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Unexpected formation of $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PH}(\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2)_2\text{O})_2)(\text{PPh}_3)_2]\text{BF}_4$ – the first “piano-stool” ruthenium complex bearing a secondary aminomethylphosphane ligand†

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In this paper we report the reaction of $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}(\text{PPh}_3)_2]$ with $\text{P}(\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2)_2\text{O})_3$ in the presence of NaBF_4 , in which, apart from the Cl^- substitution, an unexpected P–C bond cleavage in the tertiary phosphane is observed. It results in the formation of $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PH}(\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2)_2\text{O})_2)(\text{PPh}_3)_2]\text{BF}_4$ (1) – the first “piano-stool” ruthenium complex with a secondary aminomethylphosphane ligand.

Metal complexes have been investigated as potential chemotherapeutic agents during the past few decades.¹ The discovery of therapeutic activity of $(\text{ImH})[\text{trans-RuCl}_4(\text{DMSO})\text{Im}]$ (NAMI-A) and $(\text{IndH})[\text{trans-RuCl}_4(\text{Ind})_2]$ (KP1019) allowed the ruthenium complexes to achieve status of promising candidates for novel cancer therapy.² The ruthenium ion in both complexes has an oxidation state of +3. Nevertheless, it is suggested that reduction of Ru(III) to Ru(II) takes place inside the cell prior to DNA binding, which is known as the activation by reduction mechanism.³ The hypothesis that ruthenium(II) agents are much more active factors in biological system than their ruthenium(III) analogues caused that more attention has been paid in the investigations of Ru(II) coordination compounds. Nowadays, ruthenium(II) compounds, especially “piano-stool” $[\text{Ru}(\text{arene})(\text{L}_1)(\text{L}_2)(\text{L}_3)]$ complexes, are one of the most explored groups of potential drugs.⁴ Moreover, the easy introduction of different L ligands (e.g. halides, phosphanes or amines) enables significant modifications of not only stability and physico-chemical properties but also biological activity of these compounds.

In recent years, we have been interested in photochemical and biological properties of ruthenium compounds.⁵ Currently, we are focused on the synthesis of novel “piano-stool” ruthenium complexes. Our preliminary goal was to substitute of triphenylphosphane molecules or chloride ion in $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}(\text{PPh}_3)_2]$ complex, as it was shown by Ashby *et al.*⁶ For the Cl^- replacement we chose a method presented by Romerosa *et al.*⁷ involving the presence of sodium tetrafluoroborate. As the replacing ligands we decided to use tris(aminomethyl)phosphanes. These ligands are the large and interesting class of phosphanes for several reasons. Firstly, they are stable in water solution and, to some extent, in the presence of oxygen.⁸ Secondly, these ligands can be easily functionalised. For example, aminomethylphosphanes derived from amino acids⁹ or prepared from the highly water-soluble aliphatic secondary amines,¹⁰ seem to be interesting in terms of the formation of potential conjugates with a wide range of biomolecules. Moreover, in our previous papers we presented a group of copper(I) complexes with tris(aminomethyl)phosphanes derived from morpholine $\text{P}(\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2)_2\text{O})_3$ or piperazine $\text{P}(\text{CH}_2\text{-N}(\text{CH}_2\text{CH}_2)_2\text{N-R})_3$.⁸ Promising *in vitro* cytotoxicity of these complexes encouraged us to extend our studies to ruthenium compounds.

Herein, we report the reaction of $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}(\text{PPh}_3)_2]$ with $\text{P}(\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2)_2\text{O})_3$ ($\text{P}(\text{CH}_2\text{-morph})_3$) in the presence of NaBF_4 , which did not lead to a straightforward substitution of the Cl^- ion, but involved a simultaneous P–C bond cleavage in $\text{P}(\text{CH}_2\text{-morph})_3$, resulting in formation of the secondary phosphane – $\text{PH}(\text{CH}_2\text{-morph})_2$, which gave the $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PH}(\text{CH}_2\text{-morph})_2)(\text{PPh}_3)_2]\text{BF}_4$ complex (1) (Fig. 1).

