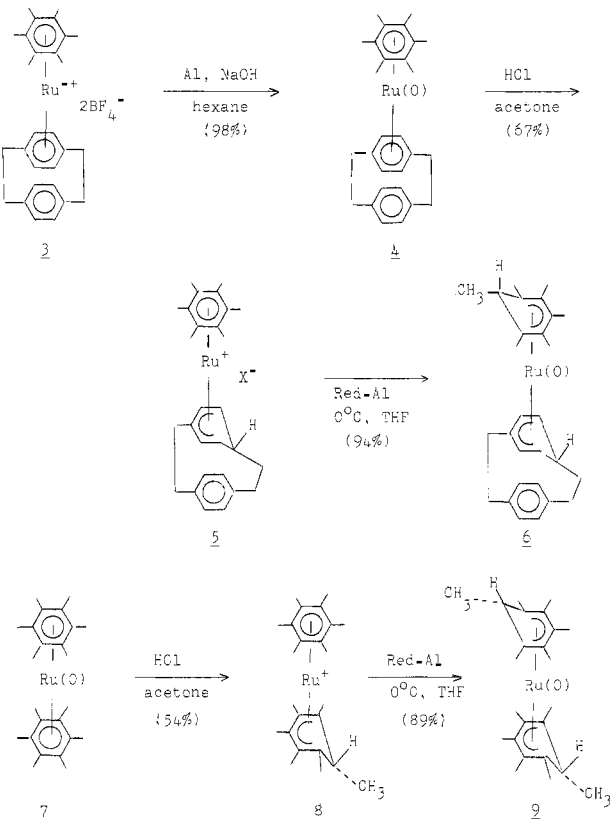


Figure 1. (η^5 -Hexamethylbenzene)(η^5 -3H-[2₂])(1,4)cyclophane)ruthenium(II) hydrogen dichloride (**5**). A view of the metal-organic ion (H atoms omitted). Ru-C bonds range from 2.17 (1) to 2.24 (1) Å. Some C-C distances: 3-2, 1.56 (2); 3-4, 1.53 (2); 3-8, 1.51 (2); 4-5, 1.42 (2); 7-8, 1.40 (2); 5-6, 1.41 (2); 6-7, 1.42 (2) Å. Other C-C distances and angles are generally consistent with the proposed formulation.

Scheme 1



methylbenzene ring to give the cyclohexadienyl analogue of ruthenocene, compound **6**, as relatively air-stable, yellow crystals.

To test the generality of this reaction sequence bis(hexamethylbenzene)ruthenium(0)⁴ was then carried through in the same fashion to give **8** and **9**, both being formed in good yield.

Although we have no firm evidence regarding the mechanism of the reaction of these η^4, η^6 -bis(arene)ruthenium(0) compounds with acid, there occurred in each reaction an immediate formation of a deep red color that rapidly faded. One can speculate that the red color is associated with the formation of a hydrido-ruthenium intermediate. Transfer of hydrogen then from ruthenium to an arene ring is an obvious possible explanation for the formation of **5** and **8**. For **5** the choice of transfer of hydrogen to the cyclophane moiety rather than to the hexamethylbenzene is probably determined by the relief of strain of the cyclophane ring. Also, the X-ray analysis of **5** shows the hydrogen has been added in an endo fashion as would be predicted for transfer from the ruthenium atom. Since Red-Al reduction places hydrogen exo,³ the overall consequence is that both **6** and **9** must have one "extra" hydrogen exo and the other endo. The assignment of

infrared stretching frequencies to the endo and exo C-H bonds in metal complexes of cyclohexadienyl anions has been a subject of controversy.¹⁰⁻¹³ However, it is now generally agreed that endo-C-H bonds absorb in the 2950-cm⁻¹ region whereas exo-C-H bonds absorb around 2750 cm⁻¹, and this is in accord with our infrared measurements of **5**, **6**, **8**, and **9** and the X-ray analysis of **5**.

