Inorganic Chemistry

Phosphenium Hydride Reduction of $[(cod)MX_2]$ (M = Pd, Pt; X = Cl, Br): Snapshots on the Way to Phosphenium Metal(0) Halides and Synthesis of Metal Nanoparticles

Jan Nickolaus,[†] Dominik A. Imbrich,^{†,§} Simon H. Schlindwein,[†] Adrian H. Geyer,[†] Martin Nieger,[‡] and Dietrich Gudat^{*,†}

[†]Institute of Inorganic Chemistry, University of Stuttgart, Pfaffenwaldring 55, 70550 Stuttgart, Germany [‡]Department of Chemistry, University of Helsinki, P.O Box 55 (A.I. Virtasen Aukio 1), 00014 Helsinki, Finland

Supporting Information

ABSTRACT: The outcome of the reduction of $[(cod)PtX_2]$ (X = Cl, Br; cod = 1,5-cyclooctadiene) with N-heterocyclic phosphenium hydrides ^RNHP–H depends strongly on the steric demand of the *N*-aryl group R and the nature of X. Reaction of $[(cod)PtCl_2]$ with ^{Dipp}NHP–H featuring bulky N-Dipp groups produced an unprecedented monomeric phosphenium metal(0) halide $[(^{Dipp}NHP)(^{Dipp}NHP-H)PtCl]$ stabilized by a single phosphine ligand. The phosphenium unit exhibits a pyramidal coordination geometry at the phosphorus atom and may according to DFT calculations be classified as a Z-type ligand. In contrast, reaction of $[(cod)PtBr_2]$ with the sterically less



protected ^{Mes}NHP–H afforded a mixture of donor-ligand free oligonuclear complexes $[\{(MesNHP)PtBr\}_n]$ (n = 2, 3), which are structural analogues of known palladium complexes with μ_2 -bridging phosphenium units. All reductions studied proceed via spectroscopically detectable intermediates, several of which could be unambiguously identified by means of multinuclear (¹H, ³¹P, ¹⁹⁵Pt) NMR spectroscopy and computational studies. The experimental findings reveal that the phosphenium hydrides in these multistep processes adopt a dual function as ligands and hydride transfer reagents. The preference for the observed intricate pathways over seemingly simpler ligand exchange processes is presumably due to kinetic reasons. The attempt to exchange the bulky phosphine ligand in [(DipPNHP)(DipPNHP-H)PtCl] by Me₃P resulted in an unexpected isomerization to a platinum(0) chlorophosphine complex via a formal chloride migration from platinum to phosphorus, which accentuates the electrophilic nature of the phosphenium ligand. Phosphenium metal(0) halides of platinum further show a surprising thermal stability, whereas the palladium complexes easily disintegrate upon gentle heating in dimethyl sulfoxide to yield metal nanoparticles, which were characterized by TEM and XRD studies.

INTRODUCTION

N-Heterocyclic phosphenium (NHP) ions of types Ia and Ib^{1-3} (Chart 1) are isovalent analogues of the widely studied N-heterocyclic carbenes (NHC), which have found eminent application in coordination chemistry and catalysis.⁴ Although





^{*a*}Dipp = $2,6-i\Pr_2C_6H_3$, Xyl = $2,6-Me_2C_6H_3$.

the carbenes have strong σ -donor and only weak π -acceptor character, NHPs act predominantly as π -acceptors, and the metal-ligand bonding in their complexes is in most cases described as superposition of a dominating dative M \rightarrow L π -bond and a weaker dative $L \rightarrow M \sigma$ -bond.^{3c,5-8} As has been demonstrated recently, these features make NHPs excellent ligands for the stabilization of complexes with low-valent platinum group metals.^{7,9-15} Particular attention has been devoted to phosphenium metal halides in which a formally cationic NHP unit is used to support a negatively charged $\{M^{(0)}X\}^-$ fragment (M = Pd, Pt) featuring a zerovalent metal atom with d¹⁰ electron count. Electronic saturation of the resulting neutral {(NHP)MX} units is achieved by either attachment of additional phosphine donors to give mononuclear complexes $(1-3)^{10-12}$ or by oligomerization to yield di- (4, 5) or trinuclear arrays (6, 7) of metal centers held together by μ_2 -bridging phosphenium ligands.^{13,15}

The phosphenium metal(0) halide complexes are accessed via either insertion of an existing metal(0) center into the P–X bond

Received: January 4, 2017

Scheme 1. Synthetic Pathways to Oligomeric Phosphenium Metal(0) Halides of Platinum-Group $Metals^{a13,15}$



of a halophosphine precursor^{10–13} or treatment of metal(II) salts like $[(cod)MCl_2]$ (cod = 1,5-cyclooctadiene) with an electronrich diphosphine (for M = Pd, Pt) or phosphenium hydride (for M = Pd) (Scheme 1).¹³

Reaction (1) is viewed as a "nonoxidative" process⁹ that leaves the formal metal oxidation state unchanged, and (2) and (3) involve reduction of the metal center and constitute new variants of reductive syntheses that are a standard method for the preparation of low valent metal complexes or metal nanoparticles.¹⁶ In particular, we consider pathway (2) noteworthy because on the one hand it is closely related to commonly applied reductions with complex hydrides (in particular BH_4^{-})¹⁷ but on the other hand remains peculiar in that the phosphenium hydride has a dual function by providing both the reduction equivalents for the generation of the product and the ligand for its stabilization. The reaction is further mechanistically appealing because besides the NHP cation the phosphenium hydride may also act as a supporting ligand that can control the course and outcome of the reaction. Having established that the phosphenium hydride reduction of [(cod)PdCl₂] proceeds rapidly without observable intermediates,¹³ we turned to study the behavior of analogous platinum salts, expecting that their higher kinetic stability might render transient intermediates more easily detectable and thus help in the elucidation of the reaction pathway. We report here that the phosphenium hydride reduction of $[(cod)PtX_2]$ (X = Cl, Br) meets this expectation but also demonstrate that different reaction kinetics have a crucial effect on the outcome of individual reactions. Furthermore, we will show that oligomeric phosphenium halides of platinum and palladium exhibit surprisingly different thermal stabilities, which has a pronounced effect on their usability for the synthesis of metal nanoparticles.

EXPERIMENTAL SECTION

All manipulations were carried out under a dry argon atmosphere and by using standard vacuum line techniques. Solvents were dried by literature-known procedures. The NMR spectra were recorded on Bruker Avance 400 (¹H, 400.1 MHz; ³¹P, 161.9 MHz; ¹⁹⁵Pt, 86.7 MHz) Avance 250 (¹H, 250.1 MHz; ³¹P, 101.2 MHz; ¹⁹⁵Pt, 54.2 MHz) NMR spectrometers at ambient temperature if not stated otherwise. Chemical shifts are referenced to external TMS (¹H, Ξ = 100.000000 MHz) using 85% H₃PO₄ (³¹P, Ξ = 40.480742 MHz) and 1.2 M Na₂PtCl₆ (¹⁹⁵Pt, Ξ = 21.496784 MHz) as secondary references. ¹⁹⁵Pt chemical shifts were obtained from ¹H-detected ¹H, ¹⁹⁵Pt HMQC spectra. Coupling constants are given as absolute values. (+)ESI mass spectra were recorded in MeOH solution on a Bruker Daltonics Micro TOF Q instrument. Elemental analyses were determined on a Thermo Micro Cube CHN/S analyzer. The secondary diazaphospholene 8^{Dipp18} was prepared as described. High-resolution transmission electron microscopy (HRTEM) images were recorded on a Tecnai G2 Sphera transmission electron microscope operated at an accelerating voltage of 200 kV.

Electron-beam microprobe measurements were performed on a CAMECA SX 100 electron probe microanalyzer with a semiconducting crystal and an excitation voltage of 15 kV. Powder diffraction data were recorded on a STOE and Cie STADI P with a Cu K α_1 X-ray source.

Synthesis of Complex 9^{Dipp}. A solution of 8^{Dipp} (440 mg, 1.10 mmol) in THF (5 mL) was cooled to 0 °C, and solid [(cod)PtCl₂] (200 mg, 0.55 mmol) was added. The mixture was stirred for 1 h during which the color changed from yellow to green and then brown. The solvent was removed under reduced pressure, and the solid residue was washed three times with 10 mL of acetonitrile. Drying of the remaining yellow solid under reduced pressure gave 370 mg (0.93 mmol, yield 86%) of spectroscopically pure product. A crystalline sample suitable for X-ray diffraction studies was obtained by recrystallization from THF/dichloromethane (DCM) at -20 °C.

¹H NMR (THF-*d*₈): δ 8.20 (dd, 1 H, ¹*J*_{PH} = 381 Hz, ³*J*_{PH} = 3.0 Hz, ²*J*_{PtH} = 427 Hz, PH), 7.23 (t, 2 H, ³*J*_{HH} = 7.7 Hz, *p*-CH), 7.16 (t, 2 H, ³*J*_{HH} = 7.7 Hz, *p*-CH), 7.09 (d, 4 H, ³*J*_{HH} = 7.7 Hz, *m*-CH), 6.91 (d, 2 H, ³*J*_{HH} = 7.7 Hz, *m*-CH), 6.76 (d, 2 H, ³*J*_{HH} = 7.7 Hz, *m*-CH), 6.30 (s, 2 H, NCH), 6.00 (d, 2 H, ³*J*_{PH} = 10.2 Hz, NCH), 3.96 (sept, 2 H, ³*J*_{HH} = 6.8 Hz, CHCH₃), 3.38 (sept, 2 H, ³*J*_{HH} = 6.8 Hz, CHCH₃), 3.04 (sept, 2 H, ³*J*_{HH} = 6.8 Hz, CHCH₃), 2.89 (sept, 2 H, ³*J*_{HH} = 6.8 Hz, CHCH₃), 1.31 (d, 12 H, ³*J*_{HH} = 6.8 Hz, CHCH₃), 1.13 (d, 6 H, ³*J*_{HH} = 6.8 Hz, CHCH₃), 0.33 (d, 6 H, ³*J*_{HH} = 6.8 Hz, CHCH₃), 0.94 (d, 6 H, ³*J*_{HH} = 6.8 Hz, CHCH₃), 0.33 (d, 6 H, ³*J*_{HH} = 6.8 Hz, CHCH₃), 0.26 (d, 6 H, ³*J*_{HH} = 6.8 Hz, CHCH₃), 8.14 (d, ¹*J*_{PP} = 283 Hz, PN₂), 81.4 (d, ⁵*J*_{PP} = 283 Hz, PN₂), 81.4 (d, ¹*J*_{PP} = 7677 Hz, ²*J*_{PP} = 283 Hz, ¹*J*_{PH} = 381 Hz, PH). ¹⁹⁵Pt NMR (THF-*d*₈): δ -4128 (d, ¹*J*_{PP} = 7677 Hz). Anal. calcd for C₅₂H₇₃ClN₄P₂Pt (1046.64): C S9.67, H 7.03, N 5.35. Found: C 55.23, H 6.95, N 5.02 (the carbon value that is significantly too low can be explained by incomplete combustion due to the formation of nonvolatile platinum carbides).

