A Novel Bifunctional Ligand for the Synthesis of Polynuclear Alkynyl Complexes

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Dedicated to Professor Hubert Schmidbaur on the occasion of his 80th birthday

The synthesis of 2-(1-(prop-2-yn-1-yl)-1*H*-pyrazol-3-yl)pyridine is presented. This ligand contains both, an alkynyl function being suitable for metal-carbon bond formation with electron-rich late transition metal sites, and a pyrazolylpyridine unit, which is well-known to undergo chelation reactions similar to 2,2′-bipyridine. This strategy allows building up polynuclear complexes with broad combinations of different metal sites. Two platinum alkynyl complexes were structurally characterized, and a trinuclear Ru_2Pt complex was indentified by means of NMR spectroscopy and ESI mass spectrometry.

Key words: Alkynyl Ligand, Pyrazole, Pyridine, Platinum, Ruthenium

Introduction

The acidity of hydrogen atoms attached to alkyne groups [1 – 3] already allows their deprotonation by bases of medium basicity. Using terminal alkynes and organometallic bases such as organolithium compounds, Grignard reagents or alkylaluminum derivatives gives the corresponding ionic acetylides R-C≡CLi, (R-C≡C)$_2$Mg or (R-C≡C)AlR′$_2$ in almost quantitative yields [4 – 7]. These compounds can be used to transfer the alkynyl moiety to more electronegative main group elements such as silicon or tin, resulting in terminal metal acetylides with mainly covalent character. Alkynyltin derivatives of the type R$_3$Sn–C≡C-R′ (R = Me, Bu) turned out to show high reactivities in the Stille cross-coupling reaction [8 – 13]. Additionally, transition metal and *f*-block element acetylides have been known for long [14 – 24]. Due to the strongly directed free electron pair of the alkynyl anion and the absence of β-hydrogen atoms, these terminally coordinated alkynyl ligands are excellent σ donors, even allowing to stabilize metal centers in higher oxidation states [25 – 28]. In this context H. Schmidbaur *et al.* have obtained homo and heteroleptic gold(III) alkynyl complexes [29 – 31]. However, the low bulkiness of terminal alkynyl ligands may lead to kinetic instability, and metal sites which can easily undergo one-electron reductions such as copper(II) may lead to the oxidation of the alkynyl anion resulting in C–C coupling reactions (Glaser coupling) [32 – 36]. Nevertheless, alkynyl copper(I) species have turned out to be crucial intermediates in the Sonogashira coupling [37 – 39] and in "Click" chemistry [40]. The outstanding stability of many σ-bound alkynyl transition metal compounds has stimulated ongoing investigations with this class of compounds. Depending on the metal site, the nature and the length of the alkynyl group, a series of interesting properties, such as luminescence [41 – 43], non-linear optic effects [15, 16, 44, 45], liquid crystallinity [41, 46], and electronic communication [47, 48] have been documented as well as the use of such compounds in catalysis [14, 49, 50].

In addition to "classical" terminal alkynyl complexes, there are compounds where one metal site is bound *via* a σ interaction to the terminal carbon atom of the C≡C triple bond and another is undergoing a π interaction to the C≡C bond [51 – 58]. Furthermore,

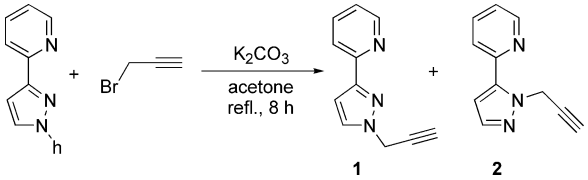
mainly aromatic alkynyl units have been designed bearing additional nitrogen, phosphorous or oxygen donor sites to obtain polynuclear complexes [59 – 64]. The highly reactive propargylic bromide is a versatile starting compound to generate functionalized alkynes carrying a methylene unit between the alkyne and the second donor site by simple nucleophilic substitution reactions. Surprisingly there are just a few reports on the coordination chemistry of such alkynes in the literature. F. Mohr *et al.* reported the synthesis of such aliphatically substituted alkynyl ligands equipped with monodentate donor sites and used them to create bi- and multinuclear compounds [65 – 67].

In this paper we present the synthesis of the new 2-(1-(prop-2-yn-1-yl)-1*H*-pyrazol-3-yl)pyridine (**1**) bearing a pyrazolylpyridine site, and of two σ-bound platinum alkynyl complexes derived from **1**. The latter compounds were used to generate bimetallic Pt/Ru_2 compounds with ruthenium being coordinated to the N,N'-donor site of ligand **1**.

