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Article

Si–N Bond Hydrolysis Furnishes a Planar 4-Coordinate 14-Electron Ru(II) Complex with a Triplet Ground State

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Reaction of stoichiometric (2:1) water with $[(^t\mathrm{Bu}_2\mathrm{PCH}_2\mathrm{SiMe}_2)_2\mathrm{N}]\mathrm{Ru}(\mathrm{OSO}_2\mathrm{CF}_3)$ produces planar, 14-valence-electron spin triplet *trans*-$\mathrm{Ru}(^t\mathrm{Bu}_2\mathrm{PCH}_2\mathrm{SiMe}_2\mathrm{O})_2$. A possible mechanism for this hydrolysis is discussed. This molecule reacts rapidly with CO to give a monocarbonyl, then a cis-dicarbonyl. Reaction with HCCR (R = H or Ph) yields the vinylidene $(^t\mathrm{Bu}_2\mathrm{PCH}_2\mathrm{SiMe}_2\mathrm{O})_2\mathrm{Ru{=}C{=}CHR}$.

Introduction

Each ligand has its vulnerabilities,[1−6] which really refers to reaction conditions (e.g., oxidative, reductive, nucleophilic, electrophilic) which yield attack on the ligand rather than the intended metal center binding. The present report details mechanistic features of one such reaction, which forms very strong Si−O bonds at the expense of Si−N bonds, all assisted by proton transfers. The fact that the reaction forms a metal complex whose characterization expands our understanding of highly unsaturated, low-coordination number, and unusually structured ruthenium complexes is an added dividend.

The Fryzuk ligand class[7−9] $(\mathrm{R}_2\mathrm{PCH}_2\mathrm{SiMe}_2)_2\mathrm{N}^{-1}$ enables synthesis of a 4-coordinate, 14-valence-electron, spin triplet planar molecule (PNP)RuCl[10] when the R group in the ligand is ^{t}Bu.[11,12] It is possible to do metal-centered reaction chemistry with the nucleophilic reagents N_3^-,[13] $[\mathrm{NMe}_4]\mathrm{F}$,[14] and MeLi.[15] Reactions with H_2 and RCCH[16] have revealed that the coordinated amide nitrogen is subject to bonding to H and vinyl groups, and the original work by the Fryzuk group showed examples of amide nitrogen protonation or of *N*-acetylation by a C(O)Me initially on nickel. The Si−N bonds persist in all these reactions. We report here on the reaction of (PNP)RuX with water.

Results

Synthesis. Yellow (PNP)Ru(OTf) in benzene reacts with water or with wet acetone (for benzene/water miscibility) in time of mixing at 22 °C to form a paramagnetic product (judging by chemical shift values) showing one ^{t}Bu (−9.1 ppm), one SiMe (21.9 ppm), and one CH_2 (−25.4 ppm) chemical shift; no ^{31}P NMR signal is detectable due to the rapid relaxation caused by paramagnetism. The reaction (Scheme 1) also proceeds, but more slowly, for the chloride and fluoride analogues (PNP)RuX.

Since PNPRuCl was shown to be a spin triplet, the parmagnetic shifts of the ^{1}H NMR signals and the absence of a ^{31}P NMR signal are attributed to this same intrinsic paramagnetism. The alternative hypothesis, that the paramagnetic shifts are due to a singlet/triplet thermal equilibrium, is excluded because we observe no thermochromism when

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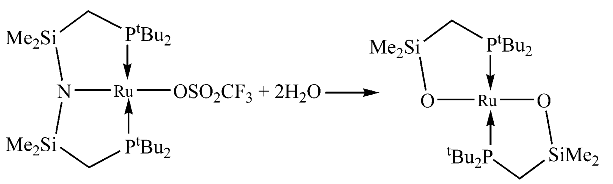
Scheme 1



a solution is cooled, which should convert the hypothesized mixture of spin isomers to a different mole fraction, hence different color. We likewise observe no growth of NMR signals of a diamagnetic spin isomer at low temperature. The possibility that these shifts are caused by Ru(III) impurities is rendered untenable since reaction(see below) of Ru(O−P)$_2$ with three different Lewis bases gives, in time of mixing, complete conversion to diamagnetic products whose NMR show no effects of the hypothesized Ru(III) and which shows no further paramagnetic constituents (the hypothesized Ru(III)). Finally, the chemical shifts are reproducible in different preparations.