Preparation of 8^{Mes}. A stoichiometric amount of LiAlH₄ (120 μ L of 1 M solution in THF, 0.12 mmol) was added to a precooled (-78 °C), stirred solution of 2-halogeno-diazaphospholene (^{Mes}NHP–Br 14^{Mes;19} 200 mg, 0.48 mmol; ^{Mes}NHP–Cl 10^{Mes;20} 172 mg, 0.48 mmol) in THF (5 mL). The mixture was warmed to ambient temperature and stirred for 1 h. Reaction control (³¹P NMR) indicated that formation of 8^{Mes} was quantitative, and the solution was used for subsequent reactions without further purification. If depletion of the formed LiAlX₄ was intended, the reaction mixture was evaporated to dryness, and 8^{Mes} was then extracted with hexane. The filtrate of the extraction was evaporated once more, and the residue was dissolved in THF.

¹H NMR (THF- d_8): δ 6.98 (d, 1 H, ¹ J_{PH} = 136 Hz, PH), 6.90 (s, 4 H, m-CH), 6.13 (d, 2 H, ³ J_{PH} = 1.7 Hz, NCH), 2.34 (s, 6 H, p-CH₃), 2.28 (s, 12 H, o-CH₃), ³¹P{¹H} NMR (THF- d_8): δ 63.8 (s).

Reaction of [(cod)PtCl₂] with 8^{Mes}. A light yellow solution of crude 8^{Mes} prepared as described was treated at room temperature with [(cod)PtCl₂] (90 mg, 0.24 mmol) and stirred until a homogeneous phase was obtained. The progress of the reaction was monitored by ³¹P NMR spectroscopy until the spectra indicated complete consumption of 8^{Mes}. Recording of ¹H and ³¹P NMR spectra revealed that cod and 10^{Mes} had formed as major products along with a minor amount of complex 11^{Mes} (\leq 10% of phosphorus-containing species by integration of the ³¹P NMR spectrum). Attempts to identify or isolate a platinum-containing reaction product failed.

containing reaction product failed. For 11^{Mes}, ¹H NMR (THF- d_8): δ 8.56 (A-part of AA'XX' pattern, ¹⁺³ $J_{\rm PH}$ = 404 Hz, 2 H, PH), 6.74 (broad s, 4 H, *m*-CH), 6.63 (broad s, 4 H, *m*-CH), 6.10 (m, 4 H, NCH), 2.30 (broad s, 24H, CH₃), 2.13 (broad s, 12H, CH₃), -15.24 (t, 1 H, ² $J_{\rm PH}$ = 8.5 Hz, ¹ $J_{\rm PtH}$ = 1197 Hz, PtH). ³¹P{¹H} NMR (THF- d_8): δ 80.0 (s, ¹ $J_{\rm PtP}$ = 3505 Hz). ³¹P NMR (THF- d_8): δ 80.0 (X-part of AA'XX'-pattern, ¹⁺³ $J_{\rm PH}$ = 405 Hz, ¹ $J_{\rm PtP}$ = 3505 Hz). ¹⁹⁵Pt NMR (THF- d_8): δ -4872 (t, ¹ $J_{\rm PtP}$ = 3505 Hz). **Reaction of [(cod)PtBr₂] with 8^{Mes}.** A light yellow solution of

Reaction of [(cod)PtBr₂] with 8^{Mes}. A light yellow solution of crude 8^{Mes} prepared as described was treated at room temperature with [(cod)PtBr₂] (111 mg, 0.24 mmol) and stirred for 2 days. During this time, the solution turned deep red, and a reddish precipitate formed. The mixture was evaporated to dryness, and the residue was washed two times with water (2 mL), two times with MeOH (2 mL), and five times

with Et₂O (5 mL). Analytical and spectroscopic studies revealed that the crude product contained a mixture of complexes $[(NHP)PtBr]_n$ (n = 2, 3; 12^{Mes}, 13^{Mes}) as major components and minor amounts of residual solvents and unidentified impurities (no yield determined). Anal. calcd for {C₂₀H₂₄N₂BrPPt}_n (n = 598.37): C 40.14, H 4.04, N 4.68. Found: C 40.00, H 4.36, N 4.29. Attempts to recrystallize the crude product yielded a few crystals (no yield determined) of 13^{Mes}, which were identified by a single-crystal X-ray diffraction study. When reaction monitoring was intended, the initial solution of 8^{Mes} in THF- d_8 was cooled to -70 °C prior to the addition of [(cod)PtBr₂], and multinuclear (¹H, ³¹P, ¹⁹⁵Pt) NMR spectra were then recorded while the temperature was stepwise increased to rt. The spectral data of all identified intermediates and products detected are listed below.

For [**B**]Br, ¹H NMR (THF- d_8 , -50 °C): δ 8.63 (m, 2 H, ¹⁺³ J_{PH} = 368 Hz, ² J_{PtH} = 393 Hz, PH), 7.67 (m, 2 H, ³ J_{PH} = 5 Hz, NCH(NHP)), 6.18 (m, 2 H, NCH(phosphine)), 6.02 (m, 2 H, NCH(phosphine)); signals of NMes substituents could not be unambiguously identified. ³¹P{¹H} NMR (THF- d_8 , -50 °C): δ 248 (t, ² J_{PP} = 202 Hz, ¹ J_{PtP} = 5623 Hz, PN₂), 102 (d, ² J_{PP} = 202 Hz, ¹ J_{PtP} = 5310 Hz, PH). ³¹P NMR (THF- d_8 , -50 °C): δ 248 (broad t, ² J_{PP} = 202 Hz, ¹ J_{PtP} = 5623 Hz, PN₂), 102 (d, ² J_{PP} = 202 Hz, ¹ J_{PtP} = 5610 Hz, PH). ³¹P NMR (THF- d_8 , -50 °C): δ 248 (broad t, ² J_{PP} = 202 Hz, ¹ J_{PtP} = 5623 Hz, PN₂), 102 (X-part of AA'XX' pattern with ² J_{PP} = 202 Hz, ¹ J_{PH} = 268 Hz, ³ J_{PH} = 56 Hz, ¹ J_{PtP} = 5310 Hz, PH). ¹⁹⁵Pt NMR (d_8 -THF, -50 °C): δ -4623 (q, ¹ J_{PtP} ≈ 5400 Hz).

(q, ${}^{1}J_{PtP} \approx 5400$ Hz). For 15^{Mes}, ¹H NMR (THF- d_8): δ 8.75 (A-part of AA'XX' pattern with ${}^{1}J_{PH} = 369$ Hz, ${}^{3}J_{PH} = 41$ Hz, ${}^{2}J_{PP} = 622$ Hz, 2 H, ${}^{4}J_{PtH} = 171$ Hz, PH), 7.01 (s, 4 H, m-CH), 6.78 (s, 4 H, m-CH), 6.01 (m, ${}^{3+5}J_{PH} = 12.1$ Hz, 4 H, NCH), 2.28 (s, 12 H, CH₃), 2.11 (s, 12 H, CH₃), 1.94 (s, 12 H, CH₃), -13.64 (t, 1 H, ${}^{2}J_{PH} = 8$ Hz, ${}^{1}J_{PtH} = 1272$ Hz, PtH). ${}^{31}P{}^{1}H{}$ NMR (THF- d_8): δ 78.5 (s, ${}^{1}J_{PtP} = 3444$ Hz). ${}^{31}P$ NMR (THF- d_8): δ 78.5 (X-part of AA'XX'-pattern with ${}^{1+3}J_{PH} = 410$ Hz, ${}^{1}J_{PtP} = 3444$ Hz). ${}^{19}F{}^{1}$ NMR (THF- d_8): δ -5007 (t, ${}^{1}J_{PtP} = 3444$ Hz).