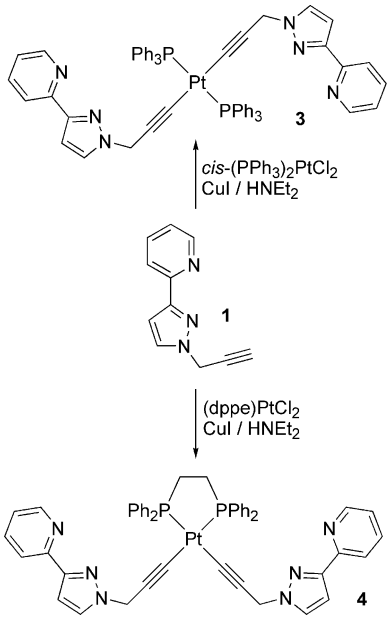
Results and Discussion

Ligand **1** was obtained by propargylation of pyrazolylpyridine with propargyl bromide in the presence of a base (Scheme 1). From a series of experiments, it turned out that the combination of K_2CO_3/acetone gave the best results. The use of strong bases such as NaOH has to be avoided since this will lead to a rearrangement of the alkyne unit (R-CH_2–C≡C–H) into the corresponding allene (R-CH_2=C=CH_2) [68 – 70]. The target compound **1** was obtained in pure form from the viscous brown raw product, that contains a small amount of the structural isomer **2**, by first performing a flash chromatography (SiO_2, ethyl acetate) followed by a gradient MPLC (SiO_2, *n*-hexane-ethyl acetate).

The reaction of *cis*-dichloridobis(triphenylphosphane)platinum(II) resp. dichlorido(1,2-diphenylphosphinoethane)platinum(II) with a slight excess of **1** in the presence of diethylamine and copper(I) in ethanol [67] leads to the formation of the corresponding dialkynyl platinum(II) complexes **3** and **4** (Scheme 2). There is a pronounced difference in the reactivity of the two precursors: The platinum triphenylphosphine complex is converted into **3** in just 1 h with 80 % yield. Hereby the configuration of the platinum complex changes from *cis* to *trans* (see crystal structure and discussion of the NMR data below). In



Scheme 1. Synthesis of 2-(1-(prop-2-yn-1-yl)-1*H*-pyrazol-3-yl)pyridine (**1**) and its structural isomer **2**.



Scheme 2. Synthesis of the platinum(II) complexes **3** and **4**.

contrast, the sterically more hindered dppe precursor gives compound **4** in just 54 % yield after 5 h.

Compound **3** crystallizes in the triclinic space group $P\bar{1}$ with two independent molecules in the unit cell. Fig. 1 shows the molecular structure of one of these units of **3** in the solid state, and selected structural parameters are given in the figure caption. The parameters of the second unit, which is not shown in Fig. 1, differ only marginally from these values.

Compound **4** crystallizes in the monoclinic space group *Cc* with $Z = 4$. Fig. 2 shows the molecular structure of **4** in the solid state, and selected structural parameters are given in the figure caption.

As expected, the platinum(II) ions in compounds **3** and **4** are found in square-planar coordination environments. The Pt–P and Pt–C distances are close to the data reported in the literature for related compounds [66, 71 – 74]. The Pt–P distances in **3** are found

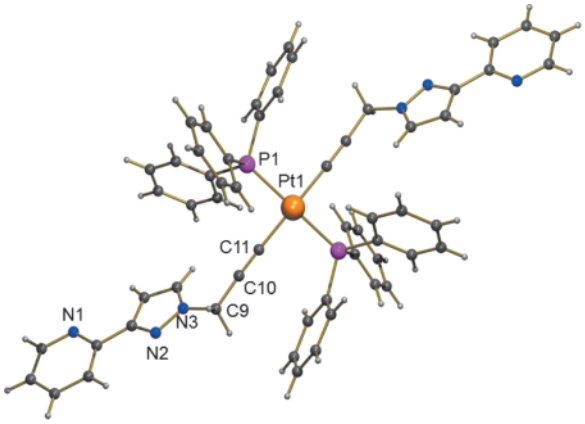


Fig. 1 (color online). Molecular structure of compound **3** in the solid state. The second crystallographically independent molecule is not shown. Selected bond lengths (Å) and angles (deg): Pt1–P1 2.301(1), Pt1–C11 2.005(3), C9–C10 1.457(4), C10–C11 1.207(4); P1–Pt1–C11 88.7(1), P1–Pt1–P1_a 180, P1–Pt1–C11_a 91.3(1), P1_a–Pt1–C11 91.3(1); C11–Pt1–C11_a 180, P1_a–Pt1–C11_a 88.7 (1), Pt1–C11–C10 178.2(2), C9–C10–C11 176.6(3).