Structure. An X-ray structure determination of crystals grown from benzene (Figure 1) shows the chemical formula Ru(^{t}Bu$_2$PCH$_2$SiMe$_2$O)$_2$, **1**. Crystals of two distinct polymorphs, both with space groups $P1$, were grown from benzene and from pentane and both structures were solved. The two polymorphs contain identical molecules (and no solvent guest) but packed differently. The molecules have a crystallographic center of symmetry, so the two identical ^{t}BuP$_2$CH$_2$SiMe$_2$O$^-$ ligands[17] have trans stereochemistry and the RuO$_2$P$_2$ core is rigorously planar. The Ru−P distance, 2.37772(5) Å, is unexceptional, and the Ru−O distance, 1.9889(9) Å, is short (cf. >2.1 Å[18,19]). Cis angles are all 90 ± 5° and are smaller within a chelate ring. The angles Ru−P−C are 110−116° and thus show no evidence for bending to achieve agostic Ru/CH$_3$ interactions; Ru/C(H$_3$) distances exceed 3.61 (on ^{t}Bu) and 4.33 Å (on Si). A least-squares fit of the molecules in the two polymorphs shows the RuPCSiO cores identical to within 0.07 Å, with the largest deviations (0.29 Å) being at the silyl methyl carbons; even the ^{t}Bu groups have the same rotational conformation in the two polymorphs.

Mechanistic Features. We anticipated that Si−O bond formation would be more favorable from OH$^-$ than from H$_2$O, although coordinated hydroxide within any proposed (PNP)RuOH species has too great a distance between Si and O to allow intramolecular reaction; bimolecular reaction of Ru−OH with Si on a different molecule would suffer steric problems.

The necessity to produce hydroxide is supported by the fact that (PNP)RuCl shows, by ^{1}H NMR, no evidence for binding H$_2$O; clearly, production of Ru(^{t}Bu$_2$PCH$_2$SiMe$_2$O)$_2$ from the chloride is much slower than it is from (PNP)Ru(OTf) (see Experimental Section). Coordination of water to Ru is thus a necessary step, but this does not effectively take place by addition to (PNP)RuCl (^{1}H NMR evidence). Only anionic ligand *displacement* is effective, and we propose that this happens with triflate but not effectively with chloride (Scheme 2).

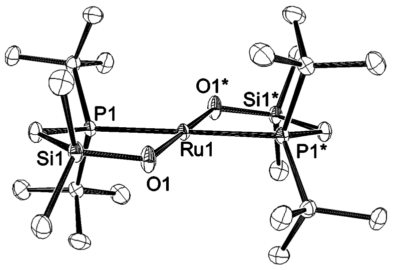
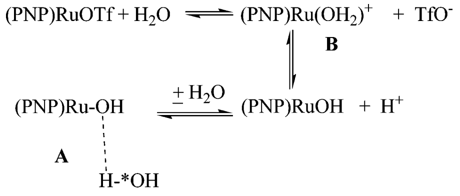


Figure 1. ORTEP view (50% probability) of the non-hydrogen atoms of Ru(^{t}Bu$_2$PCH$_2$SiMe$_2$O)$_2$, showing selected atom labeling. Unlabeled atoms are carbons. Ru−P1, 2.37772(5); Ru−O1, 1.9884(9) Å; ∠P1−Ru01, 86.62(3)°; P1−Ru−01*, 93.38(3)°.