The NMR spectral data for **6** and **9** require a high degree of symmetry, but whether this is due to free rotation about the π -metal bonds or due rather to frozen conformations, such as those drawn for **6** and **9**, has not yet been determined.

The formation of **5** and **6** represent the first [2_n]cyclophane having a cyclohexadienyl anion deck. Of interest is the possible extension of these methods to form [2_n]cyclophanes, where both decks are cyclohexadienyl moieties, as well as the polymers of such cyclophanes with transition metals. These results also are of interest in relation to the recent studies of the bis(pentadienyl)iron analogues of ferrocene.^{14,15}

Acknowledgment. This work was supported in part by the National Science Foundation, Grant CHE-8210282.

Registry No. **3**, 77089-82-8; **4**, 88453-36-5; **5** ($X^- = PF_6^-$), 88453-38-7; **5** ($X^- = HCl_2^-$), 88453-43-4; **6**, 88453-39-8; **7**, 32732-05-1; **8**, 88453-41-2; **9**, 88453-42-3; HCl, 7647-01-0.

Supplementary Material Available: Properties of the new compounds and the X-ray crystal structure analysis of (η^6 -hexamethylbenzene)(η^5 -3H-[2₂])(1,4)cyclophane)ruthenium(II) hydrogen dichloride (**5**), C₂₈H₃₆Cl₂Ru (83 pages). Ordering information is given on any current masthead page.

(10) Jones, D.; Wilkinson, G. *J. Chem. Soc.* **1964**, 2479-2481. Jones, D.; Pratt, L.; Wilkinson, G. *Ibid.* **1962**, 4458-4463.

(11) Khand, I. U.; Pauson, P. L.; Watts, W. E. *J. Chem. Soc. C* **1969**, 2024-2030.

(12) Bird, P. H.; Churchill, M. R. *Chem. Commun.* **1967**, 777-778.

(13) Treichel, P. M.; Shubkin, R. L. *Inorg. Chem.* **1967**, *6*, 1328-1333.

(14) Wilson, D. R.; DiLullo, A. A.; Ernst, R. D. *J. Am. Chem. Soc.* **1980**, *102*, 5928-5930.

(15) Böhn, M. C.; Eckert-Makić, M.; Ernst, R. D.; Wilson, D. R.; Gleiter, R. *J. Am. Chem. Soc.* **1982**, *104*, 2699-2707.

X-ray Crystal Structures of the Diphenylphosphide and -arsenide Anions: Use of a Crown Ether To Effect Complete Metal Cation and Organometalloid Anion Separation

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Received October 14, 1983

The synthesis and characterization of two-coordinate derivatives of heavier main-group elements have been the subject of intense studies during the past decade.² For phosphorus such compounds include the stable dialkyl and diamide radicals,³ the phosphabenzene,⁴ two-coordinate cationic species,⁵ compounds containing double bonds to carbon or nitrogen,⁶ and more recently, compounds having stable phosphorus-phosphorus double bonds.⁷ The al-

(1) On leave from the Department of Chemistry, Peking University, Beijing, China.

(2) Fluck, E. *Top. Phosphorus Chem.* **1980**, *10*, 193-284.

(3) Gynane, M. J. S.; Hudson, A.; Lappert, M. F.; Power, P. P.; Goldwhite, H. *J. Chem. Soc., Dalton Trans.* **1980**, 2428-2433; *J. Chem. Soc., Chem. Commun.* **1976**, 623. Cetinkaya, B.; Hudson, A. H.; Lappert, M. F.; Goldwhite, H. *Ibid.* **1982**, 609-610.

(4) Markl, G. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 846-847. Markl, G. *Phosphorus Sulfur* **1977**, *3*, 77-108.

