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Side-On Bound Dinitrogen Complex of Zirconium Supported by a P_2N_2 Macrocyclic Ligand

Lara Morello, **Maria João Ferreira**, **Brian O. Patrick**, and **Michael D. Fryzuk***

Department of Chemistry, University of British Columbia, 2036 Main Mall,
Vancouver, British Columbia, Canada V6T IZ1

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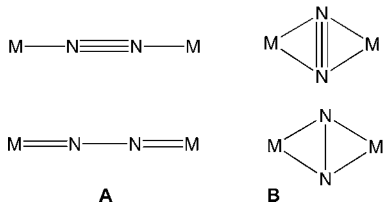
Reduction of $[P_2N_2]ZrCl_2$ (where P_2N_2 = $PhP(CH_2SiMe_2NSiMe_2CH_2)_2PPh$) by KC_8 under N_2 generates the dinuclear dinitrogen complex $([P_2N_2]Zr)_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ and impurities in varying yields depending on the solvent and temperature. The toluene complex $[P_2N_2]Zr(\eta^6\text{-}C_7H_8)$ along with a dinuclear species with bridging PC_6H_5 groups is observable. Also observable in the crude reaction mixtures is the μ-oxodiazenido derivative, $([P_2N_2]Zr)_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2H_2)(\mu\text{-}O)$, due to reaction with trace H_2O. This paper reports the full details of the preparation of $([P_2N_2]Zr)_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ including an improved method that involves reduction at low temperatures in a tetrahydrofuran solvent. Also reported is a reproducible synthesis of the oxodiazenido complex along with the X-ray structures of the dinitrogen complex and the oxodiazenido derivative.

Introduction

In the last 40 years or more, hundreds of complexes with one or more coordinated dinitrogen ligands in a variety of bonding modes have been described.[1–6] For example, in dinuclear metal complexes where the N_2 unit is symmetrically bridging, the end-on bonding mode (**A**) is very common, and becoming more prevalent is the side-on bridging motif (**B**).[6] Both of these binding modes have been reported with N−N bond lengths that range from essentially triple bond character unchanged from free N_2 (1.1 Å) to typical N−N single bonds (1.5 Å), with the latter correlated with substantial activation upon coordination.



The synthesis and characterization of the dinuclear side-on bound dinitrogen complex $([P_2N_2]Zr)_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ [**1**; where P_2N_2 = $PhP(CH_2SiMe_2NSiMe_2CH_2)_2PPh$] was first communicated in 1997 without details.[7] The solid-state structure indicated an N−N bond length of 1.43(1) Å, somewhat less that the related dinuclear zirconium complexes stabilized by other amidophosphine-type ligands,[8,9] for example, $([PNP]ZrX)_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ [**2**; where PNP = $N(SiMe_2CH_2PPr^i{}_2)_2$; X = Cl, **2**; O-2,6-$Me_2C_6H_3$, **3**], and $([NPN]ZrL)(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ [**4**; where NPN = $PhP(CH_2SiMe_2NPh)_2$ and L = tetrahydrofuran].[10,11] In this paper, we describe the full details of the original reduction of $[P_2N_2]ZrCl_2$ in the presence of N_2 in which **1** is produced along with some intriguing, but undesired side products; we also include an improved synthesis of **1**, along with full details of its solid-state X-ray crystal structure, and discuss the reaction of **1** with water.

Experimental Section

Unless otherwise specified, all procedures and manipulations were performed under an atmosphere of dry, oxygen-free dinitrogen or argon by means of standard Schlenk or glovebox techniques

