Ligand dependence of π-complex character in disilene–palladium complexes†

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The synthesis and structures of new 16-electron disilene palladium complexes with 2,6-dimethylphenyl isocyanide and phenyldimethylphosphine ligands [$L^1L^2Pd\{(t\text{-}BuMe_2Si)_2Si=Si(SiMe_2Bu\text{-}t)_2\}$], where $L^1 = L^2 = PhMe_2P$; $L^1 = $ (cyclohexyl)$_3$P, $L^2 = $ 2,6-dimethylphenyl isocyanide; $L^1 = L^2 = $ 2,6-dimethylphenyl isocyanide] are described. Comparison of the X-ray structural parameters around the disilene moiety among these complexes and related bis(trimethylphosphine)(disilene)palladium and 14-electron (tricyclohexylphosphine)(disilene)palladium revealed that the π-complex character is sensitive to the residual ligands and increases with decreasing the strength of σ-donation from the ligands.

Introduction

The bonding of an alkene to a transition metal center in alkene transition metal complexes[1] is usually understood in terms of alkene-to-metal σ-donation and metal-to-alkene π-back donation, according to the Dewar–Chatt–Duncanson model.[2] The structure of an alkene complex is significantly influenced by the relative importance between the σ-donation and the π-back donation, and hence, they are classified into either a π-complex having major contribution of σ-donation or a metallacycle having dominant π-back donation. The geometry around the alkene ligand in the π-complex is not very much different from that of the free alkene, while that in the metallacycle is significantly distorted and characterized by an elongated C^1–C^2 bond length (d) and a large bent angle (θ) defined by the angle between the R^1–C^1–R^2 (or R^3–C^2–R^4) plane and the C^1–C^2 bond (Chart 1).[3]
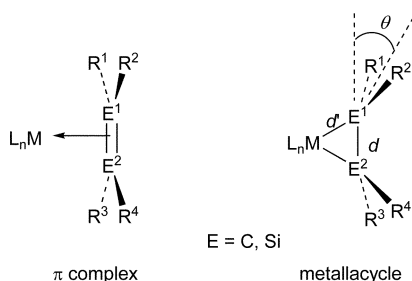

Chart 1 Qualitative bonding description of alkene and disilene complexes.

Much attention has been focused recently on the structure of transition metal complexes with η²-silicon–silicon doubly bonded species as ligands (disilene complexes).[4–8] A variety of isolable η²-disilene complexes of platinum,[4,5a] palladium,[5b,c] tungsten,[6] molybdenum,[6] iron,[7] and zirconium[8] have been synthesized and

some of them have been investigated by X-ray crystallography. We have recently synthesized 16-electron platinum and palladium complexes with a silyl-substituted η²-disilene ligand **1–3**[5a,b] and 14-electron disilene complex **4**[5c] using the reactions of the corresponding bis(phosphine)dichlorometals with 1,2-dilithiotetrakis(*tert*-butyldimethylsilyl)disilane **5**,[9] which was prepared by the reaction of stable disilene **6**[10] with lithium in THF (eqn (1)–(3)).

$$\text{(1)}$$

$$\text{(2)}$$

$$\text{(3)}$$
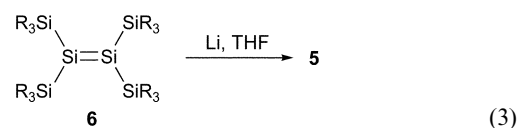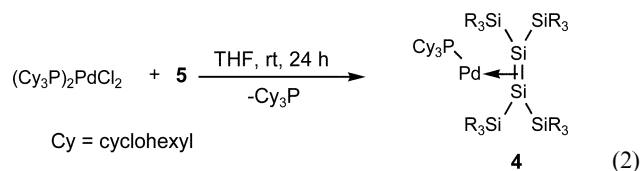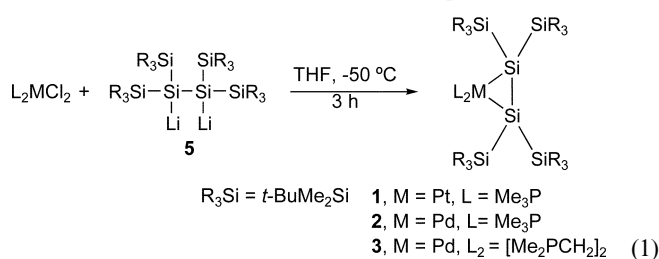
In contrast to alkene complexes, most of the disilene complexes whose X-ray structures are known[4–7] are characterized as metallacycles, by applying the Dewar–Chatt–Duncunson type bonding scheme to the disilene complexes. However, the character may depend on the central metal, ligands, and substituents on disilene. Actually, we have found that 16-electron disilene palladium complex **2** has slightly larger π-complex character than the corresponding platinum complex **1**.[5b] The first 14-electron disilene palladium complex **4** has stronger π-complex character than the related 16-electron complexes **2** and **3**.[5c]