For 16^{Mes}: ¹H NMR (THF- d_8): δ 8.65 (dd, 1 H, ¹ J_{PH} = 386 Hz, ³ J_{PH} = 45 Hz, ⁴ J_{PtH} = 153 Hz, PH), 6.89 (s, 2 H, *m*-CH), 6.83 (s, 2 H, *m*-CH), 6.82 (s, 2 H, *m*-CH), 6.77 (s, 2 H, *m*-CH), 6.07 (d, 2 H, ³ J_{PH} = 11 Hz, ⁴ J_{PtH} = 15 Hz, NCH), 5.87 (d, 2 H, ³ J_{PH} = 11 Hz, ⁴ J_{PtH} = 15 Hz, NCH), 5.87 (d, 2 H, ³ J_{PH} = 11 Hz, ⁴ J_{PtH} = 15 Hz, NCH), 5.87 (d, 2 H, ³ J_{PH} = 11 Hz, ⁴ J_{PtH} = 15 Hz, 2 H, NCH), 2.31 (s, 6 H, CH₃), 2.29 (s, 6 H, CH₃), 2.28 (s, 6 H, CH₃), 2.24 (s, 6 H, CH₃), 2.03 (s, 6 H, CH₃), 1.85 (s, 6 H, CH₃), -14.18 (d, 1 H, ² J_{PH} = 13 Hz, ¹ J_{PtH} = 1238 Hz, PtH). ³¹P{¹H} NMR (THF- d_8): δ 116.6 (d, ² J_{PP} = 700 Hz, ¹ J_{PtP} = 3487 Hz, PH). ³¹P NMR (THF- d_8): δ 116.6 (ddm, ² J_{PP} = 700 Hz, ³ J_{PH} = 45 Hz, PBr), 79.7 (ddm, ² J_{PP} = 700 Hz, ³ J_{PH} = 45 Hz, PBr), 79.7 (ddm, ² J_{PP} = 700 Hz, ¹ J_{PH} = 386 Hz, PH). ¹⁹⁵Pt{¹H} NMR (THF- d_8): δ -5051 (dd, ¹ J_{PH} ≈ 4350, 3500 Hz).

NMR (THF- d_8): δ -5051 (dd, ${}^{1}J_{\text{PtP}} \approx 4350, 3500 \text{ Hz}$). For 12^{Mes}, ${}^{1}\text{H}$ NMR (THF- d_8 , rt): δ 6.71 (s, 8 H, *m*-CH), 6.65 (m, 4 H, NCH), 2.24 (s, 12 H, *p*-CH₃), 2.20 (s, 24 H, *o*-CH₃). ${}^{31}\text{P}{}^{1}\text{H}$ NMR (d_8 -THF): δ 233.0 (s, ${}^{1}J_{\text{PtP}} = 4157 \text{ Hz}$). ${}^{195}\text{Pt}$ NMR (d_8 -THF): δ -4462 (t, ${}^{1}J_{\text{PtP}} = 4157 \text{ Hz}$).

For 13^{Mes} , ¹H NMR (THF- d_8 , rt): δ 6.91 (broad s, 6 H, NCH), 6.59 (s, 12 H, *m*-CH), 2.30 (s, 18 H, *p*-CH₃), 1.96 (s, 36 H, *o*-CH₃). ³¹P{¹H} NMR (d_8 -THF): δ 307 (s).

Synthesis of Complex 18^{Dipp}. Trimethylphosphine (170 mg, 0.23 mL, 2.25 mmol) was added via syringe to a solution of 9^{Dipp} (150 mg, 0.45 mmol) in THF (5 mL) at room temperature. The mixture was stirred for 1 h. The orange solid formed was then separated by filtration, washed with three portions of THF (5 mL), and dried under vacuum to yield 190 mg (0.34 mmol, 76%) of product. ¹H NMR (CDCl₃): δ 7.35 (t, 2 H, ³J_{HH} = 7.7 Hz, *p*-CH), 7.19 (d, 4 H, ³J_{HH} = 7.7 Hz, *m*-CH), 6.80 (d, 2 H, ³J_{PH} = 3.0 Hz, ⁴J_{HPt} = 14 Hz, NCH), 2.89 (sept, 4 H, ³J_{HH} = 6.9 Hz, CH), 1.23 (d, 12 H, ³J_{HH} = 6.9 Hz, CHCH₃), 1.13–1.05 (m, 27 H, PCH₃). ³¹P{¹H} NMR (CDCl₃): δ 175.0 (q, ²J_{PP} = 113 Hz, ¹J_{PPt} = 5659 Hz, PN₂), -47.8 (d, ²J_{PP} = 113 Hz, ¹J_{PPt} = 3473 Hz, PMe₃). ¹⁹⁵Pt NMR (CDCl₃): δ -4630 (dq, ¹J_{PtP} = 5659, 3473 Hz). (+)-ESI-MS *m*/*z*: 786.34 (M – PMe₃ – Cl). Anal. calcd for C₃₅H₆₃ClN₂P₄Pt (866.31): C 48.52, H 7.33, N 3.23. Found: C 48.01, H 7.13, N 3.17.

Reaction of 18^{Dipp} with AlCl₃. An excess of dry AlCl₃ (120 mg, 0.92 mmol) was added to a solution of 18^{Dipp} (100 mg, 0.18 mmol) in DCM (3 mL). The mixture was stirred for 12 h at rt during which time its yellow color disappeared. The solvent was evaporated, and the off-white residue was extracted with five portions (2 mL) of Et₂O.

The remaining white solid was dissolved in CDCl₃. The combined ether fractions were evaporated, and the off-white residue was likewise dissolved in CDCl₃. NMR spectra disclosed the presence of $[17^{Dipp}]$ [AlCl₄] (in the ethereal fraction) and complex [ClPt(PMe₃)₃]-[AlCl₄] (in the Et₂O-insoluble fraction), which were both identified by their known NMR data.^{48,49}

For [ClPt(PMe₃)₃][AlCl₄], ¹H NMR (CDCl₃): δ 1.93 (d, 9 H, ²J_{PH} = 10.9 Hz, ³J_{PtH} = 40 Hz), 1.75 (m, 18 H, ²⁺⁴J_{PH} = 3.9 Hz, ³J_{PtH} = 24 Hz). ³¹P{¹H} NMR (CDCl₃): δ -12.5 (d, 2 P, ²J_{PP} = 22 Hz, ¹J_{PPt} = 2265 Hz, PMe₃), -27.8 (t, 1 P, ²J_{PP} = 22 Hz, ¹J_{PPt} = 3406 Hz, PMe₃). ¹⁹⁵Pt{¹H} NMR (CDCl₃): δ -4627 (q, due to low resolution in the indirect domain of the 2D spectrum). ²⁷Al NMR (CDCl₃): δ 103.7 (s).

For $[17^{Dipp}]$ [AlCl₄], ¹H NMR (CDCl₃): δ 8.35 (s, 2 H, NCH), 7.61 (t, 2 H, ³J_{HH} = 7.64 Hz, *p*-CH), 7.41 (d, 4 H, ³J_{HH} = 7.86 Hz, *m*-CH), 2.49 (sept, 4 H, ³J_{HH} = 6.88 Hz, CH), 1.34 (d, 12 H, ³J_{HH} = 6.75 Hz, CHCH₃), 1.25 (d, 12 H, ³J_{HH} = 6.76 Hz, CHCH₃). ³¹P{¹H} NMR (CDCl₃): δ 204.9 (br s). ²⁷Al NMR (CDCl₃): δ 104.0 (s).

Attempts to Prepare Metal Nanoparticles. The phosphenium metal(0) halide (mixture of $12^{\text{Mes}}/13^{\text{Mes}}$ or 6) was dissolved in 5 mL of dimethyl sulfoxide (DMSO), and the red solution was heated for 4 h to 100 °C ($12^{\text{Mes}}/13^{\text{Mes}}$) or 50 °C (6), respectively. A ³¹P NMR assay revealed that $12^{\text{Mes}}/13^{\text{Mes}}$ did not undergo any detectable reactions, whereas in the reaction of 6, a black precipitate formed and the solution turned orange. The black solid was separated by centrifugation and decantation, washed with Et₂O (3×5 mL) and DCM (3×10 mL), dried under vacuum, and characterized as described.

Crystallographic Studies. Single-crystal X-ray diffraction data were collected on a Bruker AXS Nanostar C diffractometer equipped with a Kappa APEX II Duo CCD-detector and a KRYO-FLEX cooling device at 100(2) K for 9^{Dipp} and 7 (X = Br) and 150(2) K for 13^{Mes} using Mo K α radiation (λ = 0.71073 Å). Crystals were selected under Fomblin Y perfluoro oil mounted on nylon loops and immediately placed in a cold stream of N2. The structures were solved by direct methods (SHELXS-2014²¹) and refined with a full-matrix least-squares scheme on F^2 (SHELXL-2014²¹). Semiempirical absorption corrections from equivalents were applied for all structures. Nonhydrogen atoms were refined anisotropically. The disordered solvent molecules (DCM) cocrystallizing with complex 13^{Mes} were refined isotropically. Complex 7 cocrystallizes with two THF molecules without any disorder. Listings of crystallographic data and details on the structure solution are given in the Supporting Information. CCDC-1524319 (9^{Dipp}), CCDC-1524317 (7), and CCDC-1524318 (13^{Mes}) contain the supplementary crystallographic data for this paper. This data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data request/cif.

Computational Studies. All computational studies but the calculations of NMR properties were performed with the Gaussian09²² suite of programs. MOLDEN²³ was used for visualization. Energyoptimization of molecular structures was carried out at the bp86/def2sv(p) level, which includes relativistic pseudopotentials at the platinum atom. Calculation of harmonic vibrational frequencies at the same level of theory ensured that all stationary points located were local minima on the energy hypersurface. Final energies and population analyses were then computed at the bp86/def2-tzvp level using the previously determined geometries. The calculation of NMR properties was carried out with the Amsterdam Density Functional package (ADF 2014)²⁴ using an all-electron, triple- ζ , double-polarization TZ2P Slater basis. Relativistic two-component zero-order regular approximation (ZORA)²⁵ calculations including spin-orbit coupling²⁹⁻³² have been performed with the local density approximation (LDA) in the Vosko-Wilk-Nusair parametrization³³ with nonlocal corrections for exchange (Becke88)³⁴ and correlation (Perdew86)³⁵ included in a self-consistent manner. Chemical shifts were determined as $\delta_s = (\sigma_{ref} - \sigma_s)/(1 - \sigma_{ref})$ relative to $[PtCl_6]^{2-}$ for ¹⁹⁵Pt and as $\delta_s = (\sigma_{ref} - \sigma_s - 266.1)$ relative to 85% H₃PO₄ for ³¹P³⁶ using the magnetic shielding constants of $[PtCl_6]^{2-}$ ($\sigma_{ref} =$ 1326 ppm) and PH₃ (σ_{ref} = 590.5 ppm) calculated at the same computational level.