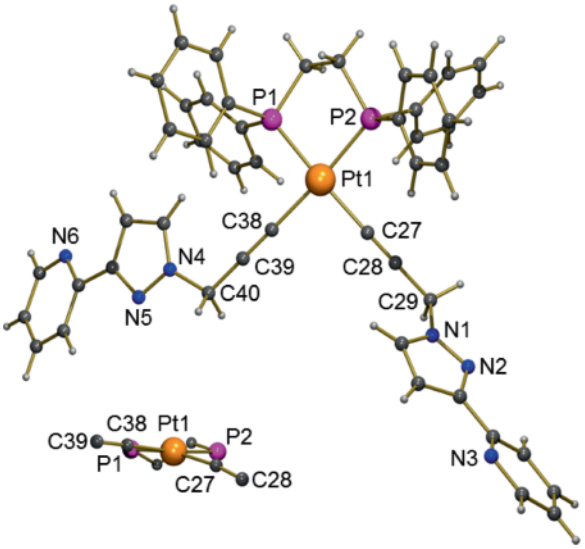
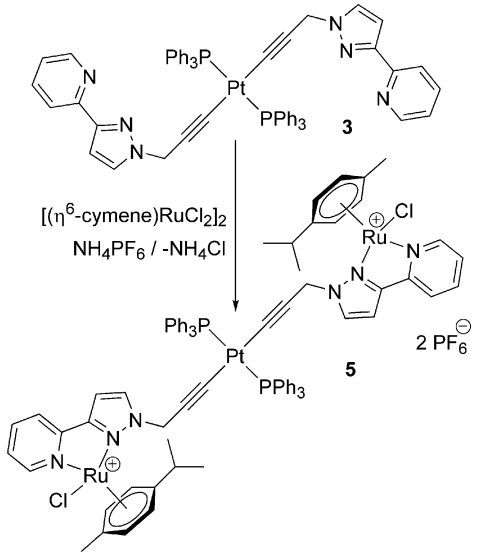


Fig. 2 (color online). Molecular structure of compound **4** in the solid state and the coordination sphere of the platinum atom (bottom left). Selected bond lengths (Å) and angles (deg): Pt1–P1 2.273(1), Pt1–P2 2.289(1), Pt1–C27 2.026(4), Pt1–C38 2.022(3), C27–C28 1.178(5), C28–C29 1.477(5), C38–C39 1.195(5), C39–C40 1.464(5); P1–Pt1–P2 85.39(3), P1–Pt1–C27 170.3(1), P1–Pt1–C38 91.2(1), P2–Pt1–C27 94.1(1), P2–Pt1–C38 173.9(1), C27–Pt1–C38 90.0(1), Pt1–C27–C28 172.6(3), C27–C28–C29 178.8(4), Pt1–C38–C39 178.6(3), C38–C39–C40 175.5(4).

to be slightly longer than those in compound **4**, while the Pt–C distances in **3** are slightly shorter than those in **4**, which can be explained by the different *trans*-influences of the phosphanes and the alkynyl ligand. Due to steric interferences of the alkynyl ligands with the phenyl groups of the dppe ligand there is a pronounced distortion of the coordination sphere around the platinum site in compound **4** (see inset in Fig. 2).

