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Sterically Controlled Synthesis and Nucleophilic Substitution Reactions of Di- and Trimeric N-Heterocyclic Phosphenium Metal(0) Halides

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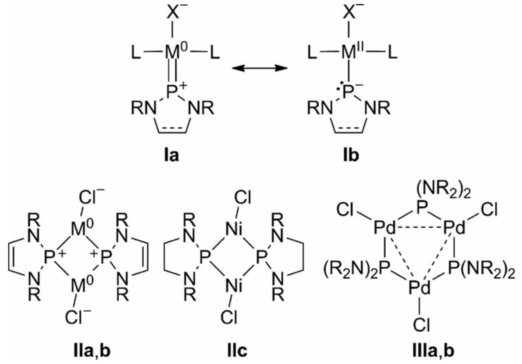
The reaction of symmetrical bis(diazaphospholenyl) compounds with $[MCl_2(cod)]$ (M = Pd, Pt; cod = 1,5-cyclooctadiene) has been used to prepare N-heterocyclic phosphenium (NHP) metal(0) halides $[M(NHP)Cl]_n$ with diverse N substituents. Characterisation by ESI-MS and NMR spectroscopy revealed that *N*-*t*Bu- and *N*-aryl-substituted NHP precursors yield trimeric ($n = 3$) and dimeric ($n = 2$) products, respectively; the degree of aggregation is presumably controlled by the different steric requirements of the NHP moiety. A single-crystal XRD study of a trimeric Pd complex confirmed the proposed constitution of the complexes with μ_2-bridging NHP and terminal chlorido ligands and allowed their metrical parameters to be analysed for the first time undisturbed by crystallographic disorder. Studies of ligand substitution and redistribution processes revealed that the complexes withstand exchange of the μ-bridging NHP units but tolerate substitution of the terminal chlorido ligands by other strong nucleophiles (SCN^-, I^-) with conservation of the oligomeric framework. Attempts to replace chlorido by thiolato ligands led to the discovery of a reaction between a phosphenium metal thiolate $[Pd(NHP)(SR)]_3$ and CH_2Cl_2 to give a formaldehyde dithioacetal $H_2C(SR)_2$ (R = benzyl). This reaction could be developed into a protocol for a C–S cross-coupling reaction in the presence of a catalytic amount of the phosphenium complex.

Introduction

Cyclic diaminophosphenium ions[1,2] (also known as N-heterocyclic phosphenium ions, NHP) have a long history in coordination chemistry because of their ability to act as σ-donor/π-acceptor ligands in transition-metal complexes.[3,4] A particularly interesting sub-class are complexes with group 10 metal atoms (M = Ni, Pd, Pt) of the general type $[MX(NHP)(L)_2]$ (**I**)[5,6] and $[MX(NHP)]_2$ (**II**;[7,8] L = phosphane, X = halide), which exhibit notable structural diversity and raise some scientifically interesting electron-counting difficulties (Scheme 1).[8] Thus, complexes **I** exist as two structural varieties in which the phosphorus atom in the NHP unit exists either in a trigonal-planar coordination sphere with a short P–M bond or in a pyramidal coordination with a lengthened P–M bond. Structures of the first type are considered to reflect the interaction of a cationic phosphenium ligand with a zero-valent metal atom to form a double bond in a bonding situation similar to Fischer-type carbene complexes (**Ia**; Scheme 1).[5,8] In contrast, the bonding in complexes of the second type has been interpreted in terms of the interaction of an anionic phosphide ligand with a divalent metal centre (**Ib**; Scheme 1), and the dichotomy between the two types of complexes is assumed to reflect a variable electron demand in the phosphenium ligands, which has allowed one to establish an analogy with the "non-innocent" behaviour of nitrosyl ligands.[6]



Scheme 1. Structures of phosphenium complexes $[MX(NHP)(L)_2]$ (**I**: R = aryl, X = halide, M = Pd, Pt, L = phosphane donor), $[MX(NHP)]_2$ (**IIa**: R = Dipp, M = Pd; **IIb**: R = Dipp, M = Pd; **IIc**: R = Mes, M = Ni) and $[PdCl\{P(NR_2)_2\}]_3$ (**IIIa**: R = Cy; **IIIb**: R = *i*Pr). Dipp = 2,6-$i Pr_2C_6H_3$.

