Polyhedron 29 (2010) 1968–1972

Contents lists available at ScienceDirect

Polyhedron

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

Cationic palladium(II), platinum(II) and ruthenium(II) complexes containing a chelating difluoro-substituted thiourea ligand

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ARTICLE INFO

Article history:
Received 19 December 2009
Accepted 12 March 2010
Available online 18 March 2010

Keywords:
Thiourea
Chelating ligand
Palladium
Platinum
Ruthenium
X-ray structure

ABSTRACT

The fluorine substituted thiourea 2,6-$F_2C_6H_3C(O)NHC(S)NEt_2$ was prepared in good yield from the reaction of 2,6-$F_2C_6H_3C(O)Cl$ with KSCN and Et_2NH in acetone. Using this compound several heteroleptic, monocationic Pd(II), Pt(II) and Ru(II) complexes of the type *cis*-[M{κ^2*S*,*O*-2,6-$F_2C_6H_3C(O)NC(S)NEt_2$}(L)]PF_6 [M = Pt, Pd; L = $(Ph_3P)_2$, $^tBu_2$bipy, 1,10-phen] as well as [Ru(η^6-*p*-cym){κ^2*S*,*O*-2,6-$F_2C_6H_3C(O)NC(S)NEt_2$}(PPh_3)]PF_6 were prepared in high yields. The compounds were characterised by spectroscopic methods and, in one case, by single crystal X-ray diffraction.

1. Introduction

N,*N*-Dialkyl-*N*-acylthiourea derivatives of the type Ar-C(O)NHC(S)NR_2 are an important class of versatile ligands which have been used in coordination chemistry for many years. These compounds are easily accessible from the reaction of an acid chloride with KSCN and subsequent reaction of the in situ formed acylthioisocyanate with an amine. Upon deprotonation these compounds can act as either monoanionic ligands *via* sulfur or as monoanionic O–S chelate ligands towards a metal (Chart 1).

Coordination solely *via* sulfur is rare and so far only known for some gold(I) compounds [1,2]. The chelating coordination mode, especially the formation of bis(chelate) metal complexes of the type *cis*-[M{κ^2*S*,*O*-ArC(O)NC(S)NR_2}$_2$] is however commonly encountered and numerous examples of such compounds have been reported. Interest in the chemistry of these metal complexes has arisen from their varied applications including precious metal separation and extraction [3,4], their use as single source precursors for nano-materials [5] as well as their biological activity [6–11]. We have been studying the synthesis, structures and applications of metal complexes containing the NHC(E)R (E = S, Se) unit with gold [12,13], palladium [14] and ruthenium [15]. In order to extend this work, we report here some platinum, palladium and ruthenium complexes containing a difluoro substituted monoanionic chelating thiourea ligand.

2. Results and discussion

The new thiourea 2,6-$F_2C_6H_3C(O)NHC(S)NEt_2$ was prepared in 95% yield as a pale yellow, crystalline solid from 2,6-$F_2C_6H_3C(O)Cl$, KSCN and Et_2NH in acetone. The compound was characterised by ^1H, ^{13}C and ^{19}F NMR spectroscopy, which unambiguously confirmed the structure as detailed in the Experimental section. Attempts to prepare the pentafluorophenyl derivative by an analogous reaction from $C_6F_5C(O)Cl$ gave only dark, oily materials which could not be purified. The reaction of metal chloro complexes of the type [MCl_2(L)] [M = Pt, Pd; L = $(Ph_3P)_2$, $^tBu_2$bipy, or 1,10-phen] with 2,6-$F_2C_6H_3C(O)NHC(S)NEt_2$ in the presence of a base gives good yields of the monocationic complexes *cis*-[M{κ^2*S*,*O*-2,6-$F_2C_6H_3C(O)NC(S)NEt_2$}(L)]$^+$ [M = Pt, Pd; L = $(Ph_3P)_2$, $^tBu_2$bipy, 1,10-phen], which were isolated as their PF_6 salts (Scheme 1). Apart from the phenanthroline complex **5** which is insoluble in common solvents except dmso, the salts **1**–**4** are soluble in methylene chloride, acetone and acetonitrile but insoluble in alcohols, ether and hexane.