Addition of $\text{P}(\text{CH}_2\text{-morph})_3$ to the orange suspension of $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}(\text{PPh}_3)_2]$ and NaBF_4 led to the formation of yellow solution after 3 hours of reflux.† $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of this solution (see ESI Fig. S3†) showed that the main product possess three phosphorus atoms – two equivalent atoms observed as a doublet and the other one, which is observed as a triplet. Such a spectrum could suggest a simple replacement of the chloride ion by the tris(aminomethyl)phosphane. However,

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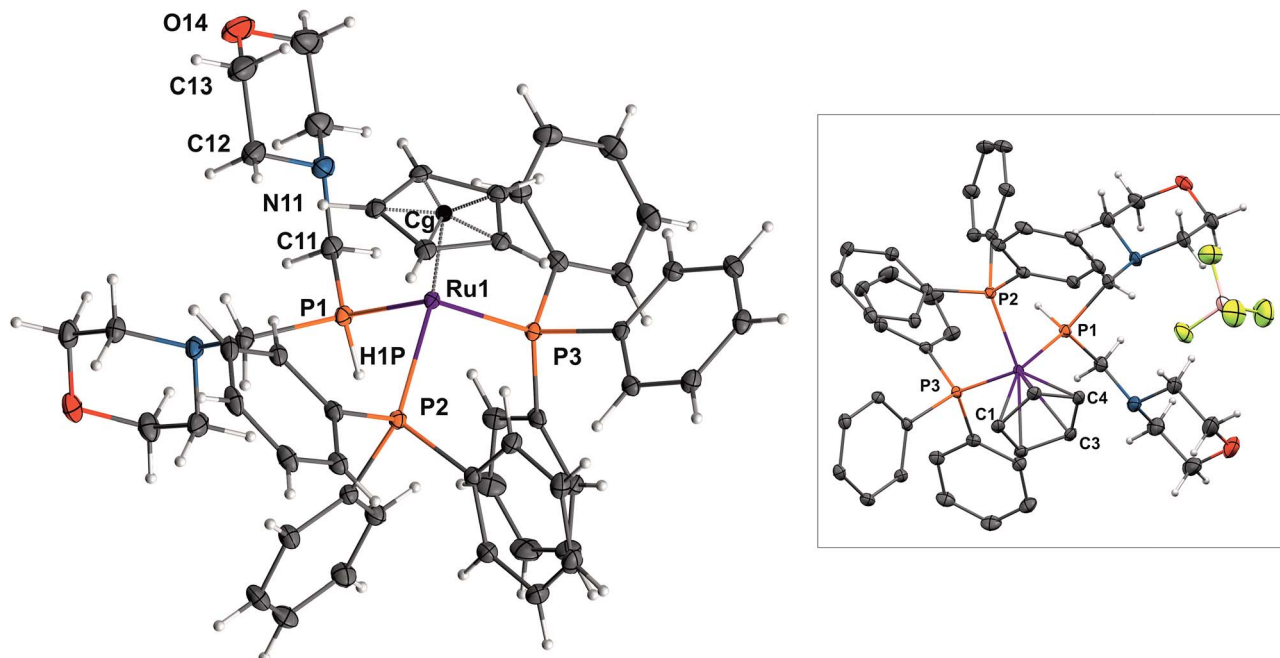


Fig. 1 Two views of the crystal structure of complex **1** (30% probability ellipsoids). Selected bond distances (Å) and angles (°): Ru(1)–C(1) = 2.250(2), Ru(2)–C(2) = 2.238(2), Ru(1)–C(3) = 2.244(2), Ru(1)–C(4) = 2.255(2), Ru(1)–C(5) = 2.253(2), Ru(1)–Cg_{Cp} (cyclopentadienyl centre of gravity) = 1.894(2), Ru(1)–P(1) = 2.294(1), Ru(1)–P(2) = 2.366(1), Ru(1)–P(3) = 2.335(1), P(1)–Ru(1)–P(2) = 89.71(2), P(1)–Ru(1)–P(3) = 92.94(2), P(2)–Ru(1)–P(3) = 102.08(2), Cg_{Cp}–Ru(1)–P(1) = 126.54(3), Cg_{Cp}–Ru(1)–P(2) = 121.71(3), Cg_{Cp}–Ru(1)–P(3) = 117.14(3).

the analysis of the crystal structure of this complex revealed that, in time of synthesis, tertiary phosphine P(CH₂-morph)₃ was rearranged to secondary PH(CH₂-morph)₂. **1** is therefore a “piano-stool” complex, in which chloride was substituted by the secondary aminomethylphosphane.