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(Vacuum Atmospheres HE-553-2 glovebox equipped with a MO-40-2H purification system and a −40 °C freezer). Argon and nitrogen were dried and deoxygenated by passing the gases through a column containing molecular sieves and MnO. Hexanes, toluene, tetrahydrofuran (THF), and diethyl ether were purchased from Aldrich, dried by passage through a tower of alumina, and degassed by passage through a tower of Q-5 catalyst under positive pressure of nitrogen. Deuterated toluene, THF, and benzene were refluxed over a sodium/potassium alloy under partial pressure, trap-to-trap distilled, and freeze–pump–thaw degassed three times. Unless otherwise stated, benzene-d_6 (C_6D_6) was the solvent used for all NMR samples. ^{1}H and ^{31}P NMR spectra were recorded on either a Bruker AMX-500, a Bruker AV-400, or a Bruker AV-300 spectrometer. ^{1}H NMR spectra were referenced to residual protons in the deuterated benzene, C_6D_5H (7.15 ppm), and deuterated THF, C_4D_7HO (3.58 ppm). ^{31}P NMR spectra were referenced to external $P(OMe)_3$ (141.0 ppm with respect to 85% H_3PO_4 at 0.0 ppm). All spectra were measured at room temperature, unless otherwise stated. Microanalyses (C, H, and N) were performed by P. Borda or M. Lakha of this department.

Caution! *All reactions that resulted in a pressure of 1.5 atm or greater within a sealed vessel upon warming to room temperature were performed with great care and always manipulated behind a blast shield.*

Materials. Potassium graphite, KC_8,[12] and $[P_2N_2]ZrCl_2$[13] were prepared according to literature procedures. Hydrazine (neat or 1 M in THF) was purchased from Aldrich. Neat hydrazine was dried and degassed according to literature procedures.[14]

Synthesis of $([P_2N_2]Zr)_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ (1). A thick-walled flask fitted with a Kontes valve adaptor was charged with $[P_2N_2]ZrCl_2$ (2.070 g, 2.98 mmol) and KC_8 (0.877 g, 6.49 mmol). The mixture was stirred and degassed prior to the addition of THF (40 mL) via a trap-to-trap transfer under static vacuum at −196 °C. The flask was warmed to −78 °C (IPA/CO_2 bath), while the mixture was stirred and supplied with a constant flow of N_2 (1 atm). Once the solvent had fully melted, the flask was sealed. The cold temperature was maintained for another 4–5 h before the slurry was warmed to room temperature. The teal slurry was stirred for another 15 h. The reaction mixture was filtered through Celite on a sintered-glass crucible, and the filtrate was evaporated to dryness. Further purification of the resulting blue-green powder, complex **1**, was unnecessary. Yield: 1.8 g, 95%. Anal. Calcd for $C_{24}H_{42}N_3P_2Si_4Zr$: C, 45.17; H, 6.63; N, 6.58. Found: C, 45.21; H, 6.83; N, 5.21. The low nitrogen value is likely due to the formation of zirconium nitrides during the combustion process. ^{1}H NMR (C_6D_6): δ 0.08 (br s, 24H, $SiCH_3$), 0.38 (s, 24H, $SiCH_3$), 1.28 (m, 8H, ring CH_2), 1.55 (m, 8H, ring CH_2), 6.93 (br m, 8H, phenyl), 7.14 (m, 8H, phenyl), 8.05 (br m, 4H, phenyl). ^{31}P{^{1}H} NMR (C_6D_6): δ −16.3 (s). ^{15}N{^{1}H} (C_6D_6): δ 466.7 (s). The ^{15}N-labeled material, $([P_2N_2]Zr)_2(\mu\text{-}\eta^2{:}\eta^2\text{-}^{15}N_2)$, was prepared identically using $^{15}N_2$ (Cambridge Isotopes).