Compounds **II** exhibit dimeric molecular structures held together by asymmetrically μ_2-bridging phosphenium li-

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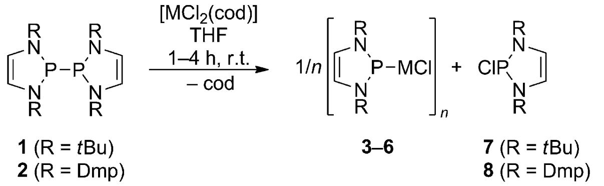
gands (Scheme 1). Based on the analysis of spectroscopic data and the outcome of ligand displacement reactions, which showed that they can act as viable sources of zero-valent metal atoms, these species were addressed as metal(0) halides with cationic phosphenium ligands.[7] Nonetheless, complexes **II** still bear a close structural resemblance to the trimers **III**, which were originally described on formal grounds as *triangulo* clusters of bridging phosphido ligands and divalent metal centres.[9]

Bearing in mind that the acyclic diaminophosphenium ions $[P(NR_2)_2]^+$, which are formal constituents of **III**, are much stronger electrophiles than the NHPs found in **II**, we were interested to establish whether the structural deviation between the two types of complexes is caused by different electronic properties of the ligand fragments, or by other factors such as steric influences. In addition, we wondered whether substitution of the halide functionalities in **II** could be used to access new multinuclear assemblies, or whether such attempts might, like reactions with phosphane donors,[7] induce a breakdown of the oligomeric structures. To address these questions, we synthesized an extended range of oligomeric NHP metal(0) halides of type **II** and studied their reactivity towards suitable nucleophiles. The results, which are reported herein, give account of the successful synthesis of trimeric NHP metal(0) halides, which are structural analogues of **III**, an unprecedented crystal structure of one such derivative, and their stoichiometric and catalytic anion substitution reactions, which culminated in the first catalytic application of a phosphenium metal halide in C–S cross-coupling reactions.

Results and Discussion

The synthesis of donor-free phosphenium metal(0) halides $[MCl(NHP)]_2$ (**IIa**,**b** in Scheme 1) has previously been described by several routes involving (1) the reaction of $[MCl_2(cod)]$ (M = Pd, Pt) with a suitable diphosphane, (2) the base-induced condensation of $[MCl_2(cod)]$ with a secondary phosphane and (3) the reaction of $[Pd_2(dba)_3]$ (dba = dibenzylideneacetone) with an N-heterocyclic chlorophosphane.[7] According to the first route, we treated $[MCl_2(cod)]$ with the symmetrical diphosphanes **1** or **2** to give the phosphenium complexes **3**–**6** and a stoichiometric amount of N-heterocyclic chlorophosphanes **7** and **8**, respectively (Scheme 2).



1 (R = *t*Bu)
2 (R = Dmp)
3–**6**
7 (R = *t*Bu)
8 (R = Dmp)

Scheme 2. Synthesis of donor-free phosphenium metal(0) halides **3**–**6** (**3**: R = *t*Bu, M = Pd, *n* = 3; **4**: R = *t*Bu, M = Pt, *n* = 3; **5**: R = Dmp, M = Pd, *n* = 2; **6**: R = Dmp, M = Pt, *n* = 2). Dmp = 2,6-$Me_2C_6H_3$; cod = cyclooctadiene).

The palladium complexes **3** and **5** precipitated from the reaction mixture and were easily isolated after washing with diethyl ether. The platinum complex **4** was obtained after evaporation of the solvent and washing of the residue several times with diethyl ether, whereas complex **6** was generated in a similar manner but could not be isolated in pure form as complete removal of all by-products proved unfeasible. All four compounds are deep-red, air-stable solids that do not dissolve in ethers (traces of the platinum complexes are soluble in THF) or hydrocarbons but are fairly soluble in dichloromethane. The products were unambiguously identified from NMR and positive-mode ESI-MS data. The mass spectra show dominant peaks of cations formed by cleavage of a chloride; the spectrum of **4** also exhibits the peak of a pseudo-molecular ion generated by attachment of Na^+ to the intact complex. Analysis of nominal masses and simulation of isotope patterns (see the Supporting Information) confirmed that *N*-*tert*-butyl-substituted complexes **3** and **4** have a trimeric nature, whereas the *N*-aryl derivative **5** is, like **IIa**,**b**, dimeric. The ^{31}P and ^{1}H NMR spectra show signals of a single NHP unit and thus confirm a symmetric molecular structure in which all the ligands are equivalent. A different degree of aggregation of the Pt complexes **4** and **6** is directly visible from the dissimilar ^{195}Pt satellite patterns in the ^{31}P NMR spectra. The habit of the spectrum of **6** matches that of **IIb**,[7] and the satellite lines are readily attributable to A_2X and A_2X_2 sub-spectra of $P_2(^{195}Pt)_1$ and $P_2(^{195}Pt)_2$ isotopomers. The spectrum of **4**, in contrast, exhibits a complicated pattern that was decomposed by spectral simulation into the AB_2X, $ABB'XX'$ and $AA'A''XX'X''$ sub-spectra expected for the $P_3(^{195}Pt)_n$ (A, B = ^{31}P; X = ^{195}Pt; n = 1–3) isotopomers of a trimer (Figure 1a). Complementary splitting was also observed in the ^{195}Pt NMR spectrum (Figure 1b). Analysis of the multiplicities associated with the large $^{1}J(^{31}P,^{195}Pt)$ couplings confirmed, as in **IIb**, the μ_2-bridging coordination of the NHP ligands.

