

feature in those spectra at about  $1700\text{ cm}^{-1}$ , in the low-energy wing of the aldehyde band, which these authors did not comment on. In our view, at least a part of this absorption can be assigned to the acyl band.

We believe, that in spite of calibration differences and differences in the nature of the group R, the reaction conditions in the two studies were similar enough to allow the conclusion that these authors observed the same type of compound as we report here, viz. a propionylrhodium tetracarbonyl rather than the ethylrhodium compound.

As our spectra demonstrate, no trace of the bridging band of  $\text{Rh}_4(\text{CO})_{12}$  at  $1886\text{ cm}^{-1}$  is present (Figures 1 and 2), whereas the terminal band at  $2065.5\text{ cm}^{-1}$  (i) has a considerable intensity, corresponding to the pattern observed with the acylcobalt tetracarbonyl compounds and (ii) is clearly a *single* band of regular shape, whereas the band of  $\text{Rh}_4(\text{CO})_{12}$  in this region consists of a sharp doublet, with a separation of  $5.4\text{ cm}^{-1}$ .<sup>22</sup>

Also, in the paper of King et al.<sup>11</sup> it seemed strange that, under the conditions used, no CO insertion took place. Our results and analysis of the spectra also show that in the case of rhodium carbonyls only the acyl derivative can be observed directly in catalytic experiments and the concentration of the alkyl derivative (as well as those of tricarbonyl species suggested frequently in studies on catalytic cycles) is below the limit of infrared detectability.

### Experimental Section

The hydroformylation reactions were carried out in a specially constructed high-pressure autoclave.<sup>14</sup> The autoclave was connected to a membrane pump and a high-pressure infrared cell containing single-crystal silicon windows. The *n*-hexane solution was continuously circulated from the high-pressure autoclave to the high-pressure infrared cell and back to the autoclave under isobaric and isothermal conditions.

**Spectra.** The spectra reported here were made on a Perkin-Elmer PE983G infrared spectrophotometer. Scanning conditions were scan

mode of 4 and noise filter of 4, corresponding to a resolution of  $3.5\text{ cm}^{-1}$ . Higher resolution was avoided to reduce noise level. This PE983G spectrophotometer was equipped with a Data Station Model 3600 computer for the manipulation of spectra. Infrared reference spectra of *n*-hexane,  $\text{Rh}_4(\text{CO})_{12}$ , 3,3-dimethyl-1-butene, and carbon monoxide dissolved in *n*-hexane were subtracted from the high-pressure *in situ* spectra of the hydroformylation solution by means of the software package included with the PE983G spectrophotometer.

**Chemicals.** All solutions were prepared by using standard Schlenk techniques under nitrogen. *n*-Hexane (Fluka, Purum) was distilled from Na/K under nitrogen. 3,3-Dimethyl-1-butene (Fluka, Puriss) was dried and stored over 4-Å molecular sieves. Carbon monoxide was prepared from the catalytic dehydration of formic acid (ETH-Z), and hydrogen was supplied by Pan Gas, Luzern.  $\text{Rh}_4(\text{CO})_{12}$  showed no  $\text{Rh}_6(\text{CO})_{16}$  impurities.

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**Note Added in Proof.** A reviewer suggested that the reaction should be repeated with ethylene as olefin. This has been performed in the meantime (conditions:  $\text{Rh}_4(\text{CO})_{12}$  0.5 mM in *n*-hexane, 15 bar of ethylene, 2 bar of hydrogen, 40 bar of CO, at  $25\text{ }^\circ\text{C}$ ). Again the formation of the corresponding *acyl* derivative, i.e. the propionylrhodium tetracarbonyl, was observed (IR bands at 2112, 2065, 2038, 2020, and  $1696\text{ cm}^{-1}$ ). Hydroformylation proceeds slowly under these conditions: the aldehyde CO band eventually appears at  $1741\text{ cm}^{-1}$ .

With carbon monoxide pressure as low as 2–5 bar and only with ethylene but not with other olefins, an unknown species is formed (IR bands at 2089, 2039, and  $2016\text{ cm}^{-1}$ ) which upon increasing the CO pressure yields the same acylrhodium derivative as mentioned above. A detailed study of this species is in progress.