Similarly, the reaction of [Ru(η^6-*p*-cym)Cl_2]$_2$ with two equivalents of the thiourea in the presence of Ph_3P, NH_4PF_6 and Et_3N affords the chiral, monocationic arene Ru(II) complex [Ru(η^6-*p*-cym){κ^2*S*,*O*-2,6-$F_2C_6H_3C(O)NC(S)NEt_2$}(PPh_3)]PF_6 in high yield (Scheme 2).

Complexes **1**–**6** were fully characterised by spectroscopic methods including NMR spectroscopy, high-resolution electrospray mass spectrometry and, in the case of complex **3**, by X-ray diffraction. The $^{31}P\{^1H\}$ NMR spectra of the palladium and platinum

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doi:10.1016/j.poly.2010.03.010

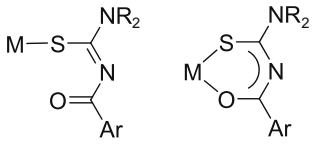


Chart 1.

complexes **1** and **2** show an AB system with P–P coupling of *ca.* 30 Hz, due to the chemical inequivalence of the two phosphorus atoms imposed by the chelating thiourea ligands. In addition, the $^{31}P\{^1H\}$ NMR spectrum of complex **1** shows platinum satellites with a coupling constant of greater than 3000 Hz, typical for *cis* platinum phosphine complexes. Loss of symmetry upon coordination of the chelating thiourea is also evident from the doubling of all signals of the $^tBu_2$bipy and 1,10-phen protons in the ^1H NMR spectra of complexes **3**–**5**. The deprotonation of the thiourea ligand is apparent from the disappearance of the NH signal in the ^1H NMR spectra of complexes **1**–**6**. The chiral Ru complex **6** shows some interesting features in its NMR spectra. Two distinct resonances for the NCH_2 groups are observed in the ^1H NMR spectrum: one quartet (2 protons) and two AB systems (1 proton each). The metal-centred chirality is also apparent from the doubling of the *p*-cymene ring resonances. For such a chiral system, two sets of signals would also be expected in the ^{19}F NMR spectrum of **6**. However, only one resonance is actually observed, probably due to coincidental overlap of the 2 signals.

High-resolution electrospray mass spectra of complexes **1**–**6** show intense signals corresponding to the molecular ions of the cations. In the case of the ruthenium complex **6**, an additional peak due to loss of one Ph_3P can be observed. The measured isotope patterns are in excellent agreement with those calculated for the proposed formulae. Overall, the spectral data is fully consistent with the structures shown in Schemes 1 and 2. The proposed structure was unambiguously confirmed by a single crystal X-ray diffraction study of complex **3**; the molecular structure of which is shown in Fig. 1.

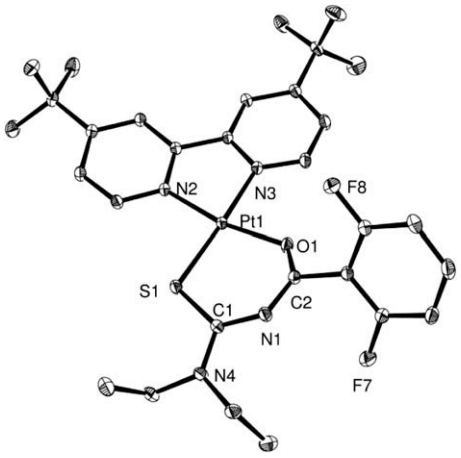
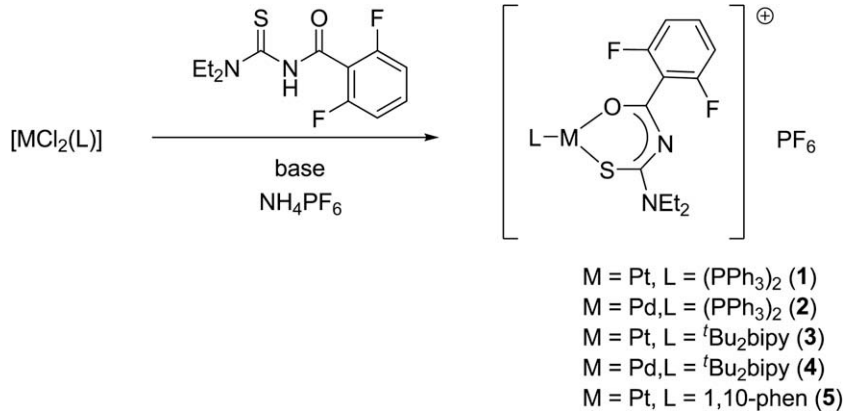
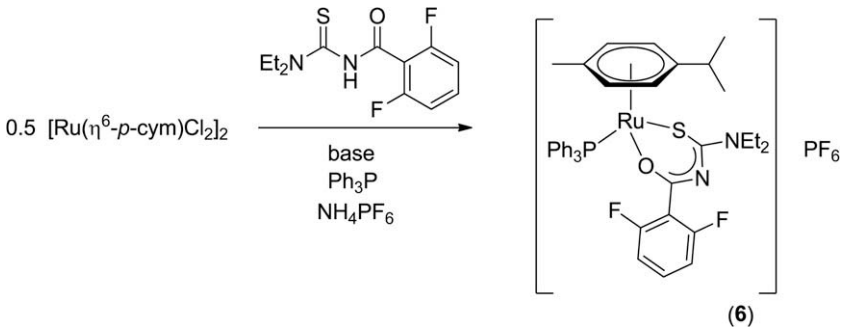