Synthesis of $([P_2N_2]Zr)_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2H_2)(\mu\text{-}O)$ (7). Degassed water (1.7 μL, 0.10 mmol) was added by microsyringe to 100 mL of THF in an addition funnel. A solution of $([P_2N_2]Zr)_2(N_2)$ (0.121 g, 0.10 mmol) in THF (100 mL) was cooled to −78 °C. The wet THF was added dropwise over a period of 4.5 h, during which the initially blue-green solution turned to yellow. The yellow mixture was filtered through Celite and evaporated until cloudy. The ^{31}P{^{1}H} NMR of the crude mixture shows only two signals, one at −12.4 ppm corresponding to **7** and one at −36.8 ppm corresponding to the free ligand, $[P_2N_2]H_2$, integrating 2:1. Yield: 60 mg, 50%. Anal. Calcd for $C_{48}H_{86}N_6OP_4Si_8Zr_2$: C, 44.54; H, 6.70; N, 6.49. Found: C, 44.85; H, 6.71; N, 6.46. ^{1}H NMR (C_6D_6): δ_H 7.7 to 6.9 (br m's, 20H, phenyl), 4.13 (s, 2H, NH), 1.80 to −0.3 (broad features for ring CH_2 and $SiMe_2$). ^{31}P{^{1}H} NMR (C_6D_6): δ_P −12.5 (s). ^{1}H NMR (C_4D_8O, 400 MHz, 228 K): δ_H 7.59 (m, 4H), 7.50 (m, 2H), 7.43 (m, 4H), 7.28 (m, 2H), 7.19 (m, 4H), 6.98 (m, 4H), 3.93 (s, 2H, NH), 1.53−0.67 (overlapping AMX m's, ring CH_2), 0.61 (s, 6H, ring $SiMe_2$), 0.30 (s, 6H, ring $SiMe_2$), 0.28 (s, 6H, ring $SiMe_2$), 0.14 (s, 6H, ring $SiMe_2$), 0.12 (s, 12H, ring $SiMe_2$), 0.08 (s, 6H, ring $SiMe_2$), −0.23 (s, 6H, ring $SiMe_2$). ^{31}P{^{1}H} NMR (C_4D_8O, 162.0 MHz, 228 K): δ_P −11.9 and −12.6 (AB doublets, J_{PP} 75.2 Hz). ($^{15}N_2$-**7**) ^{1}H NMR (C_6D_6): as with the above, except the AA′XX′ multiplet centered at 4.13 ppm.

Reaction of $[P_2N_2]ZrCl_2$ with Hydrazine and BuLi. (i) THF (25 mL) and hydrazine (0.02 mL, 0.638 mmol) were added to a Schlenk flask under an argon atmosphere. The solution was cooled to −78 °C (IPA/CO_2 bath), and BuLi (1.6 M in hexanes, 1.6 mL, 2.56 mmol) was added dropwise. The stirred yellow solution was warmed to room temperature and darkened to an orange color. This solution was cooled again to −78 °C, and a THF (35 mL) solution of $[P_2N_2]ZrCl_2$ (0.712 g, 1.02 mmol) was added via cannula. As this solution was warmed to room temperature, a color change from green to yellow was observed. THF was removed in vacuo, and the yellow residues were extracted into toluene and filtered through Celite. Toluene was also removed in vacuo, leaving a yellow residue. ^{31}P{^{1}H} NMR (C_6D_6, 81 MHz): δ 0 to −20 (many singlets, unknown sources), −36.8 (s, $[P_2N_2]H_2$).

(ii) THF (50 mL) was added to a flask containing $[P_2N_2]ZrCl_2$ (0.350 g, 0.504 mmol) and cooled to −78 °C under an argon atmosphere. A 1 M solution of hydrazine in THF (0.25 mL, 0.25 mmol) was added, followed by the dropwise addition of BuLi (1.6 M in hexanes, 0.63 mL, 1.01 mmol). The stirred solution changed from clear orange to brown and then green-yellow, with no appearance of precipitate. The cold bath was removed after 20 min, and the solution was allowed to warm to room temperature. The solvent was removed in vacuo, and the green residues were extracted into hexanes and filtered through a sintered-glass crucible. ^{31}P{^{1}H} NMR (C_6D_6, 81 MHz): δ 0 to −20 (many singlets, unknown sources), −36.8 (s, $[P_2N_2]H_2$), −37.7 (q, $[P_2N_2]Li_2(THF)$).

X-ray Crystal Structure Analyses. Selected crystals of **1** were coated in oil and mounted on a glass capillary. For **7**, the selected crystals were coated in oil, mounted on a glass fiber, and placed under a N_2 stream. For compound **1**, measurements were made on a Rigaku AFC6S equipped with a scintillation detector. Graphite-monochromated Cu Kα radiation was used (λ = 1.541 80 Å). Measurements for compound **7** were made in a Bruker X8 Apex diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). The data were collected at a temperature of 296 ± 2 K for **1** and of 193 ± 1 K for **7**. For compound **1**, data were collected and integrated using the *teXsan*[15] crystallographic software package of Molecular Structure Corp., whereas for compound **7**, the Bruker *SAINT* software package was used.[16] Data for both complexes were corrected for Lorentz and polarization effects. For complex **1**, absorption effects were corrected empirically, based on azimuthal scans for three reflections, whereas for compound **7**, the absorption correction was done by the multiscan technique