RESULTS AND DISCUSSION

Formation of Phosphenium Metal(0) Halides. Reaction of two equivalents of the secondary N-heterocyclic phosphine 8^{Dipp} with [(cod)PtCl₂] at room temperature does not proceed as with [(cod)PdCl₂]¹³ to give a mixture of a chlorophosphine and a dinuclear phosphenium metal(0) halide (Scheme 1) but yields mononuclear phosphine-phosphenium complex 9^{Dipp} (Scheme 2), which was isolated after workup as a yellow

Scheme 2. Reaction of $[(cod)PtCl_2]$ with Secondary Diazaphospholene 8^{Dippa}



solid and identified by spectral data and a single-crystal X-ray diffraction study. The product is thermally stable in solution and does not react under loss of the phosphine to the previously described¹³ dimer S^{Dipp} .

Crystalline 9^{Dipp} contains isolated molecular complexes featuring a three-coordinate platinum atom with nearly T-shaped geometry (Figure 1). The Pt-P2 (2.156(2) Å) bond to the



Figure 1. View of the molecular structure of **9**^{Dipp} (left) and a reduced plot in which the atoms of the N-Dipp substituents are omitted. Hydrogen atoms of CH bonds are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected distances [Å] and angles [deg]: Pt1–P1, 2.154(3); Pt1–Cl1, 2.313(3); Pt1–P2, 2.319(3); P1–N2, 1.692(8); P1–N1, 1.716(9); P2–N3, 1.699(9); P2–N4, 1.710(8); P1–Pt1–Cl1, 162.77(11); P1–Pt1–P2, 90.96(11); Cl1–Pt1–P2, 106.21(11).

phosphine ligand and the Pt-Cl bond (2.311(2) Å) include an angle of $162.86(8)^{\circ}$ and form the horizontal bar of the T-shape, whereas its vertical axis is associated with the Pt-P1 bond to the NHP moiety, which is nearly perpendicular to the Pt-phosphine bond (P2-Pt-P1, 90.97(7)°) and significantly elongated (Pt-P1, 2.319(2) Å). The coordination geometry at the NHPphosphorus atom P1 is pyramidal (sum of bond angles, $297.3(7)^{\circ}$) and the five-membered rings in both P-ligands display a similar degree of puckering. The perception of a lengthened Pt-P1(NHP) bond is underlined by a comparison with the distances in related NHP complexes with a zerovalent platinum atom (Pt-P, 2.2446(11)-2.2606(9) Å¹¹). In contrast, the Pt-P(phosphine) and Pt-Cl distances are significantly shorter than in structurally related complexes (Pt-P is 2.156(2) Å in 9^{Dipp} vs 2.290(2)-2.3787(6) Å in 3 (X = Br) and $[(PPP)Pt(PR_3)]^+$, where (PPP) denotes the same pincer ligand as in 3;¹¹ Pt–Cl is 2.311(2) Å in 9^{Dipp} vs 2.268(3) Å in $5^{Dipp^{13}}$). Altogether, these features suggest viewing 9^{Dipp} as containing a pseudolinear {(phosphine)PtCl} unit that is perturbed by a weakly bound secondary ligand at a right angle (see also the Discussion below).

The presence of two different P-donor ligands in 9^{Dipp} is substantiated by the ${}^{31}P{}^{1}H$ NMR spectrum, which displays an AX pattern with a large ${}^{2}J_{PP}$ coupling constant (283 Hz). The signal at lower frequency (δ 82.8 ppm) is accompanied by ¹⁹⁵Pt satellites (${}^{1}J_{PtP} = 7677 \text{ Hz}$) and splits into a doublet of doublets due to interaction with an adjacent hydrogen atom (${}^{1}J_{PH} = 380 \text{ Hz}$) when the decoupling is switched off, backing its assignment to the phosphorus atom of the secondary phosphine ligand. The second resonance is attributed to the phosphorus atom in the NHP unit and displays a substantial deshielding (δ 236.7 ppm) that had been identified as a characteristic of many phosphenium com-plexes of platinum group metals.^{9–11} This signal has no ¹⁹⁵Pt satellites, and the ¹⁹⁵Pt{¹H} NMR signal of 9^{Dipp} thus exhibits a doublet structure arising from spin-coupling to the single phosphorus atom in the phosphine ligand. The unusually small ${}^{1}J_{\rm PtP}$ coupling constant is presumably caused by the combined influences of a large interatomic distance (which decreases the magnitude of ${}^{1}J_{\rm pt,p}$ and, perhaps more importantly, the lone pair at the NHP phosphorus atom (which shifts the coupling constant from a large positive number to more negative values 39). Numerically small ${}^{1}J_{\rm ptp}$ couplings were also observed for other platinum complexes featuring P-donor ligands with lone pairs such as pyramidal PR₂ units (2659–445 Hz for [(PPP)PtX] or $[(PPP)Pt(PR_3)]^+$, where (PPP) denotes pincer ligands with a central PR_2 donor unit framed by two phosphine moieties^{11,40}) as well as phosphavinyl⁴¹ or side-on-bound phosphaalkene⁴¹ and phosphaalkyne^{42,43} ligands (19–446 Hz).

The partitioning of 9^{Dipp} into a {(phosphine)PtCl} unit and an additional secondary ligand suggests describing the bonding situation in terms of the interaction of an anionic 14 VE {(phosphine)PtCl} fragment with a phosphenium cation acting as a Z-type ligand (Chart 2(a)). The anion fragment is then

Chart 2. Limiting Descriptions of the Metal–Ligand Interaction in 9^{Dippa}



 ${}^{a}R = 2,6 \cdot i Pr_2 C_6 H_3.$

isovalent to $[AuCl_2]^-$, and the platinum atom has a formal oxidation state of zero. However, because pyramidal geometry and a long M–P bond of a metal-bound NHP unit have also been viewed as indicators of a phosphide nature of the ligand,^{8,11} 9^{Dipp} can also be depicted as a coordinatively unsaturated Pt(II) phosphido complex (Chart 2(b)). Hoping to cast further light onto this dichotomy, we carried out DFT calculations on model complex 9^{Me} featuring N-Me instead of the computationally expensive N-Dipp substituents. The molecular structure obtained after energy optimization reproduces the T-shaped metal coordination and the relative differences in Pt–P and Pt–Cl distances observed for 9^{Dipp}, even if all bond distances are overestimated by 4–7 pm. Assuming that the deviations arise, at least in part, from the structural simplification of the model compound, we refrained from using more sophisticated models and conclude that the present results should allow deductions that are qualitatively reasonable but not numerically exact.

NBO analysis⁴⁴ reveals that the partial charges on the phosphine (+0.40), NHP (+0.55), and chloro ligands (-0.53) deviate considerably from the ideal values of 0 and ± 1 , indicating the presence of substantial charge transfer and strong covalent bonding contributions. This is confirmed by Wiberg bond indexes (WBI) of 0.88 (Pt-phosphine), 0.71 (Pt-NHP), and 0.61 (Pt-Cl). The enhanced positive charge of the NHP as compared to the phosphine ligand gives a first hint to a phosphenium rather than phosphide nature of the former, which is further emphasized by the different composition of the appropriate natural bond orbitals. Thus, the NBO representing the Pt-phosphine bond (76.0% P, 24.0% Pt) is like the Pt-Cl NBO (85.4% Cl, 14.6% Pt) strongly polarized toward the ligand atom, which is commonly interpreted as indicating a dative bond dominated by $L \rightarrow M$ donation from ligand-based lone pairs to the metal center. In contrast, the Pt-NHP NBO (33.7% P, 66.3% Pt) displays a reverse polarization, which we then interpret as evidence for a "retro-dative" $M \rightarrow L$ donation and thus "phosphenium" character of the NHP ligand. These findings indicate that, even if the assignment of formal oxidation states may seem questionable in light of the large covalent contributions to the metal-ligand bonding, the phosphenium complex reference structure (Chart 2(a)) is closer to the actual electronic situation than the representation of a phosphido-complex (b), and we consider 9^{Me} , and therefore 9^{Dipp} , as another example of a phosphenium-stabilized metal(0) halide. It is further noteworthy that calculations of NMR data of 9^{Me} reveal quite good agreement of the predicted ¹⁹⁵Pt NMR chemical shift $(\delta^{195}Pt_{calcd} =$ -4118 ppm) with the observed value for 9^{Dipp} ($\delta^{195}\text{Pt}$ = -4149 ppm) and also confirm the postulated trend in ${}^{1}J_{\rm PtP}$ couplings: the coupling constant to the phosphine ligand is large and positive as expected (${}^{1}J_{PtP,calcd} = 6556$ Hz compared to 7862 Hz for 9^{Dipp}) whereas that to the NHP-phosphorus atom is smaller in magnitude and of opposite sign $({}^{1}J_{PtP,calcd} = -946 \text{ Hz})$ compared to $|\tilde{J}_{PtP}| < 30$ Hz for $\hat{9}^{Dipp}$).