Scheme 2



The enhanced acidity of coordinated water **B**, combined with hydrogen bonding to the resulting hydroxide, can furnish a hydroxide (*OH$^-$) which has the mobility to attack silicon within species **A**. The overall reaction stoichiometry (eq 1) shows the need for two water molecules and the probable fate

$$(\mathrm{PNP})\mathrm{RuOTf} + 2\mathrm{H_2O} \rightarrow \mathrm{Ru}({}^t\mathrm{Bu_2PCH_2SiMe2O})_2 + [\mathrm{NH_4}]\mathrm{OTf} \quad (1)$$

of the PNP nitrogen. The reaction is fast enough at 22 °C that no intermediates are detected, even using a 1:1 stoichiometry. Attempts to halt the reaction at intermediate stages using monoprotic acids (MeOH or ^{i}PrOH) gave only complicated mixtures.

We considered the possibility that adventitious triflic acid could catalyze this hydrolysis, thus adding an additional feature to the general mechanistic scheme already discussed. While we have not done experiments to test this, the low Brønsted basicity anticipated for an amide nitrogen serving as a π-donor to an otherwise highly unsaturated metal center makes this unnecessary; the N substituent on silicon is already electrophilic by this π-conjugation. Finally, neither PNPRuCl nor PNPRuF are hydrolyzed by the levels of HOTf which might be in our PNPRuOTf sample.

Reactivity Studies. a. CO. Compound **1** reacts completely in time of mixing in benzene with substoichiometric CO (0.9 equiv) to form exclusively a bright orange monocarbonyl which is diamagnetic and has C_2 symmetry (by ^{1}H and ^{31}P NMR). The ^{t}Bu virtual triplets indicate a transoid geometry for the phosphines. The single CO ligand makes the two sides of the Ru−P−Si−C−O rings inequivalent, which is gener-

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(17) This ligand type has been seen before: Bruce, G. C.; Stobart, S. R. *Inorg. Chem.* **1988**, *27*, 3879−3880.

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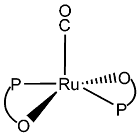
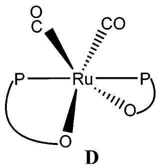
ally consistent with structure **C**. In the presence of **1**, there is no NMR line broadening of the monocarbonyl, so any CO transfer between unsaturated metal centers is slow. Addition of excess CO then produces, in time of mixing, a (colorless) dicarbonyl. The presence of two strong CO stretching frequencies is consistent with *cis*-$(CO)_2$ stereochemistry. This is confirmed by the observation of two ^1H NMR signals for ^tBu groups (i.e., two virtual triplets, indicative of mutually trans phosphorus nuclei) and two for SiMe groups. The C_2 symmetry shown in **D** is consistent with the observation of one ^{31}P chemical shift. The υ_{co} value of **C**, 1892 cm^{-1}, shows more back-bonding than even the lower of the two υ_{co} values, 1937 and 2010 cm^{-1}, of **D**. It is interesting that the dicarbonyl structure is not the obvious least motion product from **C** (i.e., trans) but implies arrival of the second CO cis to the first CO, and with bending of $\angle O-Ru-O$ near 90°. On the other hand, **D** is the isomer with the best push/pull interactions between siloxide O and CO.

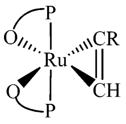


C

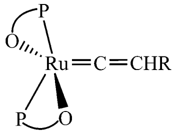


D

b. Alkynes. Reaction of equimolar **1** and PhC≡CH in C_6D_6 at 22 °C completely consumes both reagents. There is no metal hydride signal, but the $^{31}P\{^1H\}$ NMR spectrum is an AB pattern with a J_{PP} coupling constant of 366 Hz indicative of trans phosphines made inequivalent by the mode of bonding of the alkyne. The alkyne-derived proton appears as a triplet at 4.9 ppm. The lack of symmetry in the ^{31}P NMR spectrum is consistent with the complexity of the ^1H NMR: several SiMe singlets and four overlapping ^tBu signals. Variable-temperature NMR studies did not distinguish between structure **E** and **F**: the $^{31}P\{^1H\}$ NMR AB pattern persists at −60°. Combining the reagents at −196 °C, warming minimally, and mixing showed that the product was completely formed already at the lowest observation temperature, −60 °C.



