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Journal of Organometallic Chemistry 643–644 (2002) 494–497

Journal of Organometallic Chemistry

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Note

A bridging ligand featuring terminal 2-pyridylphosphole moieties: synthesis, optical properties and Ru(II)-complex

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Received 28 June 2001; accepted 19 July 2001

Abstract

2,2′-Di[2-(5-(2-pyridyl)phospholyl)]thiophene (**2a**) has been obtained in 63% yield via the Fagan–Nugent's route. Derivative **2a** possesses an extended π-conjugated system and behaves as a bis(*P*,*N*-chelate) towards cationic (*p*-cymene)RuCl fragments affording the air-stable complex **3a** in 60% yield. A diastereoselective coordination was observed and the solid state structure of the model Ru-complex **2b** featuring a related 2-(2-pyridyl)-5-(2-thienyl)phosphole ligand is presented. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Phosphole; π-Conjugated system; Ruthenium; Bridging ligand; Heterocycle

1. Introduction

Great attention has recently been paid to the synthesis and photophysical properties of dinuclear complexes containing bridging π-conjugated ligands owing to their potential applications for molecular devices [1]. The design of the bridging ligands allows tuning of the electronic properties of these dyads and has led to important progress in the field of photoinduced electron- or energy-transfer processes. Typical examples of such systems are polypyridine ligands and their Ru and Os complexes which have been widely studied due to the possible multiple structural variations [1a,1b,1c]. We have recently shown that co-oligomers alternating phosphole and thienyl rings are tunable chromophores possessing extended π-systems [2a,2b,2c,2d] and that 2-pyridylphospholes can act as tightly bonded 1,4-chelates towards Pd(II) centres [2e]. These properties prompted us to investigate a new family of derivatives possessing two terminal 2-pyridylphosphole moieties joined by a 2,5-thienyl spacer as potential bridging ligands to build bimetallic complexes. Herein, we describe the synthesis and optical properties of the first example of such derivatives and the preparation of a corresponding bimetallic Ru(II)-complex.

2. Results and discussion

The target phosphole was prepared according to the 'one-pot' Fagan–Nugent's route, an efficient method for phosphole synthesis [3]. The intramolecular oxidative coupling of 2,2′-di[8-(2-pyridyl)octa-1,7-diynyl]-thiophene (**1a**), obtained in 70% via a Sonogashira coupling involving 2,5-dibromothiophene and two equivalents of 1-(2-pyridyl)octa-1,7-diyne, with 'zirconocene' followed by addition of bromodiphenylphosphine affords 2,2′-di[2-(5-(2-pyridyl)phospholyl)]-thiophene (**2a**) (Scheme 1). This compound was isolated as an air stable solid in 63% yield after purification by flash column chromatography on basic alumina. Derivative **2a** has been characterised by high-resolution mass spectrometry and elemental analysis. Its ^{31}P-NMR spectrum consists of two lines of comparable intensity observed at + 10.6 and + 10.9 ppm, a typical range for λ^3,σ^3-phospholes [3b,3c], indicating that **2a** exists as a

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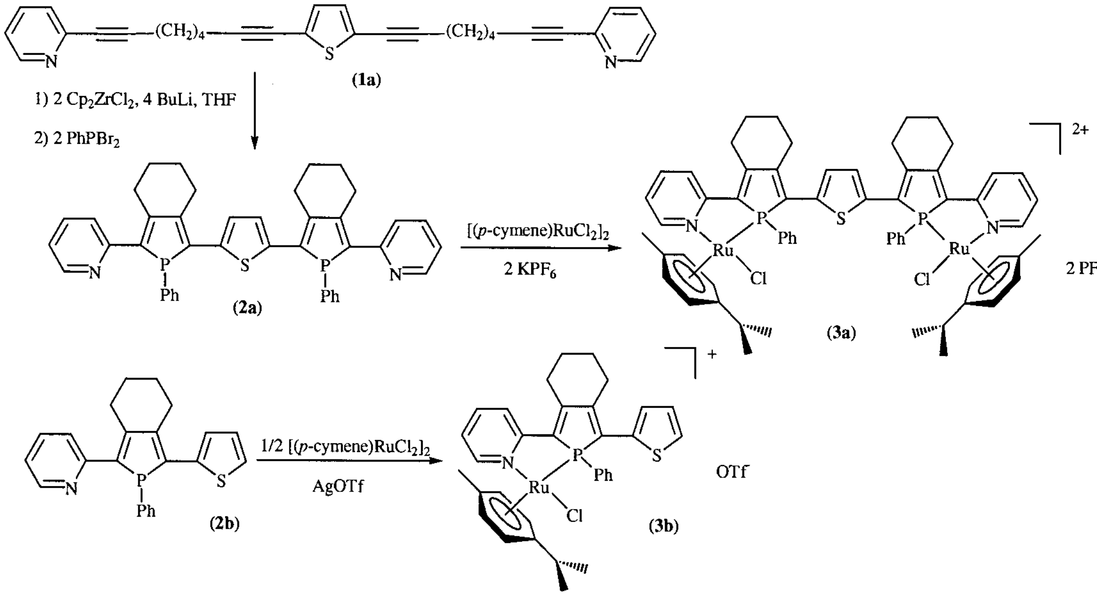
PII: S0022-328X(01)01123-8

