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Steric Protection

Steric Protection of Rhodium-Nitridyl Radical Species**

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Abstract: In an attempt to synthesize a mononuclear rhodium nitridyl complex with a reduced tendency to undergo nitridyl radical N–N coupling, we synthesized a bulky analog of Milstein's bipyridine-based PNNH ligand, bearing a *tert*-butyl group at the 6' position of the bipyridine moiety. A three-step synthetic route toward this new bulky *t*Bu₃PNNH ligand was developed, involving a selective nucleophilic substitution step, followed by a Stille coupling and a final hydrophosphination step to afford the desired 6-(*tert*-butyl)-6'-[(di-*tert*-butylphosphino)methyl]-2,2'-bipyridine (*t*Bu₃PNNH) ligand. This newly developed *t*Bu₃PNNH ligand was incorporated in the synthesis of the sterically protected azide complex [Rh(N₃)(*t*Bu₃PNNH)]. We explored N₂ elimination from this species using photolysis and thermolysis, hoping to synthesize a mononuclear rhodium com-

plex with a terminal nitrido moiety. Characterization of the reaction product(s) using NMR, coldspray HR-ESI-MS and EPR spectroscopy shows that the material is paramagnetic, and data obtained by MS spectrometry revealed masses corresponding with both monomeric and dimeric nitrido/nitridyl complexes. NMR only reveals broad uncharacteristic signals and the complex is EPR silent at 8K or above. The combined data point to formation of a paramagnetic [(*t*Bu₃PNN)Rh(μ-N)Rh(*t*Bu₃PNN)] species. It thus seems that despite its three *t*Bu groups the new ligand is not bulky enough to prevent formation of Rh–N–Rh bridged species. However, the increased steric environment does prevent further reaction with carbon monoxide, which is unable to coordinate to rhodium.

Introduction

Complexes of group 9–11 metals bearing terminal multiple bonds to main group elements (e.g. O, N) are either rare or elusive, as explained by the “oxo-wall” concept.^[1] Despite this restriction set by the availability of empty *d* orbitals with matching symmetry and energetic disposition to accept π-electron density, exceptions were reported, describing the isolation of several Ir=O,^[2] Pt=O^[3] and M=NR^[4] complexes. However, the chemistry of terminal nitrides beyond Group 8 is far less developed. Stable terminal nitrido complexes have been reported in three cases.^[5] Terminal nitridyl complexes of iridium^[5c] and rhodium,^[6] wherein the nitrido N-atom bears significant spin density, have been reported and spectroscopically characterized as well.

However, those complexes are transient and react via N–N coupling to their respective dinitrogen complexes. A cobalt nitrido complex was described and characterized by EPR spec-

troscopy at 10 K.^[7] Also, a bridging nitrido complex of iridium has been reported.^[8] Furthermore, some nitrido complexes are proposed as intermediates in azido photolysis (and thermolysis) reactions of complexes of cobalt and nickel.^[9]

Dimerization of a mononuclear nitridyl intermediate plays a crucial role in formation of the nitridyl bridged species **C** (Scheme 1).^[10] Obviously, coordination to two rhodium atoms substantially stabilizes the nitridyl moiety, thus preventing any desirable atom transfer reactivity with C–H bonds of substrates, which could for example enable the synthesis of amines via C–N bond formation with azides as nitrogen source in a (hypothetical) (photo)catalyzed reaction sequence. Fast dinuclear N₂ formation involving nitridyl–nitridyl coupling is a key step in the observed rapid consumption of the mononuclear rhodium

Scheme 1. Previously reported synthesis of dimeric nitridyl species **C**.

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nitridyl intermediate formed by reagent (CO, CNR) triggered splitting of the Rh–N bond.

These aspects, unfortunately, have thus far prevented us from studying the intrinsic reactivity of the mononuclear rhodium nitridyl species, which is expectedly more reactive than the dinuclear nitridyl-bridged species towards (the C–H bonds of) organic substrates. Hence, in an attempt to prevent dimerization of the mononuclear nitridyl intermediate, we explored the effect of using a bulkier PNN pincer ligand in the nitridyl chemistry. For that reason, we decided to apply a *t*Bu₃PNNH pincer ligand containing a *tert*-butyl group at the 6' position of the pyridine ring (Figure 1). This paper describes the synthesis of this ligand, as well as our attempts to utilize it in the synthesis of a mononuclear, terminal nitrido complex of rhodium.

Figure 1. Envisioned 6'-substituted *t*Bu₃PNN pincer ligand **6** (left), and a CPK model (right) of the corresponding hypothetical mononuclear [(*t*Bu₃PNN)Rh(N')] target molecule showing steric protection of both the metal and the nitridyl radical moiety (geometry optimized at the DFT-D3, BP86, def2-TZVP level).

