Supporting spectroscopic data and discussion for

Tuning "Kappticity" of Tripodal Ligands

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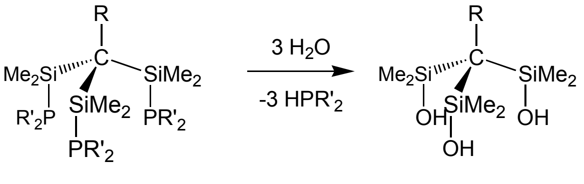
Sensitivities of tripodal ligands 3-4 to solvolysis and/or oxidation

Summary

In the presence of water and other protic reagents the P–Si bonds in compounds **3b** and **4a-b** are susceptible to cleavage, cleanly liberating the parent 2° phosphine, as determined by NMR spectroscopy (Eqn 1). Initial formation of compounds **7a/b** is followed by further condensation of these silanols to give siloxane products, as observed previously for **3a**.[9a] In air, compounds **3a-b** succumb more readily to this hydrolysis than to oxidation at phosphorus. Exposure of solid **3a** or **3b** to oxygen gas for 30 minutes resulted in only limited decomposition (primarily hydrolysis, due to trace amounts of water in the oxygen gas), while the PEt_2 derivatives (**4a-b**) decompose rapidly on exposure to the laboratory atmosphere. Although sensitivity to solvolysis is a characteristic that may limit synthetic routes to metal complexes of these ligands, we note that metal coordination does reduce the susceptibility of these Si_3 tripods to both Si-P bond cleavage and oxidation.



3a: R = H, R' = Ph
3b: R = CH_3, R' = Ph
4a: R = H, R' = Et
4b: R = CH_3, R' = Et

7a: R = H
7b: R = CH_3

(1)

Experiments performed

*Reaction of $CH_3C(Me_2SiPPh_2)_3$ (**3b**) with O_2. a) In the solid state.* In a Schlenk tube, solid $CH_3C(Me_2SiPPh_2)_3$ (**3b**, 23 mg, 0.030 mmol) was placed under an atmosphere of oxygen gas (99.9%) for 30 min, then the oxygen was removed under vacuum. The sample was dissolved in benzene-d_6 (0.6 mL) and the solution was transferred to an NMR tube for analysis by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. *b) In toluene solution.* In a Schlenk tube, oxygen gas (99.9%) was bubbled through a solution of **3b** (25 mg, 0.033 mmol) in toluene (5 mL) for 30 min. After removal of toluene and oxygen under vacuum, the remaining oily white solid was dissolved in benzene-d_6 (0.6 mL) and transferred to an NMR tube for analysis by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy.

*Reaction of $CH_3C(Me_2SiPPh_2)_3$ (**3b**) with H_2O.* Distilled water (1.5 mL, 0.083 mmol) was added under nitrogen to an NMR sample containing $CH_3C(Me_2SiPPh_2)_3$ (**3b**, 19 mg, 0.025 mmol) in C_6D_6, and the reaction was followed by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. At room temperature, 35% of **3b** was consumed within 24 h to give $HPPh_2$ and $CH_3C(SiMe_2OH)_3$, **7b**. After 24 h, significant conversion of **7b** to siloxane condensation products occurred, indicated by the appearance of new peaks in the SiMe and Me_{apical} region of the ^1H NMR. For $CH_3C(Me_2SiOH)_3$ (**7b**) : ^1H NMR (360 MHz, C_6D_6, d): 1.23 (s, 3H, $CC\mathbf{H}_3$), 0.27 (s, 18H, $SiC\mathbf{H}_3$). The signal due to SiO**H** was lost in the baseline beneath SiMe signals.

*Reaction of $HC(Me_2SiPEt_2)_3$ (**4a**) with H_2O.* Distilled water (2.0 mL, 0.11 mmol) was added under nitrogen to an NMR sample containing $HC(Me_2SiPEt_2)_3$ (**4a**, 179 mg, 0.037 mmol) in C_6D_6, and the reaction followed by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. After 24 hrs, 17% of **4a** had been hydrolyzed to give $HPEt_2$ and **7a**.

*Reaction of $CH_3C(Me_2SiPEt_2)_3$ (**4b**) with H_2O.* Distilled water (2.5 mL, 0.14 mmol) was added under nitrogen to an NMR sample containing $CH_3C(Me_2SiPEt_2)_3$ (**4b**, 18 mg, 0.038 mmol) in C_6D_6, and the reaction followed by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. Complete cleavage of all Si-P bonds occurred within 15 min of water addition, liberating $HPEt_2$ and **7b** quantitatively.