1/1 mixture of diastereoisomers. High-temperature ^{31}P-NMR experiments reveal a phosphorus inversion barrier of 16.9 kcal mol^{-1}. This low value is classical for phospholes [3b,3c] and **2a** can be regarded as a mixture of diastereoisomers interconverting slowly at room temperature. The ^{1}H- and ^{13}C-NMR spectra are quite simple and consistent with the proposed structure [4].

Subsequent additions of $[(p\text{-cymene})RuCl_2]_2$ and two equivalents of KPF_6 to a CH_2Cl_2 solution of di(2-pyridylphospholyl)thiophene (**2a**) gave rise to the air stable complex **3a** isolated in 60% yield after crystallisation (Scheme 1). In the ^{31}P-NMR spectrum of complex **3a**, the signals attributed to the phosphole rings consist in two sharp lines (+ 58.8, + 59.1) and reveal a large coordination shift effect ($\Delta\delta \approx 49$ ppm). This shift is much larger than those usually observed upon coordination of monodentate phosphole ligands such as 1-phenyl-3,4-dimethylphosphole on cationic Ru(II) centres ($\Delta\delta \approx 20$ ppm) [5]. However, such high coordination shift effects have already been observed when 2-pyridylphosphole derivatives act as chelating *P*,*N*-ligands towards Pd(II) centres [2e]. Coordination of an unsymmetrical 2-pyridylphosphole moiety to an '(arene)RuCl' fragment can give rise to two isomers. The simplicity of the ^{31}P-NMR spectrum of complex **3a** strongly suggests a diastereoselective coordination, each diastereoisomer of **2a** giving one diastereoisomer of **3a**. All attempts to separate these isomers by crystallisation failed, and the sole valuable information given by the ^{1}H- and ^{13}C-NMR spectra of the mixture is the coordination downfield shift of the ^{1}H-NMR-signal due to the NCH_6-pyridyl fragments (**2a**/**3a**, $\Delta\delta \approx 0.7$ ppm) [6]. In order to confirm that 2-pyridylphospholes act as *P*,*N*-chelates towards cationic '(arene)RuCl' fragments and undergo a diastereoselective coordination, the behaviour of the model 2-(2-pyridyl)-5-(2-thienyl)phosphole (**2b**) (Scheme 1) was investigated. Derivative **2b** was allowed to react with $[(p\text{-cymene})RuCl_2]_2$ and KPF_6 in dichloromethane at room temperature. In the ^{31}P-NMR spectrum of the crude reaction mixture, only one sharp signal at + 59.4 ppm is observed. This chemical shift compares nicely with those recorded for complex **3a**, and shows that only one of the possible diastereoisomers was formed. The half-sandwich-type complex **3b** (Scheme 1) was isolated in 95% yield after crystallisation. The simplicity of the ^{1}H- and ^{13}C-NMR spectra confirms that **3b** was obtained as a single diastereoisomer [7] and the deshielding upon coordination of the pyridyl-NCH_6 ^{1}H-NMR-signal reaches 0.6 ppm. The solid state structure of the cation of **3b** with selected bond lengths and angles is shown in Fig. 1 [8]. The chlorine atom and the *P*-phenyl substituent are pointing in the same direction. The bond lengths and bond angles around the Ru centre [Ru–P, 2.3058(8) Å; Ru–N, 2.131(3) Å, P–Ru–N, 80.29(7)°] are consistent with known literature values [5,9] and reveal no strain due to the formation of the five-membered metallacycle. The thiophene and the slightly puckered phosphole rings are almost coplanar [twist angle, 3.8°(3)] and the dihedral angle between the coordinated pyridine and phosphole moieties [P1–C1–C13–N1] reaches 24.3°(4). The C2–C1–C13–C14 twist angle [45.6(5)°] is larger than those recorded for other 2-pyridylphosphole derivatives [1.8(16)–25.6(5)°] [2], but does not prevent an extended π-conjugation since the orbital overlap varies approximately with the cosine of the twist angle.



