

# 비스(트리메틸실릴메틸) 1, 2-비스(디페닐포스포노) 에탄니켈(II)의 합성 및 반응

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## Preparation and Reactions of Bis(trimethylsilylmethyl)- 1, 2-bis(diphenylphosphino)ethanenickel(II)

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**요약.** 새로운 니켈(II) 화합물, 비스(트리메틸실릴메틸) 1, 2-비스(디페닐포스포노) 에탄니켈(II) (1)이 디클로로-1, 2-비스(디페닐포스포노)에탄니켈(II)와 트리메틸실릴메틸리튬의 반응으로부터 합성되었다. 화합물 1은 질소하, 상온에서 안정하다. 화합물 1은 열분해하여 환원성착지음 생성물, 1, 2-비스(트리메틸실릴)에탄을 생성한다. 화합물 1은 상온에서 일산화탄소 및 산소와, 그리고 80°C에서 1, 2-비스(디페닐포스포노)에탄과 반응하여 역시 1, 2-비스(트리메틸실릴)에탄을 생성한다.

**ABSTRACT.** A new nickel(II) compound,  $\text{Ni}(\text{CH}_2\text{SiMe}_3)_2((\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2)$ , **1**, has been prepared by the reaction of  $\text{NiCl}_2((\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2)$  with  $\text{Me}_3\text{SiCH}_2\text{Li}$ . The compound, **1**, is stable under nitrogen at room temperature both in solution and in the solid state. Thermal decomposition of **1** in solution or in the solid state produces the reductive coupling product,  $\text{Me}_3\text{SiCH}_2\text{CH}_2\text{SiMe}_3$  which is also afforded by the reactions of **1** with CO and  $\text{O}_2$  at room temperature, and with  $(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2$  at 80°C.

### 1. INTRODUCTION

Studies of trimethylsilylmethyl and neopentyl complexes of transition metals have yielded interesting observations. (1) Transition metal complexes containing  $\text{Me}_3\text{SiCH}_2^-$  and  $\text{Me}_3\text{CCH}_2^-$  are much more stable than the analogous compounds of  $\text{CH}_3^-$  and  $\text{C}_2\text{H}_5^-$  ligands.<sup>1-4</sup> In some cases, the difference in thermal stability is remarkable, e.g.,  $(\text{Me}_3\text{SiCH}_2)_4\text{Ti}$  and  $(\text{Me}_3\text{C}-$

$\text{CH}_2)_4\text{Ti}$  are much more stable than  $\text{Me}_4\text{Ti}$  and  $(\text{C}_2\text{H}_5)_4\text{Ti}$ .<sup>4</sup> This has been explained in terms of (a) kinetic stabilization due to the absence of  $\beta$ -hydrogen in  $\text{Me}_3\text{SiCH}_2^-$  and  $\text{Me}_3\text{CCH}_2^-$ , precluding the well known olefin elimination decomposition pathways,<sup>5</sup> and (b) steric effects of the bulky  $\text{Me}_3\text{SiCH}_2^-$  and  $\text{Me}_3\text{CCH}_2^-$  ligands, making inter- or intramolecular reactions high activation energy processes.<sup>1-4</sup> (2) It has been shown that  $\text{Me}_3\text{SiCH}_2^-$  groups

