Phosphine-substituted porphyrins as supramolecular building blocks

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A route to alkyne-phosphine-substituted metalloporphyrins is presented. The X-ray structure of the methanol adduct of a diphenylphosphine Zn(II) porphyrin reveals solid state dimerisation accompanied by proton transfer from coordinated methanol to phosphine in a process reminiscent of carbonic anhydrase. The ability of the phosphine-substituted porphyrins to form non-covalent arrays with a Ru(II) porphyrin was explored using $^{1}H/^{31}P$ NMR and UV/vis spectroscopy as well as MALDI-TOF mass spectrometry.

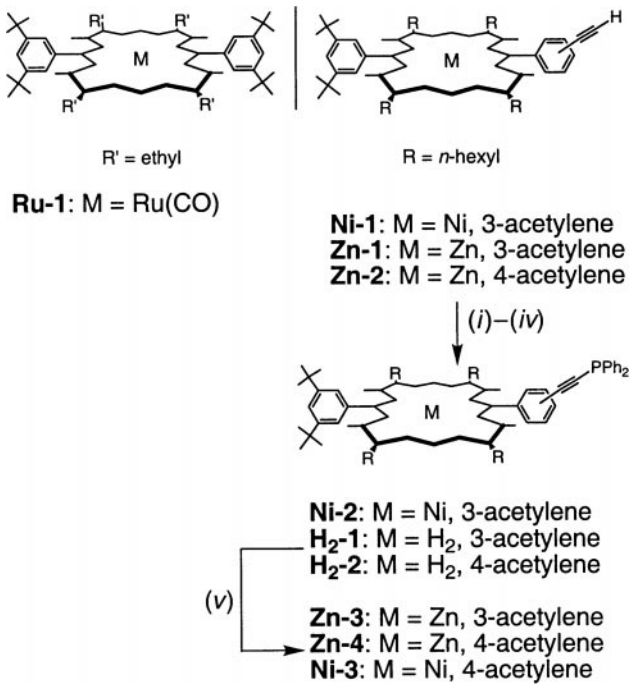
In pursuit of new building blocks capable of forming supramolecular arrays *via* non-covalent interactions,[1] we have begun to explore the coordination of phosphines to Ru(II) porphyrins. In particular, we describe here the synthesis of metalloporphyrins linked *via* rigid alkynes to phosphine groups, which can then generate oligoporphyrin arrays by coordinating to Ru(II) porphyrins. To our knowledge no such compounds have been reported previously.

Phosphine donors are known to coordinate strongly to Ru(II).[2] In porphyrins, the octahedral geometry of Ru is satisfied by the four equatorial nitrogens of the heterocyclic core, CO and a molecule of solvent, which can be exchanged by a suitable ligand at ambient temperature to produce mono(phosphine) complexes, while bis(phosphine) complexes are obtained *via* thermal displacement of the CO ligand.[3] To date, Ru(II) porphyrins have been used to study the oxidation of phosphines to phosphine oxides;[4] if the porphyrin has a chiral superstructure, then enantioselectivity can be obtained when binding racemic phosphines.[5]

Bis(triarylphosphine) complexes of ruthenium porphyrins have been reported to be labile in solution and dissociate to the corresponding mono-phosphine complex as revealed by UV/vis studies.[3a] After mixing 1 : 1 or 1 : 2 ratios of **Ru-1** with PPh_3 or PFu_3 (Fu = 2-furyl), both ^{1}H and ^{31}P NMR spectra exhibited extremely broad lines at room temperature, indicating a dynamic exchange between free and bound species on the chemical shift timescale, thus confirming the lability of these systems. In contrast, a sterically less hindered tertiary phosphine such as diphenylphosphinoacetylene (DPA) showed, upon addition of 1 equiv. to **Ru-1**, rapid formation of the mono-substituted complex at room temperature, exhibiting sharp signals in the ^{31}P NMR spectrum [δ(free) −34, δ(bound) −15]. A bis(phosphine) complex was observed when using 2 equiv. of DPA and the sample was warmed to 40 °C, as judged by the appearance of a sharp signal at δ (^{31}P) 2. As we have already synthesised alkyne-substituted porphyrins in our laboratory,[6] these porphyrins seem to be the precursors of choice to attach a diphenylphosphine, thus creating a supramolecular building block with reduced steric hindrance compared with triarylphosphines.