Results and Discussion

We started our investigations with the synthesis of the new bulky *t*Bu₃PNNH ligand **6**, 6-(*tert*-butyl)-6'-(di-*tert*-butylphosphino)-methyl]-2,2'-bipyridine. The ligand bears a *tert*-butyl group at the 6-position of the bipy moiety (Scheme 2), and was obtained by a three-step synthesis following modified literature procedures.^[11–13] Selective mono-substitution of 2,6-dibromopyridine by a *tert*-butyl group using lithium chloride, *tert*-butyllithium and copper cyanide gave the desired 2-bromo-6-(*tert*-butyl)pyridine in 97 % yield, which was reacted in the second step under Stille coupling conditions with 2-methyl-6-(tributylstannyl)pyridine in the presence of Pd(PPh₃)₄ and LiCl to form 6-(*tert*-butyl)-6'-methyl-2,2'-bipyridine compound **5** in 83 % yield (Scheme 2). Compound **5** was pure as obtained and could be used in the next step without purification. The last step is one-pot two-stage procedure that was successfully performed by

Scheme 2. Synthesis of *t*Bu₃PNNH ligand **6**.

deprotonating the methyl group of **5** with an in situ prepared solution of LDA and subsequently quenching the mixture with di-*tert*-butylchlorophosphine, resulting in the desired *t*Bu₃PNNH ligand **6** (Scheme 2). Despite the fairly low yield of this hydrophosphination step (32 %), ligand **6** was obtained in high purity after recrystallization of the crude product from methanol at ca. 0 °C.

The main concern before starting to develop a synthetic pathway towards a terminal nitrido species bearing the new ligand was to determine the coordination number. The steric hindrance present on the bipyridine system by the presence of the 6'-*tert*-butyl group could possibly yield a monodentate or bidentate coordination mode instead of the desired tridentate one. For this purpose, a cationic CO complex was synthesized by reacting *t*BuPNNH ligand **6**, KPF₆ and [Rh(CO)₂(μ-Cl)]₂ in methanol (Scheme 3). Washing with pentane and evaporating the solvent resulted in the pure, orange, cationic [Rh(CO)(*t*Bu₃PNNH)]PF₆ complex **7**.

Scheme 3. Synthesis of [Rh(CO)(*t*Bu₃PNNH)]PF₆ complex **7**.

The X-ray structure of **7** was determined by X-ray diffraction on single crystals grown from toluene at –20 °C. Despite the steric hindrance at the pyridine 6-position, the ligand adopts the desired tridentate coordination mode in complex **7**. The molecular structure of **7** exhibits a slightly distorted square-planar geometry, establishing that the *t*Bu₃PNNH ligand can coordinate as a neutral PNN ligand to rhodium(I) (Figure 2). This

Figure 2. Molecular structure of complex **7**. Hydrogen atoms and the PF₆ counterion were omitted for clarity. Selected bond lengths [Å] and angles [°]: Rh1–P1: 2.2291(8); Rh1–C24: 1.833(3); Rh1–N1: 2.056(2); Rh1–N2: 2.244(2); C1–C2: 1.494(4); C24–O1: 1.147(4); C24–Rh1–N1: 172.79(12); P1–Rh1–N2: 161.54(7); O1–C24–Rh1: 175.4(3); C24–Rh1–P1: 89.59(9); N1–Rh1–P1: 83.88(7); C24–Rh1–N2: 108.82(11); N1–Rh1–N2: 77.67(9).

means that the bulky $t\text{Bu}_3\text{PNNH}$ ligand can probably be used for the synthesis of a much wider range of organometallic complexes in future studies.

Our starting point in attempting to synthesize a terminal nitrido complex, taking advantage of the increased steric bulk caused by the $t\text{Bu}$ group of ligand **6**, was the chlorido $[\text{RhCl}(t\text{Bu}_3\text{PNNH})]$ complex **8**, bearing the new $t\text{Bu}_3\text{PNNH}$ ligand **6**. Complex **8** was prepared by the reaction of $[\text{Rh}(\mu\text{-Cl})(\text{coe})_2]_2$ (coe =cyclooctene) with ligand **6** in 86 % yield. Suitable crystals for X-ray diffraction were not obtained, and chlorido complex **8** was characterized based on ^1H , ^{31}P and ^{13}C NMR spectroscopy (Figures S8–S10) and ESI-MS data, consistently confirming formation of the desired chlorido complex. Upon coordination of the ligand the ^{31}P signal shifts strongly downfield (from 35.41 to 87.70 ppm) and becomes a doublet due to Rh-P coupling.