may bridge two metal atoms to form binuclear<sup>6</sup> and polynuclear<sup>7</sup> complexes. (3) Some  $M-CH_2SiMe_3$  groups react with CO to give CO insertion products,  $M-COCH_2SiMe_3$ .<sup>8</sup> (4) Various transition metal complexes of  $Me_3SiCH_2^-$  and  $Me_3CCH_2^-$  ligands undergo  $\gamma$ -hydrogen elimination reaction to give metallacycles.  $Mo_2(O_2CMe)_4$ , for example, reacts with an excess of  $Mg(CH_2SiMe_3)_2$  and  $PMe_3$  to give a dimeric compound where two molybdenum atoms are bridged by one  $-CH_2Si(Me_2)CH_2^-$  group forming a five membered metallacycle,  $(Me_3SiCH_2)_2-Mo-CH_2Si(Me_2)-CH_2-Mo(PMe_3)_3$ .<sup>6</sup> Mononuclear metallacycles,  $(Me_3P)_2(Me_3SiCH_2)Rh-CH_2Si(Me_2)-CH_2$ ,  $(Me_3P)_4Ru-CH_2Si(Me_2)-CH_2$  and  $(Me_3P)_4Ru-CH_2C(Me_2)-CH_2$  have been also prepared by the reactions of  $Mg(CH_2SiMe_3)_2$  or  $Mg(CH_2CMe_3)_2$  with  $Rh_2(O_2CMe)_4$  and  $Ru_2(O_2CMe)_4Cl$ , respectively, in the presence of  $PMe_3$ .<sup>6</sup> Small-ring metallacycles have attracted much attention since they are considered to be intermediates in a large number of reactions catalyzed by transition metal complexes.<sup>9</sup>

There has been only one reported attempt to prepare  $Me_3SiCH_2^-$  complexes of nickel, namely  $(C_6H_5)((C_6H_5)_3P)Ni-CH_2SiMe_3$  and  $Ni-(CH_2SiMe_3)_2$ , but no details or characterization were given.<sup>10</sup> However, numerous  $Me_3SiCH_2^-$  complexes of various other transition metals have been well characterized.<sup>1-10</sup>

We have prepared a new Ni(II) compound,  $Ni(CH_2SiMe_3)_2(diphos)$ , **1**, where diphos is 1,2-bis(diphenylphosphino)ethane, and investigated its physical properties, thermal decomposition, and reactions with CO, diphos and  $O_2$ .

## 2. EXPERIMENTAL

All reactions, except for those of **1** with  $O_2$  and CO, were carried out under nitrogen using

Schlenk type ware techniques. GC-MS spectra of liquids were obtained on a Du Pont Dimispec 321 instrument(column: OV-17 liquid phase on a acid-washed Chromosorb W support). IR spectra were determined on a Perkin-Elmer 457 spectrometer.  $^1H$  NMR spectra were obtained on a Varian A-60. Trimethylsilylmethylchloride was purchased from Petrarch System Inc. and used without further purification. 1,2-bis(diphenylphosphino)ethane was obtained from Strem Chemicals and used as supplied. All volatile products from the reactions of **1** were identified by GC-MS (Mass spectra were compared with those of authentic samples).

**Dichloro-1,2-bis(diphenylphosphino)ethanenickel(II)** ( $NiCl_2(diphos)$ ) was prepared by Chatt's Method.<sup>11</sup>

**Trimethylsilylmethyl lithium** ( $Me_3SiCH_2Li$ ) was prepared by the literature method<sup>12</sup> using diethyl ether (50 ml, distilled from sodium benzophenone under nitrogen<sup>13</sup>) as solvent, lithium metal (2.0 g, 0.3 mole, pounded to thin flat pieces) and  $Me_3SiCH_2Cl$  (14.0 ml, 0.1 mole) premixed with 40 ml of diethyl ether. The colorless solution of  $Me_3SiCH_2Li$  in diethyl ether was titrated with 2-butanol (1.0 M) in xylene employing 1,10-phenanthroline as an indicator.<sup>14</sup> The concentration of  $Me_3SiCH_2Li$  was found to be 0.9 M (90% yield). The reaction should be carried out in the absolute absence of  $O_2$  and  $H_2O$ . The solution of  $Me_3SiCH_2Li$  can be stored in a freezer for 2 weeks without significant decomposition.

**Bis(trimethylsilylmethyl)1,2-bis(diphenylphosphino)ethanenickel(II)** ( $Ni(CH_2SiMe_3)_2(diphos)$ ), **1**.

A suspension of  $NiCl_2(diphos)$  (3.1 g, 6.0 mmole) in diethyl ether (100 ml) was cooled in an ice bath and 15 ml of  $Me_3SiCH_2Li$  solution in diethyl ether ( $[Me_3SiCH_2Li] = 0.9 M$ ) was added dropwise during 5 minutes. A nitro-

Table 1.  $^1\text{H}$  NMR data obtained in  $\text{C}_6\text{D}_6$  at  $25^\circ\text{C}$  ( $\delta$  values relative to TMS).  $s$ =singlet,  $d$ =doublet,  $t$ =triplet,  $m$ =multiplet.