The ^{31}P chemical shifts of **3**–**6** in general fall in the downfield region ($\delta > 200$ ppm), which is typical of the majority of related phosphenium complexes[5–9] but not for **IIb**, which exhibits a very unusual ^{31}P chemical shift at δ = 26.9 ppm,[7] nearly 200 ppm lower than in the other complexes. We attribute this amazing deviation to the rather special electronic situation[7] that presumably makes this compound an outlier. The finding that platinum complexes **4** and **6** display larger chemical shifts than their palladium analogues **3** and **5** is likewise slightly unusual and contrasts both common experience and the known trend for phosphane-stabilized Pd and Pt complexes of type **I**.[6] We therefore wish to refrain from a further interpretation of any trends in chemical shifts, because a meaningful explanation of the observed irregularities needs further studies that are beyond the scope of this work. The value of $^{1}J(^{31}P,^{195}Pt)$ in **4** (2304 Hz) is less than that in **6** (3954 Hz) and **IIb** (5000 Hz), presumably as a consequence of the higher nuclearity of the complex.

The suggested structure of **3** was confirmed by a single-crystal X-ray diffraction study of a THF solvate obtained by slow crystallization from the reaction mixture. The com-

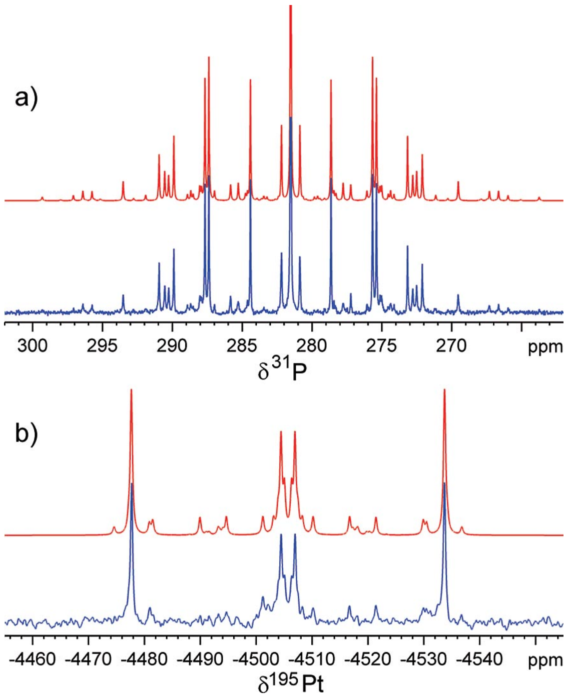


Figure 1. Experimental (blue traces) and simulated (red traces) $^{31}P\{^1H\}$ (top, the intense line of the parent isotopomer was cut off) and $^{195}Pt\{^1H\}$ NMR spectra (bottom) of **4**. The ^{31}P NMR spectrum was simulated as a superposition of A_3, AB_2X, $ABB'XX'$ and $AA'A''XX'X''$ sub-spectra and the ^{195}Pt spectrum as a superposition of AB_2X and $ABB'XX'$ sub-spectra, which were weighted appropriately to reflect the different natural abundances of individual isotopomers. Parameters used for simulation: $\delta^{31}P$ = 281.5 ppm, $\delta^{195}Pt$ = –4505 ppm; $^1J_{PtP}$ = 2304 Hz, $^2J_{PP}$ = 490 Hz, $^3J_{PtP}$ = 211 Hz, $^2J_{PtPt}$ = 129 Hz.

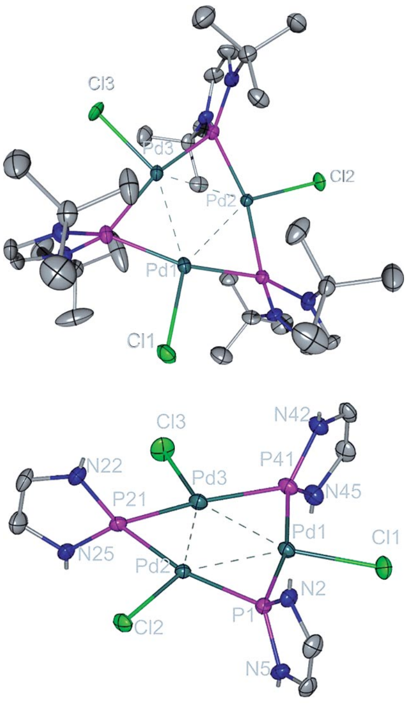


Figure 2. View of the molecular structure of **3** (top) and a reduced plot displaying only atoms in the Pd_3Cl_3 core and diazaphospholene rings (bottom). Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected distances [Å]: Pd1–P1 2.2770(12), Pd1–P41 2.2901(12), Pd1–Cl1 2.4227(12), Pd1–Pd3 2.7464(5), Pd1–Pd2 2.7743(5), Pd2–P1 2.2893(12), Pd2–P21 2.2904(11), Pd2–Cl2 2.4044(11), Pd2–Pd3 2.7643(5), Pd3–P21 2.2622(12), Pd3–P41 2.2925(13), Pd3–Cl3 2.4156(11), P1–N5 1.669(4), P1–N2 1.682(4), N2–C3 1.407(6), C3–C4 1.317(7), C4–N5 1.407(6), P21–N25 1.660(4), P21–N22 1.677(4), N22–C23 1.384(6), C23–C24 1.333(7), C24–N25 1.384(6), P41–N45 1.673(4), P41–N42 1.676(4), N42–C43 1.379(6), C43–C44 1.328(7), C44–N45 1.388(6).