Upon exposure of the sample to air, the formation of the carboxylato-bridged dimeric compound  $[\text{Rh}(\text{CO})_2(\mu\text{-C}_2\text{H}_5\text{CO}_2)]_2$  reported in ref 10 could be observed ( $\nu(\text{C-O})$  frequencies occur at 2095, 2073, 2043, and  $2023\text{ cm}^{-1}$ ).

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## First Examples of an Isomeric Methylene-Bridged Free Phosphano Phosphoranimine and a Metalated Phosphano Phosphoranimine. Synthesis, Characterization, and Isomerization of the Heterodifunctional Ligand $\text{Me}_3\text{SiNPPPh}_2\text{CH}_2\text{PPh}_2$ and the Transmetalation to the Titanium Derivative $(\eta^5\text{-C}_5\text{H}_5)\text{TiCl}_2\text{NPPPh}_2\text{CH}_2\text{PPh}_2$

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Bis(diphenylphosphino)methane (**1**) reacts cleanly with azidotrimethylsilane to give initially one isomeric form of the silylated monophosphazene  $\text{Me}_3\text{SiNPPPh}_2\text{CH}_2\text{PPh}_2$  (**2**). This new phosphano phosphoranimine undergoes a thermally induced isomerization to form three different isomeric forms as established by  $^1\text{H}$ ,  $^{31}\text{P}$ , and  $^{29}\text{Si}$  NMR spectroscopy. In solutions of  $\text{CH}_3\text{CN}$  the mixture of isomers of **2** reverts to the single isomer through a remarkable isomerization process. **2** also reacts with  $\text{CpTiCl}_3$  to give the first example of a metalated phosphoranimino phosphane,  $(\eta^5\text{-C}_5\text{H}_5)\text{TiCl}_2\text{NPPPh}_2\text{CH}_2\text{PPh}_2$  (**3**).

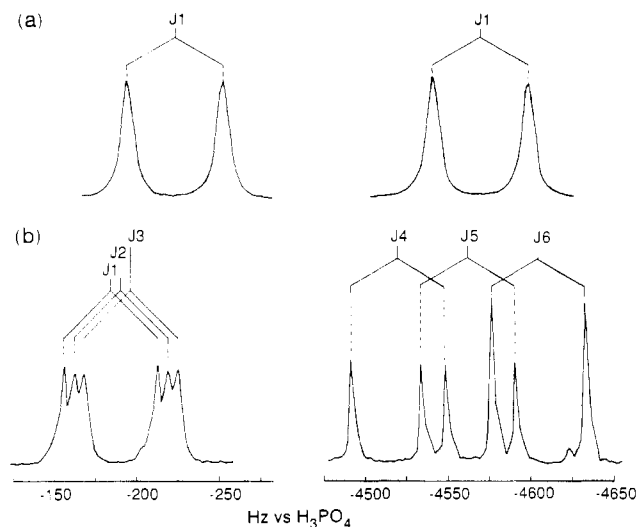
### Introduction

Increasing interest in the synthesis of heterodifunctional ligands because of their potential as backbones for a variety of catalytically active heterobimetallic compounds<sup>1–9</sup> prompted a search for

main-group skeletons containing appropriate reactive sites of different types that would be capable of holding varied heterometallic (i.e., early–late transition metal) centers together. Herein we report the first example of a methylene bridged phosphane–phosphoranimine compound,  $\text{RNPPPh}_2\text{CH}_2\text{PPh}_2$  (**2**) ( $\text{R} = \text{SiMe}_3$ ), and also the discovery of the thermally induced isomerization of

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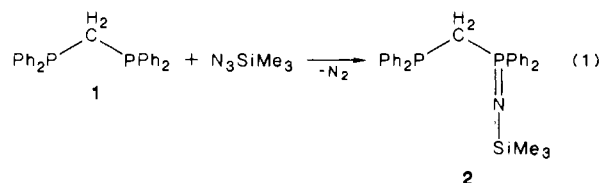


**Figure 1.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra. (a) **2R**:  $\sigma(\text{P}^{\text{III}}) = -28.20$  ppm,  $\sigma(\text{P}^{\text{V}}) = -1.38$  ppm;  $^2J_{\text{PP}} = 57.74$  ( $J_1$ ) Hz. (b) **2D**:  $\sigma(\text{P}^{\text{III}}) = -27.27, -27.53, -27.79$  ppm,  $\sigma(\text{P}^{\text{V}}) = -1.14, -1.18, -1.22$  ppm;  $^2J_{\text{PP}} = 56.87$  ( $J_1$ ),  $56.86$  ( $J_2$ ),  $56.91$  ( $J_3$ ),  $57.06$  ( $J_4$ ),  $57.34$  ( $J_5$ ),  $56.80$  ( $J_6$ ) Hz.

