

A Platinum(II) Metallonitrene with a Triplet Ground State

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ABSTRACT

Metallonitrenes (M–N) are complexes with a subvalent, atomic nitrogen ligand that have been proposed as key reactive intermediates in nitrogen atom transfer reactions. However, in contrast to the common class of nitride complexes (M≡N) and organic nitrenes (R–N), structurally and spectroscopically well-defined, authentic metallonitrenes with a monovalent, atomic nitrogen ligand remain elusive. We here report that the photolysis of a platinum(II) pincer azide complex enabled the crystallographic, spectroscopic, magnetic and computational characterization of a metallonitrene that is best described as a singly bonded, atomic nitrogen diradical ligand bound to platinum(II). The photoproduct exhibits selective C–H, B–H, and B–C nitrogen atom insertion reactivity. Despite the subvalent metallonitrene character, mechanistic analysis for aldehyde C–H amidation reveals nucleophilic reactivity of the *N*-diradical ligand. Ambiphilic reactivity of the metallonitrene is indicated by reactions with CO and PMe₃ to isocyanate and phosphoraneiminato platinum(II) complexes, respectively.

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Rational synthetic method development is driven by the ability to relate reactivity to the electronic structures of key transient intermediates. For example, organic nitrenes (R–N) are generally highly reactive, monovalent nitrogen species and detailed spectroscopic studies enabled the assignment of their diverse reaction pathways, such as C–H insertion or N–N coupling, to the accessibility of triplet *vs* (open shell) singlet spin-states.^{1,2} In comparison, the well-established class of nitrido complexes (L_nMN) commonly features trivalent nitrogen with significant covalent components to M–N σ - and π -bonding (Fig. 1a).³ Increased radical and electrophilic nitrogen character can be formally represented by divalent nitridyl all the way to monovalent metallonitrene contributions.⁴ Formal nitrido complexes with predominant subvalent metallonitrene (L_nM-N) character, which can be regarded as metal analogues of organic nitrenes, have been proposed as key intermediates in stoichiometric intra-^{5,6,7,8,9} and intermolecular^{10,11,12,13,14,15} nitrogen atom transfer reactions. However, in contrast to organic nitrenes,¹⁶ authentic metallonitrenes with a monovalent, atomic nitrogen ligand remain elusive, which impedes the development new nitrogen transfer reactions based on electronic structure/reactivity relationships.

The emergence of C–H amination and amidation *via* nitrene transfer as a powerful synthetic tool was fueled by the development of group 9-11 transition metal catalysts that facilitate selective insertion of coordinated nitrene fragments (Fig. 1b).^{17,18,19} Late transition metals are also instrumental as anode material in electrocatalytic amine oxidation for synthetic and fuel-cell applications.^{20,21,22} The dominance of late transition metals in redox transformations of nitrogenous species stimulated fundamental interest in M–N(R) bonding.³ C–H insertion by L_nM-NR species has been associated with electrophilic, subvalent nitrene (3NR)²³ or imidyl ($^2NR^-$)^{24,25,26} character that arises from low lying d-orbitals of late transition metals, which strongly reduces the imido ($^1NR^{2-}$)

contribution.^{27,28} Similar considerations might apply for metallonitrene (L_nM-N) or nitridyl ($L_nM=N^\bullet$) vs. nitrido ($L_nM\equiv N$) species (Fig. 1a). However, intermolecular C–H activation has not been reported for the few known late transition metals nitrido or nitridyl complexes.^{29,30,31} The exploitation of nitrogen atom insertion reactivity (Fig. 1b) is still in its infancy; as of yet catalytic protocols are not known and systematic advances suffer from the lack of well-defined metallonitrene platforms.

In this contribution, the first formal nitrido complex beyond group 9 is reported. Crystallographic, spectroscopic, magnetic and computational characterization shows a triplet electronic ground-state with a predominantly single-bonded metallonitrene ($L_nPt^{II}-N$) and nitrogen-centered diradical character. Facile N-atom insertion into C–H, B–H, and B–C bonds is demonstrated. In contrast to the generally observed electrophilicity of nitrenes,^{17,19} mechanistic analysis for aldehyde amidation evidences nucleophilic reactivity of the subvalent diradical metallonitrene.

RESULTS AND DISCUSSION

Generation and Characterization of Metallonitrene [Pt(N)(PNP)]. The platinum(II) azide complex [Pt(N₃)(PNP)] (**1**, PNP = N(CHCHP^tBu₂)₂) is obtained from the respective chloride precursor in a three-step synthesis (Supplementary Section 1.2). Photolysis in the solid state or in solution with a Xe arc lamp ($\lambda > 305$ nm) or a violet LED ($\lambda = 390$ nm) results in gradual bleach of the azide band in the IR spectrum at 2052 cm⁻¹. A brown product is obtained with several electronic absorption bands in the 360-600 nm range. At temperatures above approximately 223 K (toluene) or 253 K (THF), the spectroscopic signature of the photoproduct vanishes indicating thermal instability.

Structural characterization of the photoproduct was therefore carried out by photocrystallography.^{32,33,34} Photolysis of a single-crystal of **1** at 100 K with a violet LED ($\lambda = 390$

nm) gave rise to conversion over several hours. Crystallographic monitoring within space group $P\bar{1}$ revealed the depletion of electron density in the region of the azide N_β and N_γ atoms. This is accompanied by a rise of electron density in the void defined by the *t*Bu substituents of the pincer ligand. The crystallographic data was refined with a partial occupation model of azide **1** and the photoproducts, i.e. [Pt(N)(PNP)] (**2**; Fig. 2a) and free N_2 trapped in the crystal lattice at a distance of over 3 Å from the Pt–N moiety, confirming full scission of the azide N_α – N_β bond. Satisfactory crystallographic data was obtained up to a photoconversion of 76 %, offering reliable metrical parameters of the molecular structure of **2**.

