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Ru(II) and Rh(III) porphyrin complexes of primary phosphine-substituted porphyrins†

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Primary alkynyl phosphine porphyrins were prepared by $AlHCl_2$ reduction of the corresponding alkynyl phosphonates. Dephosphorylation of the alkyne proved to be a major side reaction. Using $LiAlH_4$ as reducing agent, the alkyne was found to be partially reduced to give the *trans*-alkenyl phosphine selectively. The primary phosphines coordinate to both ruthenium(II) and rhodium(III) porphyrins and readily form bis-phosphine complexes. The ^1H and ^{31}P NMR spectra for the ruthenium complexes show a pattern characteristic of an $[AX_2]_2$ spin system with an unusually large $^2J_{PP}$ coupling constant of 620.6 Hz. The IR spectrum of the complex $(PAPH_2)Ru(CO)(porphyrin)$ ($PAPH_2$ = phenylacetylenephosphine) indicates weak σ-donor properties of the ligand. In contrast to the corresponding tertiary phosphine complexes, the bis-phosphine complexes with both ruthenium(II) and rhodium(III) porphyrins are more stable than the mono-phosphine complexes, as judged by NMR spectroscopy, and they can also be detected in the gas phase by LDI-TOF MS. In all cases the complexes could not be isolated and they degrade within hours at ambient temperatures when kept in solution. These compounds may therefore not be suitable for the construction of larger multiporphyrin systems, but their accessibility makes it possible to study their coordination behaviour with other transition metals.

Introduction

In recent studies, we have used diphenyl phosphine-substituted alkynyl porphyrins for the construction of linear and cyclic multiporphyrinic arrays *via* coordination of the phosphorus to ruthenium(II) or rhodium(III) porphyrins.[1,2] The coordination of tertiary phosphines to transition metal porphyrins is well-documented and many complexes have been studied in solution and, in some cases, also in the solid state.[3,4] The binding of a primary phosphine to a metalloporphyrin, on the other hand, has not been reported to date. Indeed, reports on coordination compounds of primary phosphines are scarce,[5–7] although some air-stable primary phosphines have been reported.[8] Primary phosphines are expected to be weaker donors than tertiary phosphines due to an increased s character of the P lone pair orbital.[6,9] The acidic P–H bond is susceptible to deprotonation giving phosphido species.[7,10] Given the rich electrochemistry of Ru(II) and Rh(III) porphyrins,[3] the coordination of a primary phosphine to these acceptor porphyrins might yield complexes of unusual reactivity.

Attachment of a diphenyl phosphine group to a porphyrin is readily achieved using an alkynyl linker.[1] Thus, the report by Guillemin *et al.*[11] on a primary phenylalkynyl phosphine ($PAPH_2$, Scheme 1) and its tungsten pentacarbonyl complex attracted our interest. This ligand is comparable with other simple phenylalkynyl phosphines and phosphonites, which we have previously used to study the coordination of phosphorus to ruthenium and rhodium porphyrins.[2b,12,13] Here, we report on the synthesis of a porphyrin substituted with a primary alkynyl phosphine, as well as on the NMR and IR spectroscopic and mass spectrometric investigations of the complexes formed from both the model phosphine $PAPH_2$ and the phosphine porphyrins with ruthenium and rhodium porphyrins.

Results and discussion

Synthesis of the phosphine porphyrins

The synthetic route to the porphyrins substituted with a primary alkynyl phosphine is outlined in Scheme 1. The reduction step is adapted from the reported synthesis of $PAPH_2$.[11,14] Both *meta*- and *para*-substituted alkynyl porphyrins can be phosphonylated by our general route *via* formation of a Grignard-type cadmium-alkynyl complex[1] and using chlorodiethyl phosphate as electrophile. In this way, the phosphonates Por–C≡C–P(O)$(OEt)_2$ (Por = porphyrin, **1**) are accessible in 20 to 30% overall yield. The characteristic phosphorus chemical shift is $\delta_P = -5$ ppm, which is independent of the substitution pattern (*meta vs. para*) and of the metallation state. A major side product was isolated by column chromatography and identified by NMR spectroscopy ($\delta_P = -19$ ppm) and MALDI-TOF MS as the bis-porphyrin phosphinate $(Por–C^{\circ}≡C)_2P(O)OEt$. The bis-porphyrin phosphinate was present in up to 40% yield. Adding the Grignard reagent to a solution of the chlorophosphate did not alter the distribution of the products. The desired products can be obtained as free-base (**Fb-1**), zinc(II) (**Zn-1**) or nickel(II) (**Ni-1**) porphyrinates. However, since the difference in the substitution pattern on the *meso*-aryl group (*meta- vs. para*-alkyne) does not have a significant influence on the coordination behaviour of phosphine substituted porphyrins,[1] we focused on the *meta*-substituted zinc porphyrin (**Zn-1**) and the *para*-substituted nickel porphyrin (**Ni-1**) as representative phosphine porphyrins.

† Dedicated to the memory of Bhaskar G. Maiya.