We wish herein to report the synthesis and structures of new 16-electron disilene palladium complexes with 2,6-dimethylphenyl isocyanide (**7**) and phenyldimethylphosphine as the residual

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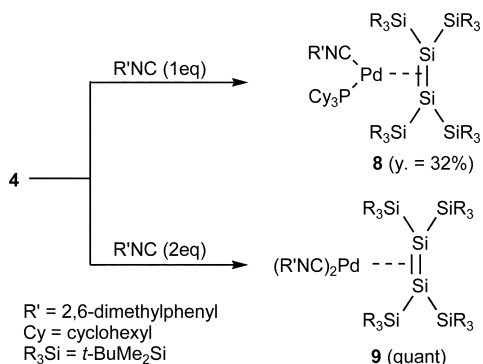
ligands. Comparison of the structural parameters around the disilene moiety revealed that the π-complex character depends remarkably on the residual ligands.

Results and discussion

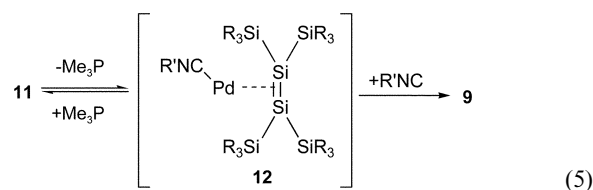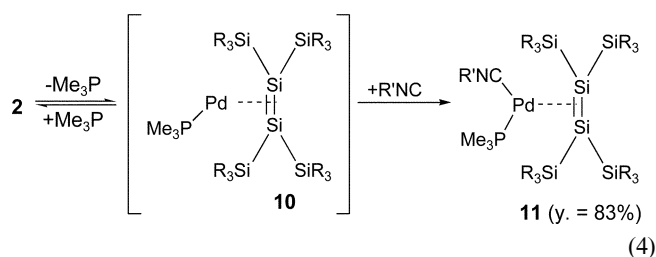### Synthesis of new 16-electron disilene palladium complexes

Very few reactions of disilene transition metal complexes have been reported to date. Disilene–platinum complexes synthesized by Pham and West react with small molecules like oxygen, hydrogen, and methanol to afford the corresponding Si–Si or Si–Pt bond cleavage products.[4] Berry *et al.* have revealed that the Si–Si and Si–metal bonds of molybdenum and tungsten complexes of tetramethyldisilene show high reactivity toward methanol, carbon dioxide and triphenylphosphine sulfide.[6] However, there have been no ligand exchange reactions of disilene complexes reported. We have found the reactions of disilene palladium complexes **2** and **4** with isocyanide **7** to afford the corresponding disilene complexes with isocyanide ligands; the disilene ligand remains intact during the reactions.

The reactions of 14-electron complex **4** with 1 and 2 equivalents of isocyanide **7** gave mono(isocyanide) complex **8** and bis(isocyanide) complex **9**, respectively (Scheme 1).

$$\begin{array}{c} \text{R'NC (1eq)} \longrightarrow \mathbf{8}\ (\text{y.} = 32\%) \\ \mathbf{4} \\ \text{R'NC (2eq)} \longrightarrow \mathbf{9}\ (\text{quant}) \end{array}$$

R' = 2,6-dimethylphenyl
Cy = cyclohexyl
R_3Si = t-$BuMe_2Si$

Scheme 1 Synthesis of disilene complexes with isocyanide ligands.