Compound	$\delta(\text{CH}_3-)$	$\delta(-\text{CH}_2\text{Si})$	$\delta(-\text{CH}_2\text{P})$	$\delta(\text{C}_6\text{H}_5-\text{P})$
$\text{Ni}(\text{CH}_2\text{SiMe}_3)_2(\text{diphos})$	0.30( $s$ )	1.88( $d$ ) <sup>b</sup>	0.90 <sup>c</sup>	$\sim 7.5(m)$
$(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2$ (diphos)	.....	.....	2.18( $t$ ) <sup>d</sup>	$\sim 7.2(m)$
$\text{Me}_3\text{SiCH}_2\text{Li}^a$	0.23( $s$ )	-1.94( $s$ )	.....	.....
$\text{Me}_3\text{SiCH}_2\text{CH}_2\text{SiMe}_3$	0.26( $s$ )	0.58( $s$ )	.....	.....

<sup>a</sup>Reference 12; <sup>b</sup> $J(\text{P}-\text{Ni}-\text{CH}_2)=15\text{ Hz}$ ; <sup>c</sup> $\text{A}_2\text{A}_2'\text{XX}'$  pattern (see Fig. 1 and text); <sup>d</sup>1:2:1 triplet,  $J(\text{P}-\text{CH}_2)=4\text{ Hz}$ .

gen atmosphere was maintained for all operations. The orange suspension immediately turned into a clear yellow solution and give a small amount of white precipitate. The reaction mixture was warmed to  $25^\circ\text{C}$  and stirred for 30 minutes. The white precipitate ( $\text{LiCl}$ ) was removed from the solution by filtration, and the yellow filtrate distilled under vacuum at  $25^\circ\text{C}$  to give yellow solid which was washed with pentane (25 ml) to remove the excess  $\text{Me}_3\text{SiCH}_2\text{Li}$ , and then dried under vacuum. The yield was 2.60g (69%). The  $^1\text{H}$  NMR spectrum is shown in Fig. 1 and spectral data are given in Table 1.

**Thermal Decomposition of Bis(trimethylsilylmethyl) 1,2-bis(diphenylphosphino) ethanenickel(II) ( $\text{Ni}(\text{CH}_2\text{SiMe}_3)_2(\text{diphos})$ ), 1.**

**Decomposition in Solution.** Thermal decomposition was carried out in  $\text{C}_6\text{D}_6$  in a 5 mm dia. NMR tube. A 0.02 g sample of 1 was dissolved in 1.5 ml of  $\text{C}_6\text{D}_6$  in an NMR tube at  $25^\circ\text{C}$  under nitrogen. The sample tube was cooled in a dry ice-acetone bath, degassed, and sealed under vacuum. The tube was then immersed in an oil bath at  $80^\circ\text{C}$ . The yellow solution turned dark brown within an hour and no additional visual change was observed for 8 hours of heating during which time the tube was removed from the oil bath and quenched in an ice-bath for  $^1\text{H}$  NMR measurements at intervals (see the next section for spectral changes).

The reaction tube was then cooled in liquid nitrogen, opened under nitrogen, and connected to a vacuum system for transferring the volatiles to a trap cooled in liquid nitrogen. The contents of the NMR tube were then allowed to warm to  $25^\circ\text{C}$  and the volatiles collected. The volatile product was analyzed by GC-MS and  $^1\text{H}$  NMR. The non-volatile residue was a dark brown-black, pyrophoric powder, the characterization of which is still incomplete.<sup>15</sup>

**Decomposition in the Solid State.** A solid sample of 1 (0.1 g) was placed in a 25 ml round bottom flask which was connected with a small trap (2.0 ml in volume). The whole system was evacuated, and the flask was placed on an oil bath at  $120^\circ\text{C}$  while the trap was immersed in liquid nitrogen. The yellow solid, 1, turned dark black within an hour. The flask was cooled down to room temperature after 3 hours of heating. The volatile material in the liquid  $\text{N}_2$  trap was analyzed by GC-MS and  $^1\text{H}$  NMR.<sup>15</sup>

