product 6 exhibits a peak at -1.8 ppm of relative area three with *two* sets of satellite patterns with areas approximately ~35% and ~3% of the total, corresponding to a trimeric molecule containing one and two ^{183}W centers, respectively.[16] This postulate was also confirmed by field-desorption mass spectroscopy. So far we know that [W-(η^5-C$_5$Me$_4$-*t*-Bu)H$_3$]$_3$ (6) is not readily converted into [W-(η^5-C$_5$Me$_4$-*t*-Bu)H$_4$]$_2$ (5) under 30 psi or H$_2$ and 5 does not readily lose H$_2$ to give 6 when it is heated to 80 °C.

The reaction of W(η^5-C$_5$Me$_4$-*t*-Bu)(CCMe$_3$)Me$_2$ with H$_2$ at 1000 psi also produces a mixture of 5 and 6 in a ratio of approximately 3:1 but a total yield of only ~30%.

It is unlikely that hydride ligands in 5 are all terminal or all bridging. A plausible structure would contain four bridging hydrides and two terminal hydrides on each metal (cf. Re$_2$H$_8$(PR$_3$)$_4$[17]). Terminal and bridging hydrides must exchange relatively rapidly since we observe only the singlet of relative area 4 in toluene-d_8 at -80 °C.

In contrast, the structure of 6 is more difficult to predict. It seems likely that the basic framework is triangular, as it is in other W(IV) clusters such as W$_3$O$_3$Cl$_4$(μ^3-Cl)-(CH$_3$CO$_2$)(PBu$_3$)$_3$[18a] or [W$_3$(μ^3-O)$_2$(CH$_3$CO$_2$)$_6$(H$_2$O)$_3$]$^{2+}$.[18b,c] Upon cooling a sample of 6 the hydride peak collapses into the base line and signals for at least two different cyclopentadienyl groups appear. Unfortunately, we have not yet been able to obtain a sensible limiting spectrum in toluene-d_8 at temperatures down to -80 °C. It is clear, however, that the hydrides in 6 are equilibrating much more slowly than those in 5.

It is interesting to compare the results observed here with those obtained upon hydrogenation of Ta(η^5-C$_5$Me$_5$)Me$_4$.[19,20] In the absence of coordinating ligands such as phosphines only unidentifiable brown to black solids or oils were obtained upon hydrogenation of Ta-(η^5-C$_5$Me$_5$)Me$_4$ at 30-1500 psi. In the presence of PMe$_3$ Ta(η^5-C$_5$Me$_5$)(PMe$_3$)$_2$H$_4$ can be isolated.[20] Therefore it appears at this point that ligand-free complexes of the type [Ta(η^5-C$_5$Me$_5$)H$_x$]$_y$ either are not formed selectively or are not stable.

We are now in the process of preparing simpler η^5-C$_5$R$_5$ analogues of 5 and 6 more directly, elucidating their structures, and studying their reactions with carbon monoxide.

Registry No. 1, 86823-25-8; 2, 86823-26-9; 3, 86823-27-0; 4, 86823-28-1; 5, 86834-30-2; 6, 86834-31-3; [W(η^5-C$_5$Me$_4$-*t*-Bu)Cl$_4$]$_2$, 83511-04-0; ZnMe$_2$, 544-97-8; Zn(CH$_2$CMe$_3$)$_2$, 54773-23-8.

(16) The theoretical distribution is (^{184}W)^3 = 63.6%, (^{184}W)^2(^{183}W) = 31.0%, (^{184}W)(^{183}W)^2 = 5.1%, and (^{183}W)^3 = 0.3%. Half of the triplet pattern for (^{184}W)(^{183}W)^2 is found under the main peak due to the hydride in (^{184}W)^3.

(17) Bau, R.; Carroll, W. E.; Teller, R. G.; Koetzle, T. F. *J. Am. Chem. Soc.* **1977**, *99*, 3872.

(18) (a) Felthouse, T. R.; Lay, D. G.; Cotton, F. A. *J. Am. Chem. Soc.* **1980**, *102*, 1431. (b) Bino, A.; Cotton, F. A.; Dori, Z.; Koch, S.; Kuppen, H.; Millar, M.; Sekutowski, J. C. *Inorg. Chem.* **1978**, *11*, 3245. (c) Bino, A.; Cotton, F. A.; Dori, Z. *J. Am. Chem. Soc.* **1979**, *101*, 3842.