In comparison with parent **1**, the structure of **2** exhibits only small deviations within the {Pt(PNP)} framework. The approximately linear N–Pt–N axis is maintained (N–Pt–N angle: 176.0(4) °) and slight elongation of the Pt– N_{PNP} bond ($\Delta d = 0.06$ Å) indicates increased *trans*-influence. In turn, the distance to the atomic nitrogen ligand ($d_{\text{Pt–N}} = 1.874(11)$ Å) is at the lower end of experimentally observed Pt–N bond lengths³⁵ and significantly shortened with respect to **1** (Pt– N_3 distance: 2.031(5) Å) or independently prepared, parent amide complex [Pt(NH₂)(PNP)] (**3**; Pt–NH₂ distance: 2.030(3) Å), respectively. A similar bond length (1.81 Å) was computed for the Pt=O core in Milstein’s platinum oxo complex.^{36,37} However, in that case the oxo ligand was predicted to be strongly bent out of the {Pt(PCN)}-plane (C–Pt–O angle: 138.2 °). Based on Pyykkö’s covalent radii, 1.94 Å, 1.72 Å, and 1.64 Å are expected for Pt–N single, double and triple bond lengths, respectively.³⁸

The observation of three paramagnetically broadened and shifted ¹H NMR signals is in agreement with an open-shell, C_{2v} symmetric ground-state, in analogy to isoelectronic ³[Ir(E)(PNP)] (E = NR, O).^{39,40} Linear dependence of $\delta(^1\text{H})$ on T^{-1} indicates population of a single electronic state in the

range 193-253 K. SQUID magnetometry data was obtained after *in situ* photolysis of solid azide **1** at 10 K ($\lambda_{\text{exc}} = 390 \text{ nm}$) leading to constant rise of the DC magnetic moment over time. Below 50 K, the $\chi_{\text{m}}T$ product of the photoproduct increases approximately linearly with temperature and assumes an almost constant value between 50-170 K (Fig. 2b). Beyond that, the magnetic moment rapidly drops, which we attribute to thermal instability of the photoproduct. The magnetic data below 170 K was nicely reproduced with a zero-field splitting (ZFS) spin-Hamiltonian for a triplet ($S = 1$) state with isotropic g -factor ($g = 2$) upon estimating the photochemical conversion by normalization to the expectation value at high temperatures. The obtained axial and rhombic ZFS parameters ($D = 85 \text{ cm}^{-1}$, $E = 0.08 D$) are in excellent agreement with the values predicted by multi-reference NEVPT2 spin-orbit computations ($D = 73 \text{ cm}^{-1}$, $E = 0.06 D$; Fig. 2b) and in line with the absence of an X-band EPR signal for **2** (in both perpendicular and parallel mode). However, the microstate splitting is considerably smaller as compared with isoelectronic [Ir(NR)(PNP)] ($D = 466 \text{ cm}^{-1}$) and [Ir(O)(PNP)] ($D = 647 \text{ cm}^{-1}$),^{39,40} respectively, indicating decreased effective spin-orbit coupling (ζ_{eff}). As an explanation, ligand-field considerations suggest increased ligand radical character for **2**.⁴¹ This is fully supported by the computational analysis, which reveals dominantly N-centered biradical character (Fig. 2c).

Quantum-chemical modeling of complex **2** gave square-planar metal coordination for DFT optimized geometries of both the triplet and singlet states. While the experimental structural parameters are nicely reproduced by the triplet state (e.g., $d_{\text{Pt-N}} = 1.89 \text{ \AA}$), the Pt–N bond length is significantly shorter for the singlet species ($d_{\text{Pt-N}} = 1.79 \text{ \AA}$). Explicitly correlated ONIOM coupled-cluster computations (Supplementary Section 4.1) confirmed that the triplet state is strongly stabilized with respect to the lowest singlet by $\Delta E_{\text{S-T}} = 15 \text{ kcal mol}^{-1}$. Spin-orbit coupling effects

have no significant influence on the spin-state energetics according to CASSCF/NEVPT2 calculations (Fig. 2d). The composition of natural localized molecular orbitals (NLMOs) evolving from a natural bond orbital (NBO) analysis of the DFT ground state wave function supports the notion of a $\{\text{Pt}^{\text{II}}\text{-N}\}$ metallonitrene (NPA charges: $q_{\text{Pt}} = +0.38$, $q_{\text{N(nitrene)}} = -0.52$). The NBO results reveal a covalent Pt–N σ -bond polarized towards nitrogen (Fig. 3a), an s-type lone-pair and two singly occupied p-type NLMOs on the nitrene N-atom (Fig. 3b) as well as four essentially nonbonding Pt d-orbitals (Fig. 3c) that share only insignificant N contributions (Pt–N Wiberg bond order: 0.94). This picture closely resembles an organic nitrene (N–R)^{42,43} with moderately spaced frontier orbitals, resulting in a triplet ground state and a first excited closed-shell singlet state, followed by an open-shell singlet, like methoxy nitrene N–OCH₃.¹ Multireference computations fully support this picture and disclose predominant (92%) triplet ground-state metallonitrene $\text{Pt}^{\text{II}}(^3\text{N})$ character. Imidyl, $\text{Pt}^{\text{III}}(^2\text{N}^-)$, or related alternative configurations contribute individually by less than 1% to the ground-state wave function (Supplementary Table 38).²³ Our results disclose **2** as a unique metallonitrene with predominant single covalent Pt–N bond character without significant π -bonding, contrasting with typical nitrido complexes.²⁹

