3,5), 8.56 (d, 2H, $^3J_{31P-1H}$ = 13.2 Hz, A3,5), 8.44 (d, 2H, ^3J = 8.0 Hz, C3), 8.32 (t, 1H, ^3J = 8.0 Hz, D4), 8.28 (d, 2H, ^3J = 8.0 Hz, B3), 7.72 (dd, 2H, ^3J = 8.0 Hz, ^3J = 7.6 Hz, C4), 7.67 (dd, 2H, ^3J = 8.0 Hz, ^3J = 7.6 Hz, B4), 7.13 (d, 2H, ^3J = 5.6 Hz, B6), 7.08 (d, 2H, ^3J = 5.6 Hz, C6), 6.95 (dd, 2H, ^3J = 7.6 Hz, ^3J = 5.6 Hz, C5), 6.74 (dd, 2H, ^3J = 7.6 Hz, ^3J = 5.6 Hz, B5), 4.29 (m, 4H, CH_2CH_3), 1.46 (t, 6H, ^3J = 7.0 Hz, CH_2CH_3). ^{13}C NMR (100 MHz, CD_3CN): δ 230.8 (A1), 168.5 (B2), 159.8 (C2), 155.6 (C6), 153.5 (D2,6), 152.9 (B6), 143.8 (A2,6, $^3J_{31P-13C}$ = 17 Hz), 136.6 (B4), 136.4 (C4), 134.1 (D4), 127.3 (C5), 126.2 (A3,5, $^2J_{31P-13C}$ = 11 Hz), 124.6 (C3), 123.5 (D3,5), 123.2 (B5), 121.0 (B3), 120.2 (A4, $^1J_{31P-13C}$ = 193 Hz), 63.2 (CH_2CH_3 $^2J_{31P-13C}$ = 5 Hz), 16.9 (CH_2CH_3). ^{31}P NMR (162 MHz, CD_3CN): δ 22.5 ($^1J_{31P-13C}$ = 193 Hz), −143.4 ($^1J_{31P-19F}$ = 707 Hz). MALDI-TOF-MS (DHB Matrix): *m/z* = 702.10 [M^+] (calcd for $C_{35}H_{31}N_5O_3PRu$, 702.12).

4.7. [Ru(Et$_2$O$_3$P-C^N^N)(tpy)](PF$_6$), [**2**]$^+$

A suspension of [$RuCl_3$(tpy)] (152 mg, 0.34 mmol), **7** (150 mg, 0.41 mmol), and *N*-methylmorpholine (10 drops) in aqueous MeOH (1:1, v/v, 60 mL) was heated under reflux for 18 h. After cooling down, the solution was filtered over Celite. The product was precipitated by the addition of an excess aqueous KPF_6 and removal of acetone *in vacuo*. The product was isolated by filtration and collected through the filter with acetone. The product was purified by column chromatography on SiO_2 (MeCN:H_2O:1 M $NaNO_3$ = 18:1:1, v/v) and Al_2O_3 (CH_2Cl_2:MeCN = 1:1, v/v), yielding the product as a purple solid (134 mg, 46%).