E



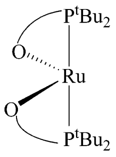
F

R = H, Ph

The structural ambiguity was resolved by forming the analogous product from **1** and HC≡CH (1 atm). These react in less than 10 min at 22 °C, and the spectra are those of a C_2 symmetric product: two ^tBu (triplets) and two SiMe chemical shifts and an intensity 2 triplet at 3.4 ppm for the C_2H_2-derived protons. The $^{31}P\{^1H\}$ NMR spectrum shows complete conversion to this single product. The $^{13}C\{^1H\}$ NMR spectrum shows a signal at 316 ppm and a second one (a triplet) at 92 ppm. An attached proton test established that the latter is a CH_2 group. These are consistent only with structure **F**, and they suggest that the inequivalence in the PhC≡CH case is due to a significant barrier to rotation around the vinylidene axis. These observations of rapid isomerization to vinylidene at low temperature indicate a remarkably low barrier for H migration between alkyne carbons in a nonpolar environment in the absence of any Brønsted acid or base catalyst.[20−24] This product is unchanged after exposure to vacuum, and this product, under excess HCCH, produces a purple-black solid within 30 min, an apparent polymerization; no such behavior was seen with PhCCH.

Discussion

The trans isomeric form of $Ru(^tBu_2PCH_2SiMe_2O)_2$ is preferred because the planar cis isomer would encounter mutual P^tBu_2 repulsion. The fact that the coordination geometry is planar, not cis-divacant octahedral (**G**), is surprising and requires re-evaluation of the idea that planar is "bad" for a 4-coordinate d^6 species or that planar requires a strong π-donor ligand (e.g., amide). Perhaps two siloxide π-donors here fill that role. The absence of agostic interactions in $Ru(^tBu_2PCH_2SiMe_2O)_2$ is attributed to its triplet spin state, where half-filled frontier orbitals diminish the Lewis acidity (unsaturation) and the energy cost of spin pairing in a spin singlet agostic species would not be repaid by the modest energy yield (~5 kcal/mol) typical of an agostic interaction.



G

In summary, while hydrolytic removal of nitrogen from an NSi_2 moiety is not unusual, the resulting product, **1**, is a 14-valence-electron 4-coordinate planar triplet d^6 molecule devoid of both π-acid and strong π-donor ligands. The siloxy ligand may show "hemi-labile" behavior,[25−27] particularly toward Brønsted acid ligands which could protonate the oxygen.

Experimental Section

General Considerations. All manipulations were performed using standard Schlenk or glovebox techniques in inert (Argon) atmosphere. All solvents, including deuterated NMR solvents, were dried over and distilled from Na/benzophenone, CaH_2, or 4 Å molecular sieves then degassed and stored in air-tight vessels. All

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other reagents were degassed and/or used as received from commercial vendors. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded on either a Varian Unity I400 (400 MHz ^1H, 101 MHz ^{13}C, 162 MHz ^{31}P, 376 MHz ^{19}F) instrument, or a Varian Gemini 2000 (300 MHz ^1H, 75 MHz ^{13}C, 121 MHz ^{31}P, 282 MHz ^{19}F) instrument, with chemical shifts reported in ppm and referenced to protio impurities in each stated solvent, with the exception of $^{31}P\{^1H\}$and $^{19}F\{^1H\}$ spectra which were externally referenced to 85% H_3PO_4 (0 ppm), and neat CF_3CO_2H (−78.5 ppm), respectively. All FT-IR spectra were recorded on a Nicolet 510P spectrophotometer. All ESI-MS spectra were generated by a PE-Sciex API III Triple Quadrupole instrument with positive ion analysis.

