



An Isolated Nitridyl Radical-Bridged {Rh(N[•])Rh} Complex**

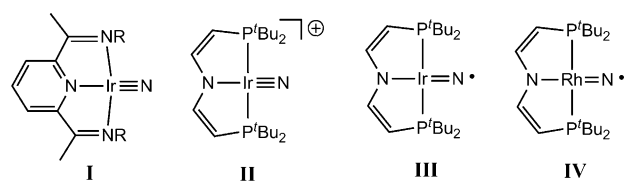
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Abstract: Photochemical activation of [(PNNH)Rh(N₃)] (PNNH = 6-di-(tert-butyl)phosphinomethyl-2,2'-bipyridine) complex **2** produced the paramagnetic ($S = 1/2$), [(PNN)Rh=N[•]-Rh(PNN)] complex **3** (PNN[•] = methylene-deprotonated PNNH), which could be crystallographically characterized. Spectroscopic investigation of **3** indicates a predominant nitridyl radical (N²⁻) character, which was confirmed computationally. Complex **3** reacts selectively with CO, producing two equivalents of [(PNN)Rh^I(CO)] complex **4**, presumably by nitridyl radical N,N-coupling.

Transition-metal complexes bearing open-shell nitrogen donors are remarkable synthetic targets that have remained elusive for a long time, in part because of their inherent high reactivity hampering isolation and characterization. Understanding their (electronic) structure, spectroscopic properties, and reactivity is important, since nitrogen-centered ligand radicals are proposed key intermediates in various catalytic reactions, and may play a key role in N₂ fixation. Despite their radical nature, they often react selectively with a variety of organic substrates.^[1] Isolated examples are extremely rare, and are thus far restricted to a few aminyl radical (R₂N[•])^[2] and nitrene radical (RN[•])^[3] complexes. Nitridyl radical complexes ([M(N[•])]) are particularly scarce, which relates to the low steric protection of the naked nitrogen atom. Thus far, only three unambiguous examples of complexes with predominant nitridyl radical (N²⁻) character have been de-

scribed; in all cases reactive intermediates that could not be isolated.^[4–6]

The availability of empty d orbitals with matching symmetry and energetic disposition to accept π -electron density is typically a prerequisite for stabilization of M=O, M $\equiv$ N, or M=NR species through multiple bonding between the transition metal and the oxo (O²⁻), nitrido (N³⁻), or imido (RN²⁻) π -donor ligands. For this reason, group 9–11 transition-metal ions with high d-electron counts are usually considered “incompatible” with oxo, nitride, and imido ligands. Exceptions were reported, describing the isolation of a few Ir=O, Pt=O, and M=NR complexes.^[7,8] Nitrido compounds of late transition metals (LTMs) are still extremely rare^[9] and only two isolated examples **I**^[10] and **II**^[5] beyond Group 8 have been



Closed-shell complexes, Isolated

Open-shell complexes, Transient

Figure 1. Reported nitrido and nitridyl radical complexes of iridium (**I**–**III**) and rhodium (**IV**).

reported, which are both closed-shell iridium–nitrido complexes (Figure 1, left). Despite recent efforts,^[11] isolated examples of rhodium and cobalt nitrido complexes are still unknown.^[12] In general, there are no reported examples of isolated nitridyl radical (N²⁻) complexes for any metal (neither terminal nor bridging).^[13,14] The recently disclosed transient (spectroscopically detected) nitridyl radical complexes **III** and **IV** (Figure 1) both rapidly transform into (bridging) N₂ complexes by N,N-coupling as a result of their N-centered radical character.^[5,6] We here report the first successful isolation and characterization of a stable, open-shell dinuclear nitridyl radical–rhodium complex. This complex was characterized by X-ray diffraction, electron spray ionization mass spectrometry (ESI-MS), EPR and NMR spectroscopy. Initial reactivity studies with carbon monoxide can be rationalized with the typical reactivity found for transient nitridyl radical complexes.