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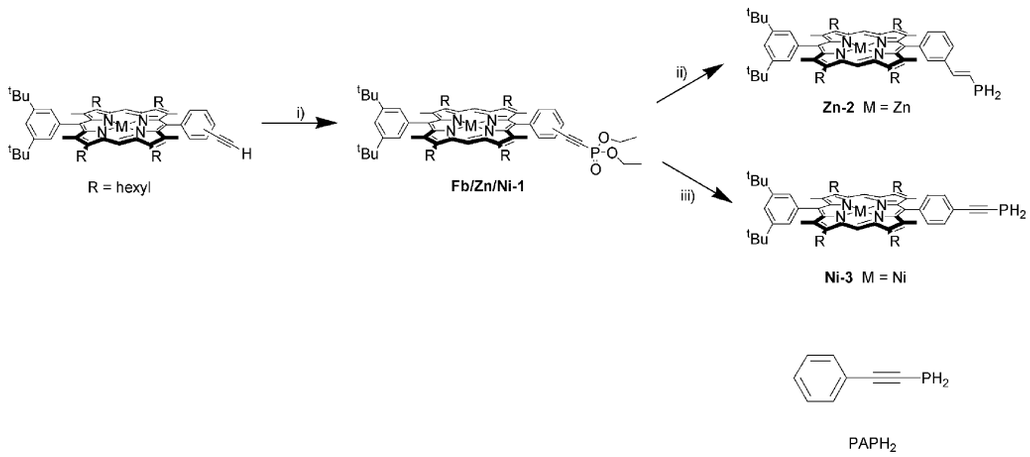


Scheme 1 Synthesis of the primary phosphines. Reagents and conditions: (i) LiHMDA, $CdCl_2$, $ClP(O)(OEt)_2$, THF, −78 °C; (ii) $LiAlH_4$, THF, −78 °C; (iii) $LiAlH_4$, $AlCl_3$, THF, −78 °C.

The phosphonates could be reduced to the corresponding primary phosphines (**2**) and (**3**) according to the procedure described by Guillemin *et al.*[11] using a mixture of $LiAlH_4$ and $AlCl_3$. The reaction resulted in almost quantitative conversion and showed only one single product by TLC. However, ^{1}H NMR and MALDI-TOF MS analysis of the collected fraction from column chromatography showed that some dephosphorylation occurred, so that in some samples up to 50% of the free alkyne was present. Due to the inherent instability of the primary phosphine towards both isomerisation and oxidation, and due to the identical R_f values of the two compounds on silica, these could not be separated. Therefore, micro-analytical data such as elemental analysis or HRMS could not be obtained. The primary alkynyl phosphine porphyrins show a characteristic ^{31}P NMR chemical shift of $\delta_P = -178$ ppm (t, $^1J_{PH} = 214$ Hz, Fig. 1). These values are essentially identical to those for $PAPH_2$ ($\delta_P = -176$ ppm, t, $^1J_{PH} = 215$ Hz). In the ^{1}H NMR spectrum, the PH_2 group is at $\delta_H = 3.78$ ppm (d, $^1J_{PH} = 214$ Hz). This corresponds to a small low-frequency shift compared to the resonance found in $PAPH_2$ ($\delta_H = 3.96$ ppm, d, $^1J_{P\text{-}H} = 215$ Hz). In decoupled spectra, the resonances for both the phosphorus and the phosphine protons appear as singlets.

When $LiAlH_4$ was used as sole reducing agent, the partially reduced alkene phosphine was isolated. The double bond shows characteristic proton resonances at $\delta_H = 7.11$ and 6.50 ppm (Fig. 1); the MALDI-TOF MS confirmed the addition of one equivalent of hydrogen. The $^3J_{HH}$ value for $H_b \leftrightarrow H_c$ could not be resolved due to the broadened multiplet resonances, but the alkene **Zn-2** was shown to be the *trans* isomer using 2D NOESY experiments. Through-space NOE connectivities between both alkene protons and the aryl group could be detected, but not from the PH_2 group (Fig. 1). Characteristic NOEs were found for H_a to H_b, H_b to H_d and H_e, and for H_c to H_d and H_e. The phosphine protons resonate at $\delta_H = 3.54$ ppm as a doublet of doublets ($^1J_{PH} = 200$ Hz, $^3J_{HH} = 5$ Hz). The ^{31}P NMR spectrum showed a resonance at $\delta_P = -136$ ppm, which appears in the proton-coupled spectrum as a triplet of triplets ($^1J_{PH} = 200$ Hz, $^2J_{PH} = 12$ Hz, $^3J_{PH} = 12$ Hz, Fig. 1), where the coupling constants to the two vinyl protons have identical values.[15]

The primary phosphines are highly unstable and must be handled under an inert atmosphere. Chloroform as solvent should be avoided, because the release of acid induces degradation of the compounds within a few hours. The phosphine porphyrins are best dissolved in benzene and can be stored in a frozen matrix of benzene at −20 °C.

NMR spectroscopy of $(PAPH_2)_2$Ru-4

To get an understanding of the coordination behaviour of primary alkynyl phosphines to metalloporphyrins, we first investigated the affinity of **Ru-4** towards $PAPH_2$. When mixing

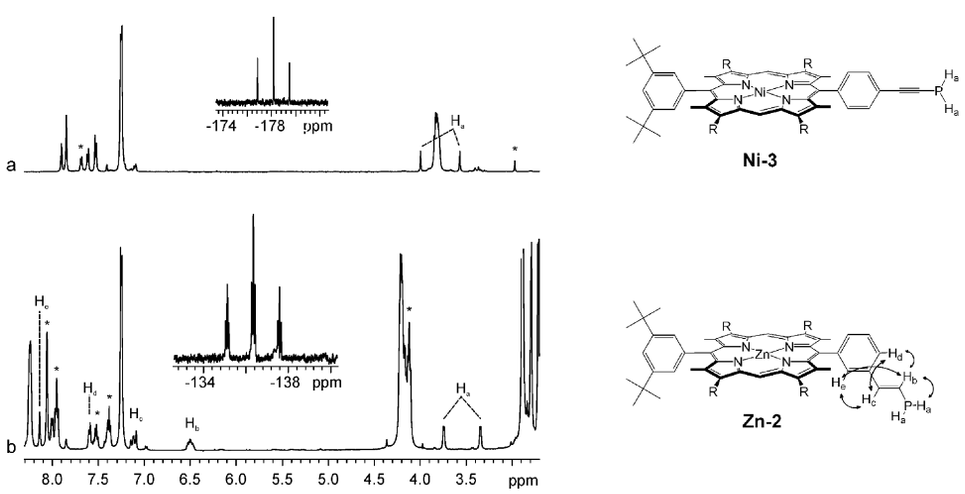
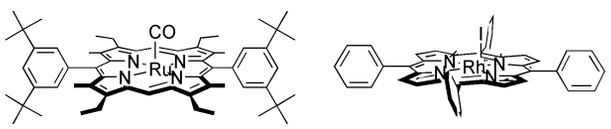


Fig. 1 Part of the 400 MHz ^{1}H NMR spectra of (a) **Ni-3** and (b) **Zn-2**; the insets show the 161.9 MHz ^{31}P NMR spectra of the phosphines. The marked (*) signals arise from the corresponding dephosphorylated alkyne porphyrins. Arrows in the structure of **Zn-2** indicate selected through-space NOE connectivities.