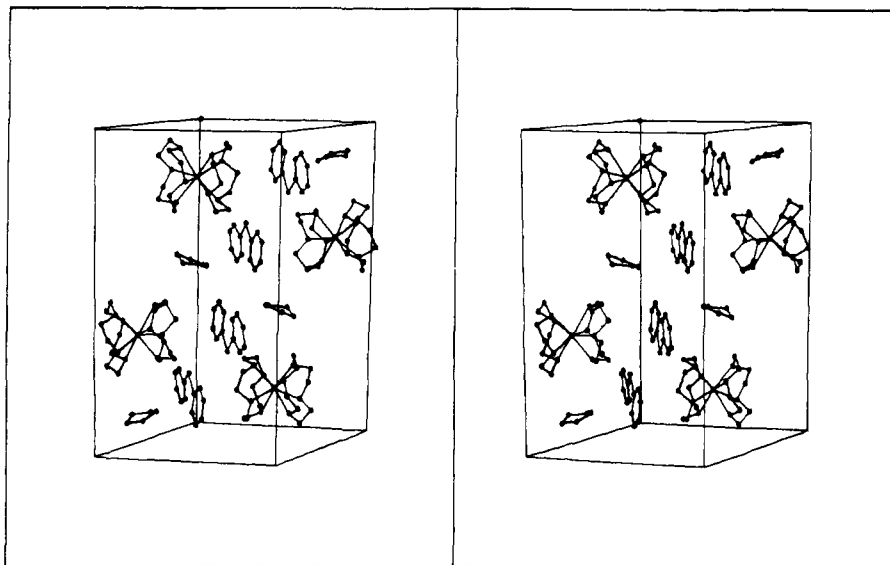


Figure 1. Stereoview of the unit cell of $[\text{Li}(12\text{-crown-4})_2][\text{AsPh}_2]\cdot\text{THF}$ (**2**) viewed between the b and c axes.

kali-metal diorganophosphides (formally MPR_2), which have been widely used as synthetic reagents in chemistry, may also exhibit two-coordination. However, detailed structures are unknown⁸ in either the solution or solid phases. ^{31}P NMR has shown that there are no free anions in THF solution, and chemical shift depends markedly on the cation.⁹ More recent work has suggested a dimeric structure for LiPPh_2 in ether¹⁰ while a tetrameric structure has been claimed for LiPPh_2 in THF solution.¹¹

Here we report the isolation and X-ray crystal structures of the first examples of two-coordinate diaryl anions of both phosphorus and arsenic. A major hindrance to structural studies has been the difficulty of obtaining suitable crystals. We overcame this problem by the addition of 2 equiv of 12-crown-4 to an ether solution of LiMPh_2 ($\text{M} = \text{P}$ or As), generated in situ from $n\text{-BuLi}$ and MHPPh_2 .¹² Recrystallization of the resultant precipitates from warm 4:1 THF/ether afforded yellow-orange crystals of $[\text{Li}(12\text{-crown-4})_2][\text{PPh}_2]$ (**1**) or $[\text{Li}(12\text{-crown-4})_2][\text{AsPh}_2]\cdot\text{THF}$ (**2**) in ca. 60% yield. Both **1** and **2** darkened on heating and softened at ca. 100 °C; **1** had fully melted by 122 °C while **2** was completely fused at 126 °C. In the molten state each compound was a red oil, which resolidified to an orange solid upon cooling.

The structures of both **1** and **2** were determined by X-ray diffraction.¹³ A stereoview of the unit cell of the arsenic com-

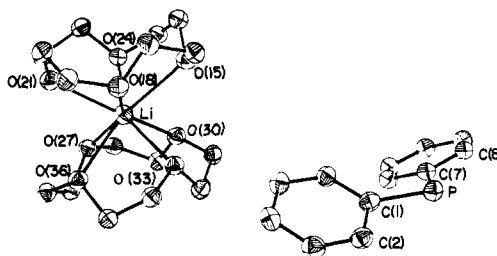


Figure 2. Thermal ellipsoid plot of $[\text{Li}(12\text{-crown-4})_2][\text{PPh}_2]$ (**1**).