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(20) Mayer, J. M.; Bercaw, J. E. *J. Am. Chem. Soc.* **1982**, *104*, 2157.

## Disilene System (R$_2$Si=SiR$_2$). The Tetra-*tert*-butyl Derivative

Satoru Masamune,* Shu Murakami, and Hiromi Tobita

Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Summary: Low-temperature photolysis of 2,3-benzo-7,7,8,8-tetra-*tert*-butyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene provides, in addition to naphthalene, tetra-*tert*-butyldisilene, which exhibits UV absorption maxima at 305 (ϵ 5200) and 433 nm (2800). This disilene is thermally unstable and has a half-life of only several hours at room temerature (ca. 10^{-2} M in methylcyclohexane).

Stable, crystalline tetramesityl-[1] and tetrakis(2,6-dimethylphenyl)disilene[2] (1 and 1a) that have been synthesized recently provide valuable chemical information on the silicon–silicon double bond. The aryl substituents

1 : R = mesityl

1a : R = 2,6-dimethylphenyl

1b : R = 1-ethylpropyl
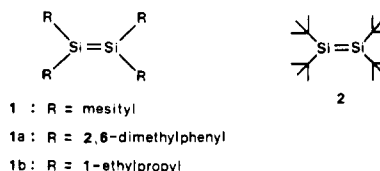
of these compounds, however, significantly perturb the intrinsic electronic structure of this double-bond system and thus create extra complications in the interpretation of physical data such as ultraviolet[3] and photoelectron spectra.[4] Obviously, the majority of these complications can be eliminated by the synthesis of alkyl (rather than aryl) substituted disilenes; therefore tetra-*tert*-butyldisilene (2)[5] has been selected as our synthetic target. We record herein that low-temperature photolysis of 2,3-benzo-7,7,8,8-tetra-*tert*-butyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene (3) leads to the formation of 2. This compound is found to be rather unstable thermally, (the half-life being approximately several hours at room temperature) and also to be extraordinarily sensitive toward air and moisture. Despite these undesirable properties, however, this disilene

(1) (a) West, R.; Fink, M. J.; Michl, J. *Science (Washington, D.C.)* **1981**, *214*, 1343. (b) Fink, M. J.; DeYoung, D. J.; West, R.; Michl, J. *J. Am. Chem. Soc.* **1983**, *105*, 1070. (c) Zilm, K. W.; Grant, D. M.; Michl, J.; Fink, M. J.; West, R. *Organometallics* **1983**, *2*, 193. (d) Boudjouk, P.; Han, B.-H.; Anderson, K. R. *J. Am. Chem. Soc.* **1982**, *104*, 4992. This communication describes the direct synthesis of 1 (~90% crude yield) from dimesityldichlorosilane and lithium, using a "common ultrasound laboratory cleaner". Several attempts to reproduce this result *in our hands* invariably led to the almost exclusive formation of the corresponding cyclotrisilane (50–60%) perhaps due to some subtle difference in experimental conditions.
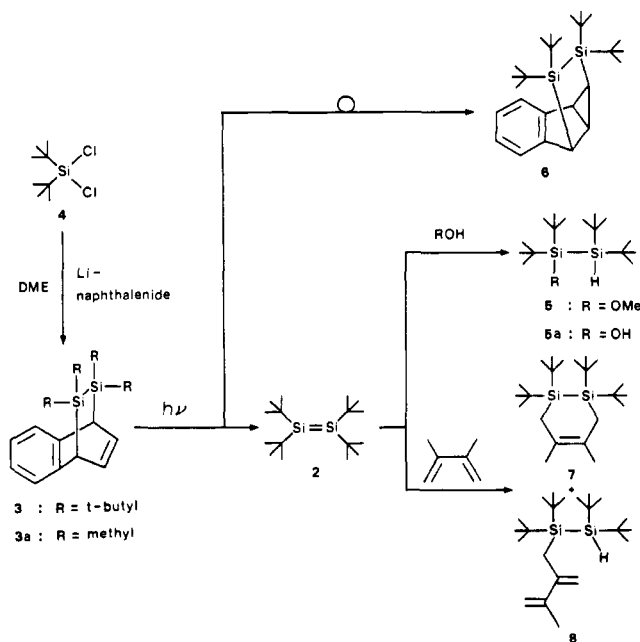
(2) (a) Masamune, S.; Hanzawa, Y.; Murakami, S.; Bally, T.; Blount, J. F. *J. Am. Chem. Soc.* **1982**, *104*, 1150. (b) For the preparation of a digermene derivative, see: Masamune, S.; Hanzawa, Y.; Williams, D. J. *Ibid.* **1982**, *104*, 6136.