The platinum complexes **3** and **4** were further characterized by means of elemental analysis, NMR and IR spectroscopy. The ^{31}P NMR resonances of **3** and **4** appear at 19.03 resp. 42.10 ppm. They show ^{195}Pt satellites with $^{1}J_{PtP}$ coupling constants of 2631 and 2313 Hz typical of platinum(II) diphosphane complexes with *trans*- resp. *cis*-coordinated phosphane ligands [74, 75], which is in agreement with the solid-state structures of both compounds. Since we started with the precursor *cis*-dichloridobis(triphenylphosphane)platinum(II) for the synthesis of **3**, a rearrangement of the configuration at the platinum site from *cis* to *trans* had occurred. Beside a series of resonances in the aromatic region, there are characteristic ^{1}H NMR resonances for the CH_2 groups appearing at 4.29 and 5.08 ppm for **3** resp. **4**. The corresponding resonance in the free ligand **1** is observed at 5.01 ppm, and we assign the pronounced shift to higher field found for compound **3** to a shielding effect of the neighboring phenyl groups of the two PPh_3 ligands. The resonances of the CH_2 groups in the ^{13}C NMR spectra are found at around 44 ppm for both complexes, slightly shifted to lower field compared to that of ligand **1**. The shielding effect of the PPh_3 ligands on the alkynyl ligands in **3** is further visible by a strong shift of the resonances assigned to the protons in the 5-position of the pyrazole rings. By applying 2D-NMR methods (HH-COSY, HMQC; see Supporting Information available online; see note at the end of the paper for availability), the resonance at 6.54 ppm can unambiguously be assigned to this proton, which is observed in the free ligand **1** at 7.68 ppm and in complex **4** at 7.12 ppm. The resonances of the pyrazole proton in the 4-position of the five-membered ring, being located further away from the center of the complexes, are found at 6.45 (for **3**) and 6.50 ppm (for **4**, for comparison: 6.94 ppm for **1**). ^{13}C NMR spectroscopy allows an assignment of the binding situation of the alkyne carbon atoms: The corresponding resonances are observed at 75.1 (≡C–H) and 76.6 (≡*C*–C)



Scheme 3. Synthesis of complex **5**.

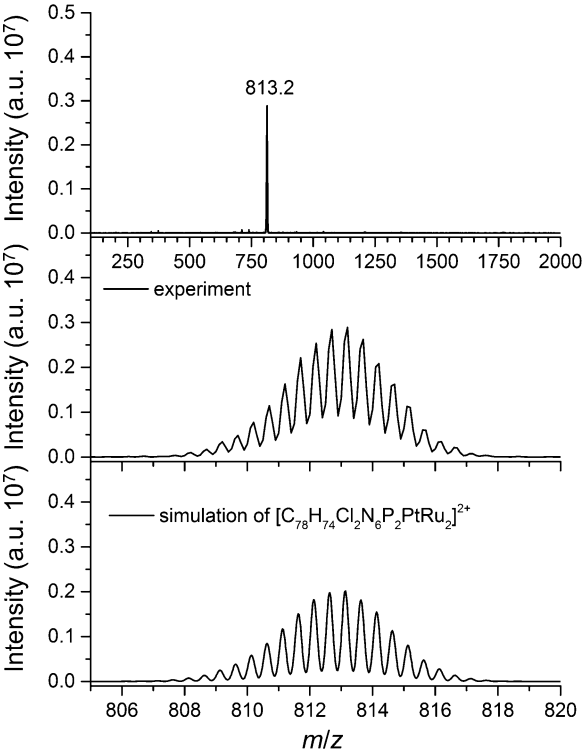


Fig. 3. top: ESI mass spectrum of the Ru_2Pt complex **5**; middle: measured isotopic peak pattern; bottom: simulated isotopic peak pattern for $[C_{78}H_{74}Cl_2N_6P_2PtRu_2]^{2+}$.

for compound **1**. After coordination of the alkynyl unit to platinum(II), they are strongly shifted to lower field and appear at 102.3 (≡*C*–C) and 105.7 ppm (≡C–Pt; d, *cis*-$^2J_{PC}$ = 15 Hz) for the *trans*-coordinated complex **3**, and at 100.3 (≡C–Pt; dd, *cis*-$^2J_{PC}$ = 15 Hz, *trans*-$^2J_{PC}$ = 143 Hz) and 102.2 ppm (≡*C*–C; d, *trans*-$^2J_{PC}$ = 34.8 Hz) for the dppe complex **4**. In the infrared spectra, the absorptions of the alkynyl units are observed at 2116 (for **1**), at 2139 (for **3**) and at 2137 cm^{-1} (for **4**).

The reaction of the *trans*-platinum complex **3** with $[(\eta^6\text{-cymene})RuCl_2]_2$ leads to the trinuclear bimetallic Ru_2Pt_1 species **5** in high yields (Scheme 3). By contrast, the *cis* complex **4** gives the analogous compound only in low yields and in a complex mixture from which it could not be isolated in pure form as yet.