To synthesise phosphine-substituted porphyrins, we envisaged deprotonation of the alkynes **Zn-1**, **Zn-2** or **Ni-1** using lithium hexamethyldisilazane (LiHMDS) in THF (−78 °C, Scheme 1), followed by transmetallation using a transition metal chloride to produce a Grignard-type alkynyl complex.† The reactivity of alkynyl metal complexes was found to increase in the order Na < Li ≈ Cu(II) ≈ Zn(II) ≪ Mg(II) ≈ Ce(III) ≪ Cd(II). This reagent reacts *in situ* with an electrophilic phosphorus such as $ClPPh_2$ to give, after acidic workup, H_2**-1**, H_2**-2** or **Ni-2**, respectively.‡ The phosphines were protected *in situ* by treatment with a slight excess of BH_3SMe_2 at −30 °C to prevent oxidation during work-up and purification.[7] Nevertheless, the reactions are best carried out using standard Schlenk techniques. Changing the central metal from Zn(II) to Ni(II) did not prevent phosphine oxidation, but the reaction was significantly retarded. The phosphine oxides, however, can be reduced using Cl_3SiH in toluene.[8] Metallation of the free base porphyrin phosphines is easily achieved by standard procedures using the metal acetates to yield quantitatively the corresponding Zn and Ni porphyrins.

The ^{31}P NMR shifts for the phosphine porphyrins are diagnostic for distinguishing the phosphines (δ − 32.2) from the phosphine oxides (δ 8.9); the nature of the metal and the substitution pattern did not show any influence on the chemical shift of either the phosphine or phosphine oxide. The ^{31}P NMR resonance for the zinc phosphine series was slightly broadened in $CDCl_3$ at room temperature, but sharpened either upon cooling to −20 °C or by recording the spectrum in C_5D_5N. This indicates a dynamic yet weak complexation of



Scheme 1 Reagents and conditions: (*i*) LiHMDS, $CdCl_2$, THF, −78 °C; (*ii*) $ClPPh_2$, −78 °C → rt; (*iii*) BH_3SMe_2, −30 °C; (*iv*) $HNEt_2$, 50 °C; (*v*) $M(OAc)_2$, $CHCl_3$–MeOH, heat.

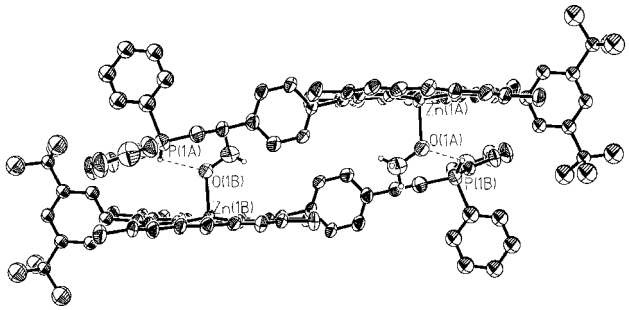


Fig. 1 X-Ray structure of the **Zn-4** dimer. Thermal ellipsoids are drawn at the 50% probability level. H atoms (except for phosphine and Zn-bound methanol) and hexyl sidechains are omitted for clarity; dashed line indicates H bonding. Alternative disordered orientations are not shown.