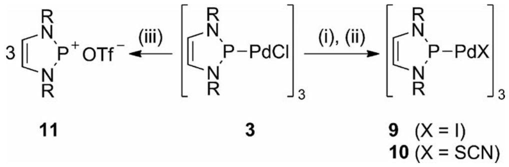
plex crystallizes in the orthorhombic space group $P2_12_12_1$ and contains isolated molecules (Figure 2, top) that exhibit a star-shaped structure similar to that of **IIIb**,[9] but lacks the strong disorder that had prevented a detailed evaluation of the structural features of this species.

The core of each complex (Figure 2, bottom) consists of a planar Pd_3P_3 unit (mean deviation from the least-squares plane 0.025 Å) in which the phosphorus atoms form a rather regular triangle and the metal atoms bisect the sides of this triangle. The Pd–Cl bonds lie nearly in the core plane (angles with the least-squares plane are 2.7–6.8°). The metal atoms adopt a planar, distorted T-shaped coordination sphere [the P–Pd–P units with angles between 164.0(1) and 165.7(1)° form the bar of the T]. The Pd–P distances [2.262(1)–2.293(1) Å, average 2.284 Å] are marginally longer than in **IIa** [2.2738(4) and 2.2401(4) Å, average 2.257 Å[7]]. The Pd–Cl distances [2.404(1)–2.423(1) Å, average 2.414 Å] lie between the corresponding distance in **IIa** [2.3361(4) Å[7]] and a **Ib**-type complex [2.4530(11) Å[6]]. The diazaphospholene rings are planar (mean deviation from the least-squares planes 0.010 Å) and perpendicular to the P_3Pd_3 plane (dihedral angles 86.9–88.9°). Intra-ligand bond lengths (cf. Figure 2) match the values in **IIa**[7] and known chlorodiazaphospholenes and NHPs.[10] The arrangement of NHP units in **3** comes close to a symmetrical μ-bridging coordination, which contrasts the definitely unsymmetrical binding mode in **II**.[7,8] Finally, the metal–metal distances in **3** [2.746(1)–2.774(1) Å, average 2.762 Å] are longer than in **IIa** [2.6410(2) Å[7]]. Even though these values are still in the range of Pd–Pd bonds in dimeric Pd^I complexes (2.72 ± 0.1 Å[11]), direct metal–metal bonding seems even less likely than in **IIa**.[7]

In summary, the molecular structure of **3** bears a close resemblance to those of the dimeric phosphenium metal(0) halide **IIa** and the *triangulo* cluster **IIIb**, but shows a nearly symmetric μ-bridging coordination of the NHP units. The observation that NHP units can stabilize both dinuclear (**IIa**) and trinuclear (**3**) assemblies has led us to conclude that the degree of aggregation in these complexes is not determined by different electronic properties of the bridging diaminophosphanyl units but rather by steric influences: it seems that paddle-shaped *N*-aryl substituents (in **II**, **5** and **6**) favour the formation of dimers, whereas more globular (and possibly sterically less-demanding) *N*-alkyl groups (in **IIIb**, **3** and **4**) tolerate a higher degree of association.

The coexistence of di- and trinuclear metal(0) halides with unlike NHP ligands stimulated us to explore the prospect of generating mixed species through intermolecular exchange processes. However, a ^{31}P NMR spectroscopic analysis of a CH_2Cl_2 solution containing equimolar amounts of trinuclear **3** and dinuclear **5** revealed that even after a prolonged time (5 d) signals from the starting materials were exclusively observed. The failure to detect even trace amounts of reaction products suggested that cluster interchange by the scrambling of μ-bridging ligands is apparently not possible.

Considering that the previously mentioned elongation of Pd–Cl distances in **3** might imply a certain bond weakening, we believed that nucleophilic replacement of the terminal ligands should offer a more promising approach to cluster modification. We therefore studied the behaviour of **3** towards suitable nucleophiles and found that the chloride ions are indeed easily displaced by soft nucleophiles such as iodide or thiocyanate (Scheme 3).[12] No ligand substitution but decomposition to give a black precipitate of palladium and phosphenium triflate **11** (Scheme 3; identified by its known chemical shift[10]) was observed upon treatment of **3** with excess trimethylsilyl triflate. We assume that this reaction is likewise initiated by Cl/OTf exchange, but that a hypothetical NHP palladium(0) triflate is unstable and decomposes. This finding is in line with previous results,[5,13] which indicated that the "push–pull" effect exerted by a combined action of π-acceptor and strong σ-donor ligands is essential for the stabilization of the zero-valent metal atom in these complexes.