Since crystallization of **5** failed, the trinuclear complex was characterized by means of spectroscopy and elemental analysis. There are two resonances found in the ^{31}P NMR spectrum: one at 18.07 ppm ($^1J_{PtP}$ = 2601 Hz) for the platinum-bound phosphine ligands and another one for the PF_6^- counter anions. Thus, there are only slight differences in the ^{31}P NMR parameters compared to the precursor **3**. The coordination of the ruthenium(II) site to the *N*,*N*′-donor sites is unambiguously proven by the strong shift of the resonance of the proton in the *ortho*-position of the pyridine ring towards lower field (**1**: 8.62; **3**: 8.57; **5**: 9.31 ppm) [76–78]. Both ruthenium sites are centers of chirality which should result in the formation of diastereomers, which, however, is not confirmed by the ^{31}P NMR data, probably due to the fact that the stereo centers are too far away from the phosphorous sites. However, the chirality at the ruthenium sites is reflected by the presence of a series of doubled signals in the ^{1}H NMR spectrum: The protons of the methylene units are diastereotopic as are the isopropyl methyl groups. Their resonances appear as two doublets at 4.75 and 4.50 ppm ($^2J_{HH}$ = 16 Hz) resp. two doublets at 0.78 and 0.73 ppm. There are four inequivalent protons and six inequivalent carbon atoms (some of them broadened) of the η^6-bound cymene ligand giving resonances in the ^{1}H resp. ^{13}C NMR spectra with chemical shifts comparable to structurally related cymene ruthenium complexes [79]. As found for the precursor **3**, the ^{1}H NMR resonance of the protons in the 5-position of the pyrazole rings is strongly shifted to

higher field due to a shielding effect of the neighboring PPh_3 ligands. However, instead of one doublet showing a small coupling to the protons in the 4-position of the pyrazole rings, there are two doublets (6.75 and 6.72 ppm; $^3J_{HH} = 2$ Hz) in an almost 1 : 1 ratio. Together with two resonances at 2.11 resp. 2.10 ppm, being assigned to the benzene-bound methyl group of the cymene ligand, these signals prove the presence of two diastereomeric species of compound **5**. In the infrared spectrum of compound **5**, there is a broad but not very intense absorption at 2131 cm^{-1} which is assigned to the alkynyl stretching vibration. Characterization of complex **5** by means of ESI mass spectrometry gives a signal at $m/z = 813.3$ a.m.u. (Fig. 3) that corresponds perfectly to the mass of the dication (1625.57 a.m.u.).

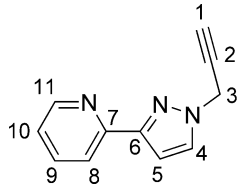
Conclusion

The synthesis of 2-(1-(prop-2-yn-1-yl)-1*H*-pyrazol-3-yl)pyridine (**1**) was accomplished by nucleophilic substitution of propargylic bromide with 2-(3(5)-pyrazolyl)pyridine in the presence of a weak base, delivering an alkynyl ligand that could be linked to two different platinum(II) precursors. One of the resulting platinum complexes leads to a trinucler Ru_2Pt compound when reacted with $[(\eta^6\text{-cymene})RuCl_2]_2$, while this transformation fails for the sterically more hindered (dppe)Pt dialkynyl complex. We are presently investigating the coordination chemistry of the platinum alkynyl complexes with other transition metal precursors as well as the reactivity of ligand **1** towards gold and other noble metals.

Experimental Section

General information

The ligand precursor 2-(3(5)-pyrazolyl)pyridine was prepared according to a procedure reported in the literature [80]. Propargylic bromide, triphenylphosphane and 1,2-bisdiphenylphosphinoethane (dppe) were purchased from Sigma-Aldrich, resp. ACROS Chemicals, $[(\eta^6\text{-cymene})Ru(Cl)(\mu^2\text{-}Cl)]_2$ was obtained from STREM Chemicals. The platinum precursors *cis*-$(PPh_3)_2PtCl_2$ and *cis*-$(dppe)PtCl_2$ were obtained from K_2PtCl_4 and the corresponding phosphane [81, 82]. Solvents for the ligand syntheses were used without further purification, solvents for the synthesis of the transition metal complexes were dried prior to use by standard methods. The NMR spectra were measured using a Bruker DPX 400 NMR spectrometer. Chemical shifts are quoted relative to the external standard, and



Scheme 4. Labelling scheme for the assignment of the NMR resonances.

the ^1H and ^{13}C NMR resonances listed below are assigned according to the numbering shown in Scheme 4. For recording the IR spectra a Perkin Elmer FT-ATR IR 1000 spectrometer equipped with a diamond-coated ZnSe window was used. Elemental analyses were carried out at the Fachbereich Chemie, column chromatography was performed with an NPLC CombiFlash RF 200 from Teledyne ISCO.