Reactivity of Metallonitrene [Pt(N)(PNP)] (2). The reactivity of metallonitrene **2** was examined by *in situ* photolysis of **1** ($\lambda_{\text{exc}} > 305$ nm). In the presence of CO (1 atm), the platinum(II) isocyanate complex [Pt(NCO)(PNP)] (**4**) was obtained with high selectivity and could be isolated in around 60 % yield (Fig. 4a). In analogy, the reaction with PMe₃ gave phosphoraneiminato complex [Pt(NPMe₃)(PNP)] (**5**) in around 75 % spectroscopic yield, which could be characterized crystallographically (Fig. 4a), indicating facile crossing onto the singlet surface upon nucleophilic attack.¹⁶ Nitrogen atom transfer was further examined with selected electrophiles. Insertion into C–H,

B–H, and B–C bonds was obtained in the presence of 1.1-1.5 equiv. benzaldehyde, 1-butanol, 4,4,5,5-tetramethyl-1,2,3-dioxaborolane (HBpin), and triphenylborane, respectively, giving the platinum(II) amido complexes **6-9** in over 80 % (**6-8**) and 39 % (**9**) isolated yields, respectively (Fig. 4a). Photolysis of **1** in toluene-*d*₈ at –70 °C and subsequent addition of benzaldehyde also gave the amide product **6** as main product after warming to room temperature in the dark, supporting thermal amide formation from the metallonitrene intermediate.

Aldehyde C–H amidation was examined in more detail to distinguish between conceivable pathways. Photolysis of **1** in the presence of PhC(O)H/PhC(O)D (5 equiv. each) indicated the absence of a kinetic isotope effect (KIE). Competition experiments with a series of *para*-substituted benzaldehydes gave rise to a *Hammett*-plot with a steep, positive slope ($\rho = +4.4$, Fig. 4b).⁴⁴ These observations are consistent with rate-determining nucleophilic attack of the metallonitrene at the carbonyl group. Importantly, the reactivity of **2** does obviously not encompass radical rebound pathways via hydrogen atom abstraction (HAA) here, despite the diradical nature of the nitrene and comparatively small aldehyde C–H bond dissociation energies.⁴⁵

Further mechanistic rationalization of aldehyde amidation is provided by computational investigations. Explicitly correlated ONIOM coupled-cluster calculations were used to compare nucleophilic vs. radical reactivity of **2** (Fig. 5). The radical HAA from benzaldehyde is connected with a free energy barrier of 20.9 kcal mol⁻¹ (**TS1**). Nucleophilic attack of triplet species **2** at benzaldehyde via **TS2** ($\Delta G^\ddagger = 16.8$ kcal mol⁻¹) is clearly favored over HAA and leads to tetrahedral intermediate **I2**. In analogy to **2**, triplet **TS2** lacks significant contributions from other configurations, excluding imidyl- or nitride-driven reactivity. The ONIOM coupled-cluster results reveal a singlet ground state for **I2**, in full accordance with multi-reference NEVPT2 results. In contrast, DFT

erroneously favors a triplet ground state (Supplementary Table 40) as similarly reported for related copper nitrene complexes.^{46,47} The singlet and triplet potential energy surfaces cross beyond transition state **TS2** along the reaction coordinate leading to **I2**. The estimated crossing point is approximately isoenergetic with **TS2**, which excludes any significant lowering of the activation barrier in the sense of a two state reactivity scenario.^{48,49} Two pathways branch off from **I2**, i.e., formation of amide **6** or alternatively ring closure to oxaziridine **I3**, as typically observed for singlet aryl nitrenes.⁵⁰ However, oxaziridine formation is reversible under the reaction conditions and both kinetically and thermodynamically disfavored. The experimentally observed product **6** is formed from **I2** with a modest barrier of 10.7 kcal mol⁻¹ via **TS3** in a highly exergonic step ($\Delta_r G = -75.9$ kcal mol⁻¹). Thus, nucleophilic attack of the triplet metallonitrene at the carbonyl group represents the overall rate determining step and neither the transition to the singlet potential energy surface nor the subsequent H-shift are kinetically significant, in full agreement with the Hammett-analysis and the absence of an H/D KIE.

CONCLUSIONS

In summary, the metallonitrene **2** was synthesized upon photolysis of azide complex **1**. Complex **2** exhibits a triplet electronic ground state with unexpectedly low microstate splitting as a result of dominant ligand radical character. Our detailed bonding analysis supports the picture of a $\{(PNP)Pt^{II}\}$ fragment with a single covalent σ -bond to an atomic nitrogen diradical ligand in distinct contrast to the common triply bonded nitrido description. Complex **2** exhibits versatile and selective ambiphilic intermolecular reactivity, exemplified, e.g. by the formation of phosphoraneiminato product **5** and reaction with aldehydes and boranes that leads to facile nitrogen atom insertion into C–H, B–H, and

B–C bonds. Experimental and computational mechanistic data for aldehyde amidation favor rate-determining, nucleophilic attack of the nitrogen atom over initial (proton coupled) electron transfer pathways, such as a HAA / radical rebound mechanism, which is surprising given its subvalent, diradical nature. This work provides a detailed view on the electronic structure of metallonitrenes and emphasizes the fact that, in contrast to intuition, neither the subvalent character nor the open-shell nature of the ground state are reliable predictors for nitrogen atom transfer reactivity.⁵¹

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ACKNOWLEDGEMENT

The authors thank the ERC (Grant Agreement 646747) and the German Research Council (DFG grants 389479699/RTG2455, SA1840/7 and SL104/10) for funding. J. M. Matys is acknowledged for help with synthetic work and single-crystal growth of [Pt(OTf)(PNP)]. C. W. thanks Dr. R. Herbst-Irmer for helpful discussion. Quantum-chemical calculations of the Frankfurt group were performed at the Center for Scientific Computing (CSC) Frankfurt on the Goethe-HLR computer cluster.