Interestingly, the reactions of 16-electron complex **2** with 1 and 2 equivalents of isocyanide **7** also gave new mono(isocyanide) complex **11** in 83% isolation yield and **9** in quantitative yield, respectively. The result suggests that 16-electron complex **2** exists in equilibrium with 14-electron complex **10** and dissociated trimethylphosphine (eqn. (4) and (5)); the subsequent dissociation of trimethylphosphine from **11** followed by the addition of the isocyanide will give bis(isocyanide) complex **9**. Because no 14-electron complexes **10** and **12** were detected in solution by NMR spectroscopy, the concentration of **10** and **12** in the equilibrium will be very low.

$$\mathbf{2} \underset{+Me_3P}{\overset{-Me_3P}{\rightleftharpoons}} \mathbf{10} \overset{+R'NC}{\longrightarrow} \mathbf{11}\ (\text{y.} = 83\%) \tag{4}$$

$$\mathbf{11} \underset{+Me_3P}{\overset{-Me_3P}{\rightleftharpoons}} \mathbf{12} \overset{+R'NC}{\longrightarrow} \mathbf{9} \tag{5}$$

To elucidate the electronic effects of phosphine ligands on the π-complex character of the 16-electron complex **2**, complex **13** was synthesized by the conventional method[5,11] (eqn (6)).

$$(PhMe_2P)_2PdCl_2^+ \ \mathbf{5} \xrightarrow[\text{3 h}]{\text{THF, -50 °C}} \mathbf{13} \tag{6}$$
$$\mathbf{14}$$
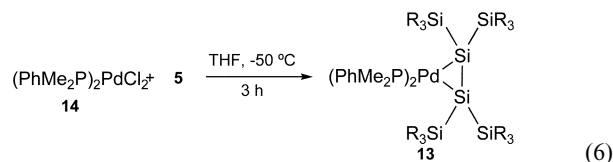
Molecular structures of 16-electron disilene complexes

Molecular structures of disilene palladium complexes **8**, **9** and **13** determined by X-ray crystallography are shown in Fig. 1–3. The structural parameters are listed in Table 1 together with those for disilene complexes **2**, **3** and **4**.[12] Because mono(isocyanide) complex **8** showed two crystallographically independent molecules in an asymmetric unit, two sets of parameters are shown in the table.

The Si(1)–Si(2) bond distances (*d*) of all the disilene palladium complexes (2.273–2.3180 Å) lie below the shortest limit of the reported Si–Si single bond (2.335–2.697 Å) but depend significantly on the ligands.[13] The central palladium atom of the disilene complexes **8**, **9** and **13** adopts highly distorted square planar geometry with the angle between Si^1–Pd–Si^2 and L^1–Pd–L^2 planes (φ in Table 1) of 36.4 (31.1), 20.0 and 31.0°, respectively; the angle φ for **2** and **3** is 31.8 and 28.5°, respectively,[5b] while the geometry around palladium in the 14-electron disilene complex **4** is almost planar.[5d] Steric repulsion between bulky trialkylsilyl substituents and other ligands could be responsible for the distorted geometry. The extent of the steric repulsion for **9** with less bulky isocyanide ligands is much smaller than that for other 16-electron disilene complexes. The Si–Pd distances (*d*$_1$ and *d*$_2$, 2.360–2.460 Å) are a little longer than those of reported bis(phosphine)(disilyl)palladium complexes (2.34–2.38 Å).[14]

The bent angles (θ_1 and θ_2), which are defined as an angle between the Si$^{1(2)}$–Si$^{2(1)}$–R plane and the Si^1–Si^2 bond, are larger than that of free disilene **6** (0.1°)[10] but the extent depends remarkably on the ligands. The bond elongation estimated by $\Delta d/d_0$ values ($\Delta d = d - d_0$, where d_0 is the Si1–Si2 bond length of free disilene **6**[10]), is not very sensitive to the ligands on palladium but decreases in the order of **3** > **2** > **13** > **8** (av.) ~ **9** > **4**. On the other hand, the *averaged bent angles* ($\theta_{av.}$) are significantly affected by the ligands and decrease in almost the same order as the bond elongation; **3** ~ **2** > **13** > **8** (av.) > **9** > **4**.[15]