(3) For a recent theoretical discussion on the UV absorption of polysilanes and polygermanes, see: Castel, A.; Rivière, P.; Saint-Roch, B.; Satgé, J.; Malrieu, J. P. *J. Organomet. Chem.* **1983**, *247*, 149.

(4) A photoelectron spectrum of 1a has been measured (private communication from Dr. T. Bally, Institut de Chimie Physique, Universite de Fribourg Suisse). The first VIP is 8.4 eV.
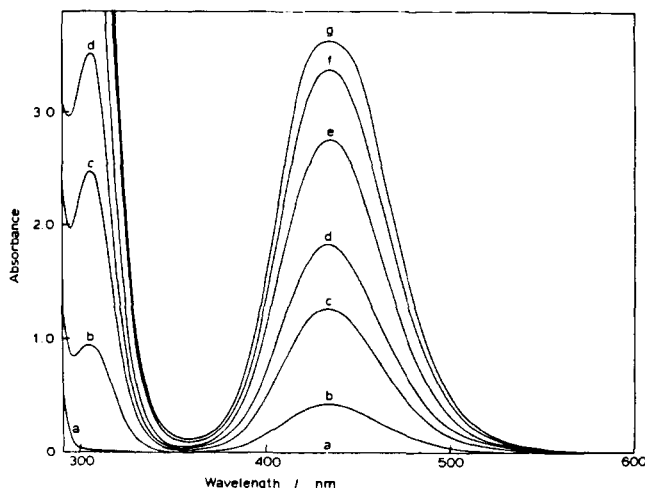
(5) For an earlier attempt at the synthesis of 2 see: Triplett, K.; Curtis, M. D. *J. Organomet. Chem.* **1976**, *107*, 23.

Scheme I

3 : R = t-butyl
3a : R = methyl

Figure 1. Photolysis of **3** (2 × 10⁻² M in cyclohexane-d_6) at −196 °C followed by ultraviolet spectroscopy: (a) before irradiation; (b) after 2 min of irradiation and warming to room temperature; (c) 4 min; (d) 6 min; (e) 10 min; (f) 18 min; (g) 24 min.

2 has been purified to an extent of approximately 40% (Scheme I).

Synthesis of 3. A reaction that was carried out with the intention to prepare hexa-*tert*-butylcyclotrisilane in the manner described earlier for the construction of the aryl-substituted three-membered ring system[2] took vastly different pathways. Thus, treatment of di-*tert*-butyldichlorosilane (**4**) (3 g, 14.1 mmol) in dimethoxyethane (25 mL) with lithium naphthalenide [prepared from lithium (30% dispersion, 625 mg, 0.0282 mol) and naphthalene (3.6 g, 28.2 mmol)] at −78 °C and then at room temperature provided several products,[6,7] from which the disilabicyclo[2.2.2]octadiene **3** (176 mg, mp 210–211 °C, was readily isolated via flash chromatography. The spectral properties of **3** are in parallel with its known tetramethyl analogue **3a**:[8] mass spectrum (electron impact) calcd for M − C₄H₉ *m/z* 355.2277, found *m/z* 355.2291, (field desorption) calcd for M *m/z* 412, found *m/z* 412; UV spectrum (cyclohexane) λ_{max} 276 (ε 870), 282 nm (870); ¹H NMR spectrum (270 MHz, CDCl₃) δ 1.01 (s, 18 H), 1.27 (s, 18 H), 3.68 (dd, 2 H, *J* = 5.0, 3.3 Hz), 6.17 (dd, 2 H, *J* = 5.0, 3.3 Hz), 6.99 (dd, 2 H, *J* = 5.5, 3.3 Hz), 7.14 (dd, 2 H, *J* = 5.5, 3.3 Hz). Reaction of 1,1,2,2-tetra-*tert*-butyl-1,2-dichlorodisilane[7,9] with lithium naphthalenide, similar to that used earlier by Peddle and co-workers for the synthesis of **3a**,[8] did not provide even a trace amount of **3**, but the product consisted of 1,1,2,2-tetra-*tert*-butyl-1-chloro-2-methyldisilane [Cl-(*t*-Bu)₂SiSi(*t*-Bu)₂Me][7] and 1,1,2,2-tetra-*tert*-butyl-1-chlorodisilane [Cl(*t*-Bu)₂SiSi(*t*-Bu)₂H].[7] The course of the naphthalenide reduction is known to be highly dependent on the substituents of either *dichlorosilanes* or *dichlorodisilanes*,[10] and the formation of **3** from **4** appears to

represent the first construction of the disilano bridge over naphthalene directly from a dichlorosilane with this reducing agent.