the phosphine to the zinc to give dimerisation; this was not observed in the free base or nickel series. The UV/vis spectra of **Zn-4** (10^{-6} M in toluene) did not show a red shift of the B-band absorption compared to its oxide, which does not form any complexes with **Ru-1** in solution (as judged by ^{31}P NMR). The Q-bands are red shifted by 2 nm, and the ratio of the intensities $Q(\alpha)/Q(\beta)$ increased from 0.56 for the oxide to 0.64 for **Zn-4**. Since these differences are small, dimerisation is a negligible phenomenon in dilute solutions, because phosphine ligands on zinc porphyrins cause large red shifts (Δ *ca.* 10 nm) and substantial changes in the intensity ratios (Δ *ca.* 0.3) due to their σ-donor properties.[9] Also the free base and nickel phosphines exhibited essentially identical absorption spectra as their phosphine oxide counterparts.

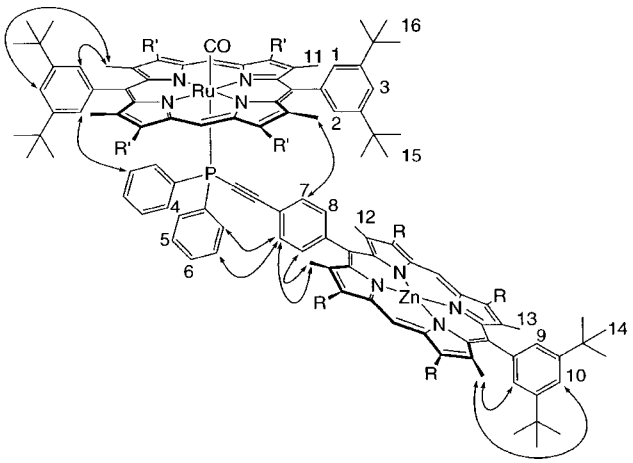


Fig. 2 Selected nOe connectivities for [**Ru-1**/**Zn-4**].

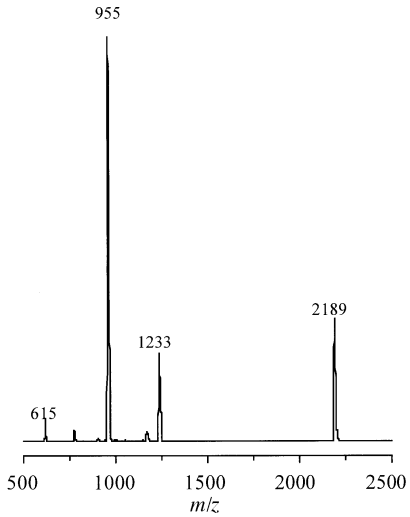


Fig. 3 MALDI-TOF mass spectrum of a 5 : 1 mixture ($CHCl_3$) of **Ni-2** with **Ru-1**, neat sample. H_2tpp (*m*/*z* 615.25) served as internal reference; for peak assignments see text.

In the solid state, however, formation of a dimeric structure was observed by X-ray analysis of a suitable crystal of **Zn-4** (Fig. 1),§ where the most striking observation is deprotonation of a metal-bound methanol by the phosphine; the proton bound to the phosphorus could be located from significant residual electron density in the difference Fourier map and (isotropically) refined. The dimer is cooperatively supported by two equivalent hydrogen bonds between the protonated phosphine and the zinc bound methoxide (P–H···O, 2.67 Å; P–H, 1.36 Å). The P–H bond length is consistent with that in other reported protonated phosphines.[10] Although there are reported examples of deprotonated zinc-bound alcohols,[11] the structure of **Zn-4** is to our knowledge the first zinc-bound methoxide to be deprotonated by a phosphine and held together by P–H···O bonds. Indeed, the structure is reminiscent of the active sites of some of the hydrolytic zinc enzymes such as carboxypeptidase A and carbonic anhydrase.[12]