A large number of ruthenium complexes with secondary and/or primary phosphanes were synthesized until now.¹¹ However, the cleavage of the phosphane P–C bond during complex formation is unprecedented not only for the aminomethylphosphanes. A similar reaction was observed by Higham *et al.*¹² only for two hydroxymethylphosphanes. They reported analogous process when fourfold excess of P(CH₂OH)₃ or P(CH₂OH)₂Ph was mixed with RuCl₃·H₂O. As a result, they obtained the coordination compounds possessing two molecules of the tertiary phosphane and two molecules of the secondary one: [Ru{PPh(CH₂OH)₂}₂{PPh(CH₂OH)H}₂Cl₂] and [Ru{P(CH₂OH)₃}₂{P(CH₂OH)₂H}₂Cl₂].

The complex **1** crystallizes in tetragonal crystal system; space group *I*4₁/*a*. The asymmetric unit contains sixteen equivalent [Ru(η⁵-C₅H₅){PH(CH₂-morph)₂}(PPh₃)₂]⁺ cations and tetrafluoroborate anions. Replacement of chloride with the PH(CH₂-morph)₂ leads to a slight elongation of one of the Ru–PPh₃ bonds compared to the parent complex.¹³ The bond lengths are equal: Ru(1)–P(3) = 2.335(1) Å, Ru(1)–P(2) = 2.366(1) Å for **1** and Ru–P(1) = 2.337(1), Ru–P(2) = 2.335(1) Å for [Ru(η⁵-C₅H₅)Cl(PPh₃)₂]. Moreover, the average distance from the carbon atoms of C₅H₅[−] ligand to Ru(1) central atom, equal to 2.248(2) Å, is also longer than for [Ru(η⁵-C₅H₅)Cl(PPh₃)₂] (2.207(3) Å). The angle between Ru–PPh₃ bonds found for **1** (P(2)–Ru(1)–P(3) = 102.08(2)°) is smaller than for [Ru(η⁵-C₅H₅)

Cl(PPh₃)₂] (P(1)–Ru–P(2) = 103.99(4)°). Above data prove steric hindrances in **1** caused by the presence of PH(CH₂-morph)₂ ligand and may be related to a facilitation of the –CH₂-morph group release.

Measurement of ³¹P NMR spectrum confirmed the presence of the secondary phosphane. The upfield signal of PH(CH₂-morph)₂, which is observed as a triplet at −12.96 ppm (²*J*(P¹–P^{2,3}) = 41.2 Hz) in the proton-decoupled ³¹P{¹H} NMR

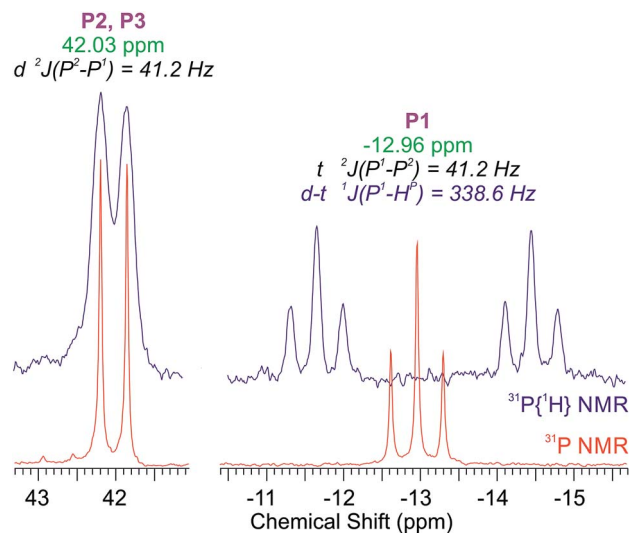


Fig. 2 Comparison of the ³¹P and ³¹P{¹H} NMR spectra (CDCl₃, 300 K) of complex **1**.