If the Dewar–Chatt–Duncanson model is applicable to disilene complexes, the $\Delta d/d_0$ value and θ value should decrease with increasing the π-complex character of the disilene complexes. On the basis of this criterion, the π-complex character is evaluated to decrease in the following order: **4** > **9** > **8** (av.) > **13** > **2** ~ **3**. As shown in a previous paper,[5c] the π-back donation in 14-electron disilene complex **4** is the smallest because one basic ligand on
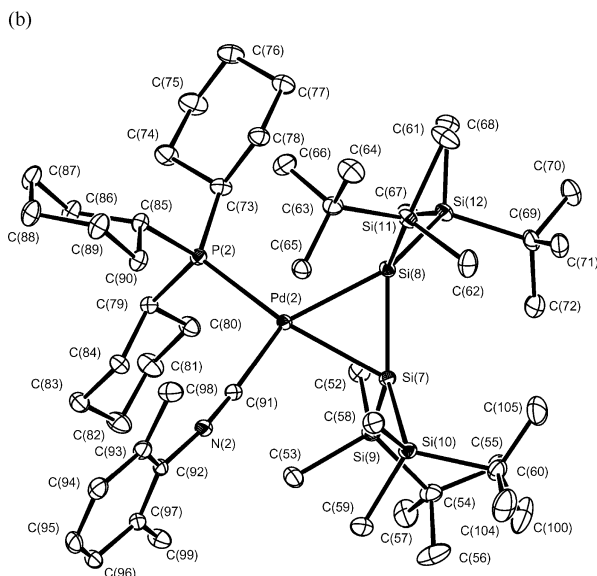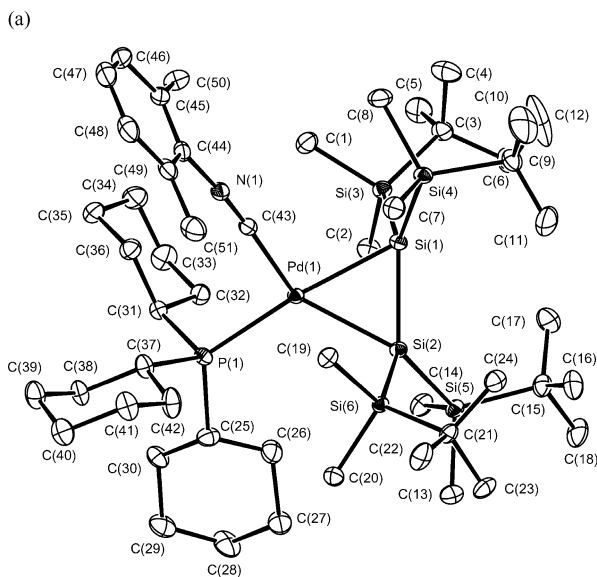
(a)

(b)

Fig. 1 Molecular structure of complex **8**. Two crystallographically independent molecules were observed in an asymmetric unit: (a) molecule 1, (b) molecule 2. Thermal ellipsoids are shown in the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Pd(1)–Si(1) 2.4597(8), Pd(1)–Si(2) 2.4581(9), Si(1)–Si(2) 2.2861(11), Pd(1)–P(1) 2.4437(8), Pd(1)–C(43) 1.989(3); Si(1)–Pd(1)–Si(2) 55.40(3), Pd(1)–Si(1)–Si(2) 62.26(3), Pd(1)–Si(2)–Si(1) 62.33(3), P(1)–Pd(1)–C(43) 96.06(9), Pd(2)–Si(7) 2.4603(8), Pd(2)–Si(8) 2.4264(8), Si(7)–Si(8) 2.2967(11), Pd(2)–P(2) 2.4352(8), Pd(2)–C(91) 2.001(3), Si(7)–Pd(2)–Si(8) 56.06(3), Pd(2)–Si(7)–Si(8) 61.22(3), Pd(2)–Si(8)–Si(7) 62.72(3), P(2)–Pd(2)–C(91) 96.48(9).

palladium is missing. The σ-donor ability of ligands is expected to decrease in the order of $Me_3P > PhMe_2P > R'NC$ on the basis of the basicity of the ligands. Thus, the π-back donation from the metal will increase in the order of **4 < 9 < 8 < 13 < 2 ∼ 3**. As expected, the order is in good accord with the observed order for the π-complex character.