When phosphine porphyrins are mixed with 1 equiv. of **Ru-1** in $CDCl_3$, complexes [**Ru-1**/Por-PPh_2] (Por = porphyrin) are readily formed with a distinct 1 : 1 stoichiometry, showing sharp lines in the ^{31}P NMR spectra. The resonances for the complexed phosphines are downfield shifted and appear at $\delta(^{31}P)$ −13.2. Again, the nature of the metal in the phosphine porphyrin and the substitution pattern had no influence on the chemical shift difference ($\Delta\delta$ 19 upon complexation), but complexation of the phosphines to ruthenium leads to more stable complexes compared to complexation to zinc, as indicated by the narrower resonance. The proton signals of the phosphine residue were typically upfield shifted in the complexes as a result of the ring current of the aromatic porphyrin core, and the observation of diagnostic nOe connectivities between the phosphine porphyrin and **Ru-1** in the NOESY spectrum of [**Ru-1**/**Zn-4**] confirmed the coordination, presumably at an angle as depicted in Fig. 2. Inequivalency of the α and β sides of the **Ru-1** moiety can be seen by the different proton chemical shifts of the H-15 and H-16 Bu^t groups at the periphery of **Ru-1**, whereas the H-14 Bu^t groups of the phosphine porphyrin moiety appear equivalent. The UV/vis spectra of 1 : 1 mixtures of the phosphine porphyrins with **Ru-1** proved to be a superposition of the absorption spectra of the individual components; therefore the conjugates do not exhibit exciton coupling in the electronic ground state.[13] We attribute the absence of electronic communication to the relatively large distance between the chromophores, as confirmed by the unaffected N–H NMR resonance in [**Ru-1**/H_2-**2**].

Mixing 2 equiv. of phosphine porphyrin with **Ru-1** and boiling the $CDCl_3$ solution for 5 h resulted in formation of a new species assigned to trimeric porphyrin arrays of the composition [Por-PPh_2/**Ru-1**/Por-PPh_2] and showing a ^{31}P NMR resonance at δ 3.0. As no free phosphine was detected in the ^{31}P NMR spectra, the formation of the trimeric complexes was virtually complete. The even larger downfield shift compared to the dimeric arrays is indicative of the much weaker π-backbonding ability of a phosphine ligand on the ruthenium compared to a CO ligand in a *trans* position. The diagnostic proton resonances were again the aryl proton signals of the phosphine residues, which have essentially identical chemical shifts as in the dimeric arrays. The isochronic resonances of H-15 and H-16 are indicative of an equivalent *trans* coordination of the two phosphines to **Ru-1**. As in the dimeric arrays, the measured UV/vis spectra of the trimeric complexes could be perfectly reproduced by calculation of the additive superposition of the individual components.

The MALDI-TOF mass spectrum of a 1 : 1 mixture of **Ni-2** with **Ru-1** showed signals at *m*/*z* 955 (**Ru-1** − CO, calcd. 955), 1234 (**Ni-2**, calcd. 1231), 1913 [(**Ru-1** − CO) dimer, calcd. 1910] and 2191 ([**Ru-1**/**Ni-2**], calcd. 2186). Raising the amount of phosphine to a 5 : 1 ratio did not increase the relative amount of complex detected in the mass spectrum, nor were peaks observed that would indicate formation of the bis(phosphine) complex in the gas phase, but significantly Ru dimerisation was completely inhibited (Fig. 3).[14] This result shows that stable arrays between phosphine-substituted porphyrins and ruthenium porphyrins are not only readily formed in solution, but remain intact in the gas phase and can even be detected by MALDI-TOF mass spectrometry.

In summary, we have developed a general synthetic route to phosphine porphyrins, and an X-ray structure revealed unexpected deprotonation of Zn-bound methanol. The phosphine porphyrins are capable of forming dimeric and trimeric hetero-dimetallic porphyrin arrays in solution, the former being also stable in the gas phase, and contribute new supramolecular building blocks exhibiting orthogonal, non-covalent binding motifs when combined with suitable central metals.

Experimental

All experiments and manipulations were performed under an Ar atmosphere using freshly distilled and carefully degassed solvents. Standard Schlenk techniques in appropriate glassware were used throughout the experiments and analysis. The molecular mass of **Ru-1** (1014.42) was calculated as the MeOH solvate.