spectrum, in ^{31}P NMR spectrum appears as a doublet of triplets (Fig. 2). Appearance of a new, large coupling (338.6 Hz) proves that phosphorous atom is directly bound with hydrogen atom. Integration of the signals in the proton spectrum also confirms that aminomethylphosphane loses one $-\text{CH}_2\text{-morph}$ moiety during of complex preparation. The PPh_3 part of the $^{13}\text{C}\{\text{H}\}$ spectrum of **1**, similarly to the spectrum of $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}(\text{PPh}_3)_2]$, consists of four signals: the multiplet of the C^{ipso} atoms, the singlet of C^{para} atoms and two pseudo-triplets of the C^{orto} and C^{meta} atoms (see ESI Fig. S6 and S8†). The latter signals arise from a second-order effect, referred to as “virtual coupling”,¹⁴ observed usually for the phosphanes in *trans* positions to one another. The $\text{PH}(\text{CH}_2\text{-morph})_2$ part consists of a doublet of C11 carbon atoms with the $^1\text{J}(\text{C-P}) = 36.1\text{ Hz}$ – much larger than observed for the free $\text{P}(\text{CH}_2\text{-morph})_3$ ligand, a doublet of C12 and a singlet of C13 atoms.

The other data are fully consistent with the crystal structure of **1**.† In the infrared spectrum the band assigned to P–H stretching is observed at 2346 cm^{-1} . The location of the band at lower wavenumber in comparison with that of $[\text{Ru}\{\text{P}(\text{CH}_2\text{-OH})_3\}_2\{\text{PH}(\text{CH}_2\text{OH})_2\text{Cl}_2\}]$ (2374 cm^{-1})¹² suggests that P–H bond in **1** is noticeably weaker. It is worth to mention that **1** is stable under normal conditions (the air and the presence of moisture). Fragmentation of the $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\{\text{PH}(\text{CH}_2\text{-morph})\}(\text{PPh}_3)_2]^+$ ion in ESI-MS takes place only in a small degree, even under acidic conditions. Among products of fragmentation it is possible to identify $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\{\text{PH}_2(\text{CH}_2\text{-morph})\}(\text{PPh}_3)_2]^+$ and $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2]^+$ ions. It suggests that $-\text{CH}_2\text{-morph}$ moiety as well as secondary phosphane $\text{PH}(\text{CH}_2\text{-morph})_2$ are more susceptible to elimination than triphenylphosphane parts of complex **1**.

Conclusions

The synthesized complex, to the best of our knowledge, is a first metal complex bearing a secondary bis(aminomethyl)phosphane ligand. The presented formation of ruthenium(II) complex containing a reactive P–H bond, offers a great scope for further ligand functionalization. Moreover, our recent studies proved that discussed process is not an individual case. The preliminary experiments showed that similar reaction takes place in the case of other tris(aminomethyl)phosphanes as well as indenyl or pentamethylcyclopentadienyl “piano-stool” starting complexes. Now we are focused on elucidation of the mechanism of the phosphane P–C bond cleavage as well as the biological properties of the resulting complex.

Notes and references

† Preparation: $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}(\text{PPh}_3)_2]$ were bought in Stream Chemicals, whereas other chemicals were from Sigma-Aldrich. $\text{P}(\text{CH}_2\text{-morph})_3$ was synthesised according to literature procedure.⁷ Each synthetic step was performed in inert atmosphere: $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}(\text{PPh}_3)_2]$ (0.116 g, 0.16 mmol) and sodium tetrafluoroborate (0.026 g, 0.24 mmol) were refluxed in methanol by 20 minutes. After this time the orange suspension was cooled to room temperature, solid aminomethylphosphane $\text{P}(\text{CH}_2\text{-morph})_3$ (0.080 g, 0.24 mmol) was added and the mixture was refluxed one more time by 3 hours. Obtained yellow solution was evaporated to 1 ml and biphasic mixture of diethyl ether and water was added.