The azido species **9** was obtained by reaction of chlorido complex **8** through salt metathesis with five equivalents of NaN_3 , which afforded the stable, neutral azido $[\text{Rh}(\text{N}_3)(t\text{Bu}_3\text{PNNH})]$ complex **9** in 82 % isolated yield (Scheme 4). Conversion of **8** to **9** can be tracked by following the ^{31}P NMR shift over time; a shift from 87.70 to 90.73 ppm can be observed. The azide stretching frequency of **9** was observed in the IR spectrum at 2017 cm^{-1} . Like complex **8**, azido complex **9** is air-sensitive and oxidation is indicated by the formation of yellow solutions upon formation of oxidized species. The X-ray structure of the O_2 adduct of complex **8** (complex **10**) is shown in the Supporting Information (Figure S18). The fate of the oxidation reaction of complex **9** was not further investigated.

Scheme 4. Synthesis of azido complex **9** and attempts to synthesize a terminal nitrido complex.

The ^1H NMR spectra of **6**, **8** and **9** are shown in Figure S6–S13. In all of these complexes, the *tert*-butyl signal significantly shifts to higher ppm value compared to the free ligand, due to influence of the Rh center. Substituting chloride for azide results in a relative shift to lower ppm values for the *tert*-butyl protons, due to the slightly lower electronegativity of the azide ion. This effect is negligible for the protons further away from the ancillary ligand. The pyridine signals of the ligand shift significantly when coordinated to rhodium. Crystals suitable for X-ray diffraction were obtained by slow diffusion of pentane into a benzene solution of **9** (Figure 3). In agreement with our expectations,

the molecular structure of **9** exhibits a slightly distorted square-planar geometry bearing a terminal Rh-N_3 moiety.

Figure 3. Molecular structure of one of the three independent molecules in the asymmetric unit cell of complex **9**. Solvent molecules and hydrogen atoms were omitted for clarity. Selected bond lengths [Å] and angles [°]: Rh1-N1 : 1.962(3), Rh1-N2 : 2.237(3), Rh1-P1 : 2.1844(11), Rh1-N3 : 2.068(4), C9-C10 : 1.363(7), N3-N4 : 1.183(4), N4-N5 : 1.166(5); N1-Rh1-N3 : 171.20(14), P1-Rh1-N2 : 162.51(10), N3-Rh1-P1 : 96.91(9); N1-Rh1-P1 : 83.84(9); N3-Rh1-N2 : 100.42(12); N1-Rh1-N2 : 78.72(12).

In an attempt to synthesize a terminal nitrido complex by N_2 -loss from complex **9**, photolysis experiments were performed. Photolysis of a solution of **9** in $[\text{D}_6]$ benzene for 4 hours using a 500 W Hg/Xe lamp emitting full spectrum light resulted in a clear color change from a dark blue to a brown solution, with complete conversion of the starting azide complex as shown by ^1H and ^{31}P NMR spectroscopy. Different solvents (THF, toluene) were also tested, causing the same color change. Despite full conversion to the photolyzed species (**11**), large scale synthesis was not feasible. The maximum amount of **9** that can be converted is approximately 20 mg. This can be attributed to the reduced homogeneity of the solution in the applied set-up. The photolyzed species is paramagnetic and no characteristic ^1H and ^{31}P NMR signals could be detected. Unfortunately, apart from indicating full conversion, NMR spectra did not provide any further information about the nature of species **11**. Repeated efforts to form crystals suitable for X-ray crystallography were not successful. Therefore, we attempted to characterize the paramagnetic species using EPR spectroscopy. Repeated attempts to measure an EPR spectrum of **11** in THF glass (8 K and 20 K) resulted only in very weak and non-informative EPR spectra (Figure S17), despite high concentrations of the species. Most likely, those signals stem from small amounts of impurities. EPR silence of complex **11** is perhaps not very surprising, as complex **C** (Scheme 1) also proved to be very difficult to detect with EPR spectroscopy (broad signals detectable only $<10\text{ K}$).^[10] The sample was also measured in different solvents such as benzene and toluene, resulting in similarly uninformative weak EPR signals.

Additionally, photolysis inside the EPR machine was studied at 20 K. To our surprise, this signal resembles a typical Rh^{II} complex, with a signal pattern and g -values close to the ones found

for earlier reported (square planar) Rh^{II} species^[14] that can presumably be attributed to the formation of a transient or unstable Rh^{II} species, not detectable under the above described photochemical reaction conditions (Figure S11).^[15] Despite the more instructive spectrum obtained in this experiment, the signal intensity is again very low, and the signal is unlikely to be representative for the bulk material.

In an attempt to gather more information about the nature of species **11**, we decided to probe the electrochemistry of this complex using cyclic voltammetry (see SI). However, multiple electron transfers were obtained, which do not provide much information about the nature of complex **11**.