The new chloride complex [(PNNH)Rh(Cl)] (**1**) was prepared by reaction of [(Rh(coe)₂Cl)₂] (coe = cyclooctene) with the bipyridine–phosphane ligand PNNH (PNNH = 6-di-(tert-butyl)phosphinomethyl-2,2'-bipyridine).^[15] Salt metathesis of **1** with excess NaN₃ afforded the stable azido complex [(PNNH)Rh(N₃)] (**2**) as a microcrystalline material. Complex **2** was characterized by ESI-MS, IR ($\tilde{\nu} = 2022\text{ cm}^{-1}$), and

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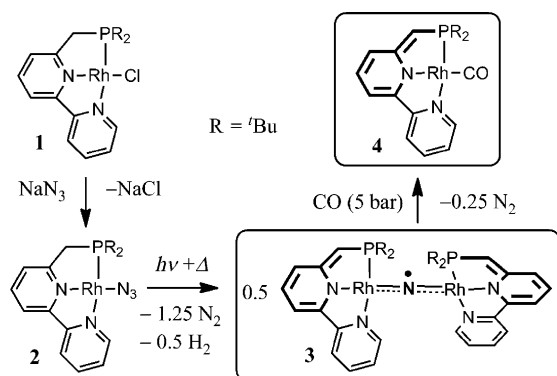
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multinuclear NMR spectroscopy. Complex **2** proved air-sensitive, but thermally stable over a wide temperature range under inert conditions. The thermal and photochemical reactivity of **2** were investigated, aiming at the formation of Rh(nitrido) species through N₂ loss. Solid-state thermolysis of **2** at temperatures < 250 °C showed no conversion, whereas decomposition into an insoluble black material was observed at temperatures greater than 250 °C. Thermolysis of **2** in refluxing toluene leads to nonselective decomposition, while **2** is stable in refluxing benzene for > 6 hours. In contrast, photolysis of a benzene suspension of **2** at 90 °C for 18 h, followed by recrystallization from benzene/heptane, fur-



Scheme 1. Complexes **1–4** and their connecting reactivity.

nished a stable black compound identified as the new Rh-N-Rh-bridged complex **3** in > 90 % isolated yield (Scheme 1). Formation of **3** is accompanied by the evolution of H₂, as detected by in situ ¹H NMR spectroscopy and GC-MS using a sample from the headspace. Single crystals, suitable for X-ray diffraction, were obtained from pentane/benzene at –20 °C. The molecular structure of **3** reveals a neutral, dinuclear compound [(PNN)Rh(N·)Rh(PNN)] (PNN[–] = anionic, methylene-deprotonated/dearomatized analogue of PNNH) with no counterions detected (Figure 2 a). This was confirmed by NMR spectroscopy and high-resolution cold-

spray-ionization ESI-MS spectrometry. The Rh1-N1 (1.814(2) Å) and Rh2-N1 (1.799(2) Å) distances are short, indicating Rh=N multiple bond character. The Rh1-N1-Rh2 angle is slightly bent (158.06(14)°). The two PNN[–] ligands adopt a near orthogonal orientation to one another (see also CPK space filling models in Figure S26), with interplane angles of 81.11(8)° and 85.14(8)° for the two independent molecules in the unit cell, indicating some rotational flexibility. Strikingly, both PNN[–] scaffolds are mono-anionic because of net deprotonation of the methylene unit, illustrated by the short CH=C_{py} bond lengths. This transforms the central pyridine into an amido donor, and in good agreement the Rh1-N21 distance (2.032(2) Å) is significantly shorter than the Rh1-N11 distance (2.101(2) Å). Complex **3** is neutral, hence it corresponds to an open-shell dinuclear Rh species containing an odd number of electrons.

The paramagnetic complex **3** is silent in ³¹P, ¹³C, and ¹⁵N NMR spectroscopy, but shows relatively sharp paramagnetically shifted ¹H NMR signals at RT [δ range from +14.9 to –11.0 ppm; C₆D₆]. The effective magnetic moment of **3** in solution ($\mu_{\text{eff}} = 1.14 \mu\text{B}$; Evans method) reveals an $S = 1/2$ species with a low g_{iso} value (about 1.31). The number and integration of the paramagnetically shifted ¹H NMR signals is consistent with two chemically inequivalent *t*Bu groups and eight signals for the chelate backbone protons, hence indicating C₂ symmetry on the NMR timescale, consistent with the molecular structure (for a tentative assignment of the signals, see Figures S7–S10^[15]). Hence, ligand rotation about the Rh-N-Rh axis is slow on the NMR time scale.