$PAPH_2$ with **Ru-4** (C_6D_6), new signals could be observed in both the ^1H NMR and ^{31}P NMR spectra. The $^1H\{^{31}P\}$ NMR spectrum showed a new singlet at $\delta_H = -0.60$ ppm. This low-frequency shift is consistent with the binding of the phosphorus in the shielding region of the porphyrin. In the $^{31}P\{^1H\}$ NMR spectrum, three signals could be found, namely a sharp singlet at $\delta_P = -102$ ppm and two broad resonances at $\delta_P = -119$ and -178 ppm, the latter being the resonance of the free $PAPH_2$ (Fig. 2). These broadened signals indicate a dynamic exchange between the free phosphine and the bound $PAPH_2$ in the mono-phosphine complex of the form $(PAPH_2)$-Ru(CO)(por).[13] Displacement of the carbonyl ligand yields the bis-phosphine complex $(PAPH_2)_2$Ru(por), which seems to be much more kinetically inert than the mono-phosphine complex. Despite all attempts made, the final complex could not be isolated. Usually, the complex degraded during the crystallisation procedure and the solutions turned from green to black overnight. However, the complex can be stored in a frozen C_6D_6 matrix at $-20\,^\circ C$.



Ru-4 **Rh-5**

The ^1H and ^{31}P (^1H coupled) NMR spectra of the PH_2 signal showed a pattern characteristic of an $[AX_2]_2$ spin system (Figs. 3 and 4). This was analysed using WINDAISY and a fit was obtained using the parameters $^2J_{PP} = 620.6$ Hz, $^1J_{PH} = 340.8$ Hz and $^3J_{PH} = 3.8$ Hz. $^2J_{PP}$ is remarkably large when compared with the 229 and 308 Hz reported for $[RuCl_2(CO)_2(PH^tBu_2)_2]$[16] (isomers).

Comparison of the IR spectra of Ru-4 and $(PAPH_2)$Ru-4

To obtain the IR spectrum of the mono-phosphine complex, a DCM solution of $PAPH_2$ was titrated into a 2.0 mM solution of **Ru-4**. The absorption of the C≡O IR stretching vibration of **Ru-4** is at $\nu = 1919$ cm^{-1} and the final spectrum of the mono-phosphine complex $(PAPH_2)$Ru(CO)(por) showed the C≡O absorption at $\nu = 1949$ cm^{-1} (Fig. 5). Further addition of $PAPH_2$ resulted in formation of the bis-phosphine complex $(PAPH_2)_2$Ru(por), visible in the loss of the CO absorption. Compared to other phosphine ligands such as PPh_3, which shows a difference in the wavenumber of $\Delta\nu = 18$ cm^{-1} upon binding,[13] this rather large shift of $\Delta\nu = 30$ cm^{-1} for $PAPH_2$ indicates very different stereoelectronic influences on the metal from the primary phosphine compared to the tertiary phosphine. The σ-donor properties of the ligands, which can be approximated by the pK_a of the protonated phosphine,[17] suggest that $PAPH_2$ (calculated $pK_a = -3.7$) is a much weaker ligand than PPh_3 ($pK_a = 2.7$).[10] The lower wavenumber observed for the PPh_3 complex is consistent with this, because PPh_3, as stronger donor, increases the electron density on the ruthenium, thus allowing more effective back-bonding to the pπ* orbital of the CO ligands, resulting in a decreased CO stretching frequency compared to $PAPH_2$.

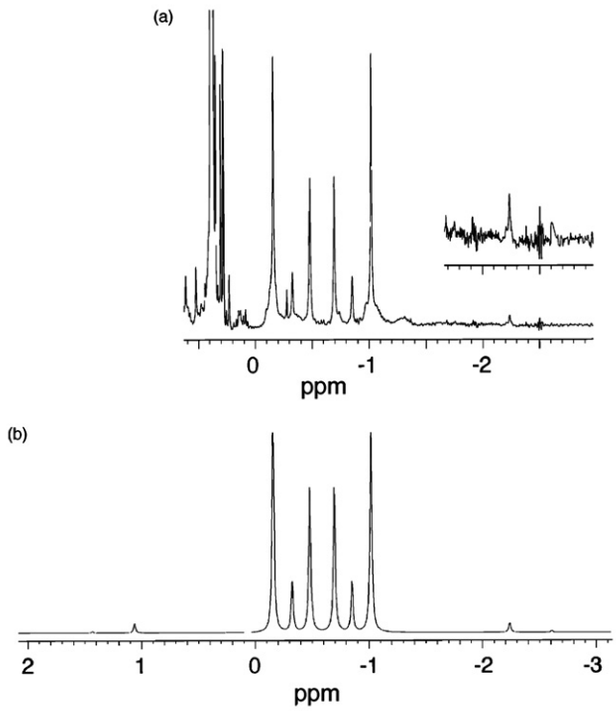


Fig. 3 (a) A partial experimental 400 MHz ^1H NMR spectrum of $(PAPH_2)_2$**Ru-4** in d_6-benzene showing the signal due to the PH_2 protons. (b) The calculated spectrum of the PH_2 protons, calculated as an $[AX_2]_2$ spectrum with the parameters $^2J_{PP} = 620.6$ Hz, $^1J_{PH} = 340.8$ Hz and $^3J_{PH} = 3.8$ Hz.