Analysis of species **11** by electron-spray ionization (ESI)-MS spectrometry proved to be more informative (Figure 4). The two peaks with largest intensity (958 & 959) correspond to $[(\text{tBu}_3\text{PNN})\text{Rh}(\mu\text{-N})\text{Rh}(\text{tBu}_3\text{PNN})]^+$ and $[(\text{tBu}_3\text{PNN})\text{Rh}(\mu\text{-N})\text{Rh}(\text{tBu}_3\text{PNNH})]^+$, suggesting that the neutral dinuclear nitrido-bridged species $[(\text{tBu}_3\text{PNN})\text{Rh}(\mu\text{-N})\text{Rh}(\text{tBu}_3\text{PNN})]$ (Figure 5, bottom) is the main product formed upon photolysis of **9** (detected in its 1e oxidized and mono-protonated cationic forms). This species is analogous to paramagnetic $[(\text{PNN})\text{Rh}(\mu\text{-N})\text{Rh}(\text{PNN})]$ species **C** in Scheme 1, which is actually only detectable by EPR at very low temperatures. Fragmentation peaks at 487 and 473 correspond to masses expected for the protonated monomeric nitrido species $[(\text{tBu}_3\text{PNNH})\text{Rh}(\text{N})]^+$ and the coordinatively unsaturated species $[(\text{tBu}_3\text{PNNH})\text{Rh}]^+$. Fragmentation peaks corresponding to loss of one or two *t*Bu groups (900 & 856) from the dinuclear species are also detectable. These data suggest that despite our efforts increasing the steric bulk of the ligand, dimerization could not be prevented. On the other hand, fragmentation of **C** in the mass spectrometer to detect the mononuclear $[(\text{PNN})\text{Rh}^{\text{IV}}(\text{N})]$ species was not observed, and

hence the Rh–N bond in **11** does seem to be weakened compared to **C**.

Figure 5. Optimized geometry of the proposed binuclear $[(\text{tBu}_3\text{PNN})\text{Rh}(\mu\text{-N})\text{Rh}(\text{tBu}_3\text{PNN})]$ structure of complex **11** optimized at the DFT-D3, BP86, def2-TZVP level (doublet) in ball-and-stick (top) and CPK (middle) representations. Bottom: CPK representation of the analogous, less hindered complex **C**. Space filing CPK models were generated with Platon.^[16]

Figure 4. Top: ESI-MS spectrum of complex **11**. Bottom: Proposed structure of complex **11** formed by photolysis of complex **9**.

Due to the difficulties we faced in determining the molecular structure of **11**, indirect characterization via its follow-up chemical reactivity with CO was attempted. We argued it might react with CO in a similar manner as described for **C** (see Scheme 1) to form the neutral carbonyl complex $[(\text{tBu}_3\text{PNN})\text{Rh}(\text{CO})]$. Thus, CO was added to **11** in C_6D_6 (5 bar, 5 min). However, no chemical transformation seemed to take place as judged from the absence of any color changes. Furthermore, the ^{31}P and ^1H NMR spectra remained silent.

It thus seems that $[(\text{tBu}_3\text{PNN})\text{Rh}(\mu\text{-N})\text{Rh}(\text{tBu}_3\text{PNN})]$ complex **11** does not fragment into mononuclear species in solution, and that the steric bulk of ligand **6** protects the rhodium ions from reacting with CO. To shed more light on the (electronic) structure and spin state of complex **10**, and to understand why it does not react with CO while complex **C** (Scheme 1) does, we decided to perform DFT calculations. The DFT-D3 optimized geometry (BP86, def2-TZVP) of complex **11** (Figure 5) reveals a rather distorted geometry compared to the previously reported structure of complex **C** determined by X-ray diffraction.^[10] Like **C**, the ground state of complex **11** {and that of its mononuclear analogue $[(\text{tBu}_3\text{PNN})\text{Rh}(\text{N})]$ } is a doublet ($S = 1/2$). The excited quartet state ($S = 3/2$) is 18 kcal mol⁻¹ higher in energy. It is clear from these calculations that the steric bulk surrounding the nitridyl moiety and the metal ions is much larger in com-

plex **11** than in complex **C**. In complex **C** only the nitridyl moiety is shielded, while the rhodium atoms are exposed enabling reaction with CO (Figure 5, bottom).^[10] In contrast, in complex **11**, both the nitridyl moiety and the metal ions are sterically shielded, thus preventing any follow-up reactivity.