Variable temperature $^{31}P\{^{1}H\}$ NMR studies of $CH_3C(SiMe_2PPh_2)_3$ (3b)

Changes in the $^{31}P\{^{1}H\}$ NMR spectra recorded for **3b** in toluene-d_8 at varying temperatures (Fig 1) correspond to a ground state solution structure similar to its solid state structure (Fig 2 in article). The sharp room temperature singlet undergoes decoalescence, when the sample is cooled to 185K, to give two broad singlets in a 2:1 ratio. Presumably these signals represent $P^{2/3}$ and P^{1}, respectively (as shown in Fig 3 in article), and complete rotation around all three tripod arms is slowed considerably at this temperature. Figure 2 below illustrates an idealized solution structure for **3b** and two exchange processes that must still be occurring at these low temperatures to render P^{2} and P^{3} equivalent yet distinct from P^{1}. When the sample is cooled to 180K, further splitting of these broad signals occurs. Slowing of either of the two exchange processes shown in Fig 2 would give rise to diastereomers, generating as many as four to six distinct P environments. This is consistent with the complexity of the $^{31}P\{^{1}H\}$ spectrum of **3b** at 180K. Changes in the $SiMe_2$ signal in the $^{1}H\{^{31}P\}$ NMR as **3b** is cooled are not inconsistent with the exchange processes shown in Fig 2, but these low T spectra are too broad to give detailed structural information. An apparent decoalescence at 195K gives three broad singlets, which may correspond to methyl groups A, B, and C.

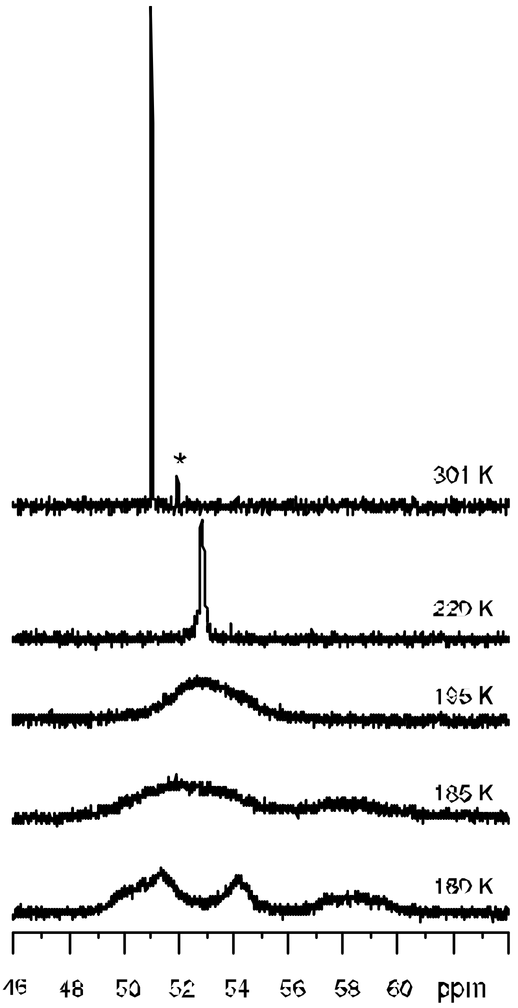


Figure 1. Variable temperature $^{31}P\{^{1}H\}$ NMR of **3b** (toluene-d$_8$, 202.43 MHz). Signals due to an impurity of the disubstituted compound, $CH_3C(Si(CH_3)_2Br)\{Si(CH_3)_2PPh_2\}_2$ are marked with “*”.

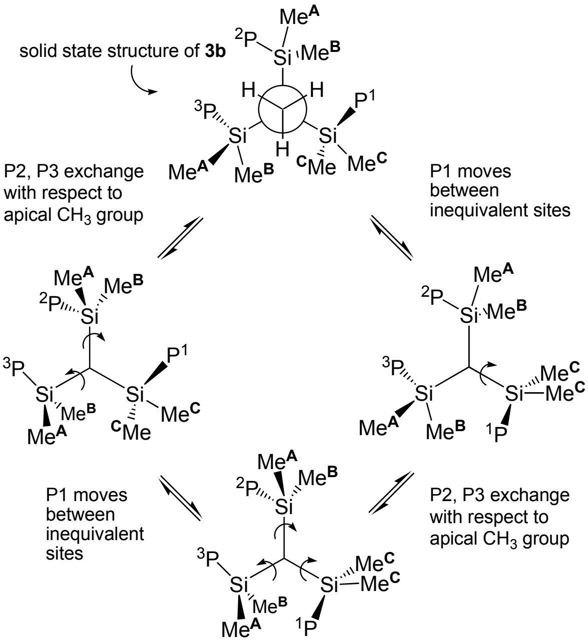


Figure 2 Mechanisms for phosphorus exchange in **3b**, based on a low temperature solution structure analogous to the solid-state structure. Views are down the apical CH_3–C bond, and Ph substituents are omitted for clarity.

Reference

1. D. M. Friesen, R. McDonald and L. Rosenberg, *Can. J. Chem.-Rev. Can. Chim.*, 1999, **77**, 1931-1940.