Ru(II) and Rh(III) complexes of 2 and 3

To obtain the complexes of the primary phosphines, both Ru(II) (**Ru-4**) and Rh(III) (**Rh-5**) porphyrins were dissolved in C_6D_6 (5 mM each) and titrated into C_6D_6 solutions of **Zn-2** and **Ni-3** (*ca.* 2–3 mM each), which were immediately used for NMR measurements. The complexation of both the alkenyl and the alkynyl phosphine to the ruthenium(II) and rhodium(III) porphyrins could be followed by ^1H NMR spectroscopy

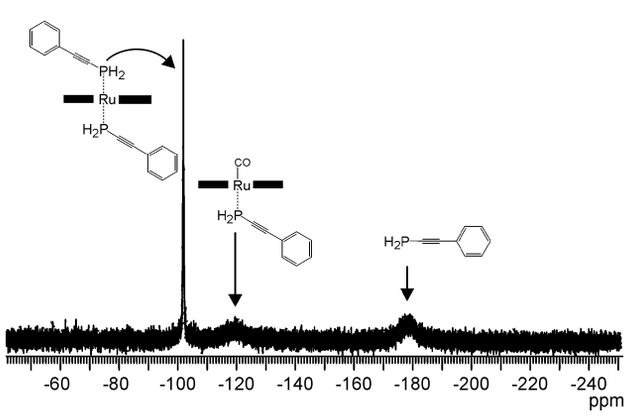


Fig. 2 161.9 MHz $^{31}P\{^1H\}$ NMR spectrum of the mixture of $PAPH_2$ with **Ru-4** in C_6D_6 (273 K).

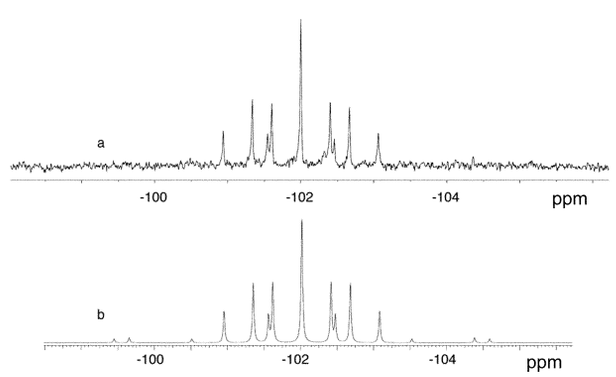


Fig. 4 (a) The experimental 161.9 MHz ^{31}P NMR spectrum of $(PAPH_2)_2$**Ru-4** in d_6-benzene. (b) The calculated spectrum of the PH_2 ^{31}P nuclei, calculated as an $[AX_2]_2$ spectrum with the parameters $^2J_{PP} = 620.6$ Hz, $^1J_{PH} = 340.8$ Hz and $^3J_{PH} = 3.8$ Hz.

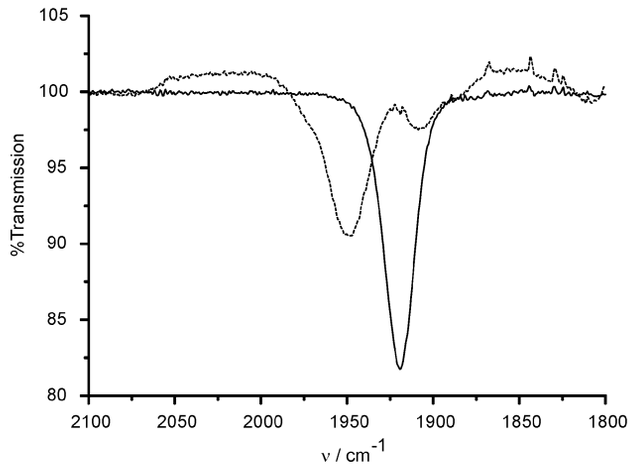


Fig. 5 C=O absorption region in the IR spectra of **Ru-4** (solid line) and of (PAPH$_2$)**Ru-4** (dashed line). Spectra are recorded in CH_2Cl_2 (2.0 mM, 25 °C).

(Fig. 6). Initially, the ^{1}H NMR spectrum of the **Ni-3**/**Rh-5** mixture displayed a signal for the RPH$_2$ group at $\delta = 1.33$ ppm ($^1J_{PH} = 403$ Hz), consistent with formation of the complex; some uncoordinated phosphine is still detectable. Re-measuring the sample after allowing it to stand for 24 h at ambient temperature showed the occurrence of new species, though some of the initial compound was still present. A signal due to another ruthenium adduct with RPH$_2$ is seen whose chemical shift values are consistent with a complexed phosphine ($\delta - 0.93$ ppm, $^1J_{PH} = 389$ Hz). Two strong signals appear at $\delta - 1.30$ ppm ($^1J_{PH} = 197$ Hz) and at $\delta - 1.33$ Hz ($^1J_{PH} = 199$ Hz); the $^1J_{PH}$ values suggest free RPH$_2$ but the chemical shifts suggest coordination, perhaps through the alkyne.[18] However, any structural assignments of the newly formed products are speculative.

The ^{1}H NMR spectrum of the **Ni-3**/**Ru-4** mixture displayed a signal at $\delta - 0.56$ ppm, which appears to be an $[AX_2]_2$ spin system (singlet in the $^1H\{^{31}P\}$ NMR spectrum). This spin system is consistent with the one obtained from the $(PAPH_2)_2$-Ru(por) complex and confirms the formation of the complex [**Ni-3**/**Ru-4**/**Ni-3**]. The values obtained are $^2J_{PP} = 603.7$ Hz, $^1J_{PH} = 339.0$ Hz and $^3J_{PH} = 6.0$ Hz. However, due to the missing outer lines, the errors may be too large to discuss these values in detail, yet they are similar to those of the PAPH$_2$ complex. This sample degraded rapidly upon standing at ambient temperature.