Immediately yellow precipitate appeared at the interface. The precipitate was washed by water, methanol and diethyl ether and dried under vacuum. Yield: 65%. Anal. Found: C, 60.25; H, 5.55; N, 2.78%. Anal. Calc. for $\text{RuC}_{51}\text{H}_{56}\text{N}_2\text{O}_2\text{P}_3\text{BF}_4$: C, 60.66; H, 5.59; N, 2.77%.

Spectroscopic data: $^{31}\text{P}\{\text{H}\}$ NMR (CDCl_3) δ (ppm), (J [Hz]): -12.96 (t, 41.2), 42.03 (d, 41.2); ^{31}P NMR (CDCl_3) δ (ppm), (J [Hz]): -12.96 (d-t, 41.2 and 338.6), 42.03 (d, 41.2); ^1H NMR (CDCl_3) δ (ppm), (J [Hz]): 2.28 (m, 8 H), 2.94 (m, 4 H), 3.62 (m, 8 H), 4.95 (s, 5 H), 6.94 (bt, 8.6, 12 H), 7.33 (t, 7.2, 12 H), 7.45 (t, 7.2, 6 H); ^{13}C NMR (CDCl_3) δ (ppm), (J [Hz]): 54.31 (d, 5.5), 55.97 (d, 36.1), 66.95 (s), 85.42 (s), 128.52 (bt, 4.1), 130.42 (s), 133.56 (bt, 4.8), 136.41 (m); IR (ATR) (ν_{max} [cm^{-1}]): 3103w, 3054w, 2954w, 2841w, 2799w, 2346w, 1480w, 1451w, 1433m, 1304w, 1285m, 1256w, 1233w, 1205w, 1186w, 1159w, 1113m, 1085m, 1058s, 1018s, 1000m, 987m, 926w, 914w, 900m, 875m, 864s, 847m, 818m, 802w, 788w, 752s, 693s, 610w, 590w, 533m, 516s, 487s, 456m, 430m; +ESI-MS (MeOH) (m/z): 953.27 (2.34%), 923.26 (100%), 824.19 (1.99%), 426.13 (1.65%); +ESI-MS (MeOH/HCOOH) (m/z): 1011.27 (3.32%), 953.27 (1.08%), 923.26 (32.84%), 824.19 (1.43%), 691.12 (2.58%), 462.13 (100%), 263.10 (3.39%), 233.14 (6.38%);

Yellow crystals suitable for the X-ray analysis were obtained by slow diffusion of diethyl ether to methanolic solution.