**Reaction of Bis(trimethylsilylmethyl) 1,2-bis(diphenylphosphino)ethanenickel(II) ( $\text{Ni}(\text{CH}_2\text{SiMe}_3)_2(\text{diphos})$ ), 1, with  $\text{O}_2$ .**

The yellow solution of 1 (0.16 g) in benzene (7.0 ml) in a 50 ml round bottom flask under nitrogen was exposed to air at  $25^\circ\text{C}$ . The solution turned pale in 10 minutes and became white suspension within 2 hours. The volatile material (including the solvent) was collected in sample tube on a liquid nitrogen bath in the

same manner described above, and analyzed by GC-MS and  $^1\text{H}$  NMR.<sup>15</sup>

**Reaction of Bis(trimethylsilylmethyl)1,2-bis(diphenylphosphino)ethanenickel(II) ( $\text{Ni}(\text{CH}_2\text{SiMe}_3)_2(\text{diphos})$ ), **1**, with CO.**

The yellow solution of **1** (0.32 g) in benzene (10 ml) under  $\text{CO}$  ( $P_{\text{CO}} \sim 1$  atm.) turned pale yellow within 20 minutes at  $25^\circ\text{C}$  and became beige suspension within 18 hours. The volatile product (including the solvent) was collected in a sample tube on liquid nitrogen bath in the same manner described above, and analyzed by GC-MS and  $^1\text{H}$  NMR.<sup>15</sup>

**Reaction of Bis(trimethylsilylmethyl)1,2-bis(diphenylphosphino)ethanenickel(II) ( $\text{Ni}(\text{CH}_2\text{SiMe}_3)_2(\text{diphos})$ ), **1**, with 1,2-Bis(diphenylphosphino)ethane, diphos.**

To the solution of **1** (0.158 g, 0.25 mmole) in benzene (7.0 ml) in 15 mm dia. reaction tube (10 cm long) was added 1,2-bis(diphenylphosphino)ethane (0.10 g, 0.25 mmole) at  $25^\circ\text{C}$ . The tube was cooled on dryice-acetone bath, degassed and sealed under vacuum. The reaction mixture in the reaction tube was heated at  $80^\circ\text{C}$  in an oil bath. The yellow solution did not show any visual change for 6 hours except that a small amount of light yellow precipitate was observed. Cooling the reaction mixture to  $25^\circ\text{C}$  resulted in precipitation of more light yellow solid which was separated by vacuum distillation of the volatile material at room temperature. The volatile product trapped on a liquid nitrogen bath was analyzed by GC-MS and  $^1\text{H}$  NMR.<sup>15</sup>

### 3. RESULTS AND DISCUSSION

$\text{Ni}(\text{CH}_2\text{SiMe}_3)_2(\text{diphos})$ , **1**, is stable under nitrogen in solution and in the solid state at room temperature. It decomposes to unknown compounds on exposure to air immediately in solution and within an hour in the solid state

at room temperature. It is very soluble in acetone, benzene, toluene, diethyl ether and tetrahydrofuran, and slightly soluble in pentane and hexane.  $^1\text{H}$  NMR spectrum of **1** is seen in Fig. 1 and the spectral data are given in Table 1. It is seen in Fig. 1 that the ratio of the signals is 2:2:9, which clearly indicates a singlet at  $\delta=0.30$  ppm to be due to  $\text{CH}_3$ . The methylene hydrogens in  $-\text{CH}_2\text{SiMe}_3$  appear as a doublet (1:1) at  $\delta=1.88$  ppm\* due to the coupling by  $^{31}\text{P}$  *trans* to  $-\text{CH}_2\text{SiMe}_3$ . The methylene hydrogens in  $(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2$  give rise to a complex  $\text{A}_2\text{A}_2'\text{XX}'$  pattern at  $\delta=0.90$  ppm\*\* due to the inequivalence of the coupling of the  $\text{CH}_2$  to the near and remote phosphorus atoms. Similar observations have been reported for iridium<sup>16</sup> and platinum<sup>17</sup> complexes in their  $^1\text{H}$  NMR spectra.