Scheme 3. Substitution reactions of **3**. Reagents and conditions: (i) excess Me_3SiI, THF, 2 h, –78 °C; (ii) excess NaSCN, THF, 1 h, room temp.; (iii) excess Me_3SiOTf, room temp.

Substitution products **9** and **10** were isolated after appropriate workup as red to purple air-stable solids that are more soluble in THF than starting material **3**. The identity of the complexes was confirmed, as before, by ^{31}P NMR and ESI-MS data (see the Exp. Sect.). Analysis of the MS data indicated that the trinuclear assembly had in all cases remained intact. The IR spectrum of thiocyanato complex **10** contains two bands at 2089 and 2106 cm^{-1}, which have been attributable to ν_{CN} stretching modes but did not allow clear discrimination between N- and S-bound ligands.[14] A clear assignment was finally made on the basis of a preliminary single-crystal X-ray diffraction study. Even though the limited quality of the data (not deposited) impeded satisfactory structure refinement, the data proved the presence of a trinuclear complex with a shape similar to that of **3** and terminal *S*-thiocyanato ligands (see the Supporting Information).

Monitoring of the progress of the halide exchange by ^{31}P NMR spectroscopy permitted the detection of transient intermediates and suggested that the reaction proceeds in a stepwise manner. This was confirmed in a detailed study of a CH_2Cl_2 solution containing a mixture of chlorido complex **3** and iodido complex **9**, which revealed that the starting materials reacted eventually to form new products. Simulation allowed us to interpret the observed spectral pattern (Figure 3) as a superposition of the A_3 spin systems of the starting materials with two A_2B spin systems, which we have assigned to trinuclear complexes with Cl_2I and ClI_2 substitution patterns. The formation of new products is readily explained as resulting from stepwise halide transfer between the starting materials, and the failure to detect any further intermediates suggests that the trinuclear structures of the starting materials is conserved in all the reaction steps. Even though the halide exchange may proceed by direct interaction between trinuclear clusters, we cannot exclude that it is promoted by trace amounts of halide impurities, and the apparent ligand redistribution is merely a special case of nucleophilic substitution.

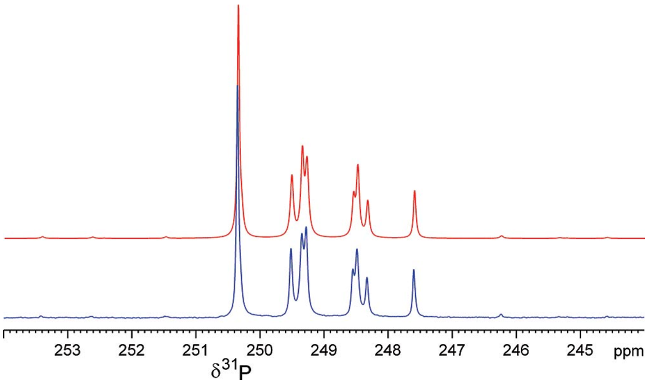
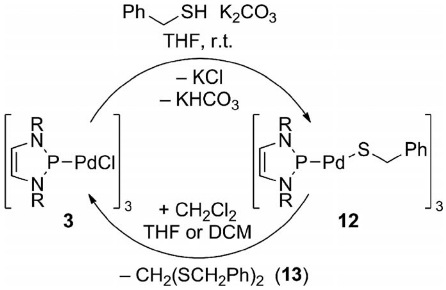


Figure 3. Experimental (blue trace) and simulated (red trace) $^{31}P\{^1H\}$ NMR spectra of a mixture of complexes $[Pd_3(NHP)_3Cl_nI_{3-n}]$ (n = 0–3; NHP = 1,3-di-*tert*-butyldiazaphospholenium) in CH_2Cl_2. The spectra of the homoleptic complexes were simulated as A_3 (Cl_3: δ = 250.4 ppm, molar fraction 0.28; I_3: δ = 247.6 ppm, molar fraction 0.05) and those of heteroleptic complexes as AB_2 spin systems (Cl_2I: δ = 250.3 and 248.9 ppm, J = 373.9 Hz, molar fraction 0.44; ClI_2: δ = 248.9 and 247.6 ppm, J = 359.9 Hz, molar fraction 0.24).

The successful synthesis of **10** stimulated us to investigate also the reactions of **3** with other sulfur nucleophiles. Treatment of a THF solution of **3** with benzylthiol in the presence of K_2CO_3 produced a purple precipitate clearly containing a mixture of the desired substitution product and inorganic salts formed as by-products. Purification of the solid material was prevented by its very low solubility in most aprotic solvents and its chemical instability in DMSO or protic media. The ^{31}P NMR spectrum of a suspension in CH_2Cl_2 allowed us to identify the signal of the substitution product as a singlet with a chemical shift (δ = 255 ppm) similar to that of **3** (δ = 250 ppm). Surprisingly, this solution proved unstable, and the species initially present transmuted slowly via spectroscopically detectable intermediates into **3** (see the Supporting Information). These observations led us to conclude that the reaction of **3** with benzylthiol and K_2CO_3 affords thiolato complex **12**, which then interacts with CH_2Cl_2 to regenerate **3** by the stepwise substitution of thiolato by chlorido ligands. The by-product of this process was later identified as formaldehyde dithioacetal **13** (Scheme 4).