The sterically distorted structure of **11** when compared to **C** might also cause differences in electronic structure and relaxation times, perhaps explaining the difficulties we encountered in detecting species **11** directly with NMR and EPR spectroscopy. The UV/Vis spectrum of **11** shows only coarse similarities to that of **C** (Figure S20), suggestive of a rather large influence of the additional *t*Bu group on the electronic structure of these complexes. Furthermore, based on the mass data, we cannot fully exclude that **11** might exist in equilibrium with the mononuclear species $[(t\text{Bu}_3\text{PNN})\text{Rh}(\text{N})]$ and $[(t\text{Bu}_3\text{PNN})\text{Rh}]$ in solution. Such an equilibrium would provide an alternative/additional explanation for the spectroscopic differences between **11** and **C**. The absence of reactivity with CO suggests otherwise, but the additional *t*Bu group might cause dinuclear **11** to be more stable than its fragments (even in the presence of CO) and steric protection of nitridyl species $[(t\text{Bu}_3\text{PNN})\text{Rh}(\text{N})]$ could actually prevent N–N coupling driving the reaction forward (as designed, see also Figure 1).

Conclusions

A new $t\text{Bu}_3\text{PNNH}$ pincer ligand was synthesized, with a *tert*-butyl group in the 6' position of the bipyridine moiety. This new ligand was successfully applied in the synthesis of new rhodium complexes. Although the ligand introduces substantial steric bulk, due to the *tert*-butyl group in close proximity to the metal, the pincer ligand binds in a tridentate fashion. This leads to slightly distorted geometries of the synthesized rhodium complexes, with the ancillary ligands bending out of the plane away from the *tert*-butyl group. The carbonyl complex **7**, the chlorido complex **8** and the azido complex **9** were successfully synthesized. We further attempted to synthesize a mononuclear terminal nitrido complex from azido complex **9** by photolysis. However, despite the steric bulk imposed by the new ligand around the nitridyl moiety, HR ESI-MS reveals formation of the dinuclear nitridyl-bridged $[(t\text{Bu}_3\text{PNN})\text{Rh}(\mu\text{-N})\text{Rh}(t\text{Bu}_3\text{PNN})]$ complex **11** as the major product. NMR only reveals broad uncharacteristic signals and the complex is EPR silent at 8K or above. DFT studies showed that complex **11** is similar to the previously reported $[(\text{PNN})\text{Rh}(\mu\text{-N})\text{Rh}(\text{PNN})]$ species **C**, but has a distorted geometry and less accessible metal ions. The steric congestion around Rh imposed by the bulky $t\text{Bu}_3\text{PNN}^-$ ligand prevents follow-up reactivity of **11** with CO, which contrasts with the reactivity of complex **C**.

Experimental Section

General Considerations: All reactions were carried out under an atmosphere of nitrogen using standard Schlenk techniques. The following compounds were prepared following literature procedures: $[\text{IrCl}(\text{DMSO})_3]$,^[17] $[\text{Rh}(\mu\text{-Cl})(\text{coe})_2]_2$,^[18] 2-methyl-6-(tributylstannyl)pyridine^[19] and 2-bromo-6-(*tert*-butyl)pyridine.^[20] Other re-

agents were purchased from commercial suppliers and used without further purification. THF, pentane, hexane and Et_2O were distilled from sodium/benzophenone ketyl, toluene from sodium under nitrogen. NMR spectra (^1H , $^1\text{H}\{^{31}\text{P}\}$, ^{31}P , $^{31}\text{P}\{^1\text{H}\}$, $^{31}\text{P}^1\text{-}^1\text{H}$, and $^{13}\text{C}\{^1\text{H}\}$) were measured on a Varian INOVA 500 MHz, a Bruker AV400 or a Varian MERCURY 300 MHz spectrometer. IR spectra were recorded with a Bruker Alpha-p FT-IR spectrometer (ATR) or with a Thermo Nicolet nexus FT-IR spectrometer (solution). Cold-spray ESI-MS measurements were performed on JEOL AccuTOFLC-plus JMS-T100LP spectrometer. Experimental X-band EPR spectra were recorded on a Bruker EMX spectrometer (Bruker BioSpin Rheinstetten) equipped with a He temperature control cryostat system (Oxford Instruments).