Syntheses

H_2-2. A solution of **Zn-2** (500 mg, 0.474 mmol) and dry $CdCl_2$ (261 mg, 1.42 mmol) in THF (20 ml) was cooled to −78 °C, and after addition of LiHMDS (1.42 ml, 1 M THF) the mixture was stirred for 2 h. Then $ClPPh_2$ (313 mg, 1.42 mmol) in THF (10 ml) was added dropwise at −78 °C and the red solution stirred for 30 min, warmed to rt and stirred for another 30 min. The mixture was again cooled to −30 °C, BH_3SMe_2 (108 mg, 1.42 mmol) was added, and the solution stirred for 45 min. The reaction was quenched by addition of H_2O–10 N HCl (20 + 2 ml) and stirred vigorously until homogenously green. Extraction from CH_2Cl_2–Na_2CO_3 sat. (50 + 100 ml) and evaporation of the dried ($MgSO_4$) organic phase yielded a brownish-red solid, which was chromatographed on silica (hexane–EtOAc–$CHCl_3$ 15 : 1 : 1). The **H_2-2**-BH_3 complex was dissolved in $HNEt_2$ (5 ml), heated to 50 °C for 45 min. and the solvent evaporated *in vacuo*. The solid was three times coevaporated with $CHCl_3$ (5 ml) and precipitated from toluene–acetonitrile (2 + 15 ml) at −20 °C overnight. Crystallisation from $CHCl_3$–methanol (2 + 15 ml) at −20 °C gave **H_2-2** (380 mg, 0.322 mmol, 68%) as brown crystals. R_f (hexane–EtOAc 5 : 1): **Zn-2** 0.70, **H_2-2** 0.68, **H_2-2**-BH_3 0.52.

Selected data for **H_2-2:** UV/vis (toluene, λ/nm, lg ε): 412 (5.39), 506 (5.01), 540 (3.79), 576 (3.95), 584 (3.85). ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 10.23 (s, 2 H, *meso*-H), 8.08 (d, *J* 7.5 Hz, 2 H, H-8), 7.92 (d, *J* 7.5 Hz, 2 H, H-7), 7.91 (s, 2 H, H-9), 7.83 (d, *J* 7.7 Hz, 4 H, H-4), 7.81 (s, 1 H, H-10), 7.47 (dd, J_1 7.7 Hz, J_2 6.8 Hz, 4 H, H-5), 7.43 (d, *J* 6.8 Hz, 2 H, H-6), 3.98 [br s, 8 H, $CH_2(CH_2)_4CH_3$], 2.53 (s, 6 H, H-12), 2.50 (s, 6 H, H-13), 2.19 [br s, 8 H, $CH_2CH_2(CH_2)_3CH_3$], 1.73 [t, *J* 6.5 Hz, $(CH_2)_2CH_2(CH_2)_2CH_3$], 1.50 (s, 18 H, H-14), 1.49 [m, 8 H, $(CH_2)_3CH_2CH_2CH_3$], 1.36 [m, 8 H, $(CH_3)_4CH_2CH_3$], 0.90 [t, *J* 7.1 Hz, 12 H, $(CH_2)_5CH_3$], −2.39 and −2.41 (2 × s, 2 H, NH). ^{13}C NMR ($CDCl_3$, 125.7 MHz): δ = 149.9 (s), 145.3 (s), 144.7 (s), 143.4 (s), 143.1 (s), 141.5 (s), 141.4 (s), 140.9 (s), 136.6 (s), 136.3 (s, $J_{P\text{-}C}$ 6.3 Hz), 135.7 (s), 133.1 (d), 132.8 (d), 132.6 (d), 131.0 (d), 129.1 (d), 128.7 (d, $J_{P\text{-}C}$ 7.5 Hz), 127.5 (d), 122.6 (s), 121.1 (d), 119.6 (s), 116.3 (s, C≡C, $J_{P\text{-}C}$ 28.8 Hz), 96.7 (d), 86.4 (s, C≡C), 34.9 (t), 33.0 (t), 31.7 (t), 31.6 (t), 31.4 (q), 29.7 (t), 29.6 (t), 26.5 (t), 22.5 (t), 22.4 (t), 14.8 (q), 14.0 (q), 13.9 (q). ^{31}P NMR ($CDCl_3$, 161.97 MHz): δ = −32.2. MALDI-TOF MS: calcd. 1176, found 1174.