Having noticed that reacting mixtures of $8^{\rm Dipp}$ and [(cod)PtCl₂] show a transient green color before adopting the orange color of 9^{Dipp}, we reckoned that the reaction involves intermediates that might possibly be spectroscopically detectable. Reaction monitoring by multinuclear (¹H, ³¹P, ¹⁹⁵Pt) NMR spectroscopy at -70 °C revealed that the formation of 9^{Dipp} was indeed preceded by that of another complex. Formation of 9^{Dipp} occurred with appreciable rates above -30 °C and thwarted attempts to isolate this intermediate. The ³¹P{¹H} NMR signal of the transient species appears as a singlet that is accompanied by satellites arising from coupling to a single ¹⁹⁵Pt nucleus. The large chemical shift ($\delta^{31}P = 206.8 \text{ ppm}$) and small magnitude of ${}^{1}J_{PtP}$ (360 Hz) suggest the presence of an NHP ligand in a similar coordination mode as in 9^{Dipp}. The ¹H NMR spectrum contains, besides the signals of the NHP unit, solely a resonance attributable to a metal-bound hydride ($\delta^1 H = -14.7$ ppm, ${}^{1}J_{\text{PtH}} = 1563 \text{ Hz}$). The signal multiplicities in ${}^{195}\text{Pt}$ and selectively decoupled ³¹P NMR spectra as well as heteronuclear correlation spectra allow for assembly of the individual building blocks to a {(NHP)₂PtH} partial structure with two equivalent NHP units. However, the data give no clue about the presence or absence of additional halide ligands, and the precise structure of the intermediate thus remains unknown.

Lacking further experimental evidence, we attempted to derive a tentative structural assignment of the intermediate from the results of computational modeling studies on a series of complexes $[{(^{Me}NHP)_2PtH}Cl_n]^{(1-n)+}$ $(n = 0-2, ^{Me}NHP =$ Me-substituted *N*-heterocyclic phosphenium; see SI for details). Using the match between predicted and observed (δ^{195} Pt = -4410 ppm) ¹⁹⁵Pt NMR chemical shifts as selection criterion,⁴⁵ a cationic complex $[(^{Me}NHP)_2PtH]^+ (\delta^{195}Pt_{calcd} = -4511 \text{ ppm})$ emerged as the best candidate. The construction of a logical scenario explaining both the formation of an intermediate $[(NHP)_2PtH][Cl]$ (A) from 8^{Dipp} and $[(cod)PtCl_2]$ and its further isomerization to 9^{Dipp} is in principle feasible, but a detailed mechanistic discussion seems premature as long as no definitive identification of A has been achieved and shall thus be postponed. We note, however, that the metal hydride nature of A proves, regardless of the incomplete constitutional assignment, that activation of the P-H bond of 8^{Dipp} and transfer of a hydrogen atom to platinum occur in a very early reaction stage and justifies viewing the studied reaction as another manifestation of the phosphenium hydride nature of the starting material.

Assuming steric protection by the bulky NHP ligand as the key reason for the surprising thermal stability of 9^{Dipp} , we decided to also study the behavior of $[(\text{cod})\text{PtCl}_2]$ toward the sterically less demanding phosphenium hydride 8^{Mes} . NMR spectroscopic studies disclosed that the reaction yielded chlorophosphine 10^{Mes} and a small amount (<10 mol %) of a phosphine platinum hydride, which we assign as 11^{Mes} (Scheme 3). Further



reaction intermediates or platinum-containing products were neither spectroscopically detected nor isolated. Gratifyingly, we observed that the reaction of 8^{Mes} with $[(cod)PtBr_2]$ took a similar course as that of phosphenium hydrides with $[(cod)-PdCl_2]^{13,15}$ (Scheme 1(2)) to yield a mixture of oligomers 12^{Mes} and 13^{Mes} , bromophosphine 14^{Mes} , and dihydrogen as the final products (Scheme 3). An analytically impure mixture of 12^{Mes} and 13^{Mes} was isolated after workup, and recrystallization produced a very small amount of crystalline 13^{Mes} , which was identified by a single-crystal X-ray diffraction study (Figure 2).

The structural features of the Pt_3Br_3 unit and the bridging NHP ligands are closely comparable to those of the previously described trimeric phosphenium platinum(0) chloride 7¹⁵ (Chart 1), the crystal structure of which had been unknown and was now newly determined for comparison (see SI for a pictorial representation and a list of metrical parameters). The Pt–Pt distances in both compounds (7, 2.6855(5)–2.7016(5) Å; 13^{Mes}, 2.6901(6)–2.6983(5) Å) do not significantly differ, whereas the Pt–P distances in 7 (2.2721(17)–2.2909(16) Å) are slightly longer than in 13^{Mes} (2.268(2)–2.269(2) Å). The deviation in Pt–X distances (13^{Mes}: Pt–Br, 2.4778(9)–2.4867(13) Å; 7: Pt–Cl, 2.357(2)–2.383(2) Å) mainly reflects the different covalent radii of the halogens, and



Figure 2. View of the molecular structure of **13**^{Mes} (left) and reduced plot (right) displaying only the Pt₃Br₃ core and the diazaphospholene rings. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected distances [Å]: Pt1–P1, 2.268(2); Pt1–Br1, 2.4867(13); Pt1–Pt2, 2.6983(5); Pt2–P2, 2.268(2); Pt2–P1, 2.269(2); Pt2–Br2, 2.4778(9); Pt2–Pt2#1, 2.6901(6).

the intraligand bond lengths in the NHP units are similar as in other complexes of type 5 and 7.^{13,15} The formation of trinuclear complex 13^{Mes} is remarkable as it contradicts earlier assumptions¹⁵ that the presence of *N*-aryl substituents in the NHP units favors the formation of dinuclear phosphenium metal(0) halides for steric reasons.

Even if the final products of the reaction of 8^{Mes} with [(cod)PtBr₂] are formed at ambient temperature, the mechanism is quite intricate and involves several detectable intermediates. Multinuclear (1H, 31P, 195Pt) VT-NMR studies disclosed that the reaction sets off at -50 °C to yield a major product along with several minor byproducts that gave strongly exchangebroadened NMR signals and could not be identified further. The main product gives rise to AM₂/AM₂X-type signal patterns (A, M = ${}^{31}P$; X = ${}^{195}Pt$) in the ${}^{31}P{}^{1}H$ and ${}^{195}Pt{}^{1}H$ NMR spectra and is therefore assigned as a mononuclear platinum complex with three P-based ligands. The ³¹P NMR spectrum reveals for the M₂-signal ($\delta^{31}P = 102 \text{ ppm}$) an additional AA'XX'type splitting, which arises from coupling with P-bound hydrogen atoms and allows for identifying two of the ligands as 8^{Mes}. The A-signal (triplet at 248 ppm) is only slightly broadened by long-range couplings and exhibits a similar chemical shift as that of the cationic units in 9^{Dipp} and other Pt-NHP complexes^{9–15} and is attributed to a metal-bound phosphenium ion. Structural assignments compatible with these data are cationic complex B and the isomeric neutral species C and D (Chart 3). Even if the spectral data allow no definite decision, we favor assignment as (solvent separated or contact) ion pair [B]...[Br] based on the finding that the computed ¹⁹⁵Pt NMR chemical shift for the model cation \mathbf{B}^{Me} of -4701 ppm gives the best match with the experimental value (δ^{195} Pt = -4623) and the similarity of the ³¹P NMR data with those of previously reported analogous complexes $[(NHP)Pt(PPh_3)_2][OTf].^{7,10}$

The initial product reacted further to yield 14^{Mes} and a new complex identified as platinum hydride 15^{Mes} (Chart 3). This irreversible transformation was very slow at -50 °C, occurred at an increased rate above -30 °C, and went rapidly to completion at 0 °C. The ³¹P, ¹⁹⁵Pt, and ¹H NMR data of 15^{Mes} are similar to

Chart 3. Possible Structures of Intermediates in the Reaction of 8^{Mes} with $[(\text{cod})\text{PtBr}_2]^a$



those of 11^{Mes}, and the ³¹P and ¹⁹⁵Pt chemical shifts match those of known complexes *trans*-[Pt(R₃P)₂(H)(Cl)],⁴⁶ which can also be readily prepared by hydride reduction of Pt(II) precursors.⁴⁷ The structural assignment is also backed by the good match of the observed ¹⁹⁵Pt NMR chemical shift with the calculated value of -5114 ppm for the N-Me substituted model compound 11^{Me}.

Further slow conversion of 15^{Mes} at room temperature proceeded under formal H/Br exchange at one phosphine ligand to vield 16^{Mes} (Chart 3), which is recognized by its AB(X)-type signal pattern in the ³¹P{¹H} and ¹⁹⁵Pt NMR spectra, a similar metal chemical shift (δ^{195} Pt -5051) as 15^{Mes}, and the persistence of ¹H NMR signals for P- and Pt-bound hydrogen atoms. This species eventually evolved into a mixture of 12^{Mes} and 13^{Mes}. Complex 12^{Mes} gives rise to a broadened line in the room temperature ³¹P{¹H} NMR spectrum, which narrows upon cooling to yield a sharp singlet ($\delta^{31}P = 233$) with two sets of satellites that form the A_2 parts of A_2X and A_2X_2 spin systems with ${}^{1}J_{PtP} =$ 4157 Hz and arise from isotopomers with one and two ${}^{195}Pt$ nuclei, respectively. The reason for the signal broadening, which is completely reversible, is currently not known (VT-NMR studies gave no indication of a relation to dynamic exchange between 12^{Mes} and 13^{Mes}). The observed splitting pattern is typical for dimeric phosphenium platinum(0) halides,¹³ and the structural analogy of 12^{Mes} and 5^{Dipp} is further corroborated by matching of the values of ${}^{1}J_{\text{PtP}}$ and $\delta^{195}P$ of both species. The ³¹P NMR signal of 13^{Mes}, which is much less intense than that of 12^{Mes} but readily detectable in ¹H and ³¹P HMQC spectra, consists of a parent singlet accompanied by a complex set of ¹⁹⁵Pt satellites. Concise analysis of the satellite spectrum was precluded by the limited resolution and signal intensity in the indirect dimension of the 2D spectrum, but the similarity to the signal pattern of 7¹⁵ is taken as a strong argument for supporting that the trinuclear structure of crystalline 13^{Mes} persists in solution.