Synthesis and Properties of 2. Photolysis of **3** is of special interest, as extrusion of the disilano bridge from **3** is a distinct possibility.[11] Indeed this photofragmentation was indicated in the initial experiments. Thus, brief irradiation of **3**[12] in methylcyclohexane glass (ca. 2 × 10⁻² M) *containing 5 equiv of methanol* with a low-pressure mercury lamp at −196 °C caused yellow coloration of the glass, which disappeared instantly upon thawing. After this sequence of processes (cooling, irradiation, and thawing) was repeated until no distinct intensification of color was discernible upon further photolysis, the photolysate was found to consist of three compounds [5 (35% isolated yield), **6** (13%), and naphthalene (~40%)] in addition to the starting material **3** (13%): **5** was identified as 1,1,2,2-tetra-*tert*-butyl-1-methoxydisilane[13] and **6** as 3,4-benzo-6,6,7,7-tetra-*tert*-butyl-6,7-disilatricyclo[3.3.0.0²,⁸]-oct-3-ene.[13] Replacement of methanol with water as a trapping agent (7 equiv) in the above experiment led to the formation of the hydroxy compound **5a**[13] instead of **5**. These experiments strongly suggest that the precursor of **5** or **5a** is tetra-*tert*-butyldisilene.

In the absence of a trapping reagent (and to the strict exclusion of air and moisture from the reaction system),[12]

(6) These products are: H(*t*-Bu)₂SiSi(*t*-Bu)₂H (3%),[5] Me(*t*-Bu)₂SiSi(*t*-Bu)₂H (5%), Me(*t*-Bu)₂SiSi(*t*-Bu)₂Me (5%), 1,4-bis(di-*tert*-butylsilyl)naphthalene (7%), and 1,4-dihydro-1,4-bis(di-*tert*-butylsilyl)-naphthalene (8%). In this reaction the lithiated silicon intermediate apparently has attached the solvent dimethoxyethane to yield the two methylated derivatives.

(7) See Supplementary Material for spectral information.

(8) (a) Peddle, G. J. D.; Roark, D. N.; Good, A. M.; McGeachin, S. G. *J. Am. Chem. Soc.* **1969**, *91*, 2807. (b) Roark, D. N.; Peddle, G. J. D. *Ibid.* **1972**, *94*, 5837.

(9) This compound was prepared by chlorination of 1,1,2,2-tetra-*tert*-butyldisilane[5] in carbon tetrachloride at 0 °C.

(10) (a) Andrianov, K. A.; Nogaideli, A. I.; Tkeshelashvili, R. Sh. *Isv. Akad. Nauk SSSR, Ser. Khim.* **1966**, 2228. (b) Smith, C. L.; Pounds, J. *J. Chem. Soc., Chem. Commun.* **1975**, 910. (c) Biernbaum, M.; West, R. *J. Organomet. Chem.* **1977**, *131*, 179. (d) Dunoguès, J.; Calas, R.; Biran, C.; Duffaut, N. *Ibid.* **1970**, *23*, C50.

(11) (a) Nakadaira, Y.; Otsuka, T.; Sakurai, H. *Tetrahedron Lett.* **1981**, *22*, 2417. (b) Rich, J. D.; Drahnak, T. J.; West, R.; Michl, J. *J. Organomet. Chem.* **1981**, *212*, C-1.

(12) Compound **3** is extremely hygroscopic but can be obtained in anhydrous form by removing water as a toluene azeotrope.