An analogous reaction using **Ni-1** yielded directly **Ni-2** in 75% yield.

Metallation reactions. Metallation of **H_2-2** was achieved by refluxing a $CHCl_3$–MeOH solution (5 + 1 ml) of **H_2-2** (100 mg, 0.085 mmol) with $Zn(OAc)_2 \cdot 2H_2O$ (187 mg, 0.85 mmol) or $Ni(OAc)_2 \cdot 4H_2O$ (211 mg, 0.85 mmol) for 1 h (Zn) or 4 h (Ni). After evaporation of the solvent, the residue was extracted with $CHCl_3$ until the filtrate appeared colourless. Crystallisation from $CHCl_3$–MeOH (1 + 15 ml) at −20 °C overnight gave the pure metallated phosphine porphyrins in quantitative yields.

Selected data for **Zn-4**: UV/vis (toluene, λ/nm, lg ε): 414 (5.53), 538 (4.28), 574 (4.09). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 10.20 (s, 2 H, *meso*-H), 8.10 (d, *J* 8.0 Hz, 2 H, H-8), 7.96 (d, *J* 1.8 Hz, 2 H, H-9), 7.94 (d, *J* 8.0 Hz, 2 H, H-7), 7.81 (m, 4 H, H-4), 7.78 (d, *J* 1.8 Hz, 1 H, H-10), 7.46 (m, 6 H, H-5/6), 3.99 [m, 8 H, $CH_2(CH_2)_4CH_3$], 2.51 (s, 6 H, H-12), 2.46 (s, 6 H, H-13), 2.21 [m, 8 H, $CH_2CH_2(CH_2)_3CH_3$], 1.78 [m, 8 H, $(CH_2)_2CH_2(CH_2)_2CH_3$], 1.54 (s, 18 H, H-14), 1.49 [m, 8 H, $(CH_2)_3CH_2CH_2CH_3$], 1.37 [m, 8 H, $(CH_3)_4CH_2CH_3$], 0.91 [t, *J* 7.3 Hz, 12 H, $(CH_2)_5CH_3$]. ^{31}P NMR ($CDCl_3$, 161.97 MHz): δ = −32.2. MALDI-TOF MS: calcd. 1240, found 1237.

Selected data for **Ni-3**: UV/vis (toluene, λ/nm, lg ε): 410 (5.35), 530 (4.19), 564 (4.33). ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 9.42 (s, 2 H, *meso*-H), 7.83 (d, *J* 8.0 Hz, 2 H, H-8), 7.79 (d, *J* 8.0 Hz, 2 H, H-7), 7.76 (m, 4 H, H-4), 7.68 (d, *J* 1.7 Hz, 2 H, H-9), 7.67 (d, *J* 1.7 Hz, 1 H, H-10), 7.42 (m, 6 H, H-5/6), 3.63 [t, *J* 7.6 Hz, 8 H, $CH_2(CH_2)_4CH_3$], 2.25 (s, 6 H, H-12), 2.23 (s, 6 H, H-13), 2.20 [qn, *J* 7.1 Hz, 8 H, $CH_2CH_2(CH_2)_3CH_3$], 1.58 [p, *J* 7.5 Hz, 8 H, $(CH_2)_2CH_2(CH_2)_2CH_3$], 1.42 (s, 18 H, H-14), 1.34 [m, 16 H, $(CH_2)_3CH_2CH_2CH_3/(CH_3)_4CH_2CH_3$], 0.88 [dt, J_1 2.3 Hz, J_2 7.2 Hz, 12 H, $(CH_2)_5CH_3$]. ^{31}P NMR ($CDCl_3$, 161.97 MHz): δ = −32.2. MALDI-TOF MS: calcd. 1233, found 1231.