The π-complex character of unsymmetrically substituted 16-electron disilene complex **8** is between those of **2** and **9**, suggesting
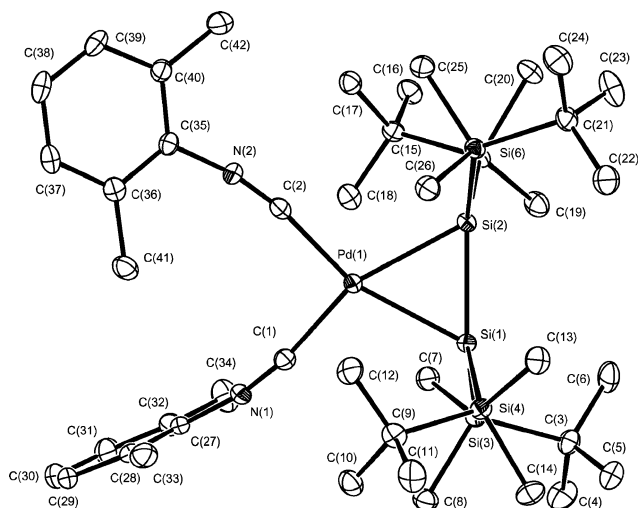

Fig. 2 Molecular structure of complex **9**. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Pd(1)–Si(1) 2.4340(11), Pd(1)–Si(2) 2.4411(11), Si(1)–Si(2) 2.2891(14), Pd(1)–C(1) 2.014(4), Pd(1)–C(2) 2.029(4); Si(1)–Pd(1)–Si(2) 56.01(4), Pd(1)–Si(1)–Si(2) 62.15(4), Pd(1)–Si(2)–Si(1) 61.84(4), C(1)–Pd(1)–C(2) 97.59(15).
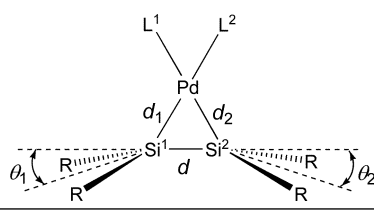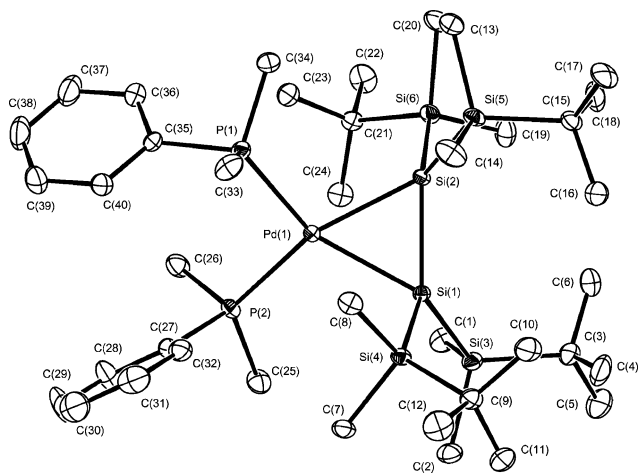

Fig. 3 Molecular structure of complex **13**. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Pd(1)–Si(1) 2.6432(10), Pd(1)–Si(2) 2.4287(10), Si(1)–Si(2) 2.2952(13), Pd(1)–P(1) 2.3574(10), Pd(1)–P(2) 2.3566(10); Si(1)–Pd(1)–Si(2) 55.96(3), Pd(1)–Si(1)–Si(2) 61.26(3), Pd(1)–Si(2)–Si(1) 62.78(3), P(1)–Pd(1)–P(2) 101.14(4).