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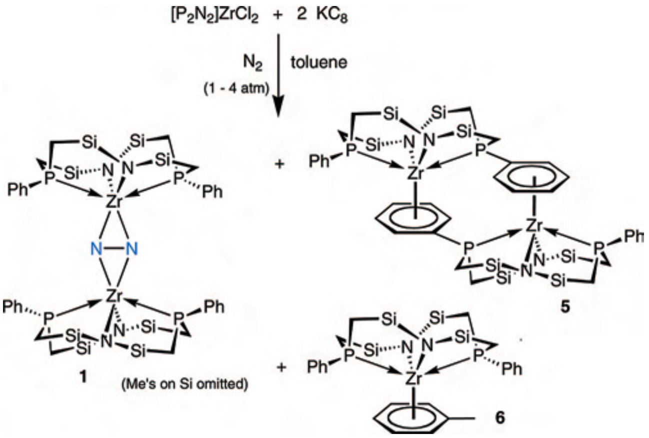
(16) *SAINT*, version 7.03A; Bruker AXS Inc.: Madison, WI, 1997–2003.

(*SADABS*).[17] For both compounds, neutral atom scattering factors were taken from Cromer and Waber.[18] Anomalous dispersion effects were included in F_{calc};[19] the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.[20] The values for the mass attenuation coefficients are those of Creagh and Hubbell.[21] The structures were solved by direct methods using *SIR-2004*.[22] All non-hydrogen atoms were refined anisotropically using *SHELXL-97*.[23] Hydrogen atoms were included in fixed positions. These programs are part of the *WinGX* software package version 1.70.01.[24] In compound **1**, the phenyl rings on the ligand are disordered and were modeled satisfactorily. The ellipsoids of these groups and of the methyl groups attached to the silicon atoms are slightly large because of movements of these groups in the crystal lattice. The residual electron density was also evident but could not be modeled successfully. In the asymmetric unit of **7**, solvents that could be modeled as 1.5 C_6H_6 appear. The residual electron density consistent with additional disordered solvent was also evident but could not be modeled successfully. The program *SQUEEZE*[25] was used to generate a data set that corrects for the scattering contribution from this disordered solvent. The ellipsoids of C_6H_6, the phenyl groups, and the methyl groups attached to the silicon atoms are slightly large because of movements of these groups in the crystal lattice.

Results and Discussion

Originally, **1** was synthesized by the addition of toluene to a 1:2 mixture of $[P_2N_2]ZrCl_2$ and potassium graphite (KC_8) under 1 (or 4) atm of N_2 at room temperature and isolated in yields that averaged around 40%. The reaction starts quickly, as suggested by the immediate formation of a dark-blue-green solution that is characteristic of the presence of complex **1** and related phosphineamido derivatives of zirconium previously reported by us. However, analysis of the crude reaction mixture that contains **1** by ^{31}P NMR spectroscopy shows additional resonances that are due to other products present under these reducing conditions. As shown in Scheme 1, two of the minor products contain activated aryl groups, the bridging P−phenyl derivative **5**, and the toluene complex **6**. Although only formed in low yields (5–10%), the bridging P−phenyl complex **5** can be synthesized independently and in high yield by performing the reduction in the absence of N_2 as reported previously.[26] The toluene complex **6**, also formed as a minor byproduct in the N_2 reaction (Scheme 1), can be prepared by hydrogenation of the zirconium dimethyl complex $[P_2N_2]ZrMe_2$ in toluene in moderate yield (58%). Both **5** and **6** have been characterized by NMR spectroscopy and X-ray crystallography.

Scheme 1



One can speculate about possible intermediates formed in the reduction of $[P_2N_2]ZrCl_2$ by a strong reducing agent such as KC_8. Complexes **5** and **6** likely result during the reduction of $[P_2N_2]ZrCl_2$ under N_2 through the intermediacy of a reduced zirconium species, perhaps a zirconium(II) intermediate that is subsequently trapped by toluene to form **6** or perhaps a zirconium(III) chloride bridged dimer, which upon further reduction may lead to **5**. Regardless of the mechanism, clearly **6** can be avoided by a change to a nonaromatic solvent. With regards to **5**, its formation seems to correlate with inadequate access to N_2, either from inefficient stirring or if pressures of N_2 of less than 1 atm are utilized.