Coordination compounds

[Ru-1/Ni-3]. NMR: **Ru-1** (5.00 mg, 4.93 μmol) in $CDCl_3$ (0.4 ml) and **Ni-3** (6.08 mg, 4.93 μmol) in $CDCl_3$ (0.3 ml) were mixed in a NMR tube fitted with a teflon seal and left to equilibrate for 1 h. ^{1}H NMR (500 MHz): δ = 9.87 (s, 2 H, **Ru-1** *meso*-H), 9.44 (s, 2 H, **Ni-3** *meso*-H), 7.83 (br s, 2 H, H-1), 7.76 (d, *J* 7.9, 2 H, H-8), 7.69 (d, *J* 1.6 Hz, 2 H, H-3), 7.68 (d, *J* 1.6 Hz, 1 H, H-10), 7.43 (br s, 2 H, H-9), 7.24 (d, *J* 7.9 Hz, 2 H, H-7), 7.15 (m, 2 H, H-2), 6.84 (br t, 2 H, H-6), 6.53 (br t, 4 H, H-5), 4.29 (br t, 4 H, H-4), 3.87 (q, *J* 7.4 Hz, 8 H, **Ru-1** CH_2CH_3), 3.66 [q, *J* 8.6, 8 H, **Ni-3** $CH_2(CH_2)_4CH_3$], 2.29 (s, 6 H, H-12), 2.25 (s, 12 H, H-11), 2.20 (s, 6H, H-13), 1.90 [m, 8 H, **Ni-3** $CH_2CH_2(CH_2)_3CH_3$], 1.80 [t, *J* 7.4 Hz, 12 H, **Ru-1** CH_2CH_3], 1.62 [m, 8 H, **Ni-3** $(CH_2)_2CH_2(CH_2)_2CH_3$], 1.51 (s, 18 H, H-16), 1.47 (s, 18 H, H-15), 1.43 (s, 18 H, H-14), 1.35 [m, 16 H, **Ni-3** $(CH_2)_3CH_2CH_2CH_3/(CH_3)_4CH_2CH_3$], 0.89 [dt, J_1 3.2 Hz, J_2 7.3 Hz, 12 H, **Ni-3** $(CH_2)_5CH_3$]. ^{31}P NMR (161.97 MHz): δ = −13.2. MALDI-TOF MS: calcd. 2186, found 2191. UV/vis: One hundred microliters each of **Ru-1** and **Ni-3** solutions (2 mM in toluene) were mixed and diluted with 800 μl toluene. After equilibration for 1 h, 15 μl of the mixture were injected into 3.0 ml of toluene in a quartz cuvette. UV/vis

(λ/nm, lg ε): 406 (5.61), 526 (4.49), 560 (4.41). Calcd:¶ 406 (5.61), 526 (4.50), 560 (4.42).