pound, **2**, is shown in Figure 1. Apart from the arsabenzenes and the recently disclosed compounds with a multiply bonded arsenic,¹⁴ this is the only structurally characterized two-coordinate arsenic compound. The structure consists of well-separated non-interacting cations and anions as well as a tetrahydrofuran molecule of crystallization. The THF molecule is not associated with either the Li or As centers. The cation and anion are, perhaps, of equal interest structurally. For the cation, the Li^+ ion has the previously unknown coordination number of 8. As expected, the Li–O distances, ca. 2.35 Å, are unusually long.¹⁵ The LiO_8 unit has approximate D_{4d} symmetry. So far as we are aware, the X-ray structure of the $[\text{Li}(12\text{-crown-4})_2]^+$ cation is the first involving 12-crown-4.¹⁶ The puckered-sandwich arrangement of two separate crowns surrounding Li^+ giving a monomeric lithium complex has not been reported before, although related metal complexes are known with macrobicyclic¹⁷ and other¹⁸ ligands. The As–C distance, 1.972 (5) Å, is quite normal; the C–As–C angle is 108.6 (2)°. The major structural features of the phosphorus analogue, **1**, are very similar (Figure 2). The P–C distances are 1.811 (4) and 1.804 (4) Å, and C–P–C angle is 105.2 (2)°. The ^{31}P NMR spectrum of **1** in THF displayed a singlet at -6.9 (relative to 85% H_3PO_4 , external D_2O lock).

(5) Fleming, S.; Lupton, M. K.; Jekot, K. *Inorg. Chem.* **1972**, *11*, 2534–2540. Thomas, M. G.; Kopp, R. W.; Bond, A. C.; Parry, R. W. *Ibid.* **1976**, *15*, 3042–3046. Cowley, A. H.; Cushner, M. C.; Szobota, J. S. *J. Am. Chem. Soc.* **1978**, *100*, 7784–7785.

(6) Niecke, E.; Flick, W. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 585. Pohl, S. Z. *Naturforsch., B* **1977**, *32B*, 1344–1345. Becker, G. Z. *Anorg. Allg. Chem.* **1976**, *423*, 242–254; *430*, 67–76.

(7) Yoshifuji, M.; Shima, I.; Inamoto, N.; Hirotsu, K.; Higuchi, T. *J. Am. Chem. Soc.* **1981**, *103*, 4587–4589. Cowley, A. H.; Kilduff, J. E.; Norman, N. C.; Pakulski, M.; Atwood, J. L.; Hunter, W. E. *Ibid.* **1983**, *105*, 4845–4846. Flynn, K. M.; Hope, H.; Murray, B. D.; Olmstead, M. M.; Power, P. P. *Ibid.*, **1983**, *105*, 7750–1.

(8) During our work the X-ray structure of the tetranuclear compound $[\text{Li}_2(\mu_3\text{-}t\text{-Bu}_2\text{P})(\mu_2\text{-}t\text{-Bu}_2\text{P})(\text{C}_4\text{H}_8\text{O})_2]$ was reported. Jones, R. A.; Stuart, A. L.; Wright, T. C. *J. Am. Chem. Soc.* **1983**, *105*, 7459–60.

(9) Fluck, E.; Issleib, K. Z. *Anorg. Allg. Chem.* **1965**, *339*, 274–280. Fluck, E.; Issleib, K. Z. *Naturforsch., B* **1965**, *20B*, 1123–1124.

(10) Colquhoun, I. J.; McFarlane, H. C. E.; McFarlane, W. J. *Chem. Soc., Chem. Commun.* **1982**, 220–221.

(11) Zschunke, A.; Bauer, E.; Schmidt, H.; Issleib, K. Z. *Anorg. Allg. Chem.* **1982**, *495*, 115–119.

(12) 12-Crown-4 (dried over molecular sieves), $n\text{-BuLi}$ (Aldrich), PPh_2 , AsHPh_2 (Pressure Chemical Co.) were used as purchased.