Fig. 1. Molecular structure of complex **3**. Ellipsoids show 50% probability. Hydrogen atoms and the $[PF_6]^-$ anion have been omitted for clarity. Selected bond distances [Å]: Pt(1)–N(2) 2.0038(9), Pt(1)–N(3) 2.0295(9), Pt(1)–O(1) 1.9939(8), Pt(1)–S(1) 2.2543(3), C(1)–N(1) 1.3566(14), C(1)–S(1) 1.7306(11), C(2)–N(1) 1.3051(14), C(2)–O(1) 1.2846(13). Selected bond angles [°]: O(1)–Pt(1)–N(2) 169.01(4), N(3)–Pt(1)–S(1) 175.02(3), O(1)–Pt(1)–S(1) 94.76(3), N(2)–Pt(1)–S(1) 95.39(3), N(2)–Pt(1)–N(3) 80.31(4).

The cation consists of a square planar coordinated platinum atom surrounded by the chelating $^tBu_2$bipy and the chelating thiourea bound to the Pt *via* oxygen and sulfur atoms, forming



Scheme 1.



Scheme 2.

five- and six-membered metallacyclic rings, respectively. There are no interactions between the cation and the PF_6 anion in the solid state. The Pt–O and Pt–S distances 1.9939(8) and 2.2543(3) Å lie within two standard deviations of the average values retrieved from the CSD [Cambridge Structural Database Ver. 5.30 Nov. 2008 + 4 updates] for N-acylthiourea ligands. There are 17 entries for platinum complexes with at least one N,N-dialkyl-N′-acylthiourea totalling 31 observations for distances and angles. These average values are: Pt–O 2.030(19) Å, Pt–S 2.26(2) Å, S–Pt–O 94.4(9)°, C=S 1.732(13) Å, and C=O 1.269(10) Å. This elongation of the C=O and C=S double bonds upon coordination to the metal atom was observed previously by Koch [16].

The Pt–N distances are 2.0038(9) and 2.0295(9) Å, the significantly longer one being *trans* to the Pt–S bond. The CSD contains 126 entries of bipyridyl coordinated to platinum, excluding Pt clusters. A total of 248 Pt-N distances averages 2.048(37) Å while the 145 N–Pt–N angles average 79.5(14)° encompassing within the statistical error the present results. More important is a comparison between the Pt–N distances *trans* to Pt–O and Pt–S bonds. In this case 146 *trans* N–Pt–O and 68 *trans*-N–Pt–S fragments were found, applying restraints of tetra coordinated Pt, two bonds formed by each S- and O-atom and three bonds formed by nitrogen. A *trans* conformation was assumed if the N–Pt–X angle was between 170 and 180°. The resulting Pt–N distances of 1.98(3) Å for O–Pt–N and 2.052(19) Å for S–Pt–N support the significant *trans*-effect (the difference amounts to 0.0257(13) Å) observed in the present complex, even though the two CSD values do not differ significantly.