Other impurities are also associated with the synthesis of **1**. Occasionally, we observe two additional singlets in the ^{31}P NMR spectrum of crude **1** at δ −12.5 and −36.8, which vary in relative intensity to each other and to **1**; the latter singlet resonance can be assigned to protonated macrocycle $[P_2N_2]H_2$ because we have prepared this independently; such an upfield shift for the signals due to the phosphines is consistent with being uncoordinated. The other singlet downfield of the starting dinitrogen complex **1** (δ −16.3) indicates that the phosphorus-31 nuclei are still coordinated to zirconium. Anticipating that the protonated ligand originates from adventitious moisture, it seemed reasonable to propose that water could react with **1** to generate a new complex. To confirm this, the slow addition of slightly less than 1 equiv of H_2O to **1** at low temperature was investigated, as shown in eq 1. By this method, the oxodiazenide **7** could be isolated in moderate yield and shown to display a singlet in the ^{31}P NMR spectrum at precisely δ −12.5 (at ambient temperature), identical with the above aforementioned impurity. The solid-state molecular structure (Figures 1 and 2) reveals a far less symmetrical structure than that for **1**. The nitrogen atoms of the diazenido unit no longer lie on the plane that contains both zirconium atoms but are now distorted approximately 1.5 Å away from a line that is defined by the two zirconium centers. The N−N distance is slightly shorter than the corresponding distance in **1**, attesting to the high activation of the dinitrogen ligand in **1**. The Zr−μ-O distance is comparable to the distances found in

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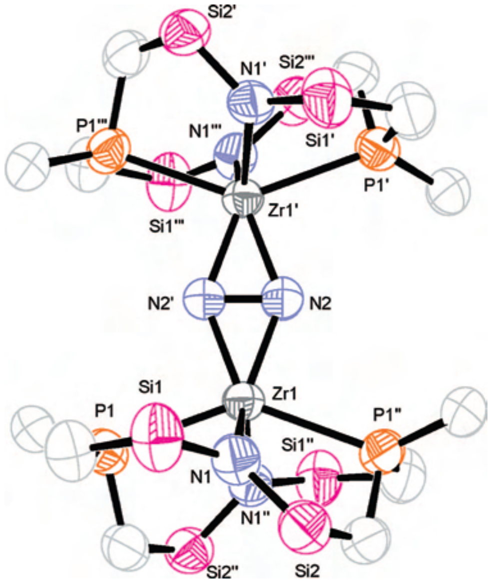


Figure 1. ORTEP drawing of the solid-state molecular structure of **1** (ellipsoid probability at 50%). The methyl groups on silicon, the phenyl rings on phosphorus (except C_{ipso}), and the hydrogen atoms are omitted for clarity. Selected bond distances (Å), angles (deg), and dihedral angles (deg): N2−N2′, 1.465(19); Zr1−N2, 2.018(3); Zr1−N1, 2.197(6); Zr1−P1, 2.736(2); Zr1−Zr1′, 3.761(15); N2−Zr1−N2′, 42.6(5); Zr1−N2−Zr1′, 137.4(5); (P1−Zr1−P1″)−(P1‴−Zr1′−P1′), 2.51(2); (N1−Zr1−N1″)−(N1‴−Zr1′−N1′), 7.90(5).

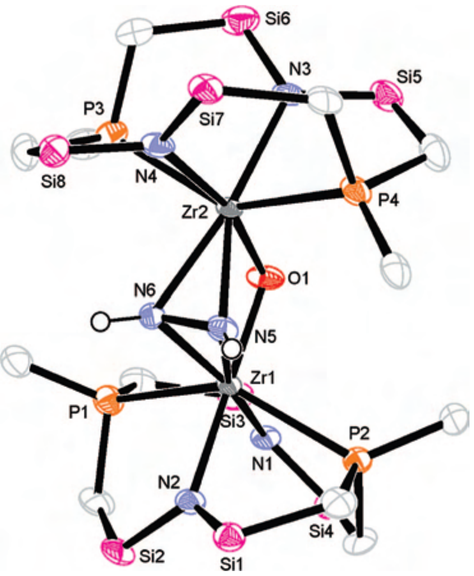
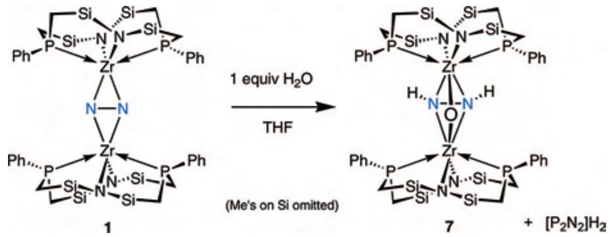