AUTHOR CONTRIBUTIONS

J.S.: Synthetic and spectroscopic work and manuscript writing. J.A.: Spectroscopic and crystallographic work. C.W.: crystallographic characterization. S.Sch.: Supervision of J.S. and J.A., conceptual design of the study and manuscript writing. B.d.B., M.D., M.C.H. (conceptual design, supervision) and H.V. carried out the quantum chemical study and wrote the theory sections of the manuscript. D.H. carried out the magnetic characterization supervised by J.v.S.

COMPETING INTERESTS

The authors declare no competing interests.

ADDITIONAL INFORMATION

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FIGURE LEGEND

Figure 1 | Lewis structures and C–H nitrogen insertion reactivity of coordinated nitrogen ligands. **a.** Lewis representations for nitrido, nitridyl and metallonitrene character. **b.** C–H functionalization via metal-mediated nitrene insertion (top) vs. nitrogen atom insertion (bottom). (L = ligands, R and R' = organic substituents).

Figure 2 | Synthesis, crystallographic and magnetic characterization of platinum(II) metallonitrene 2. **a.** Molecular structure of **2** obtained by *in situ* photolysis of a single-crystal of **1** (H atoms omitted for clarity). Selected bond lengths (Å) and angles (°) of **1**: Pt1–N1 2.011(5), Pt1–N2 2.031(5), Pt1–P1 2.3171(13), Pt1–P2 2.3125(13), P2–Pt1–P1 165.77(5), N1–Pt1–N2 174.4(2); and of **2**: Pt1–N1 2.068(7), Pt1–N2 1.874(11), Pt1–P1 2.3050(19), Pt1–P2 2.303(2), P2–Pt1–P1 164.88(8), N1–Pt1–N2 176.0(4). **b.** $\chi_M T$ vs. T data (circles) of *in situ* ($\lambda_{exc} = 390$ nm) formed **2** obtained by SQUID magnetometry with simulated (blue line) and ab initio computed (red line) values. **c.** Computed spin-density distribution

and NPA spin population (isosurface at $0.0075 a_0^{-3}$; PBE0/def2-TZVPP results). **d.** State correlation diagram from CASSCF/NEVPT2 calculations for the triplet ground state of **2** without (left) and with spin-orbit coupling (SOC).

Figure 3 | Characteristic NLMOs resulting from an NBO analysis support the platinum(II) metallonitrene description of complex 2. Isosurfaces at $\pm 0.05 a_0^{-3/2}$, results for doubly occupied orbitals were obtained by averaging over the α and β spin orbitals. **a.** Pt–N σ -bond. **b.** Singly occupied p_y and p_z orbitals and s-type lone pair localized at N. **c.** Pt-centered, doubly occupied d orbitals.

Figure 4 | Nitrogen centered reactivity of metallonitrene 2. **a.** Ambiphilic reactivity patterns of the metallonitrene with CO, PMe₃ and towards C–H, B–H, and B–C insertion reactions. **b.** The *Hammett*-plot for C–H nitrogen atom insertion with *para*-substituted benzaldehydes indicates nucleophilic reactivity of the metallonitrene.

Figure 5 | Computational examination of the reaction of metallonitrene 2 with benzaldehyde. Calculated pathways for the reaction of **2** (full model) with PhCHO (ONIOM(CCSD(T*)-F12:PBE0-D) support nucleophilic attack of the triplet metallonitrene at the carbonyl group as preferred pathway (triplet surface in black and singlet surface in red; ΔG in kcal mol⁻¹; only tertiary carbon atoms of *t*Bu groups shown for ball and stick figures).

METHODS

Synthesis and characterization of complexes 1 and 3-9.

[PtN₃(PNP)] (**1**): [PtOTf(PNP)] (**D**) (68 mg, 0.10 mmol, 1.00 eq.) and NaN₃ (34 mg, 0.52 mmol, 5.31 eq.) were suspended in 2 mL THF. After stirring for 14 h at room temperature in a brown vial, the color of the mixture changed from light yellow to almost colorless. After removal of the solvent, extraction with Et₂O (5*3 mL) and evaporation of the solvent, a white solid was obtained. Extraction with C₆H₆ (*ca.* 3 mL), filtration and removal of solvent gave **1** as white solid (52.7 mg, 90%). Crystals suitable for X-ray diffraction were obtained by slow evaporation of an Et₂O solution. ¹H NMR (300.13 MHz, C₆D₆, 298 K): δ (ppm) 6.53 (A₁₈XX'A'₁₈, N = $|^3J_{HP}+^4J_{HP}|$ = 38.1 Hz, $^3J_{H-H}$ = 5.4 Hz, $^3J_{PtH}$ = 78.1 Hz, 2H, NCH), 3.91 (A₁₈XX'A'₁₈, N = $|^2J_{HP}+^4J_{HP}|$ = 9.3 Hz, $^3J_{HH}$ = 5.2 Hz, $^3J_{PtH}$ = 33.6 Hz, 2H, PCH), 1.33 (A₁₈XX'A'₁₈, N = $|^3J_{HP}+^5J_{HP}|$ = 14.4 Hz, 36H, CMe₃); ¹³C{¹H} NMR (75.48 MHz, C₆D₆, 298 K): δ (ppm) 162.6 (t, $^2J_{PC}$ = 7.4 Hz, $^2J_{PtC}$ = 81.8 Hz, NCH), 82.8 (t, $^1J_{PC}$ = 22.8 Hz, $^2J_{PtC}$ = 53.2 Hz, CHP),