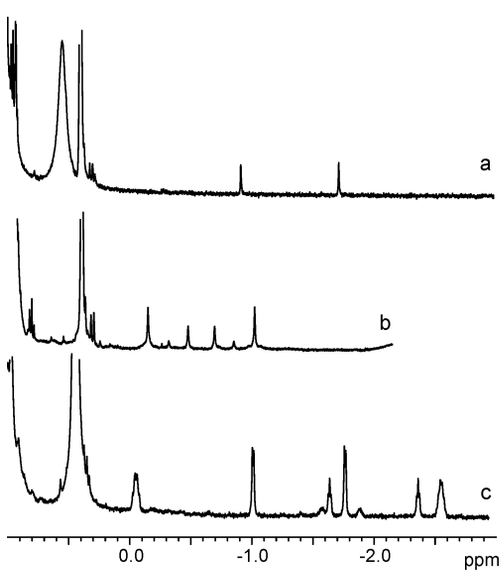


Fig. 6 Low-frequency region of the ^{1}H NMR spectra obtained from the mixtures of the primary phosphines with the ruthenium and rhodium porphyrins: (a) **Ni-3** and **Rh-5**; (b) **Ni-3** and **Ru-4**; (c) **Zn-2** and **Rh-5**.

The vinylic phosphine **Zn-2** also readily coordinates to **Rh-5**, but multiple species are observed (^{1}H NMR) immediately after mixing the two components (Fig. 6). Analogous to the complex with **Ni-3**, a signal at $\delta - 1.45$ ($^1J_{PH} = 377$ Hz, $^2J_{HH} = 6$ 6 Hz) corresponds to the coordinated primary phosphine and the alkenyl phosphine resonates at slightly lower frequency as the alkynyl phosphine. The origin of a second signal at $\delta - 2.07$ ($^1J_{PH} = 362$ Hz, $^2J_{HH} = 6$ Hz) is unclear, as the triplet coupling cannot be explained. Another signal at $\delta - 1.79$ ($^1J_{PH} = 155$ Hz) again suggests free phosphine but located within the shielding region of the porphyrin, thus complexation *via* the vinyl might explain this resonance. For this signal, the $^2J_{HH}$ could not be determined due to the low resolution. Upon mixing **Ru-4** and **Zn-2**, no spectrum with clearly resolved signals could be obtained.

LDI-TOF mass spectrometry

Since laser desorption ionisation time-of-flight (LDI-TOF) mass spectrometry is a versatile characterisation method for metalloporphyrins and their complexes,[19] we have studied the complexes of both PAPH$_2$ and **Ni-3** with **Ru-4**. A mixture of PAPH$_2$ with **Ru-4** (5 equiv of phosphine to ruthenium) showed a peak at $m/z = 1087.8$ for the mono-phosphine complex [(PAPH$_2$)**Ru-4**]$^{\bullet+}$ (calcd $m/z = 1088.5$), where the CO ligand is lost from the complex. A typical mass spectrum is displayed in Fig. 7(a). This demonstrates that the primary phosphine ligand is a sufficiently strong σ-donor to form complexes with Ru(II) porphyrins in the gas phase. In comparison, nitrogen donors such as pyridine or DMAP only form complexes in the gas phase when using large excess of the ligand (>100 equiv).[19] Upon addition of a large excess of PAPH$_2$ to **Ru-4** (approx. 50 equivalents), the bis-phosphine complex was still not observable; similar observations were made with tertiary phosphines as ligands. In contrast to measurements with tertiary phosphines, the formation of the ruthenium dimer [**Ru-4**]$_2^{\bullet+}$ was not suppressed.[19]

In the spectrum of a 5:1 mixture of **Ni-3** and **Ru-4**, additional signals to the parent mass peaks of the porphyrins could be detected at higher masses [Fig. 7(b)]. A slightly broadened mass peak at $m/z = 2032.4$ corresponds to the diporphyrin complex [**Ni-3**/**Ru-4**]$^{\bullet+}$ (calcd $m/z = 2033.2$), again with loss of CO. More surprising is the appearance of a broad peak at $m/z \sim 3110$, which can be assigned to the triporphyrin complex [**Ni-3**/**Ru-4**/**Ni-3**]$^{\bullet+}$ (calcd $m/z = 3111.8$). This contrasts to our experience with corresponding tertiary phosphine substituted porphyrins, where the triporphyrin complexes could not be detected.[1,19] The ^{31}P NMR spectrum of the mixture of PAPH$_2$ with **Ru-4** (Fig. 2) suggests that the bis-phosphine complex is more stable than the mono-phosphine complex, in contrast to tertiary phosphines where the bis-phosphine complex is usually thermodynamically less stable than the mono-phosphine complex. This solution phase behaviour seems to be retained in the gas phase for **Ni-3**. The same can be observed in mixtures of **Ni-3** with **Rh-5** [Fig. 7(c)]: the peaks for the diporphyrin complex [**Ni-3**/**Rh-5**]$^{\bullet+}$ and the triporphyrin complex [**Ni-3**/**Rh-5**/**Ni-3**]$^{\bullet+}$ were detected at $m/z = 1793.4$ (calcd $m/z = 1793.8$) and at $m/z = 2874.9$ (calcd $m/z = 2872.4$), respectively. In this case, the relative peak intensity for the free **Ni-3** is significantly higher than for **Rh-5**, indicating easier ion formation for **Ni-3** than for **Rh-5**. We had already made similar observations with different metalloporphyrins in LDI-TOF MS.[19] Another major difference compared to the measurement with **Ru-4** can be seen: the signals for the mono- and for the bis-phosphine complexes appear to be much sharper and with a higher intensity than for