The difluoro-substituted aromatic ring is twisted by 55.55° relative to the plane defined by the six-membered Pt–S–C–N–C–O ring. The root-mean-square-distance (RMSD) for the six-membered metallacycle from a least-squares plane is 0.09 Å.

In summary, we present here the preparation and full characterisation of some Pt(II), Pd(II) and Ru(II) complexes containing a fluoro-substituted chelating thiourea ligand. Further work to study this class of compounds as well as their selenium counterparts is ongoing in our laboratory.

3. Experimental

3.1. General

^1H, ^{13}C, ^{19}F and $^{31}P\{^1H\}$ NMR spectra were recorded on a 400 MHz Bruker ARX spectrometer. Chemical shifts are quoted relative to external $SiMe_4$ (^1H, ^{13}C), Freon (^{19}F) and 85% H_3PO_4 (^{31}P). High-resolution electrospray mass spectra were measured on a Bruker MicroTOF spectrometer in positive ion mode using acetonitrile solutions of the compounds. Elemental analyses were performed by staff of the microanalytical laboratory of the University of Wuppertal. Chemicals and solvents (HPLC grade) were sourced commercially and used as received. The metal precursors *cis*-$[MCl_2(PPh_3)_2]$ (M = Pt, Pd) [17] and $[Ru(\eta^6\text{-}p\text{-cym})Cl_2]_2$ [18] and were prepared by procedures as described in the literature. The ^{t}Bu$_2$bipy and 1,10-phenanthroline metal complexes *cis*-$[MCl_2(N\text{-}N)]$ (M = Pd, Pt) were prepared by reaction of the appropriate nitrogen base with $[PdCl_2(PhCN)_2]$ or $K_2[PtCl_4]$, respectively.

3.2. 2,6-$F_2C_6H_3C(O)NHC(S)NEt_2$

To a solution of KSCN (2.43 g, 25 mmol) in acetone (20 mL) was added 2,6-$F_2C_6H_3C(O)Cl$ (4.41 g, 25 mmol). The resulting suspension was heated to reflux for *ca.* 2 h. After this time, Et_2NH (2.6 mL, 25 mmol) was added and the mixture refluxed once again for *ca.* 30 min. The yellow suspension was poured into water (400 mL) and the solid that precipitated was isolated by filtration, washed with H_2O and dried in air. 5.8 g (95%) of a pale yellow solid was obtained. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.82 (br. s, 1 H, NH), 7.38 (m, 1 H, *p*-H), 6.92 (t, *J* = 8.1 Hz, 2 H, *m*-H), 3.58–4.01 (m, 4 H, NCH_2), 1.29 (t, *J* = 7.1 Hz, 6 H, NCH_2CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 177.73 (C=O), 161.17 (d, *J* = 6.4 Hz, CF), 158.64 (d, *J* = 6.4 Hz, CF), 157.78 (C=S), 132.57 (t, *J* = 9.6 Hz, *p*-C), 113.10 (t, *J* = 18.5 Hz, *ipso*-C), 111.96 (d, *J* = 25.7 Hz, *m*-C), 47.62 (NCH_2), 12.94 (NCH_2CH_3), 11.19 (NCH_2CH_3). ^{19}F NMR (376 MHz, $CDCl_3$, 25 °C): δ = −111.99 (t, *J* = 9.1 Hz). *Anal.* Calc. for $C_{12}H_{14}F_2N_2OS$ (272.31): C, 52.93; H, 5.18; N, 10.29. Found: C, 53.04; H, 5.19; N, 10.54%.

3.3. Preparation of cationic cis-[M{κ²S,O-2,6-$F_2C_6H_3C(O)NC(S)NEt_2$}(L)]⁺ complexes

A mixture of the metal precursor (0.050 g), 2,6-$F_2C_6H_3C(O)NHC(S)NEt_2$ (1 equiv) and NH_4PF_6 (slight excess) in MeCN (10 mL) and excess base (Et_3N or NaOAc) was heated to reflux until a clear solution had formed. The solution was concentrated in vacuum to a volume of *ca.* 2 mL and H_2O was added, resulting in precipitation of the product. The solid was isolated by filtration, washed with H_2O, Et_2O and was subsequently dried in vacuum.