36.2 (t, $^1J_{PC} = 13.0$ Hz, $PCMe_3$), 29.1 (t, $^2J_{PC} = 3.1$ Hz, $^3J_{PtC} = 12.8$ Hz, $PCMe_3$); $^{31}P\{^1H\}$ NMR (121.49 MHz, C_6D_6 , 298 K): δ (ppm) 66.8 (s, $^1J_{PtP} = 2686.5$ Hz); $^{195}Pt\{^1H\}$ NMR (107.14 MHz, toluene- d_8 , 298 K): δ (ppm) -3917.4 (t, $^1J_{PtP} = 2719.7$ Hz). IR (ATR): 2052 (N₃), 1530 (C=C) cm^{-1} ; UV-vis (THF): $\lambda_{max}(\epsilon, M^{-1}cm^{-1}) = 233$ (17160), 260 (7760), 312 (19980) nm; MS (LIFDI): m/z (%) 593.2 (100); analysis (calcd., found for $C_{20}H_{40}N_4P_2Pt$): C (40.47, 40.31), H (6.79, 6.74), N (9.44, 9.35).

[PtNH₂(PNP)] (3): [PtOTf(PNP)] (**D**) (23.7 mg, 0.034 mmol, 1.00 eq.) and NaNH₂ (8.8 mg, 0.22 mmol, 6.67 eq.) were suspended in 1 mL THF. After stirring at room temperature for 2 h and removal of the solvent, the residue was extracted by Et₂O (3 mL). After filtration and removal of Et₂O, the residue was extracted by C₆H₆ (2 mL). After filtration and removal of C₆H₆, **3** was obtained as white solid (15.0 mg, 78%). Crystals suitable for X-ray diffraction were obtained by crystallization from a saturated solution in Et₂O at -36°C. 1H NMR (400.25 MHz, C_6D_6 , 298 K): δ (ppm) 7.00 ($A_{18}XX'A'_{18}$, N = $|^3J_{HP}+^4J_{HP}| = 39.2$ Hz, $^3J_{HH} = 5.2$ Hz, $^3J_{PtH} = 53.2$ Hz, 2H, NCH), 4.08 ($A_{18}XX'A'_{18}$, N = $|^2J_{HP}+^4J_{HP}| = 8.9$ Hz, $^3J_{HH} = 5.2$ Hz, $^3J_{PtH} = 33.6$ Hz, 2H, PCH), 1.35 ($A_{18}XX'A'_{18}$, N = $|^3J_{HP}+^5J_{HP}| = 14.0$ Hz, 36H, CMe_3), 0.52 (s, 2H, NH₂); $^{13}C\{^1H\}$ NMR (100.65 MHz, C_6D_6 , 298 K): δ (ppm) 161.9 (t, $^2J_{PC} = 7.5$ Hz, $^2J_{PtC} = 65.5$ Hz, NCH), 82.3 (t, $^1J_{PC} = 23.1$ Hz, $^2J_{PtC} = 35.0$ Hz, CHP), 36.0 (t, $^1J_{PC} = 12.8$ Hz, $^2J_{PtC} = 37.1$ Hz, $PCMe_3$), 29.2 (t, $^2J_{PC} = 3.1$ Hz, $^3J_{PtC} = 15.7$ Hz, $PCMe_3$); $^{31}P\{^1H\}$ NMR (162.02 MHz, C_6D_6 , 298 K): δ (ppm) 60.6 (s, $^1J_{PtP} = 2839.6$ Hz); $^{195}Pt\{^1H\}$ NMR (107.13 MHz, C_6D_6 , 298 K): δ (ppm) -3819.8 (t, $^1J_{PtP} = 2864.7$ Hz); IR (ATR): 3288 (N-H), 1516 (C=C) cm^{-1} ; UV-vis (THF): $\lambda_{max}(\epsilon, M^{-1}cm^{-1}) = 240$ (15740), 332 (16718) nm; MS (LIFDI): m/z (%) 567.2 (100); analysis (calcd., found for $C_{20}H_{42}N_2P_2Pt$): C (42.32, 42.49), H (7.46, 7.45), N (4.94, 4.84).

[PtNCO(PNP)] (4): Complex **1** (11.0 mg, 0.019 mmol, 1.00 eq.) was dissolved in 0.4 mL C_6D_6 . The vessel was degassed by three freeze-pump-thaw cycles and refilled with CO (1 atm). The solution was photolyzed ($\lambda_{exc} > 305$ nm) at room temperature for 2 h. Removal of the solvent *in vacuo* and washing of the residue with pentane (2x1 mL) gave analytically pure complex **4** (6.5 mg, 59%). 1H NMR (400.25 MHz, C_6D_6 , 298 K): δ (ppm) 6.52 ($A_{18}XX'A'_{18}$, N = $|^3J_{HP}+^4J_{HP}| = 38.8$ Hz, $^3J_{HH} = 5.6$ Hz, $^3J_{PtH} = 80.3$ Hz, 2H, NCH), 3.89 ($A_{18}XX'A'_{18}$, N = $|^2J_{HP}+^4J_{HP}| = 9.6$ Hz, $^3J_{HH} = 5.2$ Hz, $^3J_{PtH} = 32.0$ Hz, 2H, PCH), 1.27 ($A_{18}XX'A'_{18}$, N = $|^3J_{HP}+^5J_{HP}| = 14.4$ Hz, 36H, CMe_3); $^{13}C\{^1H\}$ NMR (100.65 MHz, C_6D_6 , 298 K): δ (ppm) 162.8 (t, $^2J_{PC} = 7.4$ Hz, $^2J_{PtC} = 83.0$ Hz, NCH), 82.7 (t, $^1J_{PC} = 22.6$ Hz, CHP), 36.2 (t, $^1J_{PC} = 13.2$ Hz, $PCMe_3$), 29.1 (t, $^2J_{PC} = 3.0$ Hz, $PCMe_3$); $^{31}P\{^1H\}$ NMR (162.02 MHz, C_6D_6 , 298 K): δ (ppm) 66.4 (s, $^1J_{PtP} = 2608.5$ Hz); IR (ATR): 2253 (NCO), 1529 (C=C) cm^{-1} ; UV/Vis (THF): $\lambda_{max}(\epsilon, M^{-1}cm^{-1}) = 237$ (12110), 248 (11600), 319 (12080) nm; MS (LIFDI): m/z (%) 593.2 (100); analysis (calcd., found for $C_{21}H_{40}N_2OP_2Pt$): C (42.49, 42.86), H (6.79, 6.87), N (4.72, 4.72).