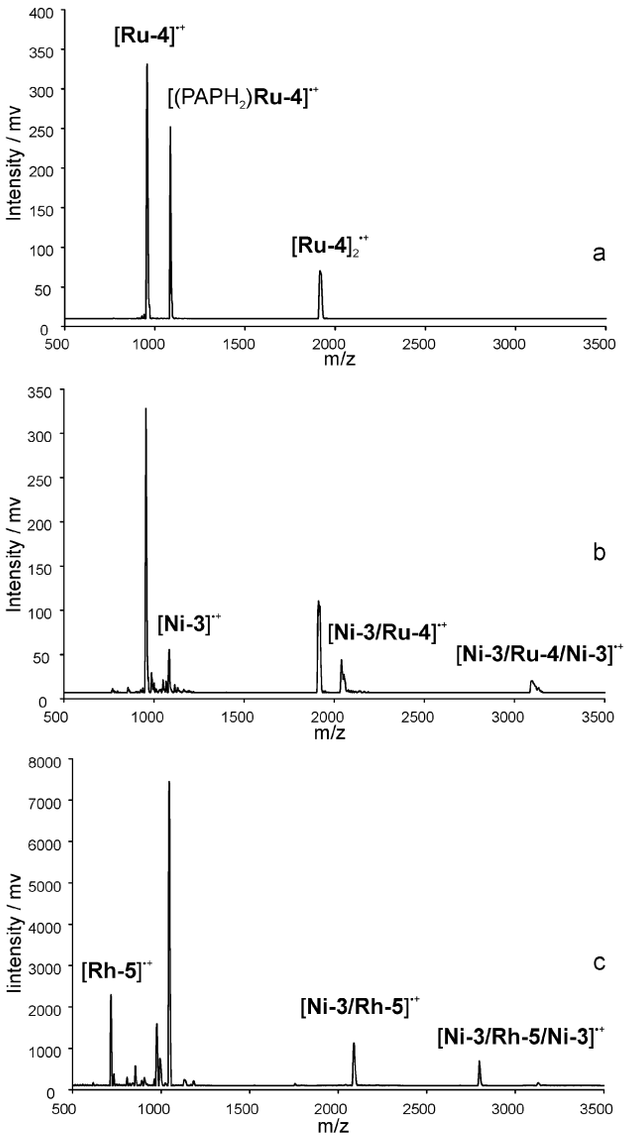


Fig. 7 LDI-TOF MS of porphyrin complexes with primary phosphines: (a) mixture of $PAPH_2$ with **Ru-4**; (b) mixture of **Ni-3** with **Ru-4**; (c) mixture of **Ni-3** with **Rh-5**.

the corresponding **Ru-4** complexes. Thus, changing the acceptor porphyrin in the array has a dramatic influence on the outcome of the mass spectrum. This could hint at different photophysical behaviour of the arrays in the gas phase upon irradiation with the laser.

Conclusions

The first syntheses of the primary alkenyl and alkynyl phosphines **Ni-3** and **Zn-4** are reported. The primary phosphines can be synthesised with variable substitution pattern on the porphyrin (*meta*- or *para*-substituted at the *meso*-phenyl groups) or with variable central metal, such as Ni(II) or Zn(II). The primary phosphines coordinate to both Ru(II) and Rh(III) porphyrins, readily forming bis-phosphine complexes. In the ^1H and ^{31}P NMR spectra, the complex of $PAPH_2$ with the Ru(II) porphyrin showed a pattern characteristic of an $[AX_2]_2$ spin system with a remarkably large $^2J_{PP}$ coupling constant of 620.6 Hz. A similar signal pattern was obtained by complexing **Ni-3** to **Ru-4**.

All the complexes are unstable in solution and thus could not be isolated. This might not be surprising given the possibility of activating alkenes and alkynes with ruthenium and rhodium porphyrins.[20] These compounds may therefore not be suitable for the construction of larger multiporphyrin systems. For this purpose, we would recommend to use either tertiary phosphines or phosphonates, because they are stable under standard inert atmosphere. But the accessibility of the primary phosphine porphyrins makes it possible to study their coordination behaviour with other transition metals and probably get more insight into the reactivity of unsaturated phosphines in the presence of Ru(II) and Rh(III) complexes *via* NMR spectroscopy or LDI-TOF mass spectrometry. This could be of particular interest to those working in the field of catalytic hydrogenation of alkenes and alkynes with ruthenium and rhodium complexes.

Experimental

General

All manipulations were performed using standard inert atmosphere techniques and freshly distilled and degassed solvents according to standard procedures; $CDCl_3$ and C_6D_6 (Eurisotop, France) were filtered over basic alumina and degassed by purging with Ar prior to use. 3-(3-Hydroxy-3-methylbut-1-ynyl)benzaldehyde and 4-(3-hydroxy-3-methylbut-1-ynyl)-benzaldehyde were prepared according to literature procedures.[21] LiHMDA (1 M THF), $ClP(O)(OEt)_2$, $LiAlH_4$ and $AlCl_3$ were purchased from Aldrich and used as received. $CdCl_2$ (Aldrich) was dried prior to use (1 mbar, 150 °C, 3 h). The general procedure for the synthesis of the acetylenic porphyrins has been described earlier.[22] **Ru-4** and **Rh-5** were prepared as described previously.[23]

NMR spectra were recorded on a Bruker DPX250 NMR spectrometer (250.13 MHz for ^1H, solvent as internal standard; 101 MHz for $^{31}P\{^1H\}$, H_3PO_4 external standard), on a Bruker DPX400 NMR spectrometer (400.13 MHz for ^1H, solvent as internal standard; 161.98 MHz for $^{31}P\{^1H\}$, H_3PO_4 external standard), or on a Bruker Avance 500 Cryo NMR spectrometer at 500.13 MHz (^1H). Abbreviations for ^1H NMR spectra used are: s, singlet; d, doublet; t, triplet; q, quartet; p, pentet; m, multiplet; b, broad. LDI-TOF mass spectra were recorded on a Kompact MALDI 4 mass spectrometer (Kratos Analytical Ltd), operated in the linear positive mode, using neat samples.