The outcome of the reaction monitoring allows for outlining a mechanistic description of the reduction of $[(cod)PtBr_2]$ by 8^{Mes} (Scheme 4). We propose that the reactants undergo an initial

Scheme 4. Proposed Mechanism of the Reaction of 8^{Mes} with $[(\text{cod})\text{PtBr}_2]^{a}$



metathesis to give HBr (formation of HCl as a coproduct is proven for reactions of phosphenium hydrides with $[(cod)PdCl_2]$ under similar conditions¹³) and a phosphenium complex, which is stabilized by incorporation of two further molecules of 8^{Mes} as the observable intermediate B[Br]. Action of the HBr formed on this species is then considered to give bromo-diazaphospholene 14^{Mes} and complex 15^{Mes}, which reacts further by hydride/halide exchange at one phosphine ligand to give 16^{Mes}. This transformation may once more be initiated by HBr as shown in Scheme 4 or, alternatively, by the bromo-diazaphospholene 14^{Mes} (intermolecular hydride/halide-exchange processes between free diazaphospholenes have precedence¹⁸). Finally, formation of 12^{Mes} and 13^{Mes} can be rationalized by oligomerization of a $\{(^{R}NHP)PtBr\}$ unit arising from formal cleavage of 8^{Mes} and HBr from 16^{Mes}. Dihydrogen, which was also positively identified as reaction product by ^IH NMR spectroscopy, can arise from the action of HBr on 15^{Mes} (see Scheme 4) as well as from a side-reaction²⁰ of HBr with 8^{Mes} . We note that the initial consumption of an overstoichiometric amount of 8^{Mes} (three instead of two equivalents as suggested by reaction (2) in Scheme 1) is also in accordance with the finding that the ¹H NMR signal of [(cod)PtBr₂] remained visible during a major part of the reaction, which indicates that total consumption of this starting material occurred only during a later reaction stage.

It is noteworthy that a reaction of key intermediate **B** via capture of the halide anion and cleavage of the two phosphine ligands would provide a more direct route to 12^{Mes} and 13^{Mes} than the detour via 15^{Mes} and 16^{Mes} . The failure to observe this pathway is obviously due to kinetic reasons. A hint to a possible explanation can be derived from population analysis of the computed electron density for the model intermediate B^{Me} . The LUMO of this species is centered on the platinum and the phosphorus atom of the NHP unit with a slightly larger coefficient on the latter, and the natural charges are positive on the phosphorus (+1.13) but negative on the metal atom (-0.62). In the light of these findings, attack of an anion on **B** should be

directed to the NHP-phosphorus atom, and this initial attack may then be assumed to facilitate breakdown into a bromophosphine and a neutral fragment $\{(8)_2Pt\}$, which is in turn trapped by HBr to yield 15. The formation of 16^{Mes} from 15^{Mes} may likewise be considered a phosphorus- rather than a platinum-centered reaction, which proceeds as in free phosphenium hydrides^{18,20} via P–H/P–Br bond metathesis; as this process leaves the Pt–P bond intact, it may be kinetically preferable to an exchange of the complete phosphine ligand, which is often notoriously slow.

Reactions of Phosphenium Metal(0) Complexes. The electronically unsaturated nature of the metal atom suggests that 9^{Dipp} can in principle add further ligands. Because the increase in metal electron density associated with such extra ligation should strengthen the bonding to a Z-type (phosphenium) and weaken the bonding to an X-type (phosphide) ligand, characterization of the reaction products might help to cast further light on the electronic properties of the NHP unit. Anticipating that sterically nondemanding and strongly σ -donating ligands are particularly effective, we considered PMe₃ an ideal substrate for these studies.

Treatment of 9^{Dipp} with an excess of PMe₃ gave an orange precipitate, which was separated by filtration from the liberated phosphenium hydride 8^{Dipp} and purified by several washings with THF. The ³¹P{¹H} and ¹⁹⁵Pt NMR spectra of the product display an AM₃(X) (A, M = ³¹P, X = ¹⁹⁵Pt) pattern. The downfield ³¹P NMR signal at 175 ppm is attributable to an NHP unit that carries no hydrogen atom and the upfield signal at -47.8 ppm to a set of three equivalent PMe₃ ligands. These data led us to anticipate an ionic product with cation E (Scheme 5), which is

Scheme 5. Reaction of 9^{Dipp} with an Excess of PMe₃ and Constitution of Complex Cation E



structurally related to the cations in salts $[(NHP)M(PMe_3)_3]$ -OTf (M = Pd, Pt) that had been accessed via analogous phosphine exchange reactions.⁷ Interestingly, further reaction with AlCl₃ did not only result in a simple conversion of free chloride into [AlCl₄]⁻ but induced a breakdown of the original complex into phosphenium salt $[17^{\text{Dipp}}][\text{AlCl}_4]^{48}$ and complex [ClPt(PMe₃)₃][AlCl₄],⁴⁹ which were identified by their known NMR data (Scheme 5; the additional chlorides originate presumably from disintegration of the solvent DCM). These findings imply that the chloride anion is an essential constituent of the original PMe3 complex and led us to reassign its constitution as 18^{Dipp} with a neutral Cl-NHP ligand.⁵⁰ Such a structure is not only well in accordance with the close match of the computed ¹⁹⁵Pt NMR chemical shift of model compound 18^{Me} (-4439 ppm) with the value for 18^{Dipp} (-4630 ppm) but can also explain the fact that the ³¹P NMR chemical shift of the NHP unit in 18^{Dipp} seems too low for a cationic phosphenium complex. Furthermore, even if the reaction of $9^{D_{1}^{i}pp}$ with PMe₃

did not result in the expected cationic complex, the proposed constitution of 18^{Me} may still serve as corroboration of the electrophilic rather than nucleophilic character of the metal-bound NHP fragment.

Knowing that 4^{Dipp} disassembles in the presence of strongly donating phosphines to yield defined metal(0) complexes,¹³ we wondered if oligonuclear phosphenium halides [(NHP)MX]_n (M = Pd, Pt; n = 2, 3) might in the absence of a stabilizing Lewis base form metal nanoparticles. The Pt-based oligomers $12^{\text{Mes}}/13^{\text{Mes}}$ proved, like 9^{Dipp} , thermally quite stable and suffered no visible disintegration even upon prolonged heating to 100 °C in DMSO. In contrast, the previously described¹⁵ trinuclear palladium(0) complex 6 (X = Cl) reacted in the same solvent at 50 °C to yield elemental palladium and a solution containing several unidentified decomposition products of chloro-NHP 10^{tBu} . The solid was identified by micro probe analysis and a powder diffraction study (Figure 3). Further characterization by trans-



Figure 3. X-ray powder diffraction pattern of Pd nanoparticles resulting from thermal disintegration of **6** at 50 $^{\circ}$ C in DMSO. The black and red curves represent experimental results and simulated data for elemental Pd, respectively.



Figure 4. TEM image of Pd nanoparticles produced by thermolysis of 6 at 50 $^\circ C$ in DMSO.

mission electron microscopy (TEM) revealed the presence of small nanoparticles that assemble to yield irregularly shaped larger aggregates (Figure 4). Analysis of 60 randomly selected particles resulted in an average diameter of 3.3 ± 1 nm, which is in reasonable agreement with a value of 2.9 ± 0.4 nm computed from the width of the (111) reflection in the powder diffractogram using a modified version of the Scherrer equation.⁵¹ The particle size and distribution compare to those of reported monodisperse nanoparticles generated by size-controlled synthetic approaches.^{52,53} In summary, these findings indicate that the synthesis of metal nanoparticles from oligomeric phosphenium metal(0) halides is in principle feasible, but platinum complexes $12^{Mes}/13^{Mes}$ failed to react due to their superior thermal stability, which is, like in the case of 9^{Dipp} , presumably a consequence of their increased kinetic inertness.

CONCLUSIONS

The reactions of phosphenium hydrides 8^{Dipp} and 8^{Mes} with $[(\text{cod})\text{PtX}_2]$ (X = Cl, Br) proceed less uniformly than those with analogous palladium salts and yield different types of

products depending on the nature of the N-aryl substituent in the phosphorus and the halogen atom in the platinumcontaining reactant. Oligomeric phosphenium platinum(0) halides $[\{(^{Mes}NHP)PtBr\}_n]$ (12^{Mes}: n = 2; 13^{Mes}: n = 3) accessible from 8^{Mes} and $[(cod)PtBr_2]$ are structural analogues to known palladium complexes, but phosphine-stabilized complex 9^{Dipp} is unprecedented in representing the first coordinatively unsaturated monomeric phosphenium metal(0) halide featuring a formal 14 VE count at the metal center. The reactions leading to these products are slower than those of analogous palladium compounds and proceed via detectable intermediates. Even if not all transient species were unambiguously identified, their observation provides some insight into a rather complicated mechanistic pathway and confirms that the phosphenium hydrides adopt a dual function in the reactions studied in acting both as ligands and (reducing) hydride donors. Accordingly, all reactions involve the transfer of a hydride from phosphorus to platinum in an early reaction stage, which is subsequently eliminated, presumably as HX or H₂, when the final products (mostly phosphenium metal(0) halides) are formed. The preference for the observed multistep mechanisms can be explained by assuming that transformations initiated by nucleophilic attack at the ligating phosphorus atoms may be kinetically favored over the displacement of intact phosphine ligands from the metal. The outcome of the reaction of 9^{Dipp} with trimethyl phosphine, which proceeds under formal migration of a chloride from platinum to phosphorus to yield a platinum(0) chlorophosphine complex, is in line with evidence from quantum chemical studies suggesting that the phosphenium unit in monomeric complex 9^{Dipp} still exhibits electrophilic character and might thus be classified as a Z-type ligand.

Phosphenium platinum(0) halides derived from platinum and palladium show further remarkable differences in their thermal stability. The kinetically inert platinum complexes are surprisingly thermally stable, whereas the kinetically more labile palladium complexes are easily disintegrated by gentle heating in DMSO to yield metal nanoparticles. Further investigations to explore the use of these reactions as a new approach to the deposition of nanoparticles on suitable carrier materials and to test the catalytic activity of these materials are in progress.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.7b00022.