[Ni-3/Ru-1/Ni-3]. NMR: **Ru-1** (3.00 mg, 2.95 μmol) and **Ni-3** (7.30 mg, 5.90 μmol) were dissolved in $CDCl_3$ (1.0 ml) and heated to reflux for 5 h. The resulting solution was directly used for measurements. ^{1}H NMR (500 MHz): $\delta = 9.53$ (br s, 2 H, **Ru-1** *meso*-H), 9.46 (br s, 4 H, **Ni-3** *meso*-H), 7.75 (d, *J* 7.9 Hz, 4 H, H-8), 7.72 (d, *J* 1.5 Hz, 2 H, H-3), 7.70 (d, *J* 1.7 Hz, 2 H, H-10), 7.61 (br s, 2 H, H-1), 7.41 (d, *J* 1.7 Hz, 4 H, H-9), 7.30 (d, *J* 7.9 Hz, 4 H, H-7), 7.17 (m, 2 H, H-2), 6.83 (t, *J* 7.2 Hz, 4 H, H-6), 6.55 (t, *J* 7.5, 8 H, H-5), 4.59 (m, 8 H, H-4), 3.74 (q, *J* 7.5, 8 H, **Ru-1** CH_2CH_3), 3.68 [m, 16 H, **Ni-3** $CH_2(CH_2)_4CH_3$], 2.36 (s, 12 H, H-12), 2.22 (s, 12 H, H-13), 2.10 (br s, 12 H, H-11), 2.04 [m, 16 H, **Ni-3** $CH_2CH_2(CH_2)_3CH_3$], 1.77 (t, *J* 7.5 Hz, 12 H, **Ru-1** CH_2CH_3), 1.65 [m, 16 H, **Ni-3** $(CH_2)_2CH_2(CH_2)_2CH_3$], 1.50 (s, 36 H, H-15/H-16), 1.45 (s, 36 H, H-14), 1.44 [m, 16 H, **Ni-3** $(CH_2)_3CH_2CH_2CH_3$], 1.36 [m, 16 H, $(CH_3)_4CH_2CH_3$], 0.92 [dt, J_1 1.4 Hz, J_2 7.2 Hz, 12 H, **Ni-3** $(CH_2)_5CH_3$]. ^{31}P NMR (161.97 MHz): $\delta = 3.0$. UV/vis: One hundred microliters of a **Ru-1** solution (2 mM in toluene) and 200 μl **Ni-3** solution (2 mM in toluene) were mixed and diluted with 700 μl toluene. After equilibration for 5 h at 70 °C, 15 μl of the mixture were injected into 3.0 ml of toluene in a quartz cuvette. UV/vis (λ/nm, lg ε): 408 (5.78), 526 (4.75), 564 (4.75). Calcd:¶ 408 (5.78), 526 (4.67), 560 (4.67).

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Notes and references

† The Na^+ alkynyl reagent was formed by deprotonation of the alkyne using NaH, while the Mg^{2+} complex was formed by treatment of the alkyne with EtMgBr.

‡ Preliminary experiments showed that reaction of the alkynyl-Grignard reagent with chloro diethyl phosphate followed by reduction using LAH yields the corresponding primary phosphine, which is also a potentially useful building block.

§ Crystals were grown from layered addition of methanol to a sat. CH_2Cl_2 solution. Crystal data for $C_{83}H_{105}N_4OPZn$, **Zn-4**: $M = 1271.05$, triclinic, $a = 15.835(2)$, $b = 17.762(2)$, $c = 14.503(2)$ Å, $\alpha = 92.220(1)°$, $\beta = 97.390(1)°$, $\gamma = 99.47(1)°$, $U = 3631.6(8)$ Å^3, $T = 180$ K, space group $P\bar{1}$, $Z = 2$, μ(Mo-Kα) = 0.408 mm^{-1}, 17 797 total reflections, 11 350 independent reflections, $R_{int} = 0.0903$, $R_1 = 0.1040$, $R(\sigma)$ 0.1553, $wR_2 = 0.3015$ (all data). Non-H atoms were refined anisotropically; H atoms were refined isotropically using a riding model except for the P-bound proton, which was refined isotropically from electron density. The hexyl sidechains, one aryl residue on P and the di-Bu^t-aryl substituent showed disorder and could be refined in two non-equally populated positions. CCDC reference number 440/174. See http://www.rsc.org/suppdata/nj/b0/b000482k/ for crystallographic files in .cif format.

¶ UV/vis data for **Ru-1** (toluene, λ/nm, lg ε): 404 (5.36), 524 (4.21), 554 (4.04).

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