3.4. cis-[Pt{κ²S,O-2,6-$F_2C_6H_3C(O)NC(S)NEt_2$}$(PPh_3)_2$]PF_6 (**1**)

This was prepared as described above from *cis*-$[PtCl_2(PPh_3)_2]$ (0.050 g, 0.063 mmol), 2,6-$F_2C_6H_3C(O)NHC(S)NEt_2$ (0.017 g, 0.063 mmol) and NH_4PF_6 (0.012 g, 0.074 mmol). 0.050 g (69%) of a yellow solid was obtained. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.05–7.62 (m, 31 H, Ph_3P, p-H Ar), 6.62 (t, *J* = 8.9 Hz, 2 H, *m*-H Ar), 3.64 (quart, *J* = 6.8 Hz, 2 H, NCH_2), 3.43 (quart, *J* = 6.8 Hz, 2 H, NCH_2), 1.15 (t, *J* = 6.8 Hz, 3 H, *Me*CH_2N), 1.00 (t, *J* = 6.8 Hz, 3 H, *Me*CH_2N). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, 25 °C): δ = 22.15 (d, J_{P-P} = 25 Hz, J_{P-Pt} = 3094 Hz), 10.27 (d, *J* = 27 Hz, J_{P-Pt} = 3874 Hz), −143 (sept, J_{P-F} = 706 Hz). ^{19}F NMR (376 MHz, $CDCl_3$, 25 °C): δ = −73.5 (d, *J* = 712 Hz, PF_6), −112.9 (t, *J* = 6.6 Hz, ArF). HR-ES-MS: *m/z* (observed, calculated) = 990.2183, 990.2187 $[M]^+$.

3.5. cis-[Pd{κ²S,O-2,6-$F_2C_6H_3C(O)NC(S)NEt_2$}$(PPh_3)_2$]PF_6 (**2**)

This was prepared as described above from *cis*-$[PdCl_2(PPh_3)_2]$ (0.050 g, 0.071 mmol), 2,6-$F_2C_6H_3C(O)NHC(S)NEt_2$ (0.019 g, 0.069 mmol) and NH_4PF_6 (0.014 g, 0.086 mmol). 0.061 g (81%) of a yellow solid was obtained. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.12–7.59 (m, 31 H, Ph_3P, p-H Ar), 6.63 (t, *J* = 8.3 Hz, 2 H, *m*-H Ar), 3.65 (quart, *J* = 6.8 Hz, 2 H, NCH_2), 3.45 (quart, *J* = 6.8 Hz, 2 H, NCH_2), 1.14 (t, *J* = 6.8 Hz, 3 H, *Me*CH_2N), 1.00 (t, *J* = 6.8 Hz, 3 H, *Me*CH_2N). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, 25 °C): δ = 39.43 (d, J_{P-P} = 29 Hz), 28.70 (d, *J* = 29 Hz), −143 (sept, J_{P-F} = 712 Hz). ^{19}F NMR (376 MHz, $CDCl_3$, 25 °C): δ = −74.3 (d, *J* = 712 Hz, PF_6), −113.1 (t, *J* = 7.0 Hz, ArF). HR-ES-MS: *m/z* (observed, calculated) = 901.1596, 901.1774 $[M]^+$.

3.6. cis-[Pt{κ²S,O-2,3-$F_2C_6H_3C(O)NC(S)NEt_2$}(^{t}Bu$_2$bipy)]PF_6 (**3**)

This was prepared as above from *cis*-$[PtCl_2(^tBu_2bipy)]$ (0.052 g, 0.097 mmol), 2,6-$F_2C_6H_3C(O)NHC(S)NEt_2$ (0.032 g, 0.100 mmol) and NH_4PF_6 (0.017 g, 0.104 mmol). 0.068 g (76%) of a yellow solid was obtained. ^1H NMR (400 MHz, dmso-d_6, 25 °C): δ = 8.75 (d, *J* = 2.0 Hz, 1 H, H^5-bipy), 8.69 (d, *J* = 2.0 Hz, 1 H, H^5-bipy), 8.63 (d, *J* = 6.1 Hz, 1 H, H^3-bipy), 8.56 (d, *J* = 6.1 Hz, 1 H, H^3-bipy), 8.01 (dd, *J* = 6.1/2.0 Hz, 1 H, H^4-bipy), 7.81 (dd, *J* = 6.1/2.0 Hz, 1 H, H^4-bipy), 7.66 (m, 1 H, H^4-arom), 7.26 (t, *J* = 8.6 Hz, 2 H, H^3, H^5-arom), 3.93 (quart, *J* = 7.1 Hz, 2 H, NCH_2), 3.76 (quart, *J* = 7.1 Hz, 2 H, NCH_2), 1.44 (s, 9 H, ^{t}Bu), 1.43 (s, 9 H, ^{t}Bu), 1.40 (t, *J* = 7.1 Hz, 3 H,