The volatile material obtained from the thermal decomposition of **1** in  $\text{C}_6\text{D}_6$  was identified as  $\text{Me}_3\text{SiCH}_2\text{CH}_2\text{SiMe}_3$  (very small amounts of other products were also observed<sup>15</sup>). Fig. 2 a ~d show  $^1\text{H}$  NMR spectral changes during the thermal decomposition of **1** in  $\text{C}_6\text{D}_6$  (see Experimental). Two singlets of  $\text{Me}_3\text{SiCH}_2\text{CH}_2\text{SiMe}_3$  ( $-\text{CH}_2-$ ,  $\delta=0.58$  ppm and  $\text{CH}_3-$ ,  $\delta=0.26$  ppm, and identified also by Mass spectrum) increase while the peaks of **1** ( $-\text{CH}_2-$ ,  $\delta=1.88$  ppm and  $\text{CH}_3-$ ,  $\delta=0.30$  ppm) decrease. The  $-\text{CH}_2\text{P}$  peaks shift to somewhat down field during the thermal decomposition. The colorless volatile product collected from the thermal decomposition of **1** in the solid state was found to be  $\text{Me}_3\text{SiCH}_2\text{CH}_2\text{SiMe}_3$ .<sup>15</sup> As mentioned earlier, some transi-

\*The chemical shift of the methylene hydrogens in  $\text{Me}_3\text{SiCH}_2\text{Li}$  shifts to downfield in  $(\text{Me}_3\text{SiCH}_2)_2\text{Ni}(\text{diphos})$ , which may be understood in terms of the electronegativity difference between Li and Ni ( $\chi_{\text{Ni}} > \chi_{\text{Li}}$ ).

\*\*The chemical shift of the methylene hydrogens in diphos(uncoordinated) shifts to upfield in  $(\text{Me}_3\text{SiCH}_2)_2\text{Ni}(\text{diphos})$ , which may be due to the effective  $\pi$ -back donation from Ni to P.

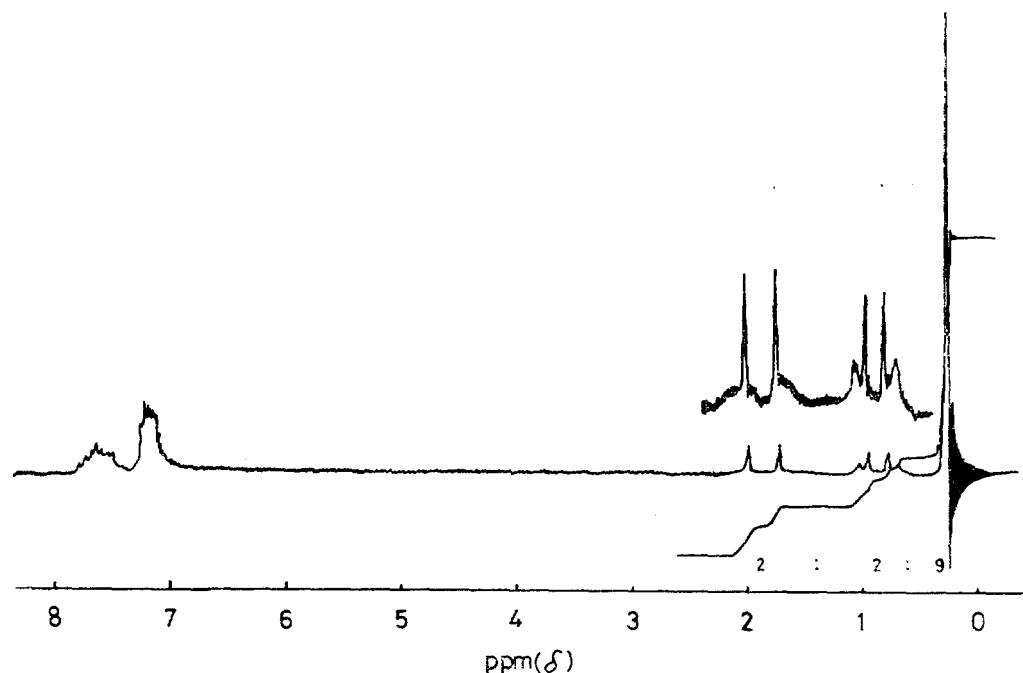
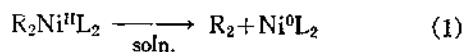
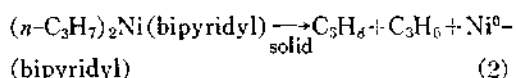