Scheme 4. Mutual transformation between **3** and benzylthiolato complex **12** and the mechanism proposed for the catalytic C–S cross-coupling reaction between PhCH$_2$SH and CH$_2$Cl$_2$. DCM = CH$_2$Cl$_2$.

Combining the formation of **12** from **3** with the regeneration of the starting material by reaction with CH$_2$Cl$_2$ forms a cycle that should in principle allow catalytic base-induced coupling of benzylthiol and dichloromethane at room temperature. To verify this hypothesis, we studied the reaction of CH$_2$Cl$_2$ with 2 equiv. of PhCH$_2$SH and K$_2$CO$_3$ in anhydrous THF at ambient temperature. Whereas only traces of the starting materials reacted in the absence of a catalyst, the thiol was quantitatively consumed within 72 h when 5 mol-% of **3** were present. The bis(benzylthio)methane (**13**) formed was isolated in 82% yield and identified by ^{1}H NMR spectroscopy. If one considers that dichloromethane was employed as stoichiometric reactant rather than solvent, the performance of this catalytic process can be considered to compare with that of other known cross-coupling reactions between thiols and polyhaloalkanes, which are induced by strong organic bases,[15] microwave irradiation[16] or the action of catalytic amounts of rhodium complexes.[17]

Conclusions

We have established that the reactions of bis(diazaphospholenyl) compounds with [MCl$_2$(cod)] (M = Pd, Pt) can serve as a general synthetic route to both di- and trimeric phosphenium metal(0) halides [MCl(NHP)]$_n$ (n = 2, 3) with μ$_2$-bridging N-heterocyclic phosphenium (NHP) ligands. The degree of aggregation in the compounds studied seems to be controlled by the steric bulk of the N substituents in the NHP moiety. A single-crystal X-ray diffraction study of a trimeric complex revealed that the NHP ligand exhibits a more symmetrical μ-bridging coordination mode than in previously reported[7] dimeric complexes. The oligomers resist attempts to exchange the μ-bridging NHP ligands, but replacement of the terminal chloride ions by other (pseudo) halides is feasible and proceeds with conservation of the oligomeric core. This behaviour contrasts the reactions of **IIa**,**b** with neutral phosphanes, which proceed with rupture of the oligomers to yield mononuclear, donor-stabilized phosphenium metal chlorides or phosphane–metal(0) complexes, respectively.[7] An attempt to exchange the chlorido ligands of **3** for thiolates led to the discovery of a catalytic cross-coupling reaction between dichloromethane and benzylthiol to give a formaldehyde dithioacetal under very mild conditions. We are currently conducting a detailed study to explore the use of phosphenium metal halides in C–S cross-coupling reactions.

Experimental Section

General: All manipulations were carried out under dry argon using standard vacuum-line techniques. Solvents were dried by using standard procedures. NMR spectra were recorded with Bruker Avance 400 (^{1}H, 400.1 MHz; ^{13}C, 100.6 MHz; ^{31}P, 161.9 MHz; ^{195}Pt, 86.7 MHz) and Avance 250 (^{1}H, 250.1 MHz; ^{13}C, 62.9 MHz; ^{31}P, 101.2 MHz) NMR spectrometers at 303 K. Chemical shifts are referenced to external TMS (^{1}H, ^{13}C), 85% H$_3$PO$_4$ (Ξ = 40.480747 MHz, ^{31}P) and 1.2 M Na$_2$[PtCl$_6$] (Ξ = 21.496784 MHz, ^{195}Pt). Coupling constants are given as absolute values. Spectral simulations were carried out by using the WinDaisy program, which is part of the spectrometer software. (+)-ESI mass spectra were recorded in MeOH solutions with a Bruker Daltonics MicroTOF Q spectrometer. Elemental analyses were performed with a Thermo Micro Cube CHN/S analyser. Melting points were determined in sealed capillaries with a Büchi B-545 melting-point apparatus.

Synthesis of Palladium Complexes 3 and 5: A solution of the appropriate diphosphane (**1**:[18] 199 mg, 0.50 mmol; **2**: [18] 295 mg, 0.50 mmol) and [PdCl$_2$(cod)] (143 mg, 0.50 mmol) in anhydrous THF (5 mL) was stirred at room temperature for 1 h. The solution turned deep red. The precipitate formed was filtered off, washed with diethyl ether (2 × 10 mL) and dried in vacuo. In the case of **3**, prolonged storage of the filtrate produced a small batch of crystalline material that was suitable for single-crystal XRD analysis.