this novel heterodifunctional ligand. This type of ligand presents the possibility of forming a metal–nitrogen  $\sigma$  bond with a high-oxidation-state early transition metal via the elimination of  $\text{Me}_3\text{SiCl}$  from a metal chloride. This route has been demonstrated herein by the synthesis of  $(\eta^5\text{-C}_5\text{H}_5)\text{TiCl}_2\text{NPPH}_2\text{CH}_2\text{PPh}_2$  (**3**).

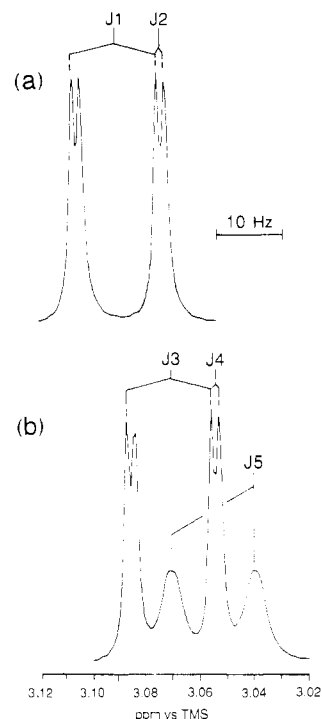
### Results and Discussion

Reaction of bis(diphenylphosphino)methane (**1**) with azido-trimethylsilane in the absence of solvents at the melting point temperature of the former (119 °C) (eq 1) yields **2** almost

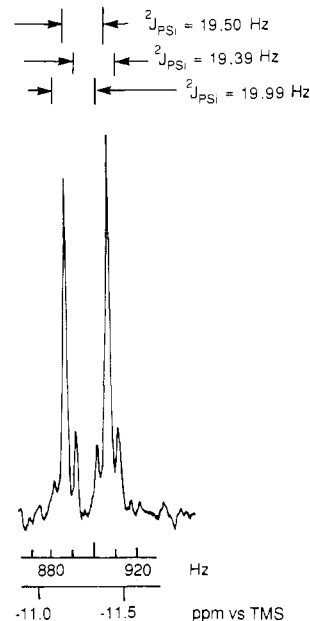


quantitatively. Although the monoxide,<sup>10</sup> monosulfide,<sup>10</sup> and monoselenide<sup>11</sup> derivatives ((E)PPh<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>; E = O, S or Se) of **1** are known, this product represents the first example of a partial oxidation of **1** with a nitrogen base. The use of solvents such as CH<sub>3</sub>CN, THF, or toluene resulted in a more complex reaction in which both phosphorus atoms are oxidized and therefore low yields of **2** were obtained. Repeated recrystallization of **2**, an air-stable microcrystalline solid, which is soluble in both polar and nonpolar organic solvents, from CH<sub>3</sub>CN removed the small traces of unreacted **1** that remained in the crude reaction product.

Attempts to separate **1** and **2** by distillation revealed that **2** can be transformed into three different isomeric forms as shown by a comparison of the  $^{31}\text{P}\{^1\text{H}\}$  and  $^1\text{H}$  NMR spectra of the recrystallized (**2R**) and distilled (**2D**) samples of **2** (Figures 1 and 2). The low- (-1.38 ppm) and the high-field (-28.20 ppm) doublets for **2R** attributable to the (P<sup>V</sup>) Ph<sub>2</sub>P(=NSiMe<sub>3</sub>) and (P<sup>III</sup>) Ph<sub>2</sub>P centers respectively appear in the spectrum of **2D** (Figure 1b) as additional closely spaced doublets of an AX spin system. The double of doublet signals (due to the methylene protons) observed in the  $^1\text{H}$  NMR spectrum of **2R** (Figure 2a) were also present in the spectrum of **2D** but were accompanied by a new broad doublet signal (Figure 2b). The  $^{29}\text{Si}$  (INEPT)<sup>12</sup>