^{1}H NMR (400 MHz, CD_3CN): δ 8.62 (d, 2H, ^3J = 8.0 Hz, E3,5), 8.60 (d, 1H, $^3J_{31P-1H}$ = 13.2. Hz, B5), 8.58 (d, 1H, ^3J = 8.0 Hz, C3), 8.42 (d, 1H, $^3J_{31P-1H}$ = 13.2 Hz, B3), 8.40 (d, 2H, ^3J = 8.0 Hz, D3), 8.10 (t, 1H, ^3J = 8.0 Hz, E4), 7.93 (d, 1H, ^3J = 7.6 Hz, A3), 7.87 (dd, 1H, ^3J = 8.0 Hz, ^3J = 7.6 Hz, C4), 7.74 (dd, 2H, ^3J = 8.0 Hz, ^3J = 7.6 Hz, D4), 7.51 (d, 1H, ^3J = 5.2 Hz, C6), 7.36 (d, 2H, ^3J = 5.6 Hz, D6), 7.11 (dd, 1H, ^3J = 7.6 Hz, ^3J = 5.2 Hz, C5), 7.01 (dd, 2H, ^3J = 7.6 Hz, ^3J = 5.6 Hz, D5), 6.77 (dd, 1H, ^3J = 7.6 Hz, ^3J = 6.8 Hz, A4), 6.57 (dd, 1H, ^3J = 7.6 Hz, ^3J = 6.8 Hz, A5), 5.79 (d, 1H, ^3J = 7.6 Hz, A6), 4.35 (m, 4H, CH_2CH_3), 1.48 (t, 6H, ^3J = 7.0 Hz, CH_2CH_3) ^{13}C NMR (100 MHz, $CDCl_3$): δ 185.0 (A1), 165.0 (B2, $^3J_{31P-13C}$ = 14 Hz), 157.8 (D2), 156.8 (C2), 155.2 (B6, $^3J_{31P-13C}$ = 15 Hz), 153.9 (E2,6), 151.8 (C6), 151.7 (D6), 147.4 (A2), 138.4 (C4),135.9 (D4), 135.7 (B4, $^1J_{31P-13C}$ = 187 Hz),135.7 (A6), 130.4 (E4), 130.1 (A5), 127.3 (C5), 127.0 (D5), 126.1 (A3), 124.7 (C3), 124.0 (D3), 123.1 (E3,5), 122.4 (A4), 121.0 (B5, $^2J_{31P-13C}$ = 10 Hz), 120.0 (B3, $^2J_{31P-13C}$ = 10 Hz), 64.1 ($^2J_{31P-13C}$ = 6 Hz), 16.9. ^{31}P NMR (162 MHz, CD_3CN): δ 15.8 ($^1J_{31P-13C}$ = 187 Hz), −143.5 ($^1J_{31P-19F}$ = 706 Hz). *Anal.* Calc. for $C_{35}H_{31}F_6N_5O_3P_2Ru$: C, 49.65; H, 3.69; N, 8.27. Found: C, 49.78; H, 3.62; N, 8.22%. MALDI-TOF-MS (DHB Matrix): *m/z* = 702.11 [M^+] (calcd for $C_{35}H_{31}N_5O_3PRu$, 702.12).

4.8. [PtCl(Et$_2$O$_3$P-N^C^N)], [**3**]

A solution of **5** (28 mg, 0.08 mmol) and K_2PtCl_6 (33 mg, 0.08 mmol) in aqueous MeCN (1:3, v/v, 8 mL) was heated under reflux for 3 days. After cooling the red solution down to rt, the resulting yellow solution was dried *in vacuo*. The dark solid was dissolved in DMSO (0.5 mL), and precipitated with water (30 mL). The yellow solid was washed with Et_2O (50 mL), yielding the product as a yellow solid (15 mg, 72%).

^{1}H NMR (400 MHz, DMSO-d_6): δ 9.14 (d, 2H, ^3J = 4.8 Hz, $^3J_{195Pt-1H}$ = 38 Hz, B6), 8.32 (d, 2H, ^3J = 7.6 Hz, B3), 8.23 (dd, 2H, ^3J = 7.6 Hz, ^3J = 7.6 Hz, B4), 8.02 (d, 2H, $^3J_{31P-1H}$ = 13.2 Hz, A3,5), 7.61 (dd, 2H, ^3J = 7.6 Hz, ^3J = 4.8 Hz, B5), 4.00–4.10 (m, 4H, CH_2CH_3), 1.25–1.35 (m, 6H, CH_2CH_3). ^{13}C NMR (100 MHz, DMSO-d6): δ 166.1, 165.4, 151.4, 140.9 ($^2J_{31P-13C}$ = 17 Hz), 140.7, 127.5 ($^3J_{31P-13C}$ = 12 Hz), 124.8, 122.7 ($^1J_{31P-13C}$ = 190 Hz), 121.3, 61.7 ($^2J_{31P-13C}$ = 5 Hz), 16.2. ^{31}P NMR (162 MHz, DMSO-d6): δ 20.6 ($^1J_{31P-13C}$ = 190 Hz). ^{195}Pt NMR (64 MHz, DMSO-d_6): δ 3574. MALDI-TOF-MS (DHB Matrix): *m/z* = 562.44 [M^+−Cl] (calcd for $C_{20}H_{20}N_2O_3PPt$, 562.09).