(13) **5**; greasy oil; ¹H NMR (C₆D₆) δ 1.17 (s, 18 H, *t*-Bu), 1.26 (s, 18 H, *t*-Bu), 3.45 (s, 3 H, OMe), 3.84 (s, 1 H, SiH); IR (CHCl₃) 2065 (ν(Si–H)), 1105 cm⁻¹ (ν(Si–O)); mass spectrum (field desorption) found *m/z* 316 (M⁺), (electron impact) *m/z* 259 (11%), 89 (24), 57 (100). **5a**: colorless oil; ¹H NMR (C₆D₆) δ 0.39 (s, 1 H, OH), 1.09 (s, 18 H, *t*-Bu), 1.23 (s, 18 H, *t*-Bu), 3.83 (s, 1 H, SiH); IR (CHCl₃) 3680 (ν(O–H)), 2065 cm⁻¹ (ν-(Si–H)); mass spectrum (field desorption) found *m/z* 302 (M⁺), (electron impact) *m/z* 245 (22%), 75 (100). **6**: mp 156–158 °C; ¹H NMR (CDCl₃) δ 0.65 [b s, 10 H, *t*-Bu and H(8)], 1.17 (s, 9 H, *t*-Bu), 1.23 (s, 9 H, *t*-Bu), 1.32 (s, 9 H, *t*-Bu), 2.72 (dd, 1 H, *J* = 9.3, 6.6 Hz) 2.82 (ddd, 1 H, *J* = 7.6, 6.6, 6.6 Hz), 3.17 (d, 1 H, *J* = 6.6 Hz), 6.97 (m, 2 H, Ar), 7.24 (m, 2 H, Ar); IR (CHCl₃) 2940, 2890, 2860 (ν(C–H)), 1475 (δ(C–H)), 1392, 1366 cm⁻¹ [δ(C–H) (*t*-Bu)]; mass spectrum (field desorption) found *m/z* 412 (M⁺), (electron impact) *m/z* 355 (9%) 284 (30), 227 (18), 172 (13), 127 (25), 73 (100).

the precursor does survive in solution at room temperature as indicated by the persistence of yellow coloration. The reaction course was followed semiquantitatively by means of both ^{1}H NMR and UV spectroscopy. When the photolysis of a sample in deuteriomethylcyclohexane containing a standard substance, 2,2,3,3-tetramethylbutane, was periodically interrupted and the photolysate, after being warmed to room temperature, was subjected to exclusion of air and moisture from the reaction system),[12] spectral measurements, a new NMR singlet at δ 1.37 appeared at the expense of the signals due to 3 (see above). The maximum height of this new signal was attained (29% yield of 2) at 74% consumption of 3. The intensity of two new UV absorptions [λ_{max} 305 (ϵ 5200), 433 nm (2800)] also increased in parallel (see Figure 1). Fractional distillation of the photolysate at 5×10^{-6} torr at 30 °C raised the purity of 2 to ca. 40%.[14]

Compound 2 is very reactive as already described in the above trapping experiments with methanol and water. In addition, after complete photolysis, quenching of 2 with 2,3-dimethylbutadiene provides the Diels–Alder adduct 7[7] (4% yield) and the ene adduct 8[7] (15%) in addition to 6 (5.7%). The disilene 2 in methylcyclohexane (ca. 10^{-2} M) has a half-life of 4–10 h.

The UV absorption maximum of 2 at 433 nm is located at a rather unexpectedly long wavelength, even compared with tetrakis(2,6-dimethylphenyl)disilene (422 nm).[2] This red shift observed for 2 coupled with its extraordinarily high reactivity suggests that the four quaternary carbon atoms of the bulky substituents in 2 may not attain coplanarity due to steric repulsion.[15] This inference has indeed led us to attempt the synthesis of tetrakis(1-ethylpropyl)disilene (1b), the silicon–silicon double bond of which, according to molecular models, is well "shielded" against external attack (and also polymerization) and yet can take a conformation of D_{2h} or C_{2h} symmetry.[15] Indeed, compound 1b exhibits a UV maximum at 390 nm.[16,17] Details of the chemistry of this compound will be reported in due course.

Registry No. 1b, 86766-28-1; 2, 86766-29-2; 3, 86766-30-5; 4, 18395-90-9; 5, 86766-31-6; 5a, 86766-35-0; 6, 86766-32-7; 7, 86766-33-8; 8, 86766-34-9.

Supplementary Material Available: A listing of physical properties of new compounds (2 pages). Ordering information is given on any current masthead page.

(14) The purity of **2** is equated to the ratio of the intensity of the singlet δ 1.37 to the total intensity of the signals between δ 0 and δ 4.