**Figure 2.** (a) Methylene proton signals in the  $^1\text{H}$  NMR spectrum of **2R**:  $\delta(\text{CH}_2) = 3.07$  ppm;  $^2J_{\text{P}^{\text{V}}\text{H}} = 12.40$  Hz ( $J_1$ ),  $^2J_{\text{P}^{\text{III}}\text{H}} = 1.20$  Hz ( $J_2$ ). (b) Methylene proton signals in the  $^1\text{H}$  NMR spectrum of **2D**:  $\delta(\text{CH}_2) = 3.06, 3.055$  ppm;  $^2J_{\text{P}^{\text{V}}\text{H}} = 12.37$  ( $J_3$ ) Hz,  $^2J_{\text{P}^{\text{III}}\text{H}} = 1.19$  ( $J_4$ ) Hz,  $^2J_{\text{P}^{\text{V}}\text{H}} = 12.43$  ( $J_5$ ) Hz. The line half-width of 1.1 Hz in the pair of lines defining  $J_5$  may be in part due to  $^2J_{\text{P}^{\text{III}}\text{H}}$  coupling.

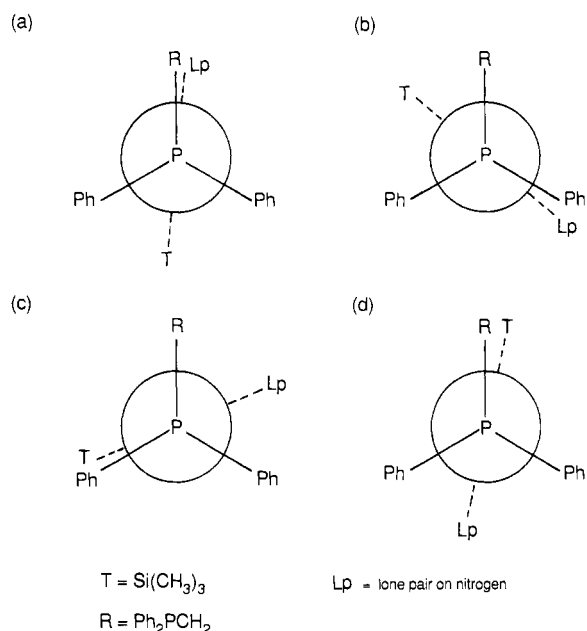


**Figure 3.**  $^{29}\text{Si}$  NMR spectrum of **2D**:  $\delta(\text{Si}) = -11.27, -11.33, -11.20$  ppm;  $^2J_{\text{SiP}} = 19.5, 19.39, 19.99$  Hz.

NMR spectrum of **2R** showed a doublet due to coupling with the phosphoramidine phosphorus across two bonds ( $^2J_{\text{PSi}} = 21.80$  Hz). The spectrum of **2D** consisted of three closely spaced doublets with almost identical  $^2J_{\text{PSi}}$  values as observed for **2R** (Figure 3). We therefore conclude that the Si–N=P linkage in **2R** remains intact even after heating to 240 °C. Furthermore molecular weight data indicates that all forms are monomeric.

The different isomeric forms for **2** probably arise from the different dispositions of the substituents around the tetrahedral P(V) center. Four different major isomeric forms of **2** may be envisaged as shown by Newman projections in Figure 4. The simple doublet of doublet signal due to the methylene protons (Figure 2a) is suggestive of one of the gauche forms (a or b) in

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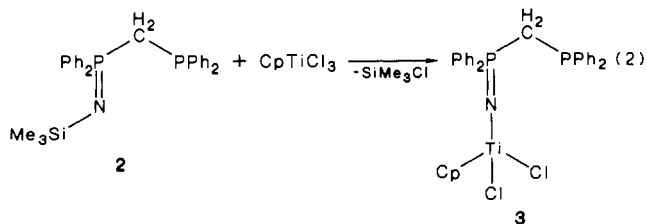


**Figure 4.** Newman projections representing the four isomeric forms of **2**. Note that R is a potentially flexible composite group (CH<sub>2</sub>PPh<sub>2</sub>) that will present further conformational orientations relative to the center depicted.