General Reaction of (PNP)RuX with H_2O (X = Cl, F, OTf). To a sample (10 mg or 0.017 mmol) of (PNP)RuX (X = OTf), in C_6H_6, 2 molar equiv of H_2O was added. Upon addition of H_2O and vigorous shaking of the reaction vessel, a red-orange precipitate of ammonium triflate formed and was immediately separated from the yellow $(P^tBu_2CH_2SiMe_2O)_2Ru$-containing solution. The solvent was stripped by vacuum from the solution, and the yellow $(P^tBu_2CH_2SiMe_2O)_2Ru$ was redissolved in C_6D_6 for recording NMR spectra. This reaction occurs for all (PNP)RuX where X = Cl, F, OTf, with maximum conversion occurring when X = OTf, with 60% isolated yield $(P^tBu_2CH_2SiMe_2O)_2Ru$ within 5 min, while when X = Cl or F, maximum conversion is 10% after 1 day. It is important to note that if the ammonium triflate precipitate is not immediately separated, then further degradation of the sample to intractable materials ensues. For each anion X, the solvent was stripped from the supernatant and the yellow solid was redissolved in C_6D_6.

$(P^tBu_2CH_2SiMe_2O)_2Ru$. ^1H NMR (400 MHz, C_6D_6): δ 21.92 (s, 12H, Si*Me*$_2$), −9.08 (s, 36H, PC*Me*$_3$), −25.39 (s, 4H, Si−C*H*$_2$−P). $^{31}P\{^1H\}$ NMR (161.2 MHz, C_6D_6): No signal in −500 − +500 ppm. $^{19}F\{^1H\}$ NMR (376 MHz, C_6D_6): No signal from +100 to −500 ppm. ESI-MS: 568.0 *m/z*.

Reaction of $(P^tBu_2CH_2SiMe_2O)_2Ru$ with CO (<1 equiv and Excess). A 10 mg (0.0176 mmol) sample of $(P^tBu_2CH_2SiMe_2O)_2Ru$ in C_6D_6 was exposed to 145 mm Hg (2.5 mL; 0.90 molar equiv) of CO gas. After 5 min of mixing, the solution turned from yellow to bright intense orange, yielding quantitatively a monocarbonyl species: ^1H NMR (300 MHz, C_6D_6): δ 1.37 (t, 18H, PC*Me*$_3$), 1.32 (t, 18H, PC*Me*$_3$), 0.45 (s, 6H, Si*Me*$_2$), 0.37 (s, 6H, Si*Me*$_2$). $^{31}P\{^1H\}$ NMR (121 MHz, C_6D_6): δ 65.8 (s). FT-IR: $\nu_{CO} = 1892\ cm^{-1}$.

A 10 mg (0.0176 mmol) sample of $(P^tBu_2CH_2SiMe_2O)_2Ru$ in C_6D_6 was exposed to CO gas (2.5 mL; 1 atm). After 15 min of mixing, the solution turned from yellow to a very pale peach color, almost colorless, yielding quantitatively a dicarbonyl species: ^1H NMR (300 MHz, C_6D_6): δ 1.43 (t, J_{P-H} = 6.3 Hz, 18H, PC*Me*$_3$), 1.23 (t, J_{P-H} = 6.3 Hz, 18H, PC*Me*$_3$), 0.51 (s, 6H, Si*Me*$_2$), 0.44 (s, 6H, Si*Me*$_2$). $^{31}P\{^1H\}$ NMR (121 MHz, C_6D_6): δ 74.5 (s). FT-IR: $\nu_{CO} = 2010, 1937\ cm^{-1}$.