MeCH_2N), 1.18 (t, J = 7.1 Hz, 3 H, *Me*CH_2N). ^{19}F NMR (376 MHz, dmso-d_6, 25 °C): δ = −70.7 (d, J = 711 Hz, PF_6), −112.9 (t, J = 7.2 Hz, ArF). HR- ES-MS: m/z (observed, calculated) = 782.1749, 782.1748 $[M]^+$. Crystals suitable for X-ray diffraction were grown by slow diffusion of Et_2O into a CH_2Cl_2 solution of the complex.

3.7. *cis*-[Pd{κ^2*S*,*O*-2,3-$F_2C_6H_3C(O)NC(S)NEt_2$}(^{t}Bu_2bipy)]PF_6 (**4**)

This was prepared as above from *cis*-[$PdCl_2$(^{t}Bu_2bipy)] (0.050 g, 0.112 mmol), 2,6-$F_2C_6H_3C(O)NHC(S)NEt_2$ (0.031 g, 0.114 mmol) and NH_4PF_6 (0.027 g, 0.166 mmol). 0.068 g (76%) of a yellow solid was obtained. ^{1}H NMR (400 MHz, acetone-d_6, 25 °C): δ = 8.75 (d, J = 2.0 Hz, 1 H, H^5-bipy), 8.74 (d, J = 2.0 Hz, 1 H, H^5-bipy), 8.65 (d, J = 6.1 Hz, 1 H, H^3-bipy), 8.48 (d, J = 6.1 Hz, 1 H, H^3-bipy), 7.98 (dd, J = 6.1/2.0 Hz, 1 H, H^4-bipy), 7.90 (dd, J = 6.1/2.0 Hz, 1 H, H^4-bipy), 7.63 (m, 1 H, H^4-arom), 7.18 (t, J = 8.6 Hz, 2 H, H^3, H^5-arom), 4.09 (quart, J = 7.1 Hz, 2 H, NCH_2), 3.92 (quart, J = 7.1 Hz, 2 H, NCH_2), 1.48 (m, 21 H, ^{t}Bu, *Me*CH_2N), 1.27 (t, J = 7.1 Hz, 3 H, *Me*CH_2N). ^{19}F NMR (376 MHz, acetone-d_6, 25 °C): δ = −73.1 (d, J = 705 Hz, PF_6), −113.8 (t, J = 9.2 Hz, ArF). HR-ES-MS: m/z (observed, calculated) = 645.1689, 645.1691 $[M]^+$.

3.8. *cis*-[Pt{κ^2*S*,*O*-2,3-$F_2C_6H_3C(O)NC(S)NEt_2$}(phen)]PF_6 (**5**)

This was prepared as above from *cis*-[$PtCl_2$(1,10-phen)] (0.050 g, 0.112 mmol), 2,6-$F_2C_6H_3C(O)NHC(S)NEt_2$ (0.032 g, 0.117 mmol) and NH_4PF_6 (0.027 g, 0.166 mmol). 0.042 g (47%) of a yellow solid was obtained. ^{1}H NMR (400 MHz, dmso-d_6, 25 °C): δ = 9.00 (m, 2 H, H^2-phen, 8.89 (m, 2H, H^5-phen), 8.25 (m, 2H, H^4-phen), 8.04 (t, J = 5.4 Hz, 2H, H^3-phen), 7.64 (t, J = 7.6 Hz, 2H, H^3, H^5-arom), 3.95 (quart, J = 6.8 Hz, 2 H, NCH_2), 3.79 (quart, J = 6.8 Hz, 2 H, NCH_2), 1.42 (t, J = 6.8 Hz, 3 H, *Me*CH_2N), 1.23 (t, J = 6.8 Hz, 3 H, *Me*CH_2N). ^{19}F NMR (376 MHz, dmso-d_6, 25 °C): δ = −70.7 (d, J = 707.9 Hz, PF_6), −112.6 (t, J = 9.4 Hz, ArF). HR-ES-MS: m/z (observed, calculated) = 646.1112, 646.1052 $[M]^+$.