Complex 3: Yield: 153 mg (0.15 mmol, 90%), m.p. 306 °C (dec.). ^{1}H NMR (CDCl$_3$): δ = 7.14 (m, 6 H, CH-N), 1.65 (s, 54 H, CH_3) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 124.9 (m, CH-N), 59.1 [s, C(CH$_3$)], 32.0 (m, CH$_3$) ppm. ^{31}P{^{1}H} NMR (CDCl$_3$): δ = 249.0 (s) ppm. MS [(+)-ESI]: m/z (%) = 987.06 (100) [M – Cl]$^+$. C$_{30}$H$_{60}$Cl$_3$N$_6$P$_3$Pd$_3$ (1023.39): calcd. C 35.21, H 5.91, N 8.21; found C 34.57, H 6.10, N 7.92.

Complex 5: Yield: 153 mg (0.17 mmol, 70%), m.p. 306 °C (dec.). ^{1}H NMR (CDCl$_3$): δ = 7.60–6.90 (m, 12 H, C$_6$H$_3$), 6.84 (s, 4 H, CH-N), 2.44 (s, 24 H, CH_3) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 135.9 (s), 134.8 (s), 128.7 (m), 127.2 (m, CH-N), 19.1 (s, CH$_3$) ppm. ^{31}P{^{1}H} NMR (CDCl$_3$): δ = 214.7 (s) ppm. MS [(+)-ESI]: m/z (%) = 837.05 (100) [M – Cl – H$_2$]$^+$. C$_{36}$H$_{40}$Cl$_2$N$_4$P$_2$Pd$_2$ (874.43): calcd. C 49.45, H 4.61, N 6.41; found C 49.03, H 4.62, N 6.22.

Synthesis of Platinum Complexes 4 and 6: A solution of the appropriate diphosphane (**1**:[18] 199 mg, 0.50 mmol; **2**:[18] 295 mg, 0.50 mmol) and [PtCl$_2$(cod)] (187 mg, 0.50 mmol) in anhydrous THF (10 mL) was stirred at room temperature for 4 h. The solution turned deep red. The solvent was evaporated, and the remaining red solid was washed with diethyl ether (5 × 5 mL) and then with hexane (2 × 5 mL) and finally dried in vacuo.

Complex 4: Yield: 168 mg (0.13 mmol, 79%), m.p. >350 °C (dec.). ^{1}H NMR (CDCl$_3$): δ = 7.07 (m, 6 H, CH=N), 1.48 (s, 54 H, CH_3) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 123.4 (m, CH-N), 58.2 [s, C(CH$_3$)], 31.6 (m, CH$_3$) ppm. ^{31}P{^{1}H} NMR (CDCl$_3$): δ = 281.5 (s; simulation of the ^{195}Pt satellite spectrum gave: m, $^2J_{PP}$ = 490 Hz, $^1J_{PtP}$ = 2304 Hz, $^3J_{PtP}$ = 211 Hz) ppm. ^{195}Pt NMR (CDCl$_3$): δ =

–4505 (m, ${}^1J_{PtP}$ = 2304 Hz, ${}^3J_{PtP}$ = 211 Hz, ${}^2J_{PtPt}$ = 129 Hz) ppm. MS [(+)-ESI]: *m/z* (%) = 1311.21 (100) [M + Na]$^+$, 1253.20 (25) [M – Cl]$^+$. $C_{30}H_{40}Cl_3N_6P_3Pt_3$ (1269.21): calcd. C 27.95, H 4.69, N 6.52; found C 28.13, H 4.80, N 6.51.

Complex 6: Complex **6** could not be obtained in pure form as quantitative separation of by-products formed during the reaction was not possible. The complex was, however, unambiguously identified by spectroscopic data. ^{1}H NMR ($CDCl_3$): δ = 7.16–6.76 (m, 12 H, C_6H_3), 6.70 (s, 4 H, C*H*=N), 2.20 (s, 24 H, C*H*$_3$) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 247.0 (s, ${}^1J_{PtP}$ = 3954 Hz) ppm. ^{195}Pt NMR ($CDCl_3$): δ = –4369 (t, ${}^1J_{PtP}$ = 3969 Hz) ppm.

Synthesis of Complex 9: Me_3SiI (22 mg, 0.11 mmol) was added slowly through a syringe to a cooled (–78 °C) solution of complex **3** (37 mg, 36 µmol) in anhydrous THF (20 mL). The mixture was stirred for 1 h and warmed to room temperature. The solvent was then removed in vacuo, and the deep-red residue was washed hexane (2 × 5 mL) and dried in vacuo to yield 42 mg (32 µmol, 90 %) of the product. M.p. 306 °C (dec.). ^{1}H NMR ($CDCl_3$): δ = 7.23 (br. s, 6 H, C*H*=N), 1.60 (s, 54 H, C*H*$_3$) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 125.9 (m, *C*H-N), 58.7 [s, *C*(CH$_3$)], 31.0 (m, *C*H$_3$) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 247.9 (s) ppm. MS [(+)-ESI]: *m/z* (%) = 1320.83 (100) [M + Na]$^+$. $C_{30}H_{60}I_3N_6P_3Pd_3$ (1297.74): calcd. C 27.77, H 4.66, N 6.48; found C 26.87, H 4.82, N 6.89.