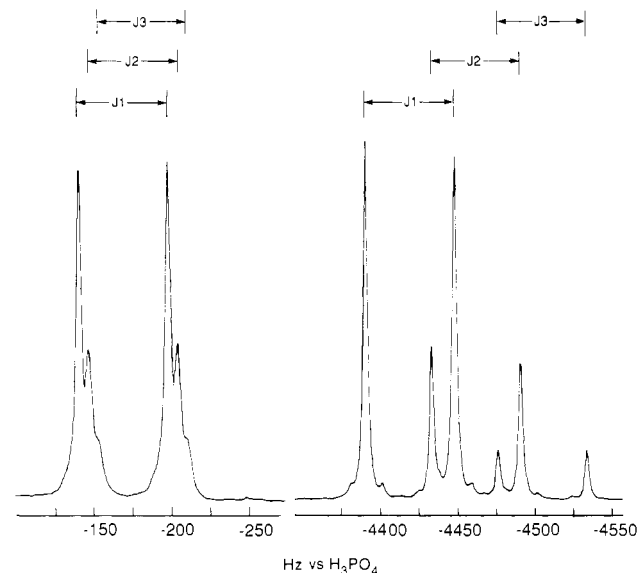
Figure 4). We prefer isomeric form b over a because interaction of the methylene group protons within the CH<sub>2</sub>PPh<sub>2</sub> substituent (depicted by R) with the proximate lone pair (LP) would probably make these protons magnetically nonequivalent. Forms c or d would probably generate similar inequivalencies in the methylene proton signals. The broad doublet signal observed in the <sup>1</sup>H NMR spectrum of **2D** is presumably a consequence of such an effect, although overlap of the signals due to the other gauche form of **2** cannot be ruled out.

Markedly different relative proportions of the isomers of **2** are formed (based on the <sup>31</sup>P and <sup>1</sup>H NMR spectroscopic data), depending on the temperature of isomerization. The <sup>31</sup>P NMR spectrum of the product obtained by thermal isomerization of **2** at 160 °C, illustrated in Figure 5, shows the same features as those present in the spectrum of the distillate obtained at 240 °C but with a different relative intensity. Three randomly distributed isomeric forms of **2** were invariably observed throughout the temperature range so far (140–240 °C) investigated. All the different isomeric forms of **2** coexist in the form of a glassy colorless viscous oil; attempted separation by fractional crystallization in various solvents was unsuccessful. Isomerization of the mixture of isomers **2D** to produce the single isomer **2R** occurred (as confirmed by <sup>1</sup>H and <sup>31</sup>P NMR spectroscopy) when **2D** was stirred overnight in dry acetonitrile at 25 °C.

The reaction of the new ligand **2R** with CpTiCl<sub>3</sub> in diethyl ether affords the titanium(IV) functionalized phosphoranimino phosphane **3** in 90% yield (eq 2) by metathetical elimination of Me<sub>3</sub>SiCl.



Compound **3** represents the first example of a potentially large class of high-oxidation-state transition-metal-functionalized phosphoranimino phosphanes. Although related to the symmetrically substituted phosphoranimino ligands, NPR<sub>3</sub><sup>-</sup> (isoelectronic with R<sub>3</sub>PO), which have been extensively used to stabilize high-oxidation-state transition-metal and actinide-metal com-



**Figure 5.** <sup>31</sup>P NMR spectrum of **2** thermally isomerized at 160 °C. The coupling constants are <sup>2</sup>J<sub>PP</sub> = 57.11 (J<sub>1</sub>), 56.88 (J<sub>2</sub>), and 56.74 (J<sub>3</sub>) Hz. Chemical shifts are comparable with but identical with those given in Figure 1.

plexes,<sup>13</sup> the presence of the P(III) center in **3** allows further reaction of the bound ligand with a variety of low-oxidation-state transition metals.

The <sup>31</sup>P NMR spectrum of **3** (Figure 6a) consisted of an AX spin pattern with the phosphoranimino phosphorus shifted to 38.6 ppm. Although the -PPh<sub>2</sub> unit of **3** showed a chemical shift similar to that in **2R**, the signal was significantly broader and resolved into two doublets at -40 °C (Figure 6b). The relative integrations of the low- and high-field doublets for **3** clearly revealed that the low-field doublet signals (corresponding to the additional high-field doublet observed at -40 °C; Fig. 6b) had merged and appeared as a fairly sharp doublet (in the temperature range +25 to -80 °C). Such a merging of the signals in the low-field region was also a feature of the <sup>31</sup>P NMR spectrum of the ligand **2** (Figure 1).