Scheme 1.

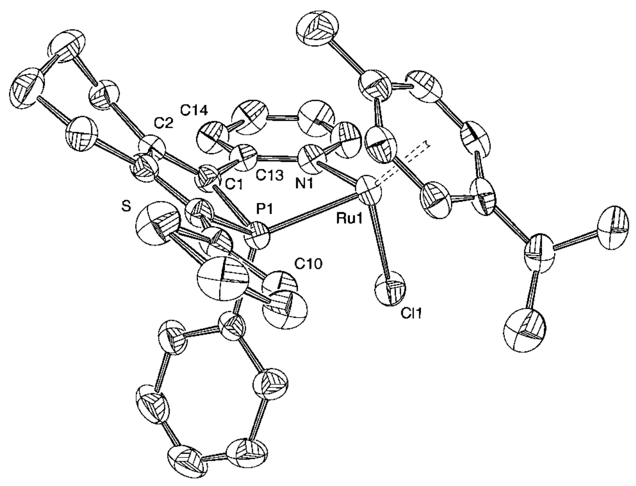


Fig. 1. ORTEP drawing (thermal ellipsoid 40% probability) of the cation of complex **3b**. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): P1–C1, 1.788(3); C1–C13, 1.464(4); C13–N1, 1.360(4); N1–Ru1, 2.131(3); Ru1–P1, 2.3058(8); Ru1–P1–C(1), 98.45(10); P1–C1–C13, 115.5(2); C1–C13–N1, 113.5(3); C13–N1–Ru1, 122.4(2); N1–Ru1–P1, 80.29(7); N1–Ru1–Cl1, 83.60(8).

Table 1
Photophysical data for compounds **2a**,**b** and **3a**,**b** in CH_2Cl_2 solutions at room temperature [a]

	λ_{max} (nm), ε (mol^{-1} l cm^{-1})	λ_{em} (nm)
2a	480 (8100)	555–585
2b	396 (4400)	500
3a	482 (4900)	
3b	435 (7500)	

[a] Absorption and emission maxima, ±3 nm.

2-Pyridyl-5-thienylphosphole (**2b**) shows an absorption maximum in the visible region at 396 nm attributed to π–π* transitions of the π-conjugated system. This value is considerably red-shifted for the bis(2-pyridylphospholyl)thiophene derivative **2a** ($\Delta\lambda_{max} = 84$ nm, Table 1), suggesting a delocalisation of the π-system over the whole molecule. Both derivatives are photoluminescent in CH_2Cl_2 solutions at room temperature, and they display emissions in the visible region upon excitation at their λ_{max}. It is noteworthy that compound **2a** exhibits two emission bands of comparable intensities (Table 1), the Stoke shifts are comparable for the two derivatives **2a** and **2b** (≈ 100 nm). Coordination of 2-pyridylphosphole **2b** to the cationic ruthenium fragment induces a bathochromic shift of 39 nm (Table 1). This red shift can be attributed to an intra-ligand-charge-transfer (ILCT) enforced by the presence of electron-rich thiophene and electron withdrawing coordinated pyridyl groups at the 2,5-position of the phosphole ring. It is very likely that this broad ligand-centred transition overlaps the possible metal-to-ligand-charge-transfer transition arising from Ru(II) to π*-orbital of the coordinated 2-pyridylphosphole moiety. In contrast, coordination of bis(2-pyridylphospholyl)thiophene **2a** has almost no influence on the λ_{max} (Table 1). This is probably due to the symmetrical structure of **2a** which prevents efficient ILCT. It is noteworthy that, in contrast to the corresponding free ligands, complexes **3a** and **3b** do not display emission in CH_2Cl_2 solutions at room temperature.

3. Conclusion

We have described the synthesis, UV–vis absorption and fluorescence data of a new π-conjugated oligomer **2a** featuring terminal 2-pyridylphosphole moieties and a thienyl spacer. The 2-pyridylphosphole fragments act as *P*,*N*-chelates and undergo diastereoselective coordination to chiral Ru(II) centres. The evaluation of the electrochemical properties of the Ru(II)-complexes **3a**,**b** and the coordination of **2a** to Ru(II)–(bipyridine)$_2$ fragments are under active investigations.

4. Supplementary material

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 165626. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

This work was financially supported by the Conseil Régional Bretagne, the Ministère de l'Education Nationale, de la Recherche et de la Technologie and the Centre National de la Recherche Scientifique.