[PtNPM₃(PNP)] (5): Complex **1** (8.2 mg, 0.014 mmol, 1.00 eq.) was dissolved in a solution of 0.4 mL C_6D_6 and PMe_3 (1M in toluene, 80 μ L, 5.79 eq.). The mixture was photolyzed ($\lambda_{exc} > 305$ nm) at room temperature for 1 h. $^1H\{^{31}P\}$ NMR spectroscopic monitoring indicated the formation of phosphoraneiminato product **5** in around 75 % yield. Isolation required repeated recrystallization from Et₂O at -36 °C, leading to low yields (< 10 %) of spectroscopically clean, light yellow crystals of **5** that were suitable for characterization by X-ray diffraction. 1H NMR (400.25 MHz, C_6D_6 , 298 K): δ (ppm) 6.93 ($A_{18}XX'A'_{18}$, N = $|^3J_{HP}+^4J_{HP}| = 38.0$ Hz, $^3J_{HH} = 5.2$ Hz, $^3J_{PtH} = 63.2$ Hz, 2H, NCH), 4.08 ($A_{18}XX'A'_{18}$, N = $|^2J_{HP}+^4J_{HP}| = 8.8$ Hz, $^3J_{HH} = 4.8$ Hz, $^3J_{PtH} = 33.6$ Hz, 2H, PCH), 1.45 ($A_{18}XX'A'_{18}$, N = $|^3J_{HP}+^5J_{HP}| = 14.0$ Hz, 36H, CMe_3), 1.42 (s, PMe_3 , slightly overlapped with the signal of CMe_3); $^{13}C\{^1H\}$ NMR (100.65 MHz, C_6D_6 , 298 K): δ (ppm) 162.4 (t, $^2J_{PC} = 7.5$ Hz, NCH), 83.0 (t, $^1J_{PC} = 22.4$ Hz, CHP), 35.6 (t, $^1J_{PC} = 11.9$ Hz, $PCMe_3$), 29.7 (t, $^2J_{PC} = 3.1$ Hz, $PCMe_3$), 24.0 (d, $^1J_{PC} = 63.1$ Hz, PMe_3); $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6 , 298 K): δ (ppm) 56.9 (s, $^1J_{PtP} = 2882$ Hz, $PCMe_3$), -29.5 (s, $^2J_{PtP} = 675$ Hz, NPM_3); MS (LIFDI): m/z (%) 641.1 (100).

[PtNH(C(O)Ph)(PNP)] (6): Complex **1** (8.0 mg, 0.013 mmol, 1.00 eq.) and PhCHO (1.5 μ L, 0.015 mmol, 1.1 eq.) were dissolved in 0.4 mL toluene- d_8 . The solution was photolyzed ($\lambda_{exc} > 305$ nm) at -30 °C for 2.5 h. After removal

of solvent and washed by cold pentane, complex **6** (7.5 mg, 83%) was obtained. Crystals suitable for X-ray diffraction were obtained by crystallization from a saturated solution in pentane at -36°C. ¹H NMR (400.25 MHz, C₆D₆, 298 K): δ (ppm) 8.14-8.08 (m, 2H, *COPh*), 7.26-7.20 (m, 2H, *COPh*), 7.15-7.10 (m, 1H, *COPh*), 6.73 (A₁₈XX'A'₁₈, N = |³J_{HP+4}J_{HP}| = 37.6 Hz, ³J_{HH} = 5.6 Hz, ³J_{PtH} = 65.6 Hz, 2H, *NCH*), 4.55 (br, ²J_{PtH} = 23.2 Hz, 1H, *NH*), 4.00 (A₁₈XX'A'₁₈, N = |²J_{HP+4}J_{HP}| = 8.8 Hz, ³J_{HH} = 5.2 Hz, ³J_{PtH} = 32.8 Hz, 2H, *PCH*), 1.35 (A₁₈XX'A'₁₈, N = |³J_{HP+5}J_{HP}| = 14.0 Hz, 36H, *CMe*₃); ¹³C{¹H} NMR (100.65 MHz, C₆D₆, 298 K): δ (ppm) 170.8 (s, *COPh*), 162.5 (t, ²J_{PC} = 7.3 Hz, *NCH*), 141.5 (s, *COPh*), 128.9 (s, *COPh*), 127.2 (s, *COPh*), 83.3 (t, ¹J_{PC} = 22.8 Hz, *CHP*), 36.4 (t, ¹J_{PC} = 12.8 Hz, *PCMe*₃), 29.2 (t, ²J_{PC} = 3.1 Hz, *PCMe*₃); ³¹P{¹H} NMR (162.02 MHz, C₆D₆, 298 K): δ (ppm) 61.9 (s, ¹J_{PtP} = 2720.5 Hz); ¹⁹⁵Pt{¹H} NMR (107.14 MHz, C₆D₆, 298 K): δ (ppm) -3905.8 (t, ¹J_{PtP} = 2744.9 Hz); IR (ATR): 3410 (N-H), 1613 (C=O), 1528 (C=C) cm⁻¹; UV-vis (THF): λ_{max} (ε, M⁻¹cm⁻¹) = 247 (13160), 288 (14650), 318 (16560) nm; MS (LIFDI): m/z (%) 671.3 (100); analysis (calcd., found for C₂₇H₄₆N₂OP₂Pt): C (48.28, 48.17), H (6.90, 7.00), N (4.17, 4.28).