Fig. 1.  $^1\text{H}$  NMR of  $\text{Ni}(\text{CH}_2\text{SiMe}_3)_2((\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2)$  measured in  $\text{C}_6\text{D}_6$  at  $25^\circ\text{C}$  ( $\delta$  values relative to tetramethylsilane).

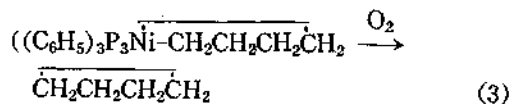
tion metal complexes of  $\text{Me}_3\text{SiCH}_2^-$  apparently undergo  $\gamma$ -hydrogen elimination reaction to produce  $\text{M}-\text{CH}_2\text{Si}(\text{Me}_2)\dot{\text{C}}\text{H}_2$  ( $\text{M}=\text{Mo}, \text{Ru}, \text{Rh}$ ) at  $0^\circ\text{C}$  under nitrogen.<sup>6</sup> An analogous metallacycle,  $(\text{Et}_3\text{P})_2\text{Pt}-\text{CH}_2\text{C}(\text{Me}_2)\dot{\text{C}}\text{H}_2$ , was obtained by the thermal decomposition of  $(\text{Et}_3\text{P})_2\text{Pt}(\text{CH}_2\text{CMe}_3)_2$  at  $157^\circ\text{C}$ .<sup>18</sup> However, no report has been made on the thermal decomposition of well characterized transition metal complexes of  $\text{Me}_3\text{SiCH}_2^-$ . It is known that the thermal decomposition of some  $\text{R}_2\text{Ni}^{\text{II}}\text{L}_2$  ( $\text{R}=\text{aryl}, \text{alkyl}$ ;  $\text{L}=\text{triaryl- or trialkylphosphine}$ ) affords the reductive coupling product,  $\text{R}_2$ , quantitatively,<sup>19,20</sup>



while others,  $(\eta\text{-C}_3\text{H}_7)_2\text{Ni}(\text{bipyridyl})$  for example, undergo reductive disproportionation reaction upon heating in the solid state (equation 2).<sup>21-23</sup>



The compound,  $\text{Ni}(\text{CH}_2\text{SiMe}_3)_2(\text{diphos})$ , seems to decompose thermally following equation (1)<sup>15</sup> either in solution or in the solid state. It was observed that the reaction of **1** with  $\text{O}_2$  in benzene also produced  $\text{Me}_3\text{SiCH}_2\text{CH}_2\text{SiMe}_3$  (very small amounts of  $\text{Me}_3\text{Si}-\text{O}-\text{SiMe}_3$ ,  $\text{Me}_4\text{Si}$  and  $\text{Me}_3\text{SiCH}=\text{CH}_2$  were found in the volatile decomposition product collected,<sup>15</sup> see Experimental). A similar reductive elimination reaction by  $\text{O}_2$  has been observed as given in equation (3), where nickel containing product was not characterized.<sup>24</sup>