Figure 2. ORTEP drawing of the solid-state molecular structure of **7** (ellipsoid probability at 50%). The methyl groups on silicon, the phenyl rings on phosphorus (except C_{ipso}), and the hydrogen atoms (except those attached to the nitrogen atoms that are placed in calculated positions) are omitted for clarity. Selected bond distances (Å), angles (deg), and dihedral angles (deg): N5−N6, 1.434(9); Zr1−O1, 1.995(5); Zr2−O1, 1.998(5); Zr1−N6, 2.183(6); Zr1−N5, 2.223(6); Zr2−N5, 2.180(7); Zr2−N6, 2.238(6); Zr1−Zr2, 3.1922(10); N5−(Zr1−Zr2), 1.5162(100); N6−(Zr1−Zr2), 1.5291(98); Zr1−O1−Zr2, 106.1(2); Zr2−N5−Zr1, 92.9(2); Zr1−N6−Zr2, 92.4(2); (P1−Zr1−P2)−(P3−Zr2−P4), 5.79(13); (N3−Zr2−N4)−(N1−Zr2−N2), 18.78(33).

the literature (1.957 Å).[27] This bridging ligand probably promotes the shortening of the Zr−Zr distance when compared to **1**, aided by the repositioning of the P_2N_2 ligands that are slightly rotated relative to each other (the angle between the planes defined by the phosphorus atoms and the zirconium on each side of the molecule is 2.51(2)° for **1** and 5.79(13)° for **7**, and the angle between the planes defined by the nitrogen atoms and the zirconium on each side of the molecule is 7.90(5)° for **1** and 18.78(33)° for **7**).

In solution, however, the NMR data for **7** are consistent with the molecule having C_s symmetry because the ^{1}H NMR data show four broad silylmethyl resonances and all four phosphine donors are equivalent. That both protons from the water molecule have been transferred to the coordinated dinitrogen unit was evident upon reaction of water with the ^{15}N-labeled dinitrogen complex **1**; in this case, the diazenido unit ($H^{15}N-^{15}NH$) appears as an AA′XX′ spin system (10-line pattern) centered at δ 4.13. This was confirmed by the careful addition of deuterated water to **1**, which resulted in the loss of the signal intensity of the N−H resonance. Interestingly, a variable-temperature ^{1}H and ^{31}P NMR spectroscopic study of **7** in THF-d_8 showed that, at low temperatures, the singlet in the ^{31}P NMR spectrum decoalesces into a doublet of doublets at δ −11.9 and −12.6 with $^2J_{PP} = 75.2$ Hz (see Figure S1 in the Supporting Information); in addition, the signals in the ^{1}H NMR spectrum become more complicated, indicating C_1 symmetry in the low-temperature limit. Thus, the low-temperature NMR data match the solid-state structure.

Attempts to isolate **1** from a crude reaction mixture that consists of **5**−**7** and $[P_2N_2]H_2$ are complicated by the similar solubilities of the dinitrogen complex and its associated impurities. Complex **1** is sufficiently soluble in a mixture of hexanes/toluene that it may be separated by extraction from dinuclear P−phenyl-bridged **5**, which is sparingly soluble in both solvents. However, **7** and $[P_2N_2]H_2$ are also removed, along with **1**, by the extraction process. A hexane rinse of the crude blue-green powder removes $[P_2N_2]H_2$ from complex **1**. However, a significant amount of **7** remains in both the washed product and the discarded filtrate, based on ^{31}P NMR spectroscopy. A portion of **1** is also sacrificed with each washing. Also, recrystallization of **1** via slow evaporation of a toluene solution is tedious and is an unreliable means of purification.