3.9. [Ru(η^6-*p*-cym){κ^2*S*,*O*-2,6-$F_2C_6H_3C(O)NC(S)NEt_2$}(PPh_3)]PF_6 (**6**)

This was prepared as described above from [Ru(η^6-*p*-cym)Cl_2]$_2$ (0.050 g, 0.082 mmol), 2,6-$F_2C_6H_3C(O)NHC(S)NEt_2$ (0.045 g, 0.165 mmol), Ph_3P (0.043 g, 0.164 mmol) and NH_4PF_6 (0.029 g, 0.1789 mmol). 0.116 g (78%) of a yellow solid was obtained. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.37–7.52 (m, 15 H, Ph_3P), 7.31 (tt, $^3J_{H-H}$ = 8.3 Hz, $^4J_{F-H}$ = 6.4 Hz, 1 H, *p*-H), 6.87 (m, 2 H, *m*-H), 5.83 (d, J = 6.1 Hz, 1 H, *p*-cym), 5.38 (d, J = 6.1 Hz, 1 H, *p*-cym), 5.34 (d, J = 6.1 Hz, 1 H, *p*-cym), 4.87 (d, J = 6.1 Hz, 1 H, *p*-cym), 3.72 (AB quart, 1 H, NCH_2), 3.57 (AB quart, 1 H, NCH_2), 3.53 (q, J = 7.1 Hz, 2 H, NCH_2), 2.77 (sept, J = 7.1 Hz, 1 H, HC *p*-cym), 1.84 (s, 3 H, Me *p*-cym), 1.21 (d, J = 7.1 Hz, 6 H, Me_2CH), 1.18 (t, J = 7.1 Hz, 3 H, *Me*CH_2N), 0.96 (t, J = 7.1 Hz, 3 H, *Me*CH_2N). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 25 °C): δ = 35.62, −143.01 (sept, J_{P-F} = 712.8 Hz, PF_6). ^{19}F NMR (376 MHz, $CDCl_3$, 25 °C): δ = −73.9 (d, J = 712.5 Hz, PF_6), −112.6 (m, ArF). HR-ES-MS: m/z (observed, calculated) = 769.1768, 769.1767 $[M]^+$, 507.0876, 507.0856 $[M\text{-}PPh_3]^+$.

3.10. X-ray crystallography

A single crystal suitable for single crystal X-ray diffraction analysis was mounted on the tip of a MiTegen MicroMount in perfluoropolyether and cooled using an Oxford Cryosystems 700 series Cryostream. Data were collected using a Bruker AXS APEX II CCD detector mounted on a Mach3 goniometer, which is placed in front of a FR591 rotating anode equipped with an Incoatec graded multilayer mirror. Data collection and integration were controlled by APEX Ver. 2 software, absorption correction was based on SADABS [19]. Structure solution was by direct methods (SHELXS-97) [20] followed by least-squares refinement (SHELXL-97) [21]. All non-hydrogen atoms were refined anisotropically, for hydrogen atoms a riding model was employed. Table 1 contains further crystallographic details, atomic coordinates together with complete bond distances and angles can be found in the CIF, which has been deposited as CCDC 758884.

Table 1
Crystallographic and refinement details of complex **3**.