The ¹H NMR signals of **3** are temperature-dependent. VT NMR of **3** in [D₈]toluene revealed signals ranging from –17.17 to +18.39 ppm at –80 °C that shift to signals in the range of –7.92 to +13.26 ppm at 105 °C. Plots of the ¹H NMR shifts versus T^{-1} for **3** are shown in Figure 3. The linear dependence of the paramagnetic shift with T^{-1} is indicative of simple Curie paramagnetic behavior associated with a single contributing state ($S = 1/2$). Estimated carbon π spin densities from these data are all well below 2%,^[15] showing that **3** bears two anionic PNN[–] ligands rather than a bipyridyl radical, in

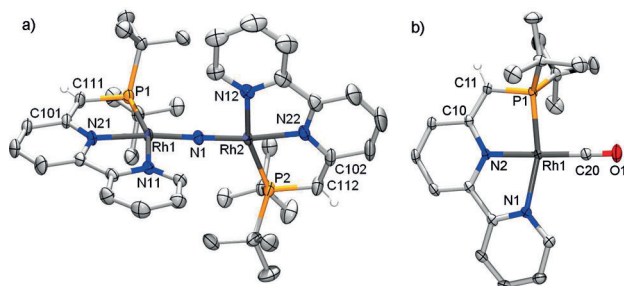


Figure 2. a) Molecular structure of **3**.^[16] Solvent molecules and hydrogen atoms (except for the methine hydrogens) were omitted for clarity. Selected bond lengths [Å] and angles [°]: Rh1-P1 2.2806(9), Rh1-N11: 2.101(2), Rh1-N21: 2.032(2), Rh1-N1: 1.814(2), Rh2-N1: 1.799(2); Rh1-N1-Rh2: 158.06(14), C101-C111: 1.364(4).^[15] b) Molecular structure of **4**.^[17] Selected bond lengths [Å]: Rh1-P1: 2.2612(4), Rh1-C20: 1.8286(17), Rh1-N1: 2.1075(13); Rh1-N2: 2.0269(13), C10-C11: 1.377(2), C20-O1: 1.152(2).^[15]

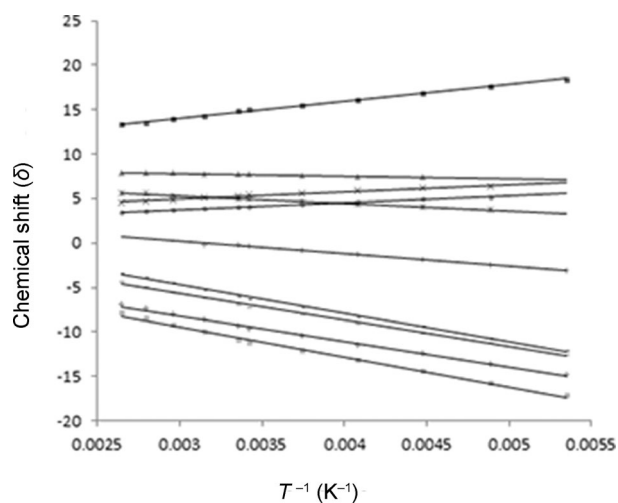


Figure 3. Curie plots of the paramagnetically shifted ¹H NMR signals of complex **3** (measured in [D₈]toluene).

good agreement with the ligand geometry in the X-ray crystal structure.

The electronic structure of **3** was examined with DFT methods, which also aided in understanding its spectroscopic properties. The SOMO (−3.188 eV) and α -LUMO (−3.086 eV) of **3** are nearly degenerate according to DFT calculations (Figure S23).^[15] The spin density of **3** (Figure 4 on the right side and Figure S23) is mainly distributed over the Rh(N)Rh moiety, with a dominating spin density at the nitrogen atom (BP86: 38 %; b3-lyp: 59 %) and smaller values at each of the two Rh atoms (BP86: 12 %; b3-lyp: 16 %). Hence, the electronic structure of **3** is best described with the resonance structures $\text{Rh}^{\text{II}}\text{--N}=\text{Rh}^{\text{III}}\leftrightarrow\text{Rh}^{\text{I}}\text{--N}^{\bullet}=\text{Rh}^{\text{III}}\leftrightarrow\text{Rh}^{\text{III}}=\text{N}^{\bullet}\text{--Rh}^{\text{I}}\leftrightarrow\text{Rh}^{\text{III}}=\text{N}\text{--Rh}^{\text{II}}\leftrightarrow\text{Rh}^{\text{II}}\text{--N}^{\bullet}=\text{Rh}^{\text{III}}$, with those containing an $\text{N}^{\bullet 2-}$ radical dominating. As such, complex **3** can be regarded as the first isolated example of a complex containing a (bridging) nitridyl radical ligand, contrasting the transient nature of the previously reported, spectroscopically detected terminal $\text{Rh}=\text{N}^{\bullet}$ and $\text{Ir}=\text{N}^{\bullet}$ species.^[5,10]