(13) Crystal data with Cu $K\alpha$ radiation ($\lambda = 1.54178$ Å), $T = 140$ K: **1**, triclinic $P\bar{1}$, $a = 8.931$ (1) Å, $b = 12.174$ (2) Å, $c = 14.902$ (3) Å, $\alpha = 90.54$ (2)°, $\beta = 105.91$ (2)°, $\gamma = 109.45$ (1)°; $Z = 2$; $\mu = 12.1$ cm⁻¹; 5469 unique data (4472 had $I > 3\sigma I$), 344 parameters; $R = 0.074$. **2**, monoclinic $P2_1/n$, $a = 12.223$ (7) Å, $b = 23.155$ (13) Å, $c = 12.969$ (8) Å, $\beta = 117.53$ (5)°; $Z = 4$; $\mu = 19.8$ cm⁻¹; 6158 unique data (3979 had $I > 3\sigma I$); 389 parameters; $R = 0.065$.

(14) Cowley, A. H.; Lasch, J. G.; Norman, N. C.; Pakulski, J. J. *Am. Chem. Soc.* **1983**, *105*, 5506–5507. Cowley, A. H.; Lasch, J. G.; Norman, N. C.; Pakulski, M.; Whittlesey, B. R. *J. Chem. Soc., Chem. Commun.* **1983**, 881–882.

(15) Shannon, R. D.; Prewitt, C. T. *Acta Crystallogr., Sect. B* **1969**, *B25*, 925–946.

(16) Shoham, G.; Lipscomb, W. N.; Olsher, U. *J. Chem. Soc., Chem. Commun.* **1983**, 208–209. This paper describes the structure of a dibenzo-14-crown-4–LiSCN complex.

(17) Mallinson, P. R.; Truter, M. R. *J. Chem. Soc., Perkin Trans.* **1972**, *2*, 1818–1823.

(18) Pedersen, C. J. *J. Am. Chem. Soc.* **1970**, *92*, 386–94. Ellaboudy, A.; Dye, J. L.; Smith, P. B. *Ibid.* **1983**, *105*, 6490–1. Drew, M. G. B.; Esho, F. S.; Nelson, S. M. *J. Chem. Soc., Dalton Trans.* **1983**, 1653–1659. Hart, S. M.; Boeyens, J. C. A.; Michael, J. P.; Hancock, R. D. *Ibid.* **1981**, 1601–1606.

The angles at the group 5 elements in the diaryl anions are somewhat larger than those in the corresponding triaryls.^{19,20} The larger angle at arsenic compared with phosphorus is somewhat surprising as are the related smaller dihedral angles between the phenyls 11.2° (As) vs. 43.4° (P). It may be that due to the greater electropositive character of carbon relative to arsenic (electronegativity of As > P),²¹ the s character of the M-C bond is increased (and as a result the C-M-C angle) in accordance with Bent's rule.²² An increased angle at the group 5 element also allows closure of the dihedral angle. The normal P-C and As-C bond lengths suggest little or no π -interaction between the phenyl ring and the metalloid atom.

Although the above structural details are of significant interest, the most remarkable feature of **1** and **2** concerns the fact that crown ethers can be used to effect separation of the metal cation and organometalloid anion in both the solid state and in solution. Efforts are under way in this laboratory to extend this technique to the structural characterization of lithium salts of alkyls, aryls, silyls, amides, alkoxides, and thiolates having non-interacting organoanions and crown ether complexed metal ions.

Acknowledgment. We thank the Research Corporation and NSF (CHE-8116355) for generous financial support.

Supplementary Material Available: Listing of atom coordinates, temperature factors, bond distances, and angles of **1** and **2** and a stereoview of **1** (8 pages). Ordering information is given on any current masthead page.

(19) Trotter, J. *Acta Crystallogr.* **1963**, *16*, 1187-1189; *Can. J. Chem.* **1963**, *41*, 14-17. Springall, H. D.; Brockway, L. O. *J. Am. Chem. Soc.* **1938**, *60*, 996-1000.

(20) Daly, J. J. *J. Chem. Soc. A* **1966**, 1020.