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[4] Selected data for **2a**: ^{1}H-NMR (200 MHz, CD$_2$Cl$_2$): $\delta = 6.95$ (m, 4H, thienyl H$_3$ and pyridyl H$_5$), 7.15 (m, 6H, phenyl H$_{meta}$ and H$_{para}$), 7.35 (m, 6H, pyridyl H$_3$ and phenyl H$_{ortho}$), 7.50 (ddd, J(H,H) = 8.1, J(H,H) = 8.1, J(H,H) = 1.9 Hz, 2H, pyridyl H$_4$), 8.45 (ddd, J(H,H) = 4.8, J(H,H) = 1.9, J(H,H) = 1.0 Hz, 2H, pyridyl H$_6$). ^{13}C–{^{1}H}-NMR (75 MHz, CD$_2$Cl$_2$): $\delta = 23.0$ (s, C=CCH$_2$CH$_2$), 23.1 (s, C=CCH$_2$CH$_2$), 29.7 (s, C=CCH$_2$), 29.6 (s, C=CCH$_2$), 120.3 (s, pyridyl C$_5$), 122.9 (d, J(P,C) = 8.2 Hz, pyridyl C$_3$), 126.3 (d, J(P,C) = 10.1 Hz, thienyl C$_3$), 128.4 (d, J(P,C) = 8.6 Hz, phenyl C$_{meta}$), 129.3 (s, phenyl C$_{para}$), 133.7 (d, J(P,C) = 19.2 Hz, phenyl C$_{ortho}$), 135.7 (d, J(P,C) = 1.6 Hz, pyridyl C$_4$), 149.3 (d, J(P,C) = 1.6 Hz, pyridyl C$_6$). ^{31}P–{^{1}H}-NMR (81 MHz, CD$_2$Cl$_2$): $\delta = +10.6$ (s) and $+10.9$ (s). MS–HR (FAB, mNBA): m/z, found 662.2084 [M]$^+$; Anal. Found: C, 76.32; H, 5.38; N, 4.34. Calc. for $C_{42}H_{36}N_2P_2S$ (662.2074): C, 76.11; H, 5.48; N, 4.23%.

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[6] Selected data for **3a**: ^{1}H-NMR (200 MHz, CD$_2$Cl$_2$): $\delta = 1.17$ (d, 6H, J(H,H) = 6.9 Hz, CHCH_3), 1.26 (d, 6H, J(H,H) = 6.9 Hz, CHCH_3), 1.60 (m, 6H, CH_3–C$_6$H$_4$), 1.80 (m, 4H, C=CCH$_2$CH_2), 2.00 (m, 4H, C=CCH$_2$CH_2), 2.77 (sept, 2H, J(H,H) = 6.9 Hz, CHCH$_3$), 2.94 (m, 8H, C=CCH_2CH$_2$), 5.44–6.10 (m, 8H, CH arom p-cymene), 7.00–7.95 (m, 18H, CH arom), 9.15 (m, 2H, pyridyl H$_6$); ^{31}P–{^{1}H}-NMR (81 MHz, CD$_2$Cl$_2$): $\delta = -140$ (s, PF$_6^-$), $+58.8$, $+59.1$ (s). Anal. Found: C, 49.96; H, 4.45; N, 1.79. Calc. for $C_{62}H_{64}Cl_2F_{12}N_2P_4Ru_2S$ (1494.1): C, 49.80; H, 4.32; N, 1.87%.