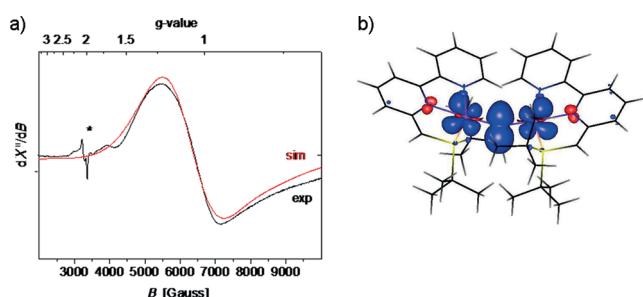


Figure 4. a) EPR spectrum of complex **3** recorded in a toluene glass at 5 K. Signal marked with * is a minor impurity (< 1 % signal intensity; possibly stemming from the EPR resonator). Frequency = 9.365432, microwave power 0.2 mW, modulation amplitude 20 G. b) Spin density plot (b3-lyp, def2-TZVP) of **3**.

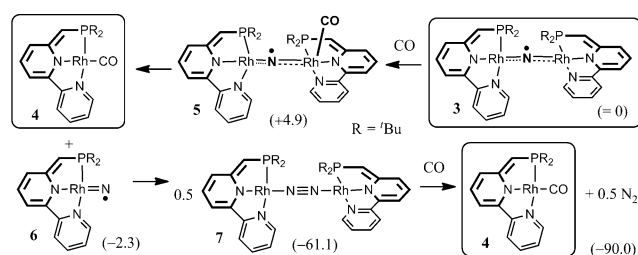
Table 1: Experimental and DFT-calculated EPR parameters of **3**.

	Experimental ^[a]	DFT ^[b]	DFT-D ^[b,c]
g_{11} (W_{11})	1.190 (1000 MHz)	1.370	1.500
g_{22} (W_{22})	1.050 (715 MHz)	0.766	1.108
g_{33} (W_{33})	0.808 (1500 MHz)	0.749	1.093

[a] Spectral simulation shown in Figure 4. [b] Turbomole optimized geometry; ADF (BP86, TZP) for EPR. [c] Geometry optimized using disp3 dispersion corrections.

The EPR spectrum of **3** (Figure 4) reveals a very broad signal with unusually low g -values,^[17,18] that are reproduced by DFT EPR property calculations (Table 1). Both the signal intensity and shape are very sensitive to temperature, which points to fast electron relaxation, in agreement with the observed ^1H NMR spectral features of **3** at RT. The low g -values, as well as the fast relaxation behaviour (which unfortunately also prevents pulse EPR experiments) are in agreement with the near degeneracy of the rotationally related SOMO and α -LUMO of **3** (Figure S23).^[5,6] The large SOC constant of Rh further contributes to the low g -values.^[18]

The mechanism for the formation of **3** from **2** remains largely unknown. However, about 50 % incorporation of ^{15}N in **3** upon using $^{14}\text{N}_2$ / ^{15}N -labeled **2** (prepared using terminally $^{14}\text{N}_2$ / ^{15}N -labeled NaN_3) confirms that the bridging nitrido ligand stems from the azide moiety.^[15] Furthermore both pincer ligands of **3** end-up as anionic PNN^- ligands, which is somehow associated with H_2 formation. Both heat and light proved necessary to drive the formation of **3**. Hence, a thermal process (e.g. enforcing a higher solubility of **2** at elevated temperatures) is likely followed by a photochemical step. Formation of H_2 could be driven by MLCT excitation, producing $\text{Rh}^{\text{II}}(\text{bipy}^-)$ excited states allowing intermolecular H_2 elimination (net $\text{H}^{\bullet}$ loss from PNNH). Precedence for $\text{H}^{\bullet}$ loss from a related $[(\text{PNPH})\text{Co}]$ complex was recently