We rationalize these spectroscopic observations by invoking different isomeric forms for **3** as illustrated in the Newman projections in Figure 7. On steric grounds isomers a and b are preferred over c and d. We did not observe any alteration of the distribution of these isomers on boiling **3** in solvents such as THF, toluene, or CH<sub>3</sub>CN, and the proportions are solvent independent. Fractional crystallization with various solvent combinations in an attempt to separate the two isomers of **3** was unsuccessful. It is also notable that the reaction of the mixture of isomers, **2D**, with CpTiCl<sub>3</sub> gave **3** with exactly the same isomeric composition as was obtained from the reaction of **2R**, according to <sup>1</sup>H and <sup>31</sup>P NMR and IR spectroscopic data.

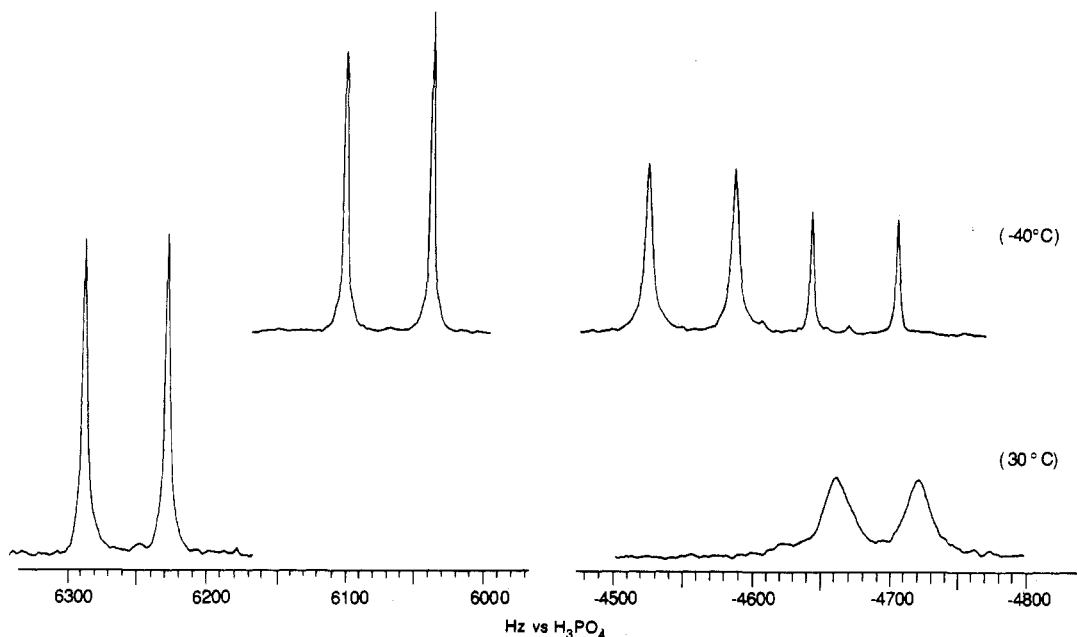
The stability of **3** with its available phosphane functionality suggests that it might be a versatile synthon for heterobimetallic compounds. Experiments in these directions are under way.

### Experimental Section

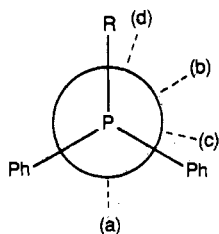
All experimental manipulations were performed under an atmosphere of dry argon. Solvents were dried and distilled prior to use. (η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)TiCl<sub>3</sub> and Me<sub>3</sub>SiN<sub>3</sub> were commercial materials obtained from Aldrich.

<sup>1</sup>H, <sup>31</sup>P, and <sup>29</sup>Si spectra were obtained on a Bruker WH 400 instrument (operating at 400.13, 161.97, and 79.50 MHz, respectively) using SiMe<sub>4</sub>, 85% H<sub>3</sub>PO<sub>4</sub>, and SiMe<sub>4</sub>, respectively, as the external standards. An INEPT sequence was employed to enhance signals in the <sup>29</sup>Si NMR spectra.<sup>13</sup> In all the spectroscopic studies CDCl<sub>3</sub> was used as the solvent

(13) Leading recent references are as follows: Cramer, R. E.; Edlmann, F.; Mori, A. L.; Roth, S.; Gilge, J. W.; Tatsumi, K.; Nakamura, A. *Organometallics* **1988**, *7*, 841. Roesky, H. W.; Seske, U.; Noltmeyer, M.; Jones, P. G.; Sheldrick, G. M. *J. Chem. Soc., Dalton Trans.* **1986**, 1309. Schmidt, I.; Kynast, U.; Hanich, J.; Dehnicke, K. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1984**, *39B*, 1248.