(21) Both the Allred-Roachow and Sanderson electronegativities are significantly greater for arsenic. The Pauling electronegativities for P and As are very nearly equal. Huheey, J. E. "Inorganic Chemistry", 3rd ed.; Harper and Row: New York, 1983; p 146.

(22) Bent, H. A. *J. Chem. Educ.* **1960**, *37*, 616; *J. Chem. Phys.* **1960**, *33*, 1258-1261; *Chem. Rev.* **1961**, *61*, 275-311. Huheey, J. E. "Inorganic Chemistry", 3rd ed.; Harper and Row: New York, 1983; p 232.

Cis and Trans Isomers of Disilenes: Photochemical and Thermal Interconversions

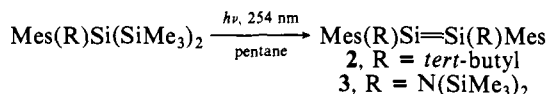
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The synthesis of tetramesityldisilene (**1**)¹ has opened the way to a new area of organosilicon chemistry.² We now report the synthesis of disilenes **2** and **3**, which exist as geometrical isomers, and observation of the facile cis-trans interconversions that they undergo.

Photolysis of 2-*tert*-butyl-2-mesitylhexamethyltrisilane at -80 °C produced more than 95% of the pale yellow disilene **2**, mostly



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(1) (a) West, R.; Fink, M. J.; Michl, J. *Science (Washington, D.C.)* **1981**, *214*, 1343. (b) Boudjouk, P.; Han, B.-H.; Anderson, K. R. *J. Am. Chem. Soc.* **1982**, *104*, 4992. (c) Masamune, S.; Hanazawa, Y.; Murakami, S.; Bally, T.; Blount, J. F. *Ibid.* **1982**, *104*, 1150. (d) Watanabe, H.; Okawa, T.; Kato, M.; Nagai, Y. *J. Chem. Soc., Chem. Commun.* **1983**, 781. (e) Masamune, S.; Murakami, S.; Tobita, H. *Organometallics* **1983**, *2*, 1464.

(2) Fink, M. J.; De Young, D. J.; West, R.; Michl, J. *J. Am. Chem. Soc.* **1983**, *105*, 1070. Zilm, K. W.; Grant, D. M.; Michl, J.; Fink, M. J.; West, R. *Organometallics* **1983**, *2*, 193.

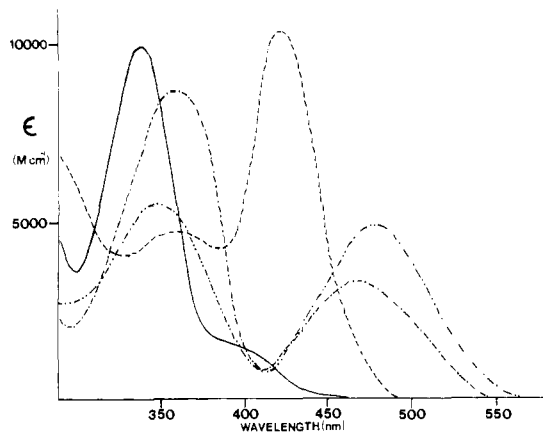
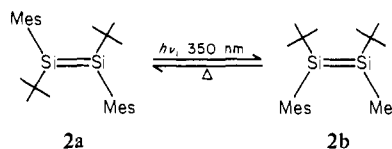


Figure 1. Electronic spectra of stable disilenes (in C₆H₆): (a) **2a** (—), (b) Mes₄Si₂ (---), (c) **3b** (-·-·-), (d) **3a** (- - - - -).

as the trans isomer **2a**.^{3,4} Compound **2a** gives a ²⁹Si NMR signal at +90.3 ppm, even more deshielded than the +63.6 ppm resonance for **1**. It exhibits UV maxima at ~400 (sh) and 338 nm (Figure 1). Irradiation at 350 nm leads to a photostationary equilibrium mixture containing 63% of **2a** and 37% of the cis isomer, **2b**.⁵ The isomerization can easily be followed by ¹H or



²⁹Si NMR; **2b** has its ²⁹Si resonance at +94.7 ppm.