Synthesis of Complex 10: A solution of **3** (56 mg, 55 µmol) and NaSCN (14 mg, 176 µmol) in anhydrous THF (10 mL) was stirred at room temperature for 2 h. During this time the deep-red solution turned pink. Undissolved solids were removed by filtration and the filtrate concentrated to dryness. The solid residue was washed diethyl ether (2 × 5 mL) and dried under reduced pressure to yield 51 mg (47 µmol, 85 %) of the product. M.p. >350 °C (dec.). ^{1}H NMR ($CDCl_3$): δ = 7.36 (m, 6 H, C*H*=N), 1.70 (s, 54 H, C*H*$_3$) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 128.3 (m, *C*H-N), 124.2 (br., SCN), 60.1 [s, *C*(CH$_3$)], 32.1 (m, *C*H$_3$) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 243.3 (s) ppm. MS [(+)-ESI; solution in $CHCl_3$/MeCN, 1:3]: *m/z* (%) = 1033.0 (20) [M – SCN]$^+$, 1114.0 (50) [M + Na]$^+$, 1195.0 (100) [M + Na + 2 MeCN]$^+$. IR: $\tilde{\nu}$ 2106, 2089 (ν_{SCN}) cm^{-1}. $C_{33}H_{60}N_9P_3Pd_3S_3$ (1091.26): calcd. C 36.32, H 5.54, N 11.55; found C 37.23, H 6.25, N 10.06.

Reaction of 3 with Benzylthiol: Complex **3** (153 mg, 0.15 mmol) and K_2CO_3 (104 mg, 0.75 mmol) were suspended in anhydrous THF, and benzylthiol (74 mg, 0.6 mmol) was added through a syringe. The mixture changed colour from deep-red to purple and was stirred for 2 h. The solid, deep-purple residue was removed by filtration and washed with THF. Complex **12** was identified by ^{1}H and ^{31}P NMR spectroscopic data; ^{13}C NMR spectra were not available due to poor solubility. Attempts to separate this species from the inorganic by-products by extraction or washing were unsuccessful. ^{1}H NMR ($CDCl_3$): δ = 7.34–7.21 (m, 15 H, C_6H_5), 7.29 (m, 6 H, C*H*=N), 3.47 (s, 6 H, C*H*$_2$S), 1.73 (s, 54 H, C*H*$_3$) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 254.8 (s) ppm.

Bis(benzylthio)methane (13): A mixture of K_2CO_3 (2.07 g, 15 mmol), dichloromethane (255 mg, 3.0 mmol) and benzylthiol (745 mg, 6.0 mmol) was suspended in anhydrous THF (10 mL), and a catalytic amount of **3** (153 mg, 0.15 mmol, 5 mol-%) was added. The red solution turned purple. The mixture was stirred for 3 d during which time the solution turned red again. The solvent was removed under reduced pressure and the remaining solid extracted with hexane (4 × 5 mL). Concentration of the combined extracts gave 600 mg (2.5 mmol, 82 %) of spectroscopically pure **13**, which was identified by ^{1}H NMR spectroscopy. ^{1}H NMR ($CDCl_3$): δ = 7.25–7.12 (m, 10 H, C_6H_5), 3.75 (s, 4 H, SC*H*$_2$), 3.30 (s, 2 H, SC*H*$_2$S) ppm.

Crystallography: The crystal structure of **3** was determined with a Bruker Kappa APEXII Duo diffractometer at 110(2) K using Mo-K_α radiation (λ = 0.71073 Å). The structure was solved by using direct methods (SHELXS-97[19]) and refined by the full-matrix least-squares method on F^2 (SHELXL-97[19]). A numerical absorption correction was applied. Non-hydrogen atoms were refined anisotropically and hydrogen atoms with a riding model on F^2. The oxygen atom of one solvent molecule is disordered. $C_{30}H_{60}Cl_3N_6P_3Pd_3 \cdot 2THF$, M = 1167.51 g mol^{-1}, crystal size 0.32 × 0.19 × 0.17 mm, orthorhombic, space group $P2_12_12_1$, a = 14.2069(7), b = 16.4980(8), c = 21.4425(12) Å, V = 5025.8(4) Å^3, Z = 4, ρ(calcd.) = 1.543 mg m^3, F(000) = 2384, θ_{max} = 27.5°, μ = 0.135 mm^{-1}, 46529 reflections measured, 11511 unique reflections (R_{int} = 0.035) for structure solution and refinement with 496 parameters and 31 restraints, max./min. transmission 0.882/0.667, $R1$ [for 9645 reflections with $I > 2\sigma(I)$] = 0.035, $wR2$ = 0.067, GoF (on F^2) = 1.03, absolute structure parameter –0.05(2), largest diff. peak/hole 0.672/–0.518 e Å^{-3}. CCDC-987716 contains 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 (see footnote on the first page of this article): Molecular structure of the crystal of **10** and selected NMR and MS data.

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