Synthesis of the New Compounds, Including NMR, IR and MS Data

6-(*tert*-Butyl)-6'-methyl-2,2'-bipyridine (5): A mixture of degassed 2-methyl-6-(tributylstannyl)pyridine (19.204 g, 50.252 mmol), 2-bromo-6-(*tert*-butyl)pyridine (9.78 g, 45.68 mmol), $\text{Pd}(\text{PPh}_3)_4$ (1.06 g, 2 mol-%) and LiCl (4.84, 114.22 mmol) were refluxed under inert conditions for 3 days in absolute toluene (230 mL). After filtration and removal of the solvent, the residue was dissolved in DCM (360 mL). Extraction with aqueous HCl (3×140 mL, 6 M) provided an aqueous layer which was carefully neutralized with 12 M solution of NH_3 . The suspension was extracted with DCM (3×500 mL), and the combined organic phases were washed with water (150 mL), brine (130 mL) and dried with anhydrous Na_2SO_4 . The volatiles were removed by means of a rotary evaporator yielding a white solid. Yield: 7.00 g, 30.92 mmol, 68 %. ^1H NMR (400 MHz, CDCl_3): δ (ppm) 8.37–8.23 (m, 2H, biPy); 7.72 (dtd, $J_{\text{HH}} = 7.8, 4.9, 2.6$ Hz, 2H); 7.34(d, $J_{\text{HH}} = 8.2$ Hz, 1H); 7.16 (d, $J_{\text{HH}} = 7.6$ Hz, 1H); 2.66 (s, 3H); 1.42 (s, 9H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ (ppm) 168.37 (s, $1\text{C}_{\text{iv-biPy}}$); 157.55 (s, $1\text{C}_{\text{iv-biPy}}$); 156.36 (s, $1\text{C}_{\text{iv-biPy}}$); 154.81 (s, $1\text{C}_{\text{iv-biPy}}$); 136.89 (s, $1\text{CH}_{\text{-biPy}}$); 136.85 (s, $1\text{CH}_{\text{-biPy}}$); 122.90 (s, $1\text{CH}_{\text{-biPy}}$); 118.81 (s, $1\text{CH}_{\text{-biPy}}$); 118.16 (s, $1\text{CH}_{\text{-biPy}}$); 117.68 (d, $J_{\text{PC}} = 8$ Hz, $1\text{CH}_{\text{-biPy}}$); 37.66 (s, $1\text{C}(\text{CH}_3)_3$); 30.32 (s, $1(\text{CH}_3)_3\text{-biPy}$); 24.70 (s, $1\text{CH}_3\text{-biPy}$). HR-MS (FAB) calcd. for $[\text{M}]^+ \text{C}_{15}\text{H}_{18}\text{N}_2\text{m/z}$, 226.1470; found 226.1471.

6-(*tert*-Butyl)-6'-[(di-*tert*-butylphosphino)methyl]-2,2'-bipyridine (6): In an flame-dried 250 mL 3-neck flask under argon atmosphere diisopropylamine (2.26 mL, 16.17 mmol) was added in 20 mL of THF. The reaction mixture was cooled to -78°C and a solution of *n*-butyllithium (11.12 mL, 1.6 M) was added dropwise over a period of 20 min. The solution was stirred at -78°C for 10 min, warmed to 0°C and stirred for 20 min. Subsequently, the reaction mixture was cooled to -78°C and a solution of 6-(*tert*-butyl)-6'-methyl-2,2'-bipyridine in Et_2O (60 mL) was added dropwise over a period of 30 min. The solution was stirred at 0°C for 2 h and then cooled to -78°C . A solution of di-*tert*-butylchlorophosphine (3.02 mL, 15.91 mmol) in Et_2O (20 mL) was added dropwise over a period of 20 min at -78°C . Afterwards, the reaction mixture was stirred for 1 h at -78°C and then allowed to reach room temperature while stirring overnight. Subsequently, the reaction solution was quenched with degassed water (20 mL) and extracted with Et_2O (3×20 mL). The combined organic layers were dried with anhydrous Na_2SO_4 , filtered and concentrated in vacuo. The crude product was purified by recrystallization from MeOH at ca. 0°C . Yield: 1.66 g, 4.51 mmol, 34 %. ^1H NMR (400 MHz, C_6D_6): δ (ppm) $\delta = 8.68$ (d, $J_{\text{HH}} = 5.2$ Hz, 1H, biPy); 8.59 (dd, $J_{\text{HH}} = 5.7, 3.2$ Hz, 1H, biPy); 7.40–7.29 (m, 3H); 7.00 (d, $J_{\text{HH}} = 7.8$ Hz, 1H, biPy); 3.14 (d, $J_{\text{PH}} = 2.6$ Hz, 2H, biPy- $\text{CH}_2\text{-P}$); 1.44 (s, 9H, biPy- $(\text{CH}_3)_3$); 1.14 (d, $J_{\text{PH}} = 10.8$ Hz, 18H, $\text{P-C}(\text{CH}_3)_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, C_6D_6): δ (ppm) 168.41 (s, $1\text{C}_{\text{iv-biPy}}$); 161.74 (d, $J_{\text{PC}} = 14.3$ Hz, $1\text{C}_{\text{iv-biPy}}$); 156.13 (s, $1\text{C}_{\text{iv-biPy}}$); 155.57 (s, $1\text{C}_{\text{iv-biPy}}$); 137.10 (s, $1\text{CH}_{\text{-biPy}}$); 136.79