The reactions of **1** with  $\text{CO}$  and  $\text{diphos}$  also

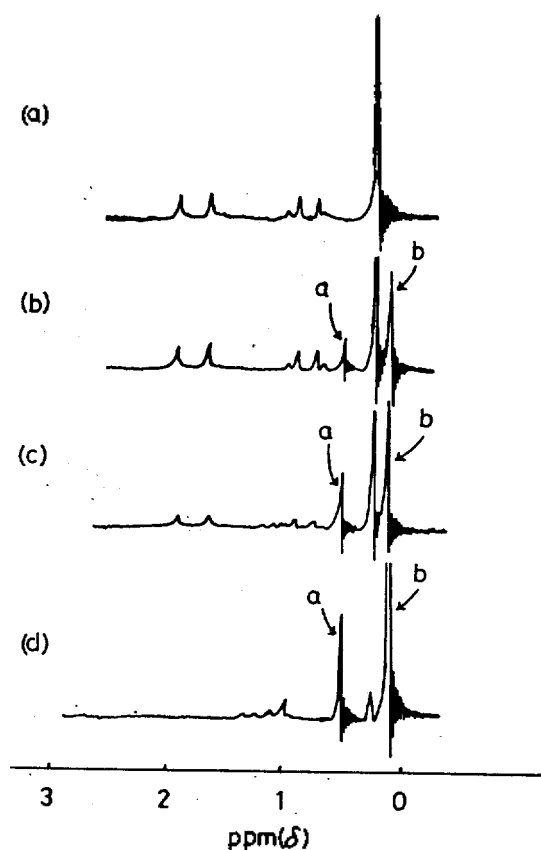
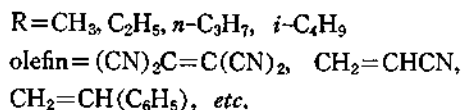
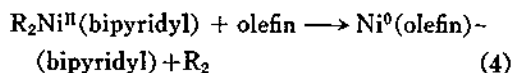


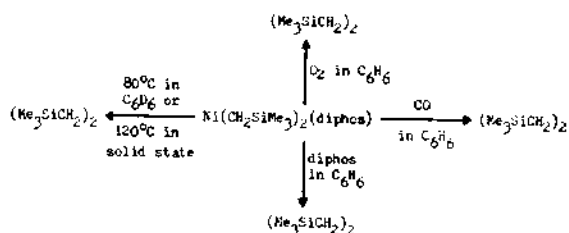
Fig. 2. Thermal decomposition of  $\text{Ni}(\text{CH}_2\text{SiMe}_3)_2$  (diphos) in  $\text{C}_6\text{D}_6$  at  $80^\circ\text{C}$  after (a) 0 min., (b) 40 min., (c) 180 min., (d) 510 min. a and b are due to  $-\text{CH}_2\text{SiMe}_3$  and  $(\text{CH}_3)_3\text{Si}-$ , respectively, in the  $\text{Me}_3\text{SiCH}_2-\text{CH}_2\text{SiMe}_3$  produced.  $\delta$  values are relative to tetramethylsilane. The phenyl hydrogen peaks are omitted since they do not show a significant change.

produced practically a single product,  $\text{Me}_3\text{SiCH}_2-\text{CH}_2\text{SiMe}_3$ , respectively.<sup>25</sup> The reactions of dialkylnickel(II) complexes with olefins are known to produce nickel(0) compounds and dialkyls quantitatively (equation (4)).<sup>21-23</sup> However, a metallacycle of nickel (II),  $((\text{C}_6\text{H}_5)_3\text{P})_2\text{Ni}-\text{CH}_2-\text{CH}_2\text{CH}_2\text{CH}_2$ , reacts tertiary phosphine  $((\text{C}_6\text{H}_5)_3\text{P})$  to give various olefins ( $\text{C}_2\text{H}_4$ ,  $\text{C}_3\text{H}_6$ ,  $\text{C}_4\text{H}_8$ ,  $\text{C}_5\text{H}_{10}$ ), cyclopentane (4~6%) and  $\text{CH}_4$ .<sup>26</sup>



Thus, the compound,  $\text{Ni}(\text{CH}_2\text{SiMe}_3)_2(\text{diphos})$ , seems to react with CO and diphos following equation (4),<sup>25</sup> rather than following a metallacycle decomposition route or inserting CO into the Ni-C bond. The latter reaction has been reported for the reaction of a  $\text{Mo}-\text{CH}_2\text{SiMe}_3$  complex.<sup>8</sup>