[PtNH(C(O)(*n*-C₃H₇))(PNP)] (7): Complex **1** (7.6 mg, 0.013 mmol, 1.00 eq.) and *n*-C₃H₇CHO (1.7 μL, 0.019 mmol, 1.5 eq.) were dissolved in 0.4 mL toluene-*d*₈. The solution was photolyzed (λ_{exc} > 305 nm) at -30 °C for 2.5 h. Removal of the solvent yielded complex **7** (7 mg, 86%). Crystals suitable for X-ray diffraction were obtained by crystallization from a saturated solution in pentane at -36°C. ¹H NMR (400.25 MHz, C₆D₆, 298 K): δ (ppm) 6.72 (A₁₈XX'A'₁₈, N = |³J_{HP+4}J_{HP}| = 37.2 Hz, ³J_{HH} = 5.2 Hz, ³J_{PtH} = 65.6 Hz, 2H, *NCH*), 4.00 (A₁₈XX'A'₁₈, N = |²J_{HP+4}J_{HP}| = 8.8 Hz, ³J_{HH} = 5.2 Hz, ³J_{PtH} = 32.8 Hz, 2H, *PCH*), 3.33 (br, ²J_{PtH} = 27.6 Hz, 1H, *NH*), 2.26 (t, ³J_{HH} = 7.5 Hz, 2H, *COCH*₂), 1.91 (sext, ³J_{HH} = 7.5 Hz, 2H, *COCH*₂*CH*₂), 1.36 (A₁₈XX'A'₁₈, N = |³J_{HP+5}J_{HP}| = 14.4 Hz, 36H, *CMe*₃), 1.04 (t, ³J_{HH} = 7.5 Hz, 3H, *CH*₂*CH*₃); ¹³C{¹H} NMR (100.65 MHz, C₆D₆, 298 K): δ (ppm) 175.4 (s, *CO*), 162.5 (t, ²J_{PC} = 7.4 Hz, *NCH*), 83.3 (t, ¹J_{PC} = 22.7 Hz, *CHP*), 42.7 (s, *COCH*₂), 36.4 (t, ¹J_{PC} = 12.7 Hz, ²J_{PtC} = 33.2 Hz, *PCMe*₃), 29.2 (t, ²J_{PC} = 3.0 Hz, *PCMe*₃), 20.7 (s, *COCH*₂*CH*₂), 14.9 (s, *CH*₂*CH*₃); ³¹P{¹H} NMR (162.02 MHz, C₆D₆, 298 K): δ (ppm) 61.2 (s, ¹J_{PtP} = 2740.9 Hz); ¹⁹⁵Pt{¹H} NMR (107.14 MHz, C₆D₆, 298 K): δ (ppm) -3895.5 (t, ¹J_{PtP} = 2759.9 Hz); IR (ATR): 3381 (N-H), 1608 (C=O), 1528 (C=C) cm⁻¹; UV/Vis (THF): λ_{max} (ε, M⁻¹cm⁻¹) = 247 (7870), 291 (10400), 320 (15070) nm; MS (LIFDI): m/z (%) 637.2 (100); analysis (calcd., found for C₂₄H₄₈N₂OP₂Pt): C (45.20, 45.48), H (7.59, 7.38), N (4.39, 4.30).

[PtNH(Bpin)(PNP)] (8): Complex **1** (8.6 mg, 0.014 mmol, 1.00 eq.) and HBpin (3 μL, 0.021 mmol, 1.5 eq.) were dissolved in 0.4 mL C₆D₆. The solution was photolyzed (λ_{exc} > 305 nm) at room temperature for 1.5 h. Removal of the solvent gave complex **8** (8.5 mg, 85%). Crystals suitable for X-ray diffraction were obtained by crystallization from a saturated solution in pentane at -36°C. ¹H NMR (300.15 MHz, C₆D₆, 298 K): δ (ppm) 6.81 (A₁₈XX'A'₁₈, N = |³J_{HP+4}J_{HP}| = 36.8 Hz, ³J_{HH} = 5.5 Hz, ³J_{PtH} = 60.0 Hz, 2H, *NCH*), 4.02 (A₁₈XX'A'₁₈, N = |²J_{HP+4}J_{HP}| = 8.6 Hz, ³J_{HH} = 5.3 Hz, ³J_{PtH} = 33.3 Hz, 2H, *PCH*), 1.39 (A₁₈XX'A'₁₈, N = |³J_{HP+5}J_{HP}| = 13.9 Hz, 36H, *CMe*₃), 1.30 (s, 12H, *OC(CH*₃*)*₂), -0.06 (br, ²J_{PtH} = 19.5 Hz, 1H, *NH*); ¹³C{¹H} NMR (100.65 MHz, C₆D₆, 298 K): δ (ppm) 162.6 (t, ²J_{PC} = 7.4 Hz, *NCH*), 83.3 (t, ¹J_{PC} = 22.3 Hz, *CHP*), 36.2 (t, ¹J_{PC} = 12.6 Hz, *PCMe*₃), 29.6 (t, ²J_{PC} = 3.0 Hz, ³J_{PtC} = 14.2 Hz, *PCMe*₃), 25.8 (s, *OC(CH*₃*)*₂); ³¹P{¹H} NMR (162.02 MHz, C₆D₆, 298 K): δ (ppm) 55.8 (s, ¹J_{PtP} = 2783.0 Hz); ¹⁹⁵Pt{¹H} NMR (107.17 MHz, C₆D₆, 298 K): δ (ppm) -3789.2 (t, ¹J_{PtP} = 2798.5 Hz); IR (ATR): 3277 (N-H), 1526 (C=C) cm⁻¹; UV-vis (THF): λ_{max} (ε, M⁻¹cm⁻¹) = 246 (7830), 306 (13270), 320 (12860) nm; MS (LIFDI): m/z (%) 693.3 (100); analysis (calcd., found for C₂₆H₅₃BN₂O₂P₂Pt): C (45.03, 45.14), H (7.70, 7.40), N (4.04, 4.14).