(s, 1CH_{biPy}); 124.08 (d, J_{PC} = 8.9 Hz, 2CH_{biPy}); 118.98 (s, 1CH_{biPy}); 118.16 (s, 1CH_{biPy}); 37.80 (s, 1C-(CH₃)₃); 32.55 (d, J_{PC} = 26.1 Hz, 1CH₂-P); 32.08 (s, P-1C-(CH₃)₃); 31.88 (s, P-1C-(CH₃)₃); 30.47 (s, 1(CH₃)₃-C); 29.93 (d, J_{PC} = 13.8 Hz, 2(CH₃)₃-C-P). ³¹P{¹H} NMR (162 MHz, C₆D₆): δ (ppm) 35.41 (s, 1P). HR-MS (FAB) calcd. for [M]⁺ C₂₃H₃₅N₂P *m/z*, 370.2538; found 370.2545.

[Rh(CO)(tBu₃PNN)]PF₆ (7): To a mixture of [Rh(μ-Cl)(CO)₂]₂ (0.210 g, 0.574 mmol) and KPF₆ (0.12 g, 0.64 mmol) in MeOH (22 mL), a solution of 6-(*tert*-butyl)-6'-[(di-*tert*-butylphosphino)-methyl]-2,2'-bipyridine in MeOH (36 mL) was added. The orange solution was stirred for 1 h at room temperature by the subsequent removal of the solvent. Extraction with DCM (40 mL) followed by filtration, evaporation and washing with pentane (50 mL) gave an orange solid. Yield: 0.31 g, 0.48 mmol, 84 %. ¹H NMR (400 MHz, [D₆]acetone): δ (ppm) 8.42 (dd, J_{HH} = 7.9, 2.8 Hz, 2H, biPy); 8.30 (t, J_{HH} = 8.0 Hz, 2H, biPy); 8.15 (d, J_{HH} = 8.0 Hz, 1H, biPy); 7.98 (d, J_{HH} = 7.8 Hz, 1H, biPy); 4.28 (d, J_{PH} = 10.3 Hz, 2H, biPy-CH₂-P); 1.86 (s, 9H); 1.50 (d, J_{PH} = 14.8 Hz, 18H, P-C(CH₃)₃). ³¹P{¹H} NMR (162 MHz, [D₆]acetone): δ (ppm) 102.68 (d, J_{RHP} = 161.7 Hz, 1P); 159.95–126.35 (m, 1PF₆). HR-MS (FAB) calcd. for [M]⁺ C₂₄H₃₅F₆N₂OP₂Rh *m/z*, 646.1184; found 646.1196. FT-IR (solid, ATR mode): $\tilde{\nu}$ 1971 cm⁻¹.

[Rh(Cl)(tBu₃PNN)] (8): To an orange suspension of [Rh(μ-Cl)(coe)₂]₂ (0.38 g, 0.53 mmol) in Et₂O (16 mL) a solution of PNNtBu ligand **2** (0.39 g, 1.053 mmol) in Et₂O (8 mL) was added. The mixture immediately turned into a black solution. After 2 h of stirring at room temperature, the solvent was removed under vacuum. Upon addition of cold pentane (20 mL, -40 °C), a black precipitate was obtained which was filtered, washed with cold pentane (7 mL) and dried, leaving complex **8** as a black powder. Yield: 0.38 g, 0.84 mmol, 80 %. ¹H NMR (400 MHz, C₆D₆): δ (ppm) 7.43 (dt, J_{HH} = 15.5, 7.9 Hz, 2H, biPy); 7.20 (d, J_{HH} = 7.5 Hz, 1H, biPy); 7.18 (m, 1H, biPy); 6.73 (d, J_{HH} = 8.0 Hz, 1H, biPy); 6.53 (d, J_{HH} = 7.6 Hz, 1H, biPy); 2.48 (d, J_{PH} = 9.3 Hz, 2H, biPy-CH₂-P); 2.09 (s, 9H, biPy-(CH₃)₃); 1.61 (d, J_{PH} = 13.0 Hz, 18H, P-C(CH₃)₃). ¹³C{¹H} NMR (100 MHz, C₆D₆): δ (ppm) 176.91 (s, 1C_{iv}-biPy); 161.13 (t, J_{PC} = 4.5 Hz, 1C_{iv}-biPy); 155.64 (s, 1C_{iv}-biPy); 155.22 (s, 1C_{iv}-biPy); 136.70 (s, 1CH_{biPy}); 127.26 (s, 1CH_{biPy}); 123.58 (d, J_{PC} = 2.3 Hz, 1CH_{biPy}); 120.91 (d, J_{PC} = 11.9 Hz, 1CH_{biPy}); 120.42 (s, 1CH_{biPy}); 116.43 (s, 1CH_{biPy}); 39.64 (s, 1C-C(CH₃)₃); 36.76 (dd, J_{PC} = 17.9 Hz, J_{RHC} = 1.2 Hz, 1CH₂-P); 35.54 (d, J_{PC} = 15.2 Hz, P-1C-(CH₃)₃); 31.96 (s, 1(CH₃)₃-C_{biPy}); 29.53 (d, J_{PC} = 6 Hz, 2(CH₃)₃-P-C). ³¹P{¹H} NMR (162 MHz, C₆D₆): δ (ppm) 87.70 (d, 1P J_{RHP} = 214.0 Hz). HR-MS (FAB) calcd. for [M]⁺ C₂₃H₃₅ClN₂PRh *m/z*, 508.1281; found 508.1295.