Crystal data: $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\{\text{PH}(\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2)_2\text{O})_2\}(\text{PPh}_3)_2]\text{BF}_4$ (**1**) $\equiv \text{C}_{51}\text{H}_{56}\text{BF}_4\text{-N}_2\text{O}_2\text{P}_3\text{Ru}$, $M = 1009.77\text{ g mol}^{-1}$, crystal size: $0.28 \times 0.25 \times 0.15\text{ mm}$, crystal system: tetragonal, space group: $I4_1/a$, $a = 28.1859(1)\text{ \AA}$, $b = 28.1859(1)\text{ \AA}$, $c = 23.7177(2)\text{ \AA}$, $\alpha = \beta = \gamma = 90^\circ$; $V = 18\,842.4(2)\text{ \AA}^3$, $D_{\text{calc}}(Z = 16) = 1.424\text{ Mg cm}^{-3}$, θ range for data collection: 2.86 to 27.50 , Mo K α radiation ($\lambda = 0.71073\text{ \AA}$), $\mu_{\text{Mo}} = 0.493\text{ mm}^{-1}$, reflections collected/unique $132\,166/10\,782$, $[R_{\text{int}} = 0.0366]$, completeness to $\theta_{\text{max}} = 99.7\%$, final R indices $[I > 2\sigma(I)]$: $R_1 = 0.0287$, $wR_2 = 0.0670$, R indices (all data): $R_1 = 0.0374$, $wR_2 = 0.0726$, GOF = 1.060, largest diff. peak and hole: 1.008 and -0.427 e \AA^{-3} , data/restraints/parameters: $10782/0/580$, $T = 119.8(5)\text{ K}$. Instruments: NMR spectra were registered using Bruker Avance III 600 MHz spectrometer in CDCl_3 with traces of CHCl_3 as an internal reference for ^1H and ^{13}C and 85% H_3PO_4 in H_2O as an external standard for ^{31}P . The infrared spectrum was recorded using Bruker Alpha FT-IR spectrometer. All spectra were collected using the Platinum-ATR-sampling module equipped with diamond crystal. 64 interferograms were recorded with a resolution of 4 cm^{-1} , in the range of 4000 cm^{-1} to 400 cm^{-1} . A mass spectrometer with a time of flight mass analyzer (MicrOTOF-Q II, Bruker, Germany) was used. ESI was used as the ion source with conditions as follows: nebulizer pressure: 0.4 bar , dry gas: 4.0 l min^{-1} heated to 180°C . Data were recorded in the positive ion mode and profile spectra were acquired in the mass range $50\text{--}3000\text{ m/z}$. End plate offset was $\sim 500\text{ V}$ and capillary voltage: 4500 V . Mass resolving power of the instrument was over $18\,000$. Mass calibration was performed using the cluster method with a mixture of 10 mM sodium formate and isopropanol ($1 : 1$, v/v) before run. Elemental analyses were performed on a Vario Micro Cube – Elementar. Single crystal X-ray diffraction was carried out on an Oxford Diffraction SuperNova diffractometer with a molybdenum source. Data were processed using *CRYSTALS*¹⁵. The structure was solved by direct methods with the program SHELXS-97 and refined by full-matrix least-squares method on F^2 with SHELXL-97.¹⁶ Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were positioned geometrically and refined using a riding model with $d(\text{CH}_{\text{arom}}) = 0.93\text{ \AA}$, $U_{\text{iso}} = 1.2U_{\text{eq}}(\text{C})$ for aromatic, 0.97 \AA , $U_{\text{iso}} = 1.2U_{\text{eq}}(\text{C})$ for CH_2 . The coordinates of the hydrogen atom H1P were refined freely with the displacement parameters $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{P1})$.

- 1 *Metallotherapeutic Drugs and Metal-Based Diagnostic Agents: The Use of Metals in Medicine*, ed. M. Gielen and E. R. Tiekink, Wiley, 2005; M. A. Hannon, *Pure Appl. Chem.*, 2007, **79**, 2243.
- 2 G. Suss-Fink, *Dalton Trans.*, 2010, **39**, 1673.
- 3 A. M. Pizarro and P. J. Sadler, *Biochimie*, 2009, **91**, 1198.
- 4 L. K. Filak, D. S. Kalinowski, T. J. Bauer, D. R. Richardson and V. B. Arion, *Inorg. Chem.*, 2014, **53**, 6934; R. Pettinari, C. Pettinari, F. Marchetti, B. W. Skelton, A. H. White, L. Bonfili, M. Cuccioloni, M. Mozzicafreddo, V. Cecarini, M. Angeletti, M. Nabissi and A. M. Eleuteri, *J. Med. Chem.*, 2014, **57**, 4532; C. M. Clavel, E. Paunescu, P. Nowak-Sliwinska, A. W. Griffioen, R. Scopelliti and P. J. Dyson, *J. Med. Chem.*, 2014, **57**, 3546; J. Kljun, A. J. Scott, T. Lanisnik