Formula	$C_{30}H_{37}F_8N_4OPPtS$
Colour	yellow
Formula weight (g mol^{-1})	879.76
T (K)	100
λ (Å)	0.71073
Crystal system	monoclinic
Space group	$P2_1/n$, (no. 14)
Unit cell dimensions	
a (Å)	9.2032(8)
b (Å)	24.425(2)
c (Å)	15.0626(13)
β (°)	104.051(2)
V (Å^3)	3284.5(5)
Z	4
D_{calc} (Mg m^{-3})	1.779
Absorption coefficient (mm^{-1})	4.461
F(0 0 0)	1736
Crystal size (mm)	0.02 × 0.02 × 0.02
θ Range for data collection (°)	1.62–36.81
Index ranges	$-15 \leqslant h \leqslant 15$, $-41 \leqslant k \leqslant 40$, $-25 \leqslant l \leqslant 25$
Reflections collected	191 684
Independent reflections (R_{int})	16 197 (0.0275)
Reflections with $I > 2\sigma(I)$	15 112
Completeness to θ = 36.81°	98.1%
Absorption correction	empirical
Maximum and minimum transmission	0.75 and 0.59
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	16 197/0/423
Goodness-of-fit (GOF) on F^2	1.125
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0166, wR^2 = 0.0367
R indices (all data)	R_1 = 0.0196, wR^2 = 0.0377
Largest difference in peak and hole (e Å^{-3})	1.324 and −0.620

Crystallographic and refinement details are shown in Table 1.

4. Supplementary data

CCDC 758884 contains the supplementary crystallographic data for complex **3**. These data can be obtained free of charge *via* 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.

Acknowledgements

F.M. gratefully acknowledges generous funding from the Fonds der Chemischen Industrie as well as the University of Wuppertal for this project.

References

[1] A. Molter, F. Mohr, unpublished results.
[2] A. Molter, F. Mohr, Coord. Chem. Rev. 254 (2010) 19.
[3] M.M. Habtu, S.A. Bourne, K.R. Koch, R.C. Luckay, New J. Chem. 30 (2005) 1155.
[4] K.R. Koch, Coord. Chem. Rev. 216–217 (2001) 473.
[5] J.C. Bruce, N. Revaprasadu, K.R. Koch, New J. Chem. 31 (2007) 1647.
[6] A. Rodger, K.K. Patel, K.J. Sanders, M. Datt, C. Sacht, M.J. Hannon, J. Chem. Soc., Dalton Trans. (2002) 3656.
[7] W. Hernández, E. Spodine, J.C. Muñoz, L. Beyer, U. Schröder, J. Ferreira, M. Pavani, Bioinorg. Chem. Appl. 1 (2003) 271.
[8] W. Hernández, E. Spodine, L. Beyer, U. Schröder, R. Richter, J. Ferreira, M. Pavani, Bioinorg. Chem. Appl. 3 (2005) 299.

[9] T.J. Egan, K.R. Koch, P.L. Swan, C. Clarkson, D.A. Van Schalkwyk, P.J. Smith, J. Med. Chem. 47 (2004) 2926.
[10] R. del Campo, J.J. Criado, R. Gheorghe, F.J. González, M.R. Hermosa, F. Sanz, J.L. Manzano, E. Monte, E. Rodríguez-Fernández, J. Inorg. Biochem. 98 (2004) 1307.
[11] R. del Campo, J.J. Criado, E. García, M.R. Hermosa, A. Jiménez-Sánchez, J.L. Manzano, E. Monte, E. Rodríguez-Fernández, F. Sanz, J. Inorg. Biochem. 89 (2002) 74.
[12] D. Gallenkamp, E.R.T. Tiekink, F. Mohr, Phosphorus, Sulfur Silicon Relat. Elem. 183 (2008) 1050.
[13] D. Gallenkamp, T. Porsch, A. Molter, E.R.T. Tiekink, F. Mohr, J. Organomet. Chem. 694 (2009) 2380.
[14] F. Fuge, C. Lehmann, F. Mohr, J. Organomet. Chem. 694 (2009) 2395.
[15] C. Alagöz, D.J. Brauer, F. Mohr, J. Organomet. Chem. 694 (2009) 1283.
[16] K.R. Koch, J. du Toit, M.R. Caira, C. Sacht, J. Chem. Soc., Dalton Trans. (1994) 785.
[17] F.R. Hartley, Organometal. Chem. Rev. A 6 (1970) 119.
[18] M.A. Bennett, R.N. Johnson, I.B. Tomkins, J. Am. Chem. Soc. 96 (1974) 61.
[19] G.M. Sheldrick, SADABS 2.03, Universität Göttingen, Germany, 2002.
[20] G.M. Sheldrick, SHELXS-97, Program for Crystal Structure Solution, University of Göttingen, Germany, 1997.
[21] G.M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement, University of Göttingen, Germany, 1997.