*2-(1-(Prop-2-yn-1-yl)-1H-pyrazol-3-yl)pyridine (**1**)*

20.17 g (138.9 mmol) of 2-(3(5)-pyrazolyl)pyridine, 37.73 g (273.0 mmol) of K_2CO_3 and 19 mL (176.3 mmol) of propargylic bromide were suspended in 500 mL of dry acetone and heated to reflux for 8 h. After filtration of the resulting brown solution containing a beige solid and washing of the solid with acetone, the acetone of the combined filtrates was stripped off resulting in 24.94 g of a dark-brown oil. The oil was adsorbed on 40 g of silica gel, and the resulting powder was put onto a silica gel column and eluted with ethylacetate. Evaporation of the solvent gave a dark-red oil which was adsorbed on a minimum amount of silica gel. The products were purified with the help of an NPLC using *n*-hexane with a gradient of ethylacetate (0 – 40 %) giving, after evaporation of the solvents, 0.92 g (4 %) of **2** and 11.67 g (46 %) of **1** as well as 3.28 g (16 %) of unreacted 2-(3(5)-pyrazolyl)pyridine. Elemental analysis for $C_{11}H_9N_3$ (183.21): calcd. C 72.12, H 4.95, N 22.94; found C 71.92, H 5.04, 22.67. – ^1H NMR (400 MHz, 25°C, $CDCl_3$): $\delta = 8.62$ (d, $^3J_{HH} = 8$ Hz, 1 H, H11), 7.91 (d, $^3J_{HH} = 8$ Hz, 1 H, H8), 7.71 (dt, $^3J_{HH} = 8$ Hz, $^4J_{HH} = 2$ Hz, 1 H, H9), 7.68 (d, $^3J_{HH} = 4$ Hz, 1 H, H4), 7.20 (ddd, 1 H, H10), 6.94 (d, 1 H, H5), 5.01 (d, $^4J_{HH} = 4$ Hz, 2 H, H3), 2.53 (t, 1 H, H1) ppm. – ^{13}C NMR (100 MHz, 25°C, $CDCl_3$): $\delta = 152.3$, 152.0 (C6, C7), 149.5 (C11), 136.7 (C9), 130.39 (C4), 122.6 (C10), 120.2 (C10), 105.0 (C5), 76.6 (C2), 75.1 (C1), 41.9 (C3) ppm. – IR (ATR): $\nu = 3188$ ($\nu_{\equiv C-H}$), 2116 ($\nu_{C\equiv C}$) cm^{-1}.

*General procedure for the synthesis of the platinum(II) complexes **3** and **4***

0.53 g (2.9 mmol) of ligand **1**, 1.26 mmol of the corresponding platinum precursor and 0.06 g CuI were heated to

reflux for 1 h for compound **3** resp. 5 h for compound **4** in 130 mL of a 1 : 1 mixture of EtOH and Et_2NH. After cooling to room temperature the suspension was filtered, and the resulting solid was washed first with H_2O, then with EtOH and finally with Et_2O and then dried in a vacuum.