General procedure for the synthesis of the phosphonates

***meta*-Zn-1.** Acetylene zinc porphyrin (100 mg, 94.3 μμmol) was dissolved in 1.5 ml THF and cooled to −78 °C. After addition of 470 μl LiHMDA (470 μmol), the solution was stirred for 15 min, after which 86 mg $CdCl_2$ (474 μmol) were added and the solution was stirred for a further 30 min at −78 °C. $ClP(O)(OEt)_2$ (82 mg, 474 μmol) in 1.5 ml THF were added dropwise and the resulting solution was stirred at −78 °C for 1.5 h, then warmed to room temperature and stirring was continued for 30 min. The reaction mixture was poured into a separating funnel containing 100 ml CH_2Cl_2 and neutralised with 50 ml saturated aqueous Na_2CO_3. The organic phase was washed with one portion of H_2O (50 ml), dried over $MgSO_4$, filtered and evaporated to dryness. Due to some demetalation during the reaction, the crude product was mixed with $Zn(OAc)_2$ (50 mg) in 20 ml $CHCl_3$–MeOH (10:1), heated to the boiling point for 5 min and evaporated to dryness. The residue was taken up in CH_2Cl_2, filtered and the residue washed with CH_2Cl_2 until colourless. Column chromatography (silica, CH_2Cl_2–MeOH 20:1, R_f 0.5) afforded 62.1 mg of *meta*-**Zn-1** (52.1 μmol; 55%). ^1H NMR (250 MHz, $CDCl_3$): $\delta = 10.21$ (s, 2H, *meso*-H), 8.32 (s, 1H, Ar–H), 8.23 (d, 1H, $J = 8$ Hz, Ar–H), 8.03 (d, 1H, $J = 8$ Hz, Ar–H), 7.93 (bs, 2H, Ar–H), 7.82 (bs, 1H, Ar–H), 7.77 (s, 1H, Ar–H), 4.24 (p, 4H, $J = 7$ Hz, P–O–CH_2–CH_3), 3.98 (t, 8H, $J = 7$ Hz, hexyl-CH_2), 2.46 (s, 6H, β-pyrrole CH_3), 2.44 (s, 6H, β-pyrrole

CH_3), 2.19 (m, 8H, hexyl-CH_2), 1.75 (m, 8H, hexyl-CH_2), 1.53 (s, 9H, ^{t}Bu–CH_3), 1.51 (s, 9H, ^{t}Bu–CH_3), 1.47 (m, 8H, hexyl-CH_2), 1.39 (t, 6H, $J = 7$ Hz, P–O–CH_2–CH_3), 1.27 (m, 8H, hexyl-CH_2), 0.92 (t, 12H, $J = 7$ Hz, hexyl-CH_3). $^{31}P\{^1H\}$ NMR (101 MHz, $CDCl_3$): $\delta = -5$. LDI-TOF MS: m/z calcd for $C_{74}H_{101}N_4O_3PZn$ 1188.69, found 1189.16.

***para*-Ni-1.** Yield 58.7 mg (49.6 μmol; 52%) from 100 mg acetylene nickel porphyrin (95.4 μmol). ^1H NMR ($CDCl_3$, 500 MHz): $\delta = 9.42$ (s, 2H, *meso*-H), 7.83 (d, $J = 8$ Hz, 2H, Ar–H), 7.79 (d, $J = 8$ Hz, 2H, Ar–H), 7.68 (d, $J = 2$ Hz, 2H, Ar–H), 7.67 (t, $J = 2$ Hz, 1H, Ar–H), 3.94 (p, 4H, $J = 7$ Hz, P–O–CH_2–CH_3), 3.63 (t, $J = 8$ Hz, 8H, hexyl-CH_2), 2.25 (s, 6H, β-pyrrole CH_3), 2.23 (s, 6H, β-pyrrole CH_3), 2.20 (p, $J = 7$ Hz, 8H, hexyl-CH_2), 1.58 (p, $J = 7$ Hz, 8H, hexyl-CH_2), 1.42 (s, 18H, ^{t}Bu–CH_3), 1.34 (m, 16H, hexyl-CH_2), 1.28 (t, 6H, $J = 7$ Hz, P–O–CH_2–CH_3), 0.88 (2 × t, $J_1 = 2$ Hz, $J_2 = 7$ Hz, 12H, hexyl-CH_3). $^{31}P\{^1H\}$ NMR (101 MHz, $CDCl_3$): $\delta = -5$. LDI-TOF MS: m/z calcd for $C_{74}H_{101}N_4O_3PNi$ 1182.70, found 1183.03.