the additivity of the extent of the σ-donation to the metal. It is expected that because of stronger *trans* influence of phosphine than isocyanide, the bent angle around an unsaturated silicon atom of complex **8** located at the *trans* position (θ_1) to tricyclohexylphosphine should be much larger than that for the other unsaturated silicon atom (θ_2). In reality, θ_1 and θ_2 in complex **8** are 5.2 (3.0) and 20.6 (36.5)°, respectively; θ_1 is much smaller than θ_2, in contrast to the above expectation. The incompatibility between the expectation and the experimental results should not be ascribed to the steric effects of bulky tricyclohexylphosphine, because the geometrical characteristics for **8** was reproduced qualitatively by the theoretical calculations for a model disilene palladium complexes (*vide infra*).

**Table 1** Comparison of structural parameters of various disilene palladium complexes (R = t-BuMe$_2$Si)

Compound	L¹	L²	d/Å	Δd/Å (%$\Delta d/d_0$)[a]	θ_1/°	θ_2/°	θ_{av}[b]/°	d_1/Å	d_2/Å	φ[c]/°	δ(^{29}Si)
2	PMe₃	PMe₃	2.3027(8)	0.101(5.2)	27.2	27.2	27.2	2.4369(5)	2.4369(5)	31.8	−46.5
3	Me₂PCH₂CH₂PMe₂		2.3180(8)	0.118(4.6)	27.3	27.3	27.3	2.4184(4)	2.4184(4)	28.5	−51.9
13	PhMe₂P	PhMe₂P	2.2952(13)	0.093(4.2)	14.4	26.8	20.6	2.4632(10)	2.4287(10)	31.0	−44.8
8 (mol. 1)	R′NC[d]	Cy₃P	2.2861(11)	0.085(3.9)	5.2	20.6	12.9	2.4597(8)	2.4581(9)	36.4	−39.4, −60.4
8 (mol. 2)	R′NC[d]	Cy₃P	2.2967(11)	0.094(4.3)	3.0	36.5	19.8	2.4603(8)	2.4264(8)	31.1	—
9	R′NC[d]	R′NC[d]	2.289(2)	0.087(4.0)	9.5	8.9	9.2	2.4340(11)	2.4411(11)	20.0	−41.2
4	Cy₃P	—	2.273(1)	0.072(3.3)	4.4	9.7	7.0	2.3610(9)	2.4168(8)	—	+65.3

[a] d_0 is the Si=Si distance in free (t-BuMe$_2$Si)$_2$Si=Si(SiMe$_2$Bu-t)$_2$ (2.202 (1) Å).[10] $\Delta d = d - d_0 = d - 2.202$. Standard deviations of %$\Delta d/d_0$ and θ are estimated to be at most 0.13 and 0.05°, respectively. [b] $\theta_{av} = (\theta_1 + \theta_2)/2$. [c] Dihedral angle between plane (L¹–Pd–L²) and plane (Si–Pd–Si). [d] R′ = 2,6-dimethylphenyl.

Interestingly, even symmetrically substituted disilene complexes **9** and **13** showed two different bent angles and Pd–Si distances. The results may be attributed to the fact that the steric and electronic environments around two unsaturated silicon atoms in these complexes are different to each other in the solid state because the two residual ligands in complex **9** or **13** adopt the different rotational conformations.

To evaluate the steric effects on the bent angles θ_1 and θ_2, theoretical calculations were performed for model 16-electron disilene–palladium complexes **8′** and **9′** at the B3LYP/6-31G* level (Chart 2).[16,17] The θ values for **2′**[5c] **8′** and **9′** are 27.9, 25.3 (av.) and 22.4, and %$\Delta d/d_0$ values for **2′**, **8′** and **9′** are 4.3, 4.4 and 4.1, respectively. Despite the geometry around palladium of all these model complexes is planar (torsion angles φ are less than 5°), the orders of θ and %$\Delta d/d_0$ values are well in accord with those for a set of **2**, **8** and **9**. The bent angle θ_{av} and the bond elongation $\Delta d/d_0$ may serve as good indices for the π-complex character of disilene complexes, even though disilene complexes are distorted significantly from the ideal square planar geometry.