4.9. X-ray structure determination of [**1**](PF$_6$)

X-ray data were collected on a Nonius KappaCCD diffractometer (Rotating anode, graphite monochromator, Mo Kα, λ = 0.71073 Å, θ(max) = 25°, 150 K). Dark red plate, orthorhombic, $P2_12_12_1$, *a* = 9.0085(4), *b* = 17.427(2), *c* = 21.7456(18) Å, *V* = 3413.9(5) Å^3, *Z* = 4, *d*(calc) = 1.647 g/cm^3. The structure is incommensurate with a Q-vector of 0.43 along (0 0 1). The reported structure was solved with DIRDIF99 [45] using the main reflections only. Refinement with SHELXL-97 [46] converged at *R* = 0.0454 for 5073 reflections with $I > 2\sigma(I)$, wR_2 = 0.1091 for all 6011 reflections, *S* = 1.036, 528 parameters. Both the PF_6 anion and the chains on *P*1 were included in the refinement with a disorder model (0.56:0.44 and 0.56:0.48, respectively). Hydrogen atoms were taken into account at calculated positions and refined riding on their carrier atoms. The ORTEP illustration and structure checking were done with PLATON [47].

Acknowledgements

The authors gratefully acknowledge the support from the European Commission through the funding of the project FULLSPECTRUM within the Sixth Framework Program under number SES6-CT-2003-502620. This work was partially supported (DMT and ALS) by the Council for Chemical Sciences of the Netherlands Organization for Scientific Research (NWO/CW).

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2009.12.008.