The cis isomer **2b** is thermodynamically unstable, reverting back to the equilibrium mixture of **2a-2b**. At 25 °C in benzene this mixture contains 98% **2a** and 2% **2b**; the half-life for equilibration under these conditions is 570 ± 30 h.

Similar photolysis of 2-mesityl-2-(bis(trimethylsilyl)amino)-hexamethyltrisilane in pentane at -60 °C gives disilene **3** in 95% yield, mainly as the *unstable* isomer **3b**. Pure solid **3b** was obtained by evaporation of solvent and subsequent recrystallization from pentane at -78 °C. At 25 °C in benzene **3b** isomerized to the equilibrium mixture **3a:3b** = 94:6, with a half-time of 40 ± 3 h. Isomers **3a** and **3b** show ²⁹Si resonances at +61.9 and +6.8 ppm and +49.4 and +6.2 ppm, respectively.⁶ The isomers cannot be identified decisively at this time, but by analogy with the behavior of **2a**, **2b** we tentatively assign **3a** as trans and **3b** as cis. The more rapid cis-trans interconversion in **3a-3b** may reflect weakening of the Si-Si π bond by electron donation from nitrogen, as is observed also for C-C double bonds substituted with π -electron-donating atoms.⁷

Disilenes **1**, **2**, and **3** all show distinctively different properties. Compound **1** is bright yellow and reversibly thermochromic, undergoing transformation to a red color when heated as a solid.

(3) **2a**: ¹H NMR (C₆D₆) δ 1.13 (s, 18 H, *t*-Bu), 2.13 (s, 6H, para CH₃), 2.88 (s, 12 H, ortho CH₃), 6.90 (s, 4 H, ArH); MS, 408 (M⁺, 52%), 351 (M - *t*-B, 10%). Exact mass for C₂₆H₄₀Si₂ calcd *m/e* 408.2658, found *m/e* 408.2671.

(4) The trans structure for **2a** was established by X-ray crystallography: Fink, M. J.; Michalczyk, M. J.; Haller, K. J.; Michl, J.; West, R. *Organometallics*, submitted for publication.

(5) **2b**: ¹H NMR (C₆D₆) δ 1.40 (s, 18 H, *t*-Bu), 1.88 (s, 6 H, para CH₃), 2.71 (s, 12 H, ortho CH₃), 6.65 (s, 4 H, ArH). A UV spectrum of the mixture of **2a** and **2b** shows a slight shift of the principal absorption band to shorter wavelength, indicating that **2b** has $\lambda_{\text{max}} \sim 332$ nm.

(6) **3a**: ¹H NMR (C₆D₆) δ 0.20 (s, 36 H, SiMe₃), 2.10 (s, 6H, para CH₃), 2.80-3.05 (br, 12 H, ortho CH₃), 6.90-6.95 (br, 4 H, Ar H); UV-vis (C₆H₆) $\lambda_{\text{max}} = 351, 483$ nm. **3b**: ¹H NMR (C₆D₆) δ 0.39 (s, 36 H, SiMe₃), 1.91 (s, 6 H, para CH₃), 2.58 (s, 12 H, ortho CH₃), 6.62 (s, 4 H, Ar H); UV-vis (C₆H₆) $\lambda_{\text{max}} = 362, 468$ nm; MS (**3b**) 614 (M⁺, 21%), 599 (M - CH₃, 0.7%), 526 (M - (CH₃)₂Si, 1.2%), 511 [M - (CH₃)₂Si - CH₃, 9.5%]. Exact Mass for C₃₀H₅₈N₂Si₆ calcd *m/e* 614.3200, found *m/e* 614.3214.

(7) Kalinowski, H.-O.; Kessler, H. In "Topics in Stereochemistry"; Allinger, N. L., Eliel, E. L., Eds.; Wiley: New York, 1973; Vol. VII, p 310.