(15) The geometry of H$_2$Si=SiH$_2$ and H$_2$Ge=GeH$_2$ has been a subject of numerous recent calculations. See: Trinquier, T.; Malrieu, J.-P.; Rivière, P. *J. Am. Chem. Soc.* **1982**, *104*, 4529 and references quoted therein. The stable conformations of these species appear to be of C_{2h} symmetry rather than D_{2h}. No experimental data have yet been available.

(16) Masamune, S.; Tobita, H.; Murakami, S. unpublished results. Details of this chemistry will be reported in due course.

(17) The carbon analogue of **2**, tetra-*tert*-butylethylene still remained unsynthesized. For a recent attempt, see: (a) Cullen, E. R.; Guziec, F. S., Jr.; Murphy, C. J. *J. Org. Chem.* **1982**, *47*, 3563. For reviews, see: (b) Tidwell, T. T. *Tetrahedron* **1978**, *34*, 1855. (c) Liebman, J. F.; Greenberg, A. *Chem. Rev.* **1976**, *76*, 311. (d) Greenberg, A.; Liebman, J. F. "Strained Organic Molecules"; Academic Press: New York, 1978.

Phosphine-Induced Reductive Elimination from *cis*-Arylmethylnickel(II) Complexes Having a 1,2-Bis(dimethylphosphino)ethane Ligand

Sanshiro Komiya*

Department of Applied Chemistry for Resources
Tokyo University of Agriculture and Technology
2-24-16 Nakamachi, Koganei, Tokyo 184, Japan

Yoshihiro Abe, Akio Yamamoto,* and Takakazu Yamamoto*

Research Laboratory of Resources Utilization
Tokyo Institute of Technology
4259 Nagatsuta, Midori-ku, Yokohama 227, Japan

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Summary: A series of *cis*-arylmethyl(1,2-bis(dimethylphosphino)ethane)nickel(II) complexes, *cis*-Ni(C$_6$H$_4$X)(Me)(dmpe) (X = *p*-OMe, *p*-Me, H, *p*-F, *o*-Me), has been prepared by the ligand exchange reaction of *trans*-Ni(C$_6$H$_4$X)(Me)(PEt$_3$)$_2$ with a stoichiometric amount of dmpe at low temperature. Addition of phosphorus ligands such as PEt$_3$, P(aryl)$_3$, dmpe, P(OEt)$_3$, and PCy$_3$ to the complexes induces facile reductive elimination of MeC$_6$H$_4$X.

Reductive elimination of alkyl and aryl ligands is the key step in nickel- or palladium-catalyzed cross-coupling reactions of aryl or alkenyl halides with alkylmagnesium halides, a process which is believed to proceed as shown in Scheme I.[1] For the reductive elimination to proceed in a concerted, nonradical pathway, the alkyl and aryl groups attached to nickel must be brought into adjacent positions, in a square-planar or tetrahedral configuration. Recent studies on thermolysis of square-planar cis-dialkyl complexes of nickel, palladium, and platinum clarified some of the reductive elimination mechanisms,[2–9] but the arylalkylnickel complexes so far isolated are only those of trans configuration[6,7] and no report is available, to our knowledge, concerning the preparation and behavior of a cis-arylalkylnickel complex, one which would have direct relevance to the catalytic cross-coupling reactions. We now report the preparation of the first cis-arylmethylnickel complexes that contain a 1,2-bis(dimethylphosphino)ethane (dmpe) ligand and the pronounced enhancement of the reductive elimination of the methyl and aryl groups by added tertiary phosphine ligands.

Preparation of *cis*-Arylmethylnickel(II) Complexes. Treatment of a homogeneous solution of trans-arylmethylbis(triethylphosphine)nickel(II),[7] 1, in ether with a stoichiometric amount of 1,2-bis(dimethylphosphino)ethane (dmpe) below 0 °C resulted in immediate precip-

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(5) (a) Braterman, P. S.; Cross, R. J.; Young, G. B. *J. Chem. Soc., Dalton Trans.* **1976**, 1310; **1977**, 1982. (b) Ertl, J.; Debaerdemaeker, T.; Brune, H. A. *Chem. Ber.* **1982**, *115*, 3860 and references cited therein.

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(9) Komiya, S.; Albright, T. A.; Hoffmann, R.; Kochi, J. K. *J. Am. Chem. Soc.* **1976**, *98*, 7255; **1977**, *99*, 8840.