- Rizner, J. Keiser and I. Turel, *Organometallics*, 2014, **33**, 1594; K. Dralle Mjos and Ch. Orvig, *Chem. Rev.*, 2014, **114**, 4540; A. Grau-Campistany, A. Massaguer, D. Carrion-Salip, F. Barragan, G. Artigas, P. Lopez-Senin, V. Moreno and V. Marchan, *Mol. Pharm.*, 2013, **10**, 1964; C. G. Hartinger, N. Metzler-Nolte and P. J. Dyson, *Organometallics*, 2012, **31**, 5677; T. Kuster, N. Lense, F. Barna, A. Hemphill, M. K. Kindermann, J. W. Heinicke and C. A. Vock, *J. Med. Chem.*, 2012, **55**, 4178.
- 5 M. Brindell, E. Kuliš, S. K. C. Elmoroth, K. Urbańska and G. Stochel, *J. Med. Chem.*, 2005, **48**, 7298; M. Brindell, D. Piotrowska, A. A. Shoukry, G. Stochel and R. Van Eldik, *JBIC, J. Biol. Inorg. Chem.*, 2007, **12**, 809; M. Brindell, I. Stawoska, J. Supel, A. Skoczowska, G. Stochel and R. Van Eldik, *JBIC, J. Biol. Inorg. Chem.*, 2008, **13**, 909; O. Mazuryk, K. Kurpiewska, K. Lewiński, G. Stochel and M. Brindell, *J. Inorg. Biochem.*, 2012, **116**, 11; M. Oszejca, E. Kuliš, G. Stochel and M. Brindell, *New J. Chem.*, 2014, **38**, 3386; O. Mazuryk, M. Maciuszek, G. Stochel, F. Suzenet and M. Brindell, *J. Inorg. Biochem.*, 2014, **134**, 83.
 - 6 G. S. Ashby, M. I. Bruce, I. B. Tomkins and R. C. Wallis, *Aust. J. Chem.*, 1979, **32**, 1003.
 - 7 A. Romerosa, M. Saoud, T. Campos-Malpartida, C. Lidrissi, M. Serrano-Ruiz, M. Peruzzini, J. A. Garrido and F. Garcia-Maroto, *Eur. J. Inorg. Chem.*, 2007, **18**, 2803.
 - 8 R. Starosta, M. Florek, J. Król, M. Puchalska and A. Kochel, *New J. Chem.*, 2010, **34**, 1441; R. Starosta, K. Stokowa, M. Florek, J. Król, A. Chwiłkowska, J. Kulbacka, J. Saczko, J. Skala and M. Jeżowska-Bojczuk, *J. Inorg. Biochem.*, 2011, **105**, 1102; R. Starosta, M. Puchalska, J. Cybińska, M. Barys and A.-V. Mudring, *Dalton Trans.*, 2011, **40**, 2459; R. Starosta, A. Bykowska, A. Kyzioł, M. Płotek, M. Florek, J. Król and M. Jeżowska-Bojczuk, *Chem. Biol. Drug Des.*, 2013, **82**, 579.
 - 9 C. Abu-Gnim and I. Amer, *J. Organomet. Chem.*, 1996, **516**, 235; F. P. Pruchnik and P. Smolenski, *Pol. J. Chem.*, 2007, **81**, 1771; K. Raghuraman, K. K. Katti, L. J. Barbour, N. Pillarsetty, C. L. Barnes and K. V. Katti, *J. Am. Chem. Soc.*, 2003, **125**, 6955; D. E. Berning, K. V. Katti, Ch. L. Barnes and W. A. Volkert, *J. Am. Chem. Soc.*, 1999, **121**, 1658.
 - 10 H. Coates and P. A. T. Hoye, *Br. Pat.*, 842593, 1960; H. Coates and P. A. T. Hoye, *US Pat.*, 3035053, 1962.
 - 11 S. I. M. Paris, F. R. Lemke, R. Sommer, P. Lonnecke and E. Hey-Hawkins, *J. Organomet. Chem.*, 2005, **690**, 1807; S. I. M. Paris, J. F. Petersen, E. Hey-Hawkins and M. P. Jensen, *Inorg. Chem.*, 2006, **45**, 5561; A. J. Blake, N. R. Champness, R. J. Forder, Ch. S. Frampton, C. A. Frost, G. Reid and R. H. Simpson, *J. Chem. Soc., Dalton Trans.*, 1994, 3377.
 - 12 L. Higham, A. K. Powell, M. K. Whittlesey, S. Wocadlo and P. T. Wood, *Chem. Commun.*, 1998, 1107; L. J. Higham, M. K. Whittlesey and P. T. Wood, *Dalton Trans.*, 2004, 4202.
 - 13 M. I. Bruce, F. S. Wong, B. W. Skelton and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1981, 1398.
 - 14 D. W. Krassowski, J. H. Nelson, K. R. Brower, D. Hauenstein and R. A. Jacobson, *Inorg. Chem.*, 1988, **27**, 4294.
 - 15 *CrysAlisPRO*, Oxford Diffraction Agilent Technologies UK Ltd, Yarnton, England.
 - 16 G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, **64**, 112.

