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DOI
10.1002/ejic.201900591

Publication date
2019

Document Version
Final published version

Published in
European Journal of Inorganic Chemistry

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Link to publication

Citation for published version (APA):

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Download date:15 May 2024
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 PNN ligand, bearing a tert-butyl group at the 6' position of the bipyridine moiety. A three-step synthetic route toward this new bulky tBu3PNN 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 (tBu3PNNH) ligand. This newly developed tBu3PNN ligand was incorporated in the synthesis of the sterically protected azide complex [Rh(N3)(tBu3PNN)]. We explored N2 elimination from this species using photolysis and thermolysis, hoping to synthesize a mononuclear rhodium complex 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 [(tBu3PNN)Rh(μ-N)Rh(tBu3PNN)] species. It thus seems that despite its three tBu 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 spectroscopy 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 species.

Scheme 1. Previously reported synthesis of dimeric nitridyl species C.
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 tBu3PNN 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 tBu3PNN pincer ligand 6 (left), and a CPK model (right) of the corresponding hypothetical mononuclear ([tBu3PNN]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 tBu3PNNH 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 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 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).

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 tBu3PNNH ligand can coordinate as a neutral PNN ligand to rhodium(I) (Figure 2). This
means that the bulky tert-Bu$_3$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 tert-butyl group of ligand 6, was the chlorido [RhCl(tert-Bu$_3$PNNH)] complex 8, bearing the new tert-Bu$_3$PNNH ligand 6. Complex 8 was prepared by the reaction of [Rh(μ-Cl)(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 $^1$H, $^{31}$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 [Rh(N$_3$)(tert-Bu$_3$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.](image)

The $^1$H 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 due to the slightly lower electronegativity of the azide ion. This influence of the Rh center. Substituting chloride for azide results in a relative shift to lower ppm values for the protons further away from the ancillary ligand.

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 [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 $^1$H 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 $^1$H 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 K). 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$^{	ext{II}}$ complex, with a signal pattern and $g$-values close to the ones found.
for earlier reported (square planar) RhII species\textsuperscript{[14]} that can presumably be attributed to the formation of a transient or unstable RhII species, not detectable under the above described photochemical reaction conditions (Figure S11).\textsuperscript{[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 [(tBu\textsubscript{3}PNN)Rh(μ-N)Rh(tBu\textsubscript{3}PNN)]\textsuperscript{+} and [(tBu\textsubscript{3}PNN)Rh(μ-N)Rh(tBu\textsubscript{3}PNNH)]\textsuperscript{+}, suggesting that the neutral dinuclear nitrido-bridged species [(tBu\textsubscript{3}PNN)Rh(μ-N)Rh(tBu\textsubscript{3}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 [(PNN)Rh(μ-N)Rh(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 [(tBu\textsubscript{3}PNNH)Rh(N)]\textsuperscript{+} and the coordinatively unsaturated species [(tBu\textsubscript{3}PNNH)Rh]\textsuperscript{+}. Fragmentation peaks corresponding to loss of one or two tBu 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 [(PNN)Rh\textsuperscript{IV}(N)] species was not observed, and hence the Rh–N bond in 11 does seem to be weakened compared to C.

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 [(tBu\textsubscript{3}PNN)Rh(CO)]. Thus, CO was added to 11 in C\textsubscript{6}D\textsubscript{6} (5 bar, 5 min). However, no chemical transformation seemed to take place as judged from the absence of any color changes. Furthermore, the \textsuperscript{31}P and \textsuperscript{1}H NMR spectra remained silent.

It thus seems that [(tBu\textsubscript{3}PNN)Rh(μ-N)Rh(tBu\textsubscript{3}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 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.\textsuperscript{[16]}
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).210 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 similar characteristics to that of C (Figure S20), suggestive of a rather large influence of the additional tBu 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 [(tBu2PNN)Rh(N)] and [(tBu2PNN)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 tBu group might cause dinuclear 11 to be more stable than its fragments (even in the presence of CO) and steric protection of nitridyl species [(tBu2PNN)Rh(N)] could actually prevent N–N coupling driving the reaction forward (as designed, see also Figure 1).