**Figure 6.**  $^{31}\text{P}$  NMR spectra of **3**. (a) At 30 °C:  $\sigma(\text{P}^{\text{III}}) = -28.95$  ppm,  $\sigma(\text{P}^{\text{V}}) = 38.64$  ppm;  $^2J_{\text{PP}} = 59.73$  Hz. (b) At -40 °C:  $\sigma(\text{P}^{\text{III}}) = -28.12, -28.85$  ppm,  $\sigma(\text{P}^{\text{V}}) = 37.47$  ppm;  $^2J_{\text{PP}} = 62.55$  Hz.



**Figure 7.** Newman projection showing possible positions of  $\text{CpTiCl}_2$  groups a-d in different isomeric forms of **3**. R represents  $\text{CH}_2\text{PPh}_2$  and may also make conformational contributions.

and as an internal lock. Positive shifts lie downfield of the standard in all cases. Solution molecular weight measurements were performed in dibromomethane solution with a Mechrolab 301A vapor-phase osmometer.

**Synthesis of 2R.** A slurry of **1** (5.12 g, 13.33 mmol) in  $\text{Me}_3\text{SiN}_3$  (1.55 g, 13.4 mmol) placed in a 100-mL round-bottomed flask was heated with stirring in an oil bath maintained at 130 °C. At the end of 6 h the clear melt was cooled to obtain a waxy solid, which when dissolved in  $\text{CH}_3\text{CN}$  and cooled to 0 °C gave **2R** as a microcrystalline solid (yield of **2R** 6.10 g, 97%; mp 85 °C). Anal. Calcd for  $\text{C}_{28}\text{H}_{31}\text{NP}_2\text{Si}$ : C, 59.44; H, 6.58; N, 2.97. Found: C, 59.2; H, 6.5; N, 2.9.  $^{29}\text{Si}$  NMR ( $\text{CDCl}_3$ ):  $\delta -12.78$  ppm (d, 1,  $\text{SiMe}_3$ ;  $^2J_{\text{SiP}} = 21.80$  Hz), MS EI ( $m/z$ ): 471 ( $M^+$ , 100%).

Solution mol wt: calcd, 471; Found, 478.

**Thermal Isomerization of 2R.** A sample of **2R** (1.512 g, 3.2 mmol) placed in a Schlenk tube was connected to a dynamic vacuum line. After the tube was evacuated for 30 min, it was placed in an oil bath and the temperature was gradually raised to 160 °C (and was maintained at this temperature for 30 min). The resulting viscous oil, which did not solidify even on cooling to 25 °C, was subjected to NMR investigations. Similar treatment of a sample at 240 °C yielded similar results. The analytical, mass spectrometric and molecular weight data for **2D** (heated to 240 °C) were identical with those of **2R**.

**Synthesis of 3.** A solution of **2R** (1.56 g, 3.3 mmol) in diethyl ether (50 mL) was added dropwise with stirring at 25 °C to a solution of  $\text{CpTiCl}_3$  (0.73 g, 3.3 mmol) also in diethyl ether (100 mL). After the mixture was stirred for 4 h, the titanium compound **3** had precipitated as a bright yellow microcrystalline solid, which was washed with diethyl ether at 0 °C (20 mL) (yield of **3** 1.74 g, 90%; mp 165 °C). Anal. Calcd for  $\text{C}_{30}\text{H}_{27}\text{Cl}_2\text{NP}_2\text{Ti}$ : C, 61.74; H, 4.63; N, 2.40. Found: C, 61.85; H, 4.50; N, 2.38.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  3.74 ppm (d, 2,  $\text{CH}_2$ ;  $^2J_{\text{P}^{\text{V}}\text{H}} = 16.00$  Hz); 6.55 (s, 5,  $\text{C}_5\text{H}_5$ ); 7.45 (m, 20,  $\text{C}_6\text{H}_5$ ). MS mol wt ( $m/z$ ): calcd, 583; found, 583.

The reaction of **2D** with  $\text{CpTiCl}_3$  was carried out under similar experimental conditions to those described above (yield of **3**: 90%). The physical constants, analytical data, and the spectroscopic data of this product were identical with those listed above.

**Registry No.** 1, 2071-20-7; 2, 116467-64-2; 3, 118378-15-7;  $\text{CpTiCl}_3$ , 1270-98-0.