The reactions of 1 described above are summarized in the following scheme.<sup>15</sup>



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#### REFERENCES

1. C. S. Cundy, B. M. Kingston and M. F. Lappert, *Advan. Organometal. Chem.*, **11**, 253 (1973).
2. G. Wilkinson, *Pure Appl. Chem.*, **30**, 627 (1972).
3. P. J. Davidson, M. F. Lappert and R. Pearce, *J. Organometal. Chem.*, **57**, 269 (1973).
4. M. R. Collier, M. F. Lappert and R. Pearce, *J. Chem. Soc., Dalton*, 445 (1973).
5. G. Yagupsky, W. Wowat, A. Shortland and G. Wilkinson, *Chem. Commun.*, 1369 (1970).
6. R. A. Anderson, R. A. Jones and G. Wilkinson, *Chem. Commun.*, 283 (1977), *J. Chem. Soc., Dalton*, 446 (1977).
7. R. A. Anderson, E. Carmona-Guzman, J. F. Gibson and G. Wilkinson, *J. Chem. Soc., Dalton*, 2204 (1976).
8. E. Carmona-Guzman, G. Wilkinson, J. L. Atwood, R. D. Rogers and M. J. Zawarotko, *Chem.*

- Commun.*, 465 (1978).
9. M.D. Curtis and J. Greene, *J. Amer. Chem. Soc.*, **100**, 6362 (1978) and references therein.
  10. M.R. Collier, M.F. Lappert and M.M. Truelock, *J. Organometal. Chem.*, **25**, C36 (1970).
  11. J. Chatt, F.A. Hart and H.R. Watson, *J. Chem. Soc.*, 2537 (1972).
  12. J. Connolly and G. Urry, *Inorg. Chem.*, **2**, 645 (1963).
  13. A.J. Gordon and R.A. Ford, "The Chemist Companion", P.439, John-Wiley and Sons, New York, U.S.A., (1972).
  14. R. J. P. Corriu and J. Masse, *J. Organometal. Chem.*, **9**, 165 (1967).
  15. Detailed data for identification of the metal-containing product(s) and the composition of the volatile products, including the minor products, will be published elsewhere. It is evident on the bases of IR and  $^1\text{H}$  NMR spectra that the non-volatile product(s), metal compound(s), does not contain  $\text{Me}_3\text{SiCH}_2-$  group or a fragment of  $\text{Me}_3\text{SiCH}_2-$ .
  16. T. Yoshida, T. Yamagata, T.H. Tulip, J. Ibers and S. Otsuka, *J. Amer. Chem. Soc.*, **100**, 2063 (1978).
  17. C.K. Brown, D. Georgiou and G. Wilkinson, *J. Chem. Soc.*, (A), 3120 (1971).
  18. P. Foley, R. DiCosino and G.M. Whitesides, *J. Amer. Chem. Soc.*, **102**, 6713 (1980).
  19. D. G. Morrell and J. K. Kochi, *J. Amer. Chem. Soc.*, **97**, 7262 (1975).
  20. M. Wada, K. Kusabe and K. Oguro, *Inorg. Chem.*, **16**, 446 (1977).
  21. T. Yamamoto, A. Yamamoto and S. Ikeda, *J. Amer. Chem. Soc.*, **93**, 3350, 3360 (1971).
  22. T. Yamamoto, Y. Nakamura and A. Yamamoto, *Bull. Chem. Soc. Japan*, **49**, 191 (1976).
  23. A. Yamamoto and T. Yamamoto, *Bull. Chem. Soc. Japan*, **49**, 1403 (1976).
  24. R. H. Grubbs, Progress in Inorganic Chemistry, Volume 24, P.33 1978.
  25. Preliminary data suggest that the nickel containing products from the reactions are nickel(0) compounds, probably  $\text{Ni}(\text{CO})_2(\text{diphos})$  and  $\text{Ni}-(\text{diphos})_2$ , respectively.
  26. R. H. Grubbs and A. Miyashita, *J. Amer. Chem. Soc.*, **100**, 7418 (1978).