Rh(N₃)(PNNtBu) (10): To a solution of **4** (0.300 g, 0.589 mmol) in THF (16 mL) a suspension of NaN₃ (0.23 g, 3.54 mmol) in THF (16 mL) was added. The dark-green mixture was stirred for 4 days in the glove box at room temperature. Upon complete conversion, based on ³¹P NMR spectroscopy, the volatiles were removed in vacuo. The black residue was successively washed with degassed water (6 × 8 mL) in order to separate both the formed NaCl and the excess of NaN₃. Subsequently, washing with pentane (2 × 10 mL) and drying overnight under vacuum in the glove box afforded the desired compound as a black solid. Yield: 0.25 g, 0.47 mmol, 82 %. ¹H NMR (400 MHz, C₆D₆): δ (ppm) 7.31 (d, J_{HH} = 8.0 Hz, 1H, biPy); 7.15–7.09 (m, 2H, biPy); 7.05 (m, 2H, biPy); 6.66 (d, J_{HH} = 7.9 Hz, 1H, biPy); 6.41 (d, J_{HH} = 7.5 Hz, 1H, biPy); 2.37 (d, J_{PH} = 9.3 Hz, 2H, biPy-CH₂-P); 1.91 (s, 9H, biPy-(CH₃)₃); 1.41 (d, J_{PH} = 13.0 Hz, 18H, P-C(CH₃)₃). ¹³C{¹H} NMR (100 MHz, C₆D₆): δ (ppm) 175.65 (s, 1C_{iv}-biPy); 161.35 (m, 1C_{iv}-biPy); 156.04 (s, 1C_{iv}-biPy); 155.92 (s, 1C_{iv}-biPy); 136.86 (s, 1CH_{biPy}); 128.36 (s, 1CH_{biPy}); 125.87 (s, 1CH_{biPy}); 123.50 (m, 1CH_{biPy}); 121.29 (m, 1CH_{biPy}); 120.45 (s, 1CH_{biPy}); 39.16 (s, 1C-C(CH₃)₃); 36.39 (d, J_{PC} = 18.5 Hz, 1CH₂-P); 35.19 (d, J_{PC} =

16.5 Hz, P-1C-(CH₃)₃); 31.04 (s, 1(CH₃)₃-C_{biPy}); 29.17 (d, J_{PC} = 6.6 Hz, 2(CH₃)₃-P-C). ³¹P{¹H} NMR (162 MHz, C₆D₆): δ (ppm) 90.73 (d, J_{RHP} = 216.0 Hz). HR-MS (FAB) calcd. for [M]⁺ C₂₃H₃₅N₅PRh *m/z*, 515.1685; found 473.1718. FT-IR (solid, ATR mode): $\tilde{\nu}$ 2017 cm⁻¹ (strong, N₃).

Photolysis Experiment: In a J-Young NMR tube, **10** (5 mg) was dissolved in degassed C₆D₆ (0.6 mL) and irradiated by using a 500W Hg/Xe lamp emitting full spectrum light. Photolysis for 4 h of **10** resulted in a clear color change from dark blue to brown solution. Full conversion was indicated by monitoring the reaction by in situ ³¹P NMR spectroscopy. **11** Was used without any isolation and purification method.

X-ray Crystal Structure Determination: CCDC 1822649 (for **7**), 1822651 (for **9**), and 1822650 (for **10**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Computational Details: Geometry optimizations were carried out with the Turbomole program package^[21] coupled to the PQS Baker optimizer^[22] via the BOpt package.^[23] We used unrestricted ri-DFT-D3 calculations at the BP86 level,^[24] in combination with the def2-TZVP basis set,^[25] and a small (m4) grid size. Grimme's dispersion corrections^[26] (version 3, disp3, "zero damping") were used to include Van der Waals interactions. All minima (no imaginary frequencies) were characterized by calculating the Hessian matrix.

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