References

[1] J.-P. Sauvage, J.P. Collin, J.C. Chambron, S. Guillerez, C. Coudret, V. Balzani, F. Barigelletti, L. De Cola, L. Flamigni, Chem. Rev. (4) (1994) 993.
[2] A. Juris, V. Balzani, F. Barigelletti, S. Campagna, P. Belser, A. Von Zelewsky, Coord. Chem. Rev. 84 (1988) 85.
[3] E.A. Medlycott, G.S. Hanan, Chem. Soc. Rev. 34 (2) (2005) 133.
[4] E. Baranoff, J.P. Collin, L. Flamigni, J.-P. Sauvage, Chem. Soc. Rev. 33 (3) (2004) 147.
[5] M. Grätzel, J. Photochem. Photobiol. A 164 (1–3) (2004) 3.
[6] K. Kalyanasundaram, M. Grätzel, Coord. Chem. Rev. 177 (1998) 347–414.
[7] M. Albrecht, G. van Koten, Angew. Chem., Int. Ed. 40 (20) (2001) 3750.
[8] J.P. Collin, P. Gavina, V. Heitz, J.-P. Sauvage, Eur. J. Inorg. Chem. (1) (1998) 1.
[9] S.H. Wadman, M. Lutz, D.M. Tooke, A.L. Spek, H. FrantiÂÀek, R.W.A. Havenith, G.P.M. Van Klink, G. Van Koten, Inorg. Chem. 48 (5) (2009) 1887.
[10] S.H. Wadman, J.M. Kroon, K. Bakker, M. Lutz, A.L. Spek, G.P.M. van Klink, G. van Koten, Chem. Commun. (19) (2007) 1907.
[11] T. Bessho, E. Yoneda, J.-H. Yum, M. Guglielmi, I. Tavernelli, H. Imai, U. Rothlisberger, M.K. Nazeeruddin, M. Graîtzel, J. Am. Chem. Soc. (16) (2009) 5930.
[12] C. Hansch, A. Leo, R.W. Taft, Chem. Rev. 91 (2) (1991) 165.
[13] H. Wolpher, S. Sinha, J. Pan, A. Johansson, M.J. Lundqvist, P. Persson, R. Lomoth, J. Bergquist, L. Sun, V. Sundstroem, B. Akermark, T. Polivka, Inorg. Chem. 46 (3) (2007) 638.
[14] S.M. Zakeeruddin, M.K. Nazeeruddin, P. Pechy, F.P. Rotzinger, R. HumphryBaker, K. Kalyanasundaram, M. Grätzel, V. Shklover, T. Haibach, Inorg. Chem. 36 (25) (1997) 5937.
[15] E. Galoppini, Coord. Chem. Rev. 248 (13–14) (2004) 1283.
[16] C.A. Kruithof, M.A. Casado, G. Guillena, M.R. Egmond, A. van der Kerk-van Hoof, A.J.R. Heck, R.J.M. klein Gebbink, G. van Koten, Chem. Eur. J. 11 (23) (2005) 6869.
[17] J.A.G. Williams, A. Beeby, E.S. Davies, J.A. Weinstein, C. Wilson, Inorg. Chem. 42 (26) (2003) 8609.
[18] W. Lu, B.X. Mi, M.C.W. Chan, Z. Hui, C.M. Che, N.Y. Zhu, S.T. Lee, J. Am. Chem. Soc. 126 (15) (2004) 4958.
[19] W. Lu, S.S.-Y. Chui, K.-M. Ng, C.-M. Che, Angew. Chem., Int. Ed. 47 (24) (2008) 4568.
[20] M. Beley, S. Chodorowski, J.P. Collin, J.-P. Sauvage, Tetrahedron Lett. 34 (18) (1993) 2933.
[21] M. Chavarot, Z. Pikramenou, Tetrahedron Lett. 40 (37) (1999) 6865.
[22] M.D. Sindkhedkar, H.R. Mulla, M.A. Wurth, A. Cammers-Goodwin, Tetrahedron 57 (15) (2001) 2991.
[23] F. Kröhnke, Synthesis (1) (1976) 1.
[24] M. Beley, J.P. Collin, R. Louis, B. Metz, J.-P. Sauvage, J. Am. Chem. Soc. 113 (22) (1991) 8521.
[25] K. Lashgari, M. Kritikos, R. Norrestam, T. Norrby, Acta Crystallogr., Sect. C C55 (1) (1999) 64.
[26] C. Houarner, E. Blart, P. Buvat, F. Odobel, Photochem. Photobiol. Sci. 4 (2) (2005) 200.
[27] F. Barigelletti, B. Ventura, J.P. Collin, R. Kayhanian, P. Gavina, J.-P. Sauvage, Eur. J. Inorg. Chem. (1) (2000) 113.
[28] M. Beley, S. Chodorowski, J.-P. Collin, J.-P. Sauvage, L. Flamigni, F. Barigelletti, Inorg. Chem. 33 (12) (1994) 2543.
[29] M. Maestri, N. Armaroli, V. Balzani, E.C. Constable, A.M.W.C. Thompson, Inorg. Chem. 34 (10) (1995) 2759.
[30] H.J. Bolink, L. Cappelli, E. Coronado, P. Gavina, Inorg. Chem. 44 (17) (2005) 5966.
[31] E.C. Constable, M.J. Hannon, Inorg. Chim. Acta 211 (1) (1993) 101.
[32] X.-Y. Wang, A. Del Guerzo, R.H. Schmehl, J. Photochem. Photobiol. C 5 (1) (2004) 55.
[33] J.A.G. Williams, A.J. Wilkinson, V.L. Whittle, Dalton Trans. (16) (2008) 2081.
[34] J.M. Calvert, J.V. Caspar, R.A. Binstead, T.D. Westmoreland, T.J. Meyer, J. Am. Chem. Soc. 104 (24) (1982) 6620.
[35] H.E. Gottlieb, V. Kotlyar, A. Nudelman, J. Org. Chem. 62 (21) (1997) 7512.
[36] P.S. Pregosin, Coord. Chem. Rev. 44 (2) (1982) 247.
[37] G.A. Crosby, J.N. Demas, J. Phys. Chem. 75 (8) (1971) 991.
[38] I.M. Kolthoff, F.G. Thomas, J. Phys. Chem. 69 (9) (1965) 3049.
[39] V.V. Pavlishchuk, A.W. Addison, Inorg. Chim. Acta 298 (1) (2000) 97.
[40] R. Ballardini, V. Balzani, M. Clemente-Leon, A. Credi, M.T. Gandolfi, E. Ishow, J. Perkins, J.F. Stoddart, H.R. Tseng, S. Wenger, J. Am. Chem. Soc. 124 (43) (2002) 12786.
[41] B.P. Sullivan, J.M. Calvert, T.J. Meyer, Inorg. Chem. 19 (5) (1980) 1404.
[42] R.A. Aitken, P.K.G. Hodgson, J.J. Morrison, A.O. Oyewale, J. Chem. Soc., Perkin Trans. (3) (2002) 402.
[43] F. Hammerschmidt, E. Zbiral, Liebigs Ann. Chem. (1979) 492.
[44] A.N. Nesmeyanov, N.K. Kochetkov, M.I. Rybinskaya, Bull. Acad. Sci. USSR Div. Chem. Sci. (Engl. Transl.) (1954) 637.
[45] P.T. Beurskens, G. Admiraal, G. Beurskens, W.P. Bosman, S. Garcia-Granda, R.O. Gould, J.M.M. Smits, C. Smykalla, The DIRDIF99 Program System, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands, 1999.
[46] G.M. Sheldrick, Acta Crystallogr., Scet. A 64 (2008) 112.
[47] A.L. Spek, J. Appl. Crystallogr. 36 (2003) 7.