Details of the crystal structure determinations of 7, 9^{Dipp} , and 13^{Mes} ; NMR spectra of 9^{Dipp} , $12^{\text{Dipp}}/13^{\text{Dipp}}$, 15^{Dipp} , 16^{Dipp} , and 18^{Dipp} ; details of the characterization of Pd metal powders, and results of DFT calculations (PDF) Crystal structure determination of 7 (CIF) Crystal structure determination of 9^{Dipp} (CIF) Crystal structure determination of 13^{Mes} (CIF)

AUTHOR INFORMATION

Corresponding Author

*E-mail: gudat@iac.uni-stuttgart.de.

ORCID [©]

Dietrich Gudat: 0000-0002-9196-0466

Present Address

[§]D.A.I.: Institute of Polymer Chemistry, University of Stuttgart, Pfaffenwaldring 55, 70550 Stuttgart, Germany

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We thank the Institut für Anorganische Chemie for financial support. We further thank B. Förtsch for elemental analyses, J. Trinkner and Dr. W. Frey (both from Institute of Organic Chemistry, University of Stuttgart) for the measurement of mass spectra and the collection of X-ray data sets, and Dr. N. Preisig and C. Schlick (both from Institute of Physical Chemistry, University of Stuttgart) for the transmission electron microscopy (TEM) measurements. The computational studies were carried out at the JUSTUS HPC facility at the University of Ulm, funded by the state of Baden-Württemberg through the bwHPC initiative and the bwHPC-C5 project and the German Research Foundation (DFG) through Grant INST 40/467-1 FUGG.

DEDICATION

This paper is dedicated to Prof. Dr. Evamarie Hey-Hawkins on the occasion of her 60th birthday.

REFERENCES

(1) Fleming, S.; Lupton, M. K.; Jekot, K. The synthesis of a Cyclic Fluorodialkylamino-phosphine and Its Coordination with Boron Acids. The Formation of a Unique Dialkylamino-phosphine Cation. *Inorg. Chem.* **1972**, *11*, 2534–2540.

(2) Denk, M.; Gupta, S.; Lough, A. J. Synthesis and Reactivity of Subvalent Compounds, 8: Aromatic Phosphenium Cations. *Eur. J. Inorg. Chem.* **1999**, 1999, 41–49.

(3) For reviews on phosphenium ions, see: (a) Cowley, A. H.; Kemp, R. A. Synthesis and Reaction Chemistry of Stable Two-Coordinate Phosphorus Cations (Phosphenium Ions). *Chem. Rev.* **1985**, *85*, 367–382. (b) Sanchez, M.; Mazières, R. M.; Lamandé, L.; Wolf, R. Phosphenium Cations. In *Multiple Bonds and Low Coordination in Phosphorus Chemistry*; Regitz, M., Scherer, O. J., Eds.; Thieme: Stuttgart, 1990; pp 129–156. (c) Gudat, D. Cationic Low Coordinated Phosphorus Compounds as Ligands: Recent Developments. Coord. Chem. Rev. **1997**, *163*, 71–106. (d) Gudat, D. Recent Developments in the Chemistry of N-Heterocyclic Phosphines. In *Topics in Heterocyclic Chemistry*; Bansal, R. K., Ed.; Springer: Berlin/Heidelberg, Germany, 2010; Vol. 21, pp 63–102.

(4) Selected reviews: (a) Crudden, C. M.; Allen, D. P. Stability and reactivity of N-heterocyclic carbene complexes. *Coord. Chem. Rev.* 2004, 248, 2247–2273. (b) Bourissou, D.; Guerret, O.; Gabbai, F. P.; Bertrand, G. Stable Carbenes. *Chem. Rev.* 2000, 100, 39–91. (c) Herrmann, W. A. N-heterocyclic carbenes: A new concept in organometallic catalysis. *Angew. Chem., Int. Ed.* 2002, 41, 1290–1309. (d) *N-Heterocyclic Carbenes in Synthesis*; Nolan, S. P., Ed.; Wiley-VCH: Weinheim, Germany, 2006. (e) N-Heterocyclic Carbenes in Transition Metal Catalysis. In *Top. Organometal. Chem.*; Glorius, F., Ed.; Springer: Berlin, Heidelberg, NY, 2007; Vol. 21.

(5) Abrams, M. B.; Scott, B. L.; Baker, R. T. Sterically Tunable Phosphenium Cations: Synthesis and Characterization of Bis-(arylamino)phosphenium Ions, Phosphinophosphenium Adducts, and the First Well-Defined Rhodium Phosphenium Complexes. *Organometallics* **2000**, *19*, 4944–4956.

(6) Nakazawa, H. Transition metal complexes bearing a phosphenium ligand. *Adv. Organomet. Chem.* **2004**, *50*, 107–143.

(7) Caputo, Č. A.; Jennings, M. C.; Tuononen, H. M.; Jones, N. D. Phospha-Fischer Carbenes: Synthesis, Structure, Bonding, and Reactions of Pd(0)- and Pt(0)-Phosphenium Complexes. *Organometallics* **2009**, 28, 990–1000.

(8) Rosenberg, L. Metal complexes of planar PR₂ ligands: Examining the carbene analogy. *Coord. Chem. Rev.* **2012**, *256*, 606–626.

(9) Hardman, N. J.; Abrams, M. B.; Pribisko, M. A.; Gilbert, T. M.; Martin, R. L.; Kubas, G. J.; Baker, R. T. Molecular and Electronic Structure of Platinum Bis(N-arylamino)phosphenium Complexes including [Pt(phosphane) (phosphenium)-(N-heterocyclic carbene)]. *Angew. Chem., Int. Ed.* **2004**, *43*, 1955–1958.

(10) Caputo, A.; Brazeau, A. L.; Hynes, Z.; Price, J. T.; Tuononen, H.; Jones, N. D. A Cation-Captured Palladium(0) Anion: Synthesis, Structure, and Bonding of $[PdBr(PPh_3)_2]^-$ Ligated by an N-Heterocyclic Phosphenium Cation. *Organometallics* **2009**, *28*, 5261–5265.

(11) Pan, B.; Xu, Z.; Bezpalko, M. W.; Foxman, B.; Thomas, C. M. N-Heterocyclic Phosphenium Ligands as Sterically and Electronically-Tunable Isolobal Analogues of Nitrosyls. *Inorg. Chem.* **2012**, *51*, 4170–4179.

(12) Pan, B.; Bezpalko, M. W.; Foxman, B. M.; Thomas, C. M. Heterolytic addition of E–H bonds across Pt–P bonds in Pt N-heterocyclic phosphenium/phosphido complexes. *Dalton Trans.* **2012**, *41*, 9083–9090.

(13) Förster, D.; Nickolaus, J.; Nieger, M.; Benkö, Z.; Ehlers, A.; Gudat, D. Donor-Free Phosphenium–Metal(0)–Halides with Unsymmetrically Bridging Phosphenium Ligands. *Inorg. Chem.* **2013**, *52*, 7699–7708.

(14) Pan, B.; Evers-McGregor, D. A.; Bezpalko, M. W.; Foxman, B. M.; Thomas, C. M. Multimetallic Complexes Featuring a Bridging Nheterocyclic Phosphido/Phosphenium Ligand: Synthesis, Structure, and Theoretical Investigation. *Inorg. Chem.* **2013**, *52*, 9583–9589.

(15) Nickolaus, J.; Bender, J.; Nieger, M.; Gudat, D. Sterically Controlled Synthesis and Nucleophilic Substitution Reactions of Diand Trimeric N-Heterocyclic-Phosphenium-Metal(0)-Halides. *Eur. J. Inorg. Chem.* **2014**, 2014, 3030–3036.

(16) Selected reading: (a) Kozitsyna, N. Yu.; Moiseev, I. I. Reductive Reactions in Synthesis of Low-valence Platinum and Palladium Cojmplexes. *Russ. Chem. Rev.* **1995**, *64*, 31–65. (b) Ellis, J. E. Adventures with substances containing metals in negative oxidation states. *Inorg. Chem.* **2006**, *45*, 3167–3186. (c) Ortiz, N.; Skrabalak, S. E. On the Dual Roles of Ligands in the Synthesis of Colloidal Metal Nanostructures. *Langmuir* **2014**, *30*, 6649–6659. (d) Roy, S.; Mondal, K. C.; Roesky, H. W. Cyclic Alkyl(amino) Carbene Stabilized Complexes with Low Coordinate Metals of Enduring Nature. *Acc. Chem. Res.* **2016**, *49*, 357–369.

(17) Brown, H. C.; Brown, C. A. Simple Preparation of Highly Active Platinum Metal Catalysts for Catalytic Hydrogenation. J. Am. Chem. Soc. 1962, 84, 1494-1495. Recent results: (a) Harada, T.; Ikeda, S.; Miyazaki, M.; Sakata, T.; Mori, H.; Matsumura, M. A simple method for preparing highly active palladium catalysts loaded on various carbon supports for liquid-phase oxidation and hydrogenation reactions. J. Mol. Catal. A: Chem. 2007, 268, 59-64. (b) Shibasaki, T.; Komine, N.; Hirano, M.; Komiya, S. Synthesis of di-, tri-, tetra- and pentacyclic arene complexes of ruthenium(II): [Ru(η^6 -polycyclic arene)-(1-5- η^5 cyclooctadienyl)]PF₆ and their reactions with NaBH₄. J. Organomet. Chem. 2007, 692, 2385-2394. (c) Li, B.; Higgins, D. C.; Zhu, S.; Li, H.; Wang, H.; Ma, J.; Chen, Z. Highly active Pt-Ru nanowire network catalysts for the methanol oxidation reaction. Catal. Commun. 2012, 18, 51-54. (d) Buitrago-Sierra, R.; Garcia-Fernandez, M. J.; Pastor-Blas, M. M.; Sepulveda-Escribano, A. Environmentally friendly reduction of a platinum catalyst precursor supported on polypyrrole. Green Chem. 2013, 15, 1981-1990. (e) Hoseini, S. J.; Bahrami, M.; Dehghani, M. Formation of snowman-like Pt/Pd thin film and Pt/Pd/reducedgraphene oxide thin film at liquid-liquid interface by use of organometallic complexes, suitable for methanol fuel cells. RSC Adv. 2014, 4, 13796-13804.