Conclusions

A new tBu3PNN 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 [(tBu2PNN)Rh(μ-N)Rh(tBu2PNN)] 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 [(PNN)Rh(μ-N)Rh(PNN)] species C, but has a distorted geometry and less accessible metal ions. The sterically congestion around Rh imposed by the bulky tBu3PNN 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: [RhCl(DMSO)]217 [Rh(μ-Cl)(coe)]218 2-methyl-6-(tributylstannylnyl)pyridine119 and 2-bromo-6-(tert-butyl)pyridine.20 Two researchers were purchased from commercial suppliers and used without further purification. THF, pentane, hexane and Et2O were distilled from sodium/benzophenone ketyl and toluene from sodium under nitrogen. NMR spectra (1H, 1H{31P}, 31P, 31P{1H}, 31P{13C}) were recorded 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 AccuTOF-FLC-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-(tributylstannylnyl)pyridine (19.204 g, 50.252 mmol), 2-bromo-6-(tert-butyl)pyridine (9.78 g, 45.68 mmol), Pd[PPPh3]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 mol/L) provided an aqueous layer which was carefully neutralized with 12 mol solution of Na2HCO3. 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 Na2SO4. The volatiles were removed by means of a rotary evaporator yielding a white solid. Yield: 7.0 g, 30.92 mmol, 68%. 1H NMR (400 MHz, CDCl3): δ (ppm) 8.37–8.23 (m, 2H, biPy); 7.72 (dt, JHH = 7.8, 4.9, 2.6 Hz, 2H); 7.34(d, JHH = 8.2 Hz, 1H); 7.16 (d, JHH = 7.6 Hz, 1H); 2.66 (s, 3H); 1.42 (s, 9H). 13C{1H} NMR (100 MHz, CDCl3): δ (ppm) 160.38 (s, 1Civ-biPy); 157.55 (s, 1Civ-biPy); 156.36 (s, 1Cv-biPy); 154.81 (s, 1Cv-biPy) 136.89 (s, 1CH3-biPy); 136.85 (s, 1CH3-biPy); 122.90 (s, 1CH-biPy); 118.81 (s, 1CH-biPy); 118.16 (s, 1CH-biPy); 117.68 (d, JCH = 8 Hz, 1CH-biPy); 37.66 (d, 1CH-2-bPy); 30.32 (t, 1Cv-biPy); 24.70 (s, 1CH3-biPy). HR-MS (FAB) calcd. for [M]+ C15H18N2O1S: 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 disopropylamine (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-butylithium (11.12 mL, 1.6 mol/L) 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 Et2O (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 Et2O (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 Et2O (3 × 20 mL). The combined organic layers were dried with anhydrous Na2SO4, 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, 41%. 1H NMR (400 MHz, CD2Cl2): δ (ppm) δ = 8.68 (d, JHH = 5.2 Hz, 1H, biPy); 8.59 (dd, JHH = 5.7, 3.2 Hz, 1H, biPy); 7.40–7.29 (m, 3H); 7.00 (d, JHH = 7.8 Hz, 1H, biPy); 3.14 (d, JHH = 2.6 Hz, 2H, biPy-C2=P); 1.44 (s, 9H, biPy-(CH2)3-P); 1.14 (d, JHH = 10.8 Hz, 18H, P-(CH2)3-P). 13C{1H} NMR (100 MHz, CD2Cl2): δ (ppm) 168.41 (s, 1Cv-biPy); 161.74 (d, JPC = 14.3 Hz, 1Cv-biPy); 156.13 (s, 1Cv-biPy); 155.57 (s, 1Cv-biPy); 137.10 (s, 1Cv-biPy); 136.79

(s, 1CH$_{3}$-P); 131.88 (s, P-1C-(CH$_{3}$)$_{3}$); 130.47 (s, 1(CH$_{3}$)$_{3}$-C); 29.93 (s, J$_{PC} = 13.8$ Hz, 2(CH$_{3}$)$_{3}$-C). $^{31}$P{1H} NMR (162 MHz, C$_{6}$D$_{6}$): δ (ppm) 35.41 (s, 1H). HR-MS (FAB) calcld. for [M]$^{+}$ C$_{23}$H$_{35}$F$_{6}$N$_{2}$OP$_{2}$Rh m/z, 515.1685; found 515.1685.

**Photolysis Experiment:** In a J-Young NMR tube, (5 mg) was dissolved in degassed C$_{6}$D$_{6}$ (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 $^{1}$H NMR spectroscopy. 11 was used without any isolation and purification method.

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

**Computational Details:** Geometry optimizations were carried out with the Turbomol program package$^{[22]}$ coupled to the PQS Baker optimizer$^{[21]}$ via the B0P package.$^{[23]}$ We used unrestricted ri-DFT-D 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.

**Acknowledgments**

We thank Ed Zuidinga for MS measurements and Jan Meine Ernsting and Andreas Ehlers for NMR advice. Financial support from the Netherlands Organization for Scientific Research (NWO-CW VICI project 016.122.613) and the University of Amsterdam (Research Priority Area Sustainable Chemistry) is gratefully acknowledged.

**Keywords:** Rhodium · Azide complexes · Photochemistry · Radicals · Bulky ligands

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[20] See ref.[12].


Received: May 25, 2019