[7] Selected data for **3b**: ^{1}H-NMR (200 MHz, CD$_2$Cl$_2$): $\delta = 1.07$ (d, 3H, J(H,H) = 6.9 Hz, CHCH_3), 1.13 (d, 3H, J(H,H) = 6.9 Hz, CHCH_3), 1.58 (s, 3H, CH_3–C$_6$H$_4$), 2.57 (sept, 1H, J(H,H) = 6.9 Hz, CHCH$_3$), 5.34 (dd, 1H, J(H,H) = 5.6 Hz, CH arom p-cymene), 5.61 (d, 1H, J(H,H) = 5.6 Hz, CH arom. p-cymene), 5.88 (d, 1H, J(H,H) = 6.2 Hz, CH arom. p-cymene), 5.96 (d, 1H, J(H,H) = 6.2 Hz, CH arom. p-cymene), 7.10–7.47 (m, 8H, thienyl H$_4$, H$_3$, pyridyl H$_5$ and phenyl H$_{ortho}$, H$_{meta}$, H$_{para}$), 7.53 (d, J(H,H) = 5.3 Hz, 1H, thienyl H$_5$), 7.59 (d,^{3}J(H,H) = 7.6 Hz, 1H, pyridyl H$_3$), 7.83 (t, J(H,H) = 7.6 Hz, J(H,H) = 7.6 Hz, 1H, pyridyl H$_4$), 9.10 (d, J(H,H) = 5.4 Hz, 1H, pyridyl H$_6$); ^{13}C–{^{1}H}-NMR (75 MHz, CD$_2$Cl$_2$): $\delta = 17.7$ (s, CH$_3$), 20.5 (s, CH$_3$), 21.7 (s, C=CCH$_2$CH$_2$), 22.3 (s, C=CCH$_2$CH$_2$), 23.5 (s, CH$_3$), 27.5 (d, J(P,C) = 7.3 Hz, C=CCH$_2$), 29.4 (d, J(P,C) = 8.5 Hz, C=CCH$_2$), 30.9 (s, CHCH$_3$), 82.1 (s, CH arom p-cymene), 88.2 (d, J(P,C) = 2.4 Hz, CH arom p-cymene), 92.5 (d, J(P,C) = 4.8 Hz, CH arom p-cymene), 93.8 (d, J(P,C) = 6.1 Hz, CH arom p-cymene), 99.1 (s, C–CH(CH$_3$)$_2$ arom. p-cymene), 111.0 (s, CH$_3$–C arom. p-cymene), 117.2 (q, ^{1}J(P,F) = 321.6 Hz, CF$_3$SO$_3$), 122.1 (d, J(P,C) = 42.2 Hz, phenyl C$_{ipso}$), 123.7 (d, J(P,C) = 8.5 Hz, pyridyl C$_3$), 124.9 (s, pyridyl C$_5$), 128.1 (s, thienyl C$_4$), 128.8 (d, J(P,C) = 10.8 Hz, phenyl C$_{meta}$), 129.0 (d, J(P,C) = 7.3 Hz, thienyl C$_3$), 129.4 (s, thienyl C$_5$), 132.0 (d, J(P,C) = 3.1 Hz phenyl C$_{para}$), 133.1 (d, J(P,C) = 9.4 Hz, phenyl C$_{ortho}$), 136.5 (d, J(P,C) = 18.8 Hz, thienyl C$_2$), 137.1 (d, J(P,C) = 50.8 Hz, C$_\alpha$), 137.7 (d, J(P,C) = 49.3 Hz, C$_\alpha$), 139.6 (s, pyridyl C$_4$), 145.9 (d, J(P,C) = 10.9 Hz, C$_\beta$), 150.8 (d, J(P,C) = 9.4 Hz, C$_\beta$), 153.3 (d, J(P,C) = 20.3 Hz, pyridyl C$_2$), 159.1 (s, pyridyl C$_6$). ^{31}P–{^{1}H}-NMR (81 MHz, CDCl$_3$): $\delta = +59.4$ (s). MS–HR (FAB, mNBA): m/z, found 644.0898 [M − OTf]$^+$; $C_{33}H_{34}ClNPRuS$ Calc. 644.0887. Anal. Found: C, 51.62; H, 4.45; N, 1.79. Calc. for $C_{34}H_{34}ClF_3NO_3PRuS_2$ (793.23): C, 51.45; H, 4.32; N, 1.77%.

[8] X-ray structural analysis for **3b**: $C_{34}H_{34}ClF_3NO_3PRuS_2$, $M = 793.23$, $0.24 \times 0.22 \times 0.18$ mm, monoclinic $P2_1/c$; $a = 12.927(2)$, $b = 18.300(2)$, $c = 14.217(4)$ Å; $\beta = 95.20(2)°$; $V = 3350(1)$ Å^3; $Z = 4$; $\mu = 7.73$ mm^{-1}. CAD4 NONIUS diffractometer; Mo–K$_\alpha$ radiation; λ(Mo–K$_\alpha$) = 0.71073 Å; $D_{calc} = 1.573$ g cm^{-3}; $F(000) = 1616$; $T = 293$ K; $2\theta_{max} = 54°$. 7287 unique reflections from which 5512 with $I > 2.0\sigma(I)$ (scan $\omega/2\theta = 1$; hkl: h, 0.16; k, 0.23; l, −18.18, calc $w = 1/[\sigma^2(F_o^2) + (0.0568P)^2 + 2.29P]$ where $P = (F_o^2 + 2F_c^2)/3$ with the resulting $R = 0.0379$, $R_w = 0.0986$ and $S_w = 1.041$ (residual $\Delta\rho \leq 1.04$ e Å^{-3})). After Lorentz and polarization corrections, the structure was solved with SIR-97, and refined with SHELXL97 by the full-matrix least-squares techniques.

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