1

7 + $[P_2N_2]H_2$

An improvement in the synthesis of **1** was achieved by changing the solvent to very dry THF and initiating the reduction reaction at a low temperature. Conditions that promote the reaction of the reduced zirconium species with N_2, and hinder the side reaction that produces **5**, are vital for the preparation of **1**. This is achieved by transferring the solvent to a cold mixture of $[P_2N_2]ZrCl_2$ and KC_8, in vacuo,

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[27] Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, S1.

such that the solvent freezes immediately and, as a result, no side reactions occur. Dinitrogen is then introduced as the frozen mixture thaws. Maintaining a cold temperature (−78 °C) for several hours, while the solution is stirred vigorously, gives the highest yield and purity of **1**: 95% with no evidence of **5**, **6**, or **7**. THF was found to be more effective than toluene or cyclohexane as a solvent.

Other methods to introduce the N_2 unit were examined. For example, the addition of tetrakis(trimethylsilyl)hydrazine, $(Me_3Si)_2NN(SiMe_3)_2$, to $NbCl_5$ in THF/CH_2Cl_2 forms $[NbCl_3(THF)_2]_2(\mu\text{-}N_2)$[28] via elimination of Me_3SiCl, without the need for additional reducing agents. Similarly, 1,2-bis(trimethylsilyl)hydrazine, $(Me_3Si)HNNH(SiMe_3)$, reacts with $TaCl_5$ to generate the corresponding tantalum(V) analogue, $[TaCl_3(THF)_2]_2(\mu\text{-}N_2)$. However, neither of these reagents were effective in installing the N_2 unit using $[P_2N_2]ZrCl_2$ because only unreacted starting materials were detected. Two additional approaches were examined in an attempt to drive the reaction using the formation of LiCl; BuLi was added to a cold solution of hydrazine in an attempt to generate N_2Li_4 in situ, followed by the addition of $[P_2N_2]ZrCl_2$, or 4 equiv of BuLi was added to a cold solution containing both N_2H_4 and $[P_2N_2]ZrCl_2$. In the former case, a yellow residue was isolated and ^{31}P NMR analysis of the crude reaction mixture showed multiple resonances, including the signal attributed to $[P_2N_2]H_2$. Green residues were isolated using the second approach, and multiple resonances, including those associated with $[P_2N_2]H_2$ and $[P_2N_2]Li_2(THF)$, were observed in the ^{31}P NMR spectrum. Because none of the attempted reactions formed complex **1**, this approach was not pursued further.

Conclusions

Reductive methods are the most widely used routes to dinitrogen complexes, particularly for the early transition metals. Exposure of a complex in a relatively high oxidation state to a reducing agent in the presence of N_2 can lead to the formation of dinitrogen complexes provided that side reactions are minimized. The factors that complicate this kind of process are (i) dinitrogen is not that good of a ligand, which makes trapping of reactive, low-oxidation-state intermediates problematic and (ii) the mechanism of dinitrogen complex formation under reducing conditions is not well established. This is especially true for zirconium systems, whereas for titanocene derivatives, reduction and coordination by N_2 is better understood.[29]

In this paper, we have documented how analysis of the products of the side reactions in the reduction of $[P_2N_2]ZrCl_2$ by potassium graphite allowed for improvement in the yield of the desired dinitrogen complex **1**. It is critical to ensure that the solvent is compatible with the reducing agent; in this case, one can conclude that substitution of toluene by THF avoids the formation of the arene complex **6** and further speculate that THF may stabilize the formation of mononuclear zirconium(III) intermediates, thus preventing the formation of the P−phenyl-bridged dimer **5**. Another important factor is stirring; because this is a heterogeneous reaction that involves solid KC_8 reacting in solution with the dissolved zirconium(IV) precursor with dissolved N_2, efficient mixing is paramount to ensure efficient trapping of lower-oxidation-state intermediates. While reduction continues to be the most common method to prepare dinitrogen complexes,[30] development of milder methods continues to be the goal of many research groups.

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Supporting Information Available: Table of crystallographic data for **1** and **7**, variable-temperature ^{31}P NMR spectra for **7** (Figure S1), and X-ray crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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