*Platinum(II) complex **3***

Yield: 80 % of a colorless microcrystalline solid. Elemental analysis for $C_{58}H_{46}N_6P_2Pt$ (1084.08): calcd. C 64.26, H 4.28, N 7.75; found C 64.08, H 4.40, N 7.86. – ^{1}H NMR (400 MHz, 25°C, $CDCl_3$): $\delta = 8.57$ (br, 2 H, H11), 7.78 – 7.73 (m, 14 H, H-*o*, H8), 7.63 (t, $^3J_{HH} = 6$ Hz, 2 H, H9), 7.41 – 7.34 (m, 18 H, H-*m*, H-*p*), 7.13 (t, $^3J_{HH} = 6$ Hz, 2 H, H10), 6.54 (s, 2 H, H4), 6.45 (s, 2 H, H5), 4.29 (s, 4 H, CH_2) ppm. – ^{13}C NMR (100 MHz, 25°C, $CDCl_3$): $\delta =$ 152.7, 151.0 (C6, C7), 149.4 (C11), 136.5 (C9), 135.1 (vt, $^2J_{PC} = 4$ Hz, C-*o*), 131.1 (vt, $^1J_{PC} = 24$ Hz, C-*i*), 130.7 (C-*p*), 130.3 (C4), 128.0 (vt, $^3J_{PC} = 6$ Hz, C-*m*), 122.1 (C10), 119.8 (C8), 105.8 (vt, $^2J_{PC} = 15$ Hz, C1), 102.9 (C5), 102.4 (C2), 44.5 (C3) ppm. – ^{31}P NMR (161 MHz, 25°C, $CDCl_3$): $\delta = 19.0$ ($^1J_{PtP} = 2631$ Hz) ppm. – IR (ATR): $\nu = 2139$ ($\nu_{C\equiv C}$) cm^{-1}.

*Platinum(II) complex **4***

Yield: 54 % of a pale-red microcrystalline solid. Elemental analysis for $C_{48}H_{40}N_6P_2Pt$ (957.91): calcd. C 60.02, H 4.21, N 8.77; found C 59.97, H 4.40, N 8.86. – ^{1}H NMR (400 MHz, 25°C, $CDCl_3$): $\delta = 8.56$ (br, 2 H, H11), 7.86 – 7.80 (m, 10 H, H-*o*, H8), 7.63 (t, $^3J_{HH} = 8$ Hz, 2 H, H9), 7.47 – 7.38 (m, 12 H, H-*m*, H-*p*), 7.15 – 7.08 (m, 4 H, H10, H4), 6.50 (s, 2 H, H5), 5.08 (s, 4 H, CH_2), 2.43 – 2.33 (m, 4 H, dppe) ppm. – ^{13}C NMR (100 MHz, 25°C, $CDCl_3$): $\delta =$ 152.5, 150.8 (C6, C7), 149.0 (C11), 136.8 (C9), 133.6 – 133.5 (m, C-*o*), 131.7 (br, C-*i*), 130.4 (C-*p*), 129.2 – 129.1 (m, C-*m*), 128.6 (t, C4), 122.1 (C10), 120.0 (C8), 103.4 (C5), 102.2 (d, *trans*-$^3J_{PC} = 35$ Hz, C2), 100.3 (dd, *cis*-$^2J_{PC} = 15$ Hz, *trans*-$^2J_{PC} = 143$ Hz, C1), 44.80 (C3), 29.0 (d, $^3J_{HH} = 48$ Hz, PCH_2) ppm. – ^{31}P NMR (161 MHz, 25°C, $CDCl_3$): $\delta = 42.1$ ($J_{PtP} = 2313$ Hz) ppm. – IR (ATR): $\nu = 2137$ ($\nu_{C\equiv C}$) cm^{-1}.