Reaction of $(P^tBu_2CH_2SiMe_2O)_2Ru$ with HC≡CH. A 10 mg (0.0176 mmol) sample of $(P^tBu_2CH_2SiMe_2O)_2Ru$, in C_6D_6, was exposed to HC≡CH (2.5 mL; 1 atm). The solution immediately turned from yellow to dark brown, quantitatively yielding the vinylidene $(P^tBu_2CH_2SiMe_2O)_2Ru{=}C{=}CH_2$. After approximately 30 min, a dark black solid, presumably polyacetylene, began to precipitate. ^1H NMR (300 MHz, C_6D_6): δ 3.43 (t, 2H, J_{P-H} = 4.2 Hz, C=C*H*$_2$), 1.45 (t, 18H, JP−H = 6.3 Hz, PC*Me*$_3$), 1.37 (t, 18H, J_{P-H} = 6.3 Hz, PC*Me*$_3$), 0.50 (s, 6H, Si*Me*$_2$), 0.17 (s, 6H, Si*Me*$_2$). $^{31}P\{^1H\}$ NMR (121 MHz, C_6D_6): δ 54.7 (s). $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6): δ 316.7 (broad s, *C*=CH$_2$), 92.8 (t, J_{P-C} = 4.2 Hz, C=*C*H$_2$), 36.0 (t, J_{P-C} = 6.1 Hz, P-*C*H$_2$−Si), 35.8 (t, J_{P-C} = 6.1 Hz, P-*C*H$_2$−Si), 30.2 (s, PC*Me*$_3$), 29. 6 (bs, P*C*Me$_3$), 29.2 (s, PC*Me*$_3$), 26.4 (bs, P*C*Me$_3$) 4.08 (s, Si*Me*$_2$), 3.48 (s, Si*Me*$_2$).

Reaction of $(P^tBu_2CH_2SiMe_2O)_2Ru$ with PhC≡CH. To a 10 mg (0.0176 mmol) sample of $(P^tBu_2CH_2SiMe_2O)_2Ru$, in C_7D_8 (d^8-toluene) at −78 °C (dry ice/acetone bath), was added 1.93 μL of PhC≡CH. The solution immediately turned from yellow to brown, quantitatively yielding the vinylidene $(P^tBu_2CH_2SiMe_2O)_2Ru{=}C{=}CPhH$. In contrast to the reaction with HC≡CH, no polyphenylacetylene was observed: ^1H NMR (400 MHz, −40 °C, C_7D_8): δ 6.87 (bm, 5H, C=CH*Ph*), 5.04 (bs, 1H, C=C*H*Ph), 1.33 (bs, 18H, PC*Me*$_3$), 1.29 (bd, J_{P-H} = 3.3 Hz, 18H, PC*Me*$_3$), 0.53 (s, 6H, Si*Me*$_2$), 0.24 (s, 6H, Si*Me*$_2$). $^{31}P\{^1H\}$ NMR (161.2 MHz, −40 °C, C_7D_8): δ 59.5 (d, J_{P-P} = 366 Hz, A of AB pattern), 52.3 (d, J_{P-P} = 366 Hz, B of AB pattern). ^1H NMR (400 MHz, 22 °C, C_7D_8): δ 7.25−7.21 (m, 5H, C=CH*Ph*), 4.91 (t, J_{P-H} = 3.2 Hz, 1H, C=C*H*Ph), 1.35 (s, 9H, PC*Me*$_3$), 1.32 (s,9H, PC*Me*$_3$), 1.30 (s, 9H, PC*Me*$_3$), 1.27 (s,9H, PC*Me*$_3$) 0.43 (s, 6H, Si*Me*$_2$), 0.14 (s, 3H, Si*Me*$_2$), 0.11 (s, 3H, Si*Me*$_2$). $^{31}P\{^1H\}$ NMR (161.2 MHz, 22 °C, C_7D_8): δ 60.7 (d, J_{P-P} = 366 Hz, A of AB pattern), 53.7 (d, J_{P-P} = 366 Hz, B of AB pattern).

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Supporting Information Available: Full crystallographic details, as a CIF file, for each polymorph. This material is available free of charge via the Internet at http://pubs.acs.org.

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