Scheme 2. Proposed mechanism for the formation of **4** from **3**. Free energies calculated by DFT ($\Delta G_{298\text{K}}$, BP86/def2-TZVP) in kcal mol^{-1} .

reported by Milstein and co-workers.^[19] Combined with N_2 loss, this would produce the $[(\text{PNN})\text{Rh}=\text{N}^{\bullet}]$ nitridyl radical intermediate **6** (Scheme 2). In analogy to transient “nitridyl radical” **IV** (Scheme 1),^[6] **6** should undergo rapid N,N-coupling to form $[(\text{PNN})\text{Rh}^{\text{I}}\text{--N}_2\text{--Rh}^{\text{I}}(\text{PNN})]$ species **7**. Diamagnetic **7** is likely to be trapped by **6** to form the isolated, paramagnetic complex **3**. However, alternative mechanisms explaining H_2 and PNN^- ligand formation are certainly conceivable, such as PPNH deprotonation by N_3^- (the acidic nature of methylene-pyridine containing ligands is well-documented^[20]) followed by decomposition of HN_3 to N_2 and H_2 .

While **3** is isolable and stable in toluene and benzene solutions, it is not unreactive. Addition of CO (5 bar, < 5 min) to a solution of **3** in C_6D_6 leads to selective formation of two equivalents of the mononuclear Rh^{I} -carbonyl complex $[(\text{PNN})\text{Rh}(\text{CO})]$ (**4**) according to ^1H NMR (calibrated against an internal standard) and IR spectroscopy, verified by independent synthesis of **4**^[15] and X-ray diffraction (Figure 2). The proposed mechanism is shown in Scheme 2. The bridging nitridyl radical ligand of **3** is sterically strongly shielded, but coordination of CO to one of the rhodium atoms is certainly possible (for a CPK space filling model of **3**, see Figure S26^[15]). This facilitates splitting of the nitridyl bridge from intermediate **5**, thus leading to formation of **4** and **6**, which is overall exergonic according to DFT calculations (Scheme 2).

The terminal nitridyl radical intermediate **6** is electronically very similar^[15] to the previously reported intermediate **IV**, and thus likely undergoes facile radical-type N,N-coupling to form N_2 -bridged dinuclear Rh^{I} intermediate **7**.

Dissociative displacement of N_2 by CO accounts for the detected second equivalent **4**. Alternative pathways cannot be fully ruled out at this point. However, isocyanates were not detected (IR) and the reaction leads to clean formation of two equivalents of **4**, which implies formal reduction of Rh^{IV} to Rh^I with complete loss of the nitridyl ligand. This can only be explained by a radical process involving the $\cdot N^{2-}$ ligand, for which the mechanism in Scheme 2 is most straightforward.

In summary, we herein report the synthesis and characterization of an isolable open-shell nitride-bridged rhodium complex with predominant nitridyl radical character. Both rhodium centers of this intriguing species (**3**) adopt a distorted square-planar coordination geometry. Complex **3** reacts selectively with CO to produce two equivalents of $[(PNN)Rh^I(CO)]$ complex **4**, presumably by N,N-coupling of the nitridyl radical. It seems that isolation of this unusual species was possible for three main reasons: 1) The square-planar coordination geometry of rhodium allows for π bonding between the filled nitrogen p orbitals and the partially empty metal d_{π} orbitals, thus avoiding serious π conflicts.^[5,6] 2) The unpaired electron of the nitridyl radical ligand $\cdot N^{2-}$ (one half-filled p -orbital) is stabilized by delocalization over the three-center $M=N-M$ π manifold as compared with the transient, terminal nitridyl species **III** and **IV**. 3) Complex **3** is sterically protected leading to kinetic stability (except towards small molecules like CO). Targeting $M=O$, $M\equiv N$, or $M=NR$ species using square-planar, sterically protected, and open-shell transition-metal complexes may well be more general, and hopefully leads to a better understanding of these intriguing, potentially reactive and catalytically relevant species.

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