*Ru_2Pt complex **5***

0.18 g (0.16 mmol) of compound **3**, 0.10 g (0.17 mmol) of $[(\eta^6\text{-cymene})Ru(Cl)(\mu^2\text{-Cl})]_2$ and 0.26 g (1.60 mmol) of NH_4PF_6 were suspended in 20 mL of dry CH_2Cl_2 and stirred for 24 h at room temperature. The reaction mixture was concentrated in a vacuum, and the resulting yellow solid was filtered off, washed first with EtOH and then with Et_2O and dried in a vacuum. Yield: 0.18 g (58 %) of a yellow microcrystalline solid. Elemental analysis for $C_{78}H_{74}Cl_2N_6P_4F_{12}PtRu_2$ (1915.48): calcd. C 48.91, H 3.89, N 4.39; found C 48.10, H 4.05, N 4.44. – ^{1}H NMR (400 MHz, 25°C, [D$_6$]DMSO): $\delta = 9.31$ (d, $^3J_{HH} = 8$ Hz, 2 H, H11), 8.13 – 8.19 (m, 4 H, H9, H8), 7.74 – 7.75 (m, 12 H, H-*o*), 7.55 – 7.61 (m, 20 H, H-*m*, H-*p*, H10), 6.75, 6.72 (2 × d, $^3J_{HH} = 2$ Hz, 2 × 2 H, H4, H5), 6.12, 6.03, 5.83, 5.57 (4 × d, $^3J_{HH} = 4$ Hz, 4 × 2 H, cymene-H), 4.73, 4.52 (2 × d, $^2J_{HH} = 16$ Hz, 2 × 2 H, H3), 2.26 – 2.33 (m, 2 H, C*H*CH$_3$), 2.11, 2.10 (2 × s, 6 H, two diastereotopic CH_3 at the cymene), 0.78, 0.73 (2 × d, $^3J_{HH} = 8.0$ Hz, 2 × 6 H, CHC*H*$_3$) ppm. – ^{13}C NMR (100 MHz, 25°C, [D$_6$]DMSO): $\delta = 155.6$ (C11), 150.1, 149.8 (C6, C7), 140.1 (C9), 135.5 (C4), 134. 6 (C-*o*), 131.3 (C-*p*), 130.4 (vt, $^1J_{PC} = 29$ Hz, C-*i*), 128.53 (C-*m*), 125.52 (C10), 122.10 (C8), 107.9 (C1), 104.7 (C5), 100.63(C2), 105.0, 102.6, 85.8, 83.3, 80.9, 80.8 (6 × cymene), 45.4 (C3), 30.2 (*C*HCH$_3$), 21.7, 21.5 (2 × CH*C*H$_3$), 18.7 (CH_3 at the cymene) ppm. – ^{31}P NMR (161 MHz, 25°C, [D$_6$]DMSO): $\delta = 18.1$ ($^1J_{PtP} = 2601$ Hz), −144.2 (sept, $^1J_{PF} = 707$ Hz, PF_6^-) ppm. – IR (ATR): $\nu =$ 2131 ($\nu_{C\equiv C}$) cm^{-1}. – MS ((+)-ESI): $m/z = 813.2$ (calculated 813.1 a.m.u.).

Table 1. Crystal structure data for **3** and **4**.

	3	**4**
Empirical formula	$C_{58}H_{46}N_6P_2Pt$	$C_{48}H_{40}N_6P_2Pt$
M_r	1084.04	957.89
Crystal size, mm^3	0.44 × 0.25 × 0.19	0.24 × 0.22 × 0.18
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	*Cc*
a, Å	11.2093(4)	9.4857(2)
b, Å	13.0415(5)	20.2480(3)
c, Å	16.7642(7)	21.2027(3)
α, deg	89.060(3)	90
β, deg	85.500(3)	100.266(2)
γ, deg	74.947(3)	90
V, Å^3	2359.28(16)	4007.13(12)
Z	2	4
$D_{calcd.}$, g cm^{-3}	1.53	1.59
μ (MoK$_\alpha$), cm^{-1}	6.6	7.6
F(000), *e*	1088	1912
hkl range	$-12 \le h \le +12$	$-10 \le h \le +10$
	$-14 \le k \le +11$	$-20 \le k \le +23$
	$-19 \le l \le +19$	$-24 \le l \le +23$
Refl. measured	16 376	12 957
Refl. unique	7500	5619
R_{int}	0.0236	0.0205
Param. refined	607	514
$R(F)/wR(F^2)$[a,b] (all refls.)	0.0257/0.0604	0.0174/0.0425
x(Flack)	–	−0.012(4)
GoF (F^2)[c]	1.107	1.084
$\Delta\rho_{fin}$ (max/min), *e* Å^{-3}	0.66/−1.61	0.38/−0.86

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; [b] $wR = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, $w = [\sigma^2(F_o^2) + (AP)^2 + BP]^{-1}$, where $P = (\mathrm{Max}(F_o^2, 0) + 2F_c^2)/3$; [c] GoF $= [\Sigma w(F_o^2 - F_c^2)^2/(n_{obs} - n_{param})]^{1/2}$.

X-Ray structure determinations

Crystal data and refinement parameters for compounds **3** and **4** are summarized in Table 1. The structures were solved using Direct Methods (SIR92 [83]), completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares procedures on F^2 [84]. Semi-empirical absorption corrections from equivalents (Multiscan) were carried out [85]. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in calculated positions and refined by using a riding model.

CCDC 1023340 (**3**) and 1023339 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Supporting information

Pictures of NMR and IR spectra, including the 2D-NMR spectra, as well as spectral data of **2** are given as Supporting Information (13 pages) available online (DOI: 10.5560/ZNB.2014-4164).

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