Zn-2. ***meta*-Zn-1** (50.0 mg, 42 μmol) was dissolved in 3.0 ml of Et_2O at 0 °C (ice bath). After addition of 4.8 mg $LiAlH_4$ (126 μmol) in one portion, the red solution was stirred at 0 °C for 2 h. Then, the solution was transferred *via canula* into a flask containing 50 ml CH_2Cl_2 and 30 ml brine and the mixture was stirred vigorously for 10 min. The organic phase was separated and concentrated *in vacuo*. The crude product was dissolved in *ca.* 2 ml THF, transferred onto a silica column *via* syringe and flash chromatographed using THF as eluent. This yielded a total of 32.5 mg of porphyrinic product. According to the ^1H NMR spectrum, the mixture contained 13.4 mg **Zn-2** (12.3 μmol, 30%); R_f (hexane–ethyl acetate 5:1) 0.8. ^1H NMR ($CDCl_3$, 500 MHz): $\delta = 10.55$ (s, 2H, *meso*-H), 8.44 (s, 2H, Ar–H), 8.25 (m, 2H, Ar–H), 8.14 (bs, 1H, Ar–H), 8.01 (d, $J = 7$ Hz, 1H, Ar–H), 7.59 (d, $J = 7$ Hz, 1H, Ar–H), 7.11 (m, 1H, alkene-H), 6.50 (m, 1H, alkene-H), 4.12 (m, 8H, hexyl-CH_2), 3.54 (dd, $^1J_{PH} = 200$ Hz, $^3J_{HH} = 5$ Hz, 2H, PH_2), 2.79 (s, 6H, β-pyrrole CH_3), 2.71 (s, 6H, β-pyrrole CH_3), 2.44 (m, 8H, hexyl-CH_2), 1.89 (m, 8H, hexyl-CH_2), 1.59 (s, 18H, ^{t}Bu–CH_3), 1.58 (m, 8H, hexyl-CH_2), 1.46 (m, 8H, hexyl-CH_2), 1.02 (m, 12H, hexyl-CH_3). $^{31}P\{^1H\}$ NMR (101 MHz, $CDCl_3$): $\delta = -136$ ($^1J_{PH} = 200$ Hz, $^2J_{PH} = 12$ Hz). LDI-TOF MS: m/z calcd for $C_{70}H_{93}N_4PZn$ 1084.64, found 1084.57.

Ni-3. To a suspension of 8.0 mg (210 μmol) $LiAlH_4$ in 15 ml dry THF were added 42 mg (315 μmol) $AlCl_3$ at −78 °C. The suspension was allowed to warm to 0 °C and cooled again to −78 °C. To the grey slurry mixture, a solution of 96.7 mg **Ni-2** in 5 ml dry THF was added slowly over a period of 30 min. After the reduction was complete (TLC check, hexane–ethyl acetate 5:1), the suspension was allowed to warm to 0 °C. The mixture was filtered through a canula fitted with a filter paper and transferred into a flask containing 20 mg sodium bicarbonate and 40 mg sodium sulfate at 0 °C. After vigorous stirring for 5 min, the solution was filtered as before and the residue was washed with dry THF until colourless. After evaporating the solvents, the red residue was flash chromatographed on silica (THF) yielding 53 mg of porphyrinic product. According to the ^1H NMR spectrum, the mixture contained 36.5 mg **Ni-3** (33.3 μmol, 41%); R_f (hexane–ethyl acetate 5:1) 0.9. ^1H NMR ($CDCl_3$, 500 MHz): $\delta = 9.86$ (s, 2H, *meso*-H), 7.90 (s, 1H, Ar–H), 7.85 (s, 2H, Ar–H), 7.61 (d, $J = 8$ Hz, 2H, Ar–H), 7.53 (d, $J = 8$ Hz, 2H, Ar–H), 3.83 (m, 8H, hexyl-CH_2), 3.78 (d, 2H, $^1J_{PH} = 214$ Hz, PH_2), 2.56 (s, 6H, β-pyrrole CH_3), 2.43 (s, 6H, β-pyrrole CH_3), 2.21 (m, 8H, hexyl-CH_2), 1.73 (m, 8H, hexyl-CH_2), 1.50 (s, 18H, ^{t}Bu–CH_3), 1.49 (m, 8H, hexyl-CH_2), 1.44 (m, 8H, hexyl-CH_2), 1.01 (m, 12H, hexyl-CH_3). $^{31}P\{^1H\}$ NMR (101 MHz, $CDCl_3$): $\delta = -176$ ($^1J_{PH} = 215$ Hz). LDI-TOF MS: m/z calcd for $C_{70}H_{93}N_4NiP$ 1078.65, found 1079.17.

NMR experiments

$(PAPH_2)_2$Ru-4. Ru-4 (50 mg, 50 μmol) was added to a solution of 60 mg (450 μmol) of $PAPH_2$ in 100 ml dry THF and the solution was stirred for 1 h at room temperature. The solvent was evaporated and the dark red residue was dried *in vacuo*. The solid was redissolved in 2.0 ml of C_6D_6 and directly used for NMR measurements. $^1H\{^{31}P\}$ NMR (C_6D_6, 500 MHz): $\delta = 10.31$ (s, 2H, *meso*-H), 8.20 (s, 4H, *o*-Ar–H), 7.99 (s, 2H, *p*-Ar–H), 6.92–6.97 (m, 10H, Ar–H of $PAPH_2$), 4.00 (m, 8H, ethyl-CH_2), 2.77 (s, 12H, β-pyrrole CH_3), 1.83 (m, 12H, hexyl-CH_3), 1.48 (s, 36H, ^{t}Bu–CH_3), −0.6 (s, 4H, PH_2). $^{31}P\{^1H\}$ NMR (C_6D_6, 101 MHz): $\delta = -102$ (s). Signals for some mono-complex at $\delta - 120$ (bs) and free phosphine at $\delta - 178$ ppm (bs) were detected as well. The $[AX_2]_2$ coupling pattern was analysed initially using the $[AX_n]_2$ spin system, which assumes that $^4J_{HH} = 0$ H. The approximate coupling constants were then refined using WINDAISY.

Ni-2/Zn-3 with Ru-4/Rh-5. Solutions of 5.0 mg of the phosphine porphyrins (500 μl C_6D_6) were titrated with 5.0 mM solutions of the acceptor porphyrins (C_6D_6) in 10 to 50 μl portions and the ^1H NMR spectra were recorded after each addition. The final spectrum was obtained when virtually all uncomplexed phosphine was consumed.

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