(18) Burck, S.; Gudat, D.; Nieger, M.; Du Mont, W.-W. P-Hydrogen-Substituted 1,3,2-Diazaphospholenes: Molecular Hydrides. *J. Am. Chem. Soc.* **2006**, *128*, 3946–3955.

(19) Dube, J. W.; Farrar, G. J.; Norton, E. L.; Szekely, K. L.; Cooper, B. F. T.; MacDonald, C. L. B. A Convenient Method for the Preparation of N-Heterocyclic Bromophosphines: Excellent Precursors to the Corresponding N-Heterocyclic Phosphenium Salts. *Organometallics* **2009**, *28*, 4377–4384.

(20) Gudat, D.; Haghverdi, A.; Nieger, M. Umpolung of P-H-Bonds. Angew. Chem., Int. Ed. 2000, 39, 3084–3087.

Inorganic Chemistry

(21) Sheldrick, G. M. A short history of SHELX. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **2008**, *64*, 112–122.

(22) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian 09, revision E.01; Gaussian, Inc.: Wallingford CT, 2009.

(23) Schaftenaar, G.; Noordik, J. H. Molden: a pre- and postprocessing program for molecular and electronic structures. *J. Comput.-Aided Mol. Des.* **2000**, *14*, 123–134.

(24) te Velde, G.; Bickelhaupt, F. M.; Baerends, E. J.; Fonseca Guerra, C.; van Gisbergen, S. J. A.; Snijders, J. G.; Ziegler, T. Chemistry with ADF. *J. Comput. Chem.* 2001, *22*, 931–967; ADF2014, SCM, Theoretical Chemistry; Vrije Universiteit: Amsterdam, The Netherlands, 2014; http://www.scm.com.

(25) Schreckenbach, G.; Ziegler, T. Calculation of NMR Shielding Tensors using Gauge-including Atomic Orbitals and modern Densityfunctional Theory. *J. Phys. Chem.* **1995**, *99*, 606–611.

(26) Schreckenbach, G.; Ziegler, T. Calculation of NMR shielding tensors based on density functional theory and a scalar relativistic Paulitype Hamiltonian. The application to transition metal complexes. *Int. J. Quantum Chem.* **1997**, *61*, 899–918.

(27) Wolff, S. K.; Ziegler, T. Calculation of DFT-GIAO NMR shifts with the inclusion of spin-orbit coupling. *J. Chem. Phys.* **1998**, *109*, 895–905.

(28) Wolff, S. K.; Ziegler, T.; van Lenthe, E.; Baerends, E. J. Density functional calculations of nuclear magnetic shieldings using the zerothorder regular approximation (ZORA) for relativistic effects: ZORA nuclear magnetic resonance. J. Chem. Phys. **1999**, *110*, 7689–7698.

(29) Dickson, R. M.; Ziegler, T. NMR spin-spin coupling constants from density functional theory with slater-type basis functions. *J. Phys. Chem.* **1996**, *100*, 5286–5290.

(30) Khandogin, J.; Ziegler, T. A density functional study of nuclear magnetic resonance spin-spin coupling constants in transition-metal systems. *Spectrochim. Acta, Part A* **1999**, *55*, 607–624.

(31) Autschbach, J.; Ziegler, T. J. Chem. Phys. 2000, 113, 936.

(32) Autschbach, J.; Ziegler, T. Nuclear spin-spin coupling constants from regular approximate relativistic density functional calculations. II. Spin-orbit coupling effects and anisotropies. *J. Chem. Phys.* **2000**, *113*, 9410–9418.

(33) Vosko, S. H.; Wilk, L.; Nusair, M. Accurate spin-dependent electron liquid correlation energies for local spin-density calculations – a critical analysis. *Can. J. Phys.* **1980**, *58*, 1200–1211.

(34) Becke, A. D. Density-functional exchange-energy approximation with correct asymptotic behavior. *Phys. Rev. A: At., Mol., Opt. Phys.* **1988**, 38, 3098–3100.

(35) Perdew, J. P. Density-functional approximation for the correlation energy of the inhomogeneous electron gas. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1986**, 33, 8822–8824.

(36) van Wüllen, C. A comparison of density functional methods for the calculation of phosphorus-31 NMR chemical shifts. *Phys. Chem. Chem. Phys.* **2000**, *2*, 2137–2144.

(37) Blau, R. J.; Espenson, J. H. Correlations of Pt-195-P-31 couplingconstants with platinum-ligand and platinum-platinum bond lengths in platinum(I) dimers and in related platinum(II) complexes. *Inorg. Chem.* **1986**, *25*, 878–880. (38) Waddell, P. G.; Slawin, A. M. Z.; Woollins, J. D. Correlating Pt-P bond lengths and Pt-P coupling constants. *Dalton Trans.* **2010**, *39*, 8620–8625.

(39) Gil, V. M. S.; Von Philipsborn, W. Effect of Electron Lone-Pairs on Nuclear Spin-Spin Coupling Constants. *Magn. Reson. Chem.* **1989**, 27, 409–430.

(40) Mazzeo, M.; Strianese, M.; Kühl, O.; Peters, J. C. Phosphido pincer complexes of platinum: synthesis, structure and reactivity. *Dalton Trans.* **2011**, *40*, 9026–9033.

(41) Gudat, D.; Meidine, M. F.; Nixon, J. F.; Niecke, E. Reaction of P-Halogeno-phospha-alkenes with Alkene Complexes of Nickel and Platinum: η^2 -Co-ordination and Unusual Oxidative Addition Behaviour. *J. Chem. Soc., Chem. Commun.* **1989**, 1206–1208.

(42) Burckett-St. Laurent, J. C. T. R.; Hitchcock, P. B.; Kroto, H. W.; Nixon, J. F. Novel transition-metal phospha-alkyne complexes – X-ray crystal and molecular structur of a side-bonded $Bu^tC = P$ complex of zerovalent platinum, Pt(PPh₃)₂(Bu^tCP). *J. Chem. Soc., Chem. Commun.* **1981**, 1141–1143.

(43) Mansell, S. M.; Green, M.; Russell, C. A. Coordination chemistry of trimethylsilylphosphaalkyne: a phosphaalkyne bearing a reactive substituent. *Dalton Trans.* **2012**, *41*, 14360–14368.

(44) Reed, A. E.; Weinstock, R. B.; Weinhold, F. Natural population analysis. *J. Chem. Phys.* **1985**, 83, 735–746.

(45) It has recently been demonstrated that, despite substantial difficulties, predictions of ¹⁹⁵Pt NMR chemical shifts by relativistic DFT calculations are sufficiently accurate to serve as a basis for structural assignments, see, e.g.: Still, B. M.; Kumar, P. G. A.; Aldrich-Wright, J. R.; Price, W. S. Pt-195 NMR - theory and application. *Chem. Soc. Rev.* 2007, 36, 665–686. Tsipis, A. C.; Karapetsas, I. N. Accurate prediction of Pt-195 NMR chemical shifts for a series of Pt(II) and Pt(IV) antitumor agents by a non-relativistic DFT computational protocol. *Dalton Trans.* 2014, 43, 5409–5426.

(46) Pregosin, P. S. Platinum NMR Spectroscopy. In *Annu. Rep. NMR Spectrosc.*; Webb, G. A., Ed.; Academic Press: London, 1986; pp 285–349.

(47) Phillips, J. R.; Trogler, W. C.; Brammer, M.; Packett, D. L. Chlorohydrido-bis(Trialkylphosphine)-Platinum(II) complexes. *Inorg. Synth.* **1992**, *29*, 189–192.

(48) Burck, S.; Gudat, D.; Nättinen, K.; Nieger, M.; Niemeyer, M.; Schmid, D. P-Chloro-1,3,2-Diazaphospholenes – A Crystal Structural Study. *Eur. J. Inorg. Chem.* **2007**, 2007, 5112–5119.

(49) Favez, R.; Roulet, R.; Pinkerton, A. A.; Schwarzenbach, D. Study of $PtX_2(PR_3)_2$ in the presence of PR_3 in CH_2Cl_2 solution and the cistrans isomerization reaction as studied by P-31 NMR – crystal structure of $[PtCl(PMe_3)_3]Cl.$ *Inorg. Chem.* **1980**, *19*, 1356–1365.

(50) An alternative formulation $[(^{R}NHP)(Me_{3}P)_{3}Pt-Cl]$ as phosphenium complex with covalent Pt-Cl bonding was ruled out as our computational studies on model compounds with R = Me failed to locate an appropriate minimum on the energy hypersurface.

(51) Borchert, H.; Shevchenko, E. V.; Robert, A.; Mekis, I.; Kornowski, A.; Grübel, G.; Weller, H. Determination of nanocrystal sizes: A comparison of TEM, SAXS, and XRD studies of highly monodisperse CoPt₃ particles. *Langmuir* **2005**, *21*, 1931–1936.

(52) Teranishi, T.; Miyake, M. Size control of palladium nanoparticles and their crystal structures. *Chem. Mater.* **1998**, *10*, 594–600.

(53) Kim, S.-W.; Park, J.; Jang, Y.; Chung, Y.; Hwang, S.; Hyeon, T.; Kim, Y. W. Synthesis of monodisperse palladium nanoparticles. *Nano Lett.* **2003**, *9*, 1289–1291.