[PtNPh(BPh₂)(PNP)] (9): Complex **1** (12.5 mg, 0.021 mmol, 1.00 eq.) and BPh₃ (5.8 mg, 0.024 mmol, 1.14 eq.) were dissolved in 0.4 mL toluene-*d*₈. The solution was photolyzed (λ_{exc} > 305 nm) at -30 °C for 2.5 h. After removal of the solvent, extraction by Et₂O/pentane and filtration, crystalline **9** (6.6 mg, 39%) was obtained after two crystallizations at -36 °C. Crystals suitable for X-ray diffraction were obtained by crystallization from a saturated solution in pentane at -36°C. ¹H NMR (400.25 MHz, C₆D₆, 298 K): δ (ppm) 8.93 (d, ³J_{HH} = 6.5 Hz, 2H, *NPh*), 7.53 (d, ³J_{HH} = 8.1 Hz, 2H, *BPh*₂), 7.44 (d, ³J_{HH} = 7.2 Hz, 2H, *BPh*₂), 7.32-7.21 (m, 3H, *NPh*), 7.21-7.17 (m, 2H,

*BPh*₂), 7.09 (t, ³*J*_{HH} = 7.5 Hz, 1H, *BPh*₂), 6.96 (t, ³*J*_{HH} = 7.7 Hz, 2H, *BPh*₂), 6.75 (t, ³*J*_{HH} = 7.2 Hz, 1H, *BPh*₂), 6.47 (A₁₈XX'A'₁₈, N = |³*J*_{HP}+⁴*J*_{HP}| = 36.4 Hz, ³*J*_{HH} = 6.0 Hz, ³*J*_{PtH} = 56.8 Hz, 2H, NCH), 3.83 (A₁₈XX'A'₁₈, N = |²*J*_{HP}+⁴*J*_{HP}| = 8.1 Hz, ³*J*_{HH} = 5.3 Hz, ³*J*_{PtH} = 30.7 Hz, 2H, PCH), 1.23-1.11 (m, 36H, *CM*₃); ¹³C{¹H} NMR (100.65 MHz, C₆D₆, 298 K): δ (ppm) 161.8 (t, ²*J*_{PC} = 6.7 Hz, NCH), 160.4 (s, *NPh*), 139.2 (s, *NPh*), 135.7 (s, *BPh*₂), 131.2 (s, *BPh*₂), 129.1 (s, *NPh*), 127.0 (s, *BPh*₂), 126.73 (s, *BPh*₂), 126.66 (s, *NPh*), 126.0 (s, *BPh*₂), 121.2 (s, *BPh*₂), 84.3 (t, ¹*J*_{PC} = 22.7 Hz, CHP), 38.5 (t, ¹*J*_{PC} = 11.9 Hz, PCMe₃), 36.2 (t, ¹*J*_{PC} = 11.4 Hz, PCMe₃), 29.5 (t, ²*J*_{PC} = 2.3 Hz, PCMe₃), 29.5 (t, ²*J*_{PC} = 2.3 Hz, PCMe₃); ³¹P{¹H} NMR (162.02 MHz, C₆D₆, 298 K): δ (ppm) 51.4 (s, ¹*J*_{PtP} = 2961.5 Hz); ¹⁹⁵Pt{¹H} NMR (107.17 MHz, C₆D₆, 298 K): δ (ppm) -3466.5 (t, ¹*J*_{PtP} = 2986.8 Hz); IR (ATR): 1547 (C=C) cm⁻¹; UV-vis (THF): λ_{max} (ε, M⁻¹cm⁻¹) = 230 (31640), 249 (24300), 310 (27510) nm; MS (LIFDI): m/z (%) 807.4 (100); analysis (calcd., found for C₃₈H₅₅BN₂P₂Pt): C (56.51, 56.39), H (6.86, 6.81), N (3.47, 3.45).

DATA AVAILABILITY

All data generated and analyzed during this study are included in this Article and its Supplementary Information or are available from the corresponding author upon reasonable request. Crystallographic data for the structures reported in this article have been deposited at the Cambridge Crystallographic Data Centre, under deposition numbers CCDC 1973273 ([PtCl{N(CH₂CH₂P^tBu)₂}] (**A**)), 1973274 ([PtCl(PNP)] (**B**)), 1973275 ([PtH(PNP)] (**C**)), 1973276 ([PtOTf(PNP)] (**D**)), 1973277 (**1**), 1973278 (**2**), 1973279 (**3**), 1994705 (**5**), 1973280 (**6**), 1973281 (**7**), 1973282 (**8**), 1973283 (**9**).

Copies of the data can be obtained free of charge via <https://www.ccdc.cam.ac.uk/structures/>.