As shown in Table 1, θ_1 is unexpectedly much smaller than θ_2 for unsymmetrically substituted disilene complex **8**. The unsymmetrical distortion is not ascribed to the steric hindrance between ligands, because the tendency was reproduced in less hindered model complex **8′** with θ_1 and θ_2 of 19.6 and 31.0°, respectively. Because θ_1 is larger than θ_2 in 14-electron disilene complex **4** whose fourth ligand is missing, sole smaller σ donor ability of aryl isocyanide than trialkylphosphine cannot explain the unsymmetrical distortion in **8** and **8′**. Further work is required to elucidate the origin of the unsymmetric bent angles in **8**.
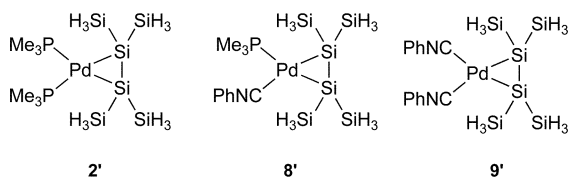
Chart 2

We have recently shown 14-electron disilene complexes **4** show the ^{29}Si resonance at very low field of +65.3 ppm compared to those of 16-electron disilene complexes **2** (−46.5 ppm) and **3** (−51.9 ppm) and the very low field resonance was taken to be an indication of the strong π-complex character.[5c] Although the ^{29}Si resonance of the unsaturated silicon nuclei for **9** (−41.2 ppm) appears at a little lower field than those for **2** and **3**, the extent of the down-field shift for **9** is much smaller than that observed for **4**. The remarkable low-field shift of the ^{29}Si resonance of **4** is characteristic of 14-electron, three-coordinate complexes.

Conclusion

We have shown that the π-complex character of disilene transition metal complexes is significantly modified by the residual ligands. The π-complex character in L₂Pd(disilene)-type 16-electron complexes remarkably increases by changing L from trialkylphosphine to aromatic isocyanide with poorer σ-donating ability, while the π-complex character is smaller than that of the previously reported 14-electron disilene complex having one trialkylphosphine ligand.

Experimental

^{1}H, ^{13}C, ^{29}Si and ^{31}P NMR spectra were recorded on a Bruker AC300P FT-NMR spectrometer at 300, 75.4, 59.6 and 121 MHz, respectively, and a Bruker Avance 400P FT-NMR spectrometer at 400, 100, 79 and 161 MHz, respectively. Mass spectra and high resolution mass spectra were recorded on a HX-110 mass spectrometer (FAB, nitrobenzyl alcohol matrix). Air-sensitive compounds were manipulated in a VAC Nexus 100027 glove box. cis-Bis(phenyl isocyanide)dichloropalladium,[18] tetrakis($tert$-butyldimethylsilyl)disilene (**6**)[10] and 1,2-dilithiotetrakis($tert$-butyldimethylsilyl)disilane (**5**)[9] were prepared according to the procedure in the literature.

[η²-Tetrakis(*tert*-butyldimethylsilyl)disilene](2,6-dimethylphenyl isocyanide)(tricyclohexylphosphine)palladium 8

To a mixture of disilene complex **4** (0.070 g, 0.077 mmol) and isocyanide **7** (0.010 g, 0.076 mmol) in a degassed Schlenk flask (50 cm³) was introduced dry THF (5 cm³) through a vacuum line at −50 °C. Increasing the temperature from −50 °C to rt during 4.5 h resulted a clear yellow solution. Evaporation of THF and then recrystallization from toluene at −20 °C afforded mono(isocyanide) complex **8** (0.080 g, 0.025 mmol) in 32% yield. **8**: Found: C, 59.07; H, 9.88. $C_{51}H_{102}PNPdSi_6$ requires C, 59.17; H, 9.93%; mp 145 °C (decomp.); δ_H (400 MHz, C_6D_6) 0.47 (s, 6 H), 0.51 (s, 6 H), 0.56 (s, 6 H), 0.63 (s, 6 H), 1.23–2.16 (m, 33 H), 1.29 (s, 18 H), 1.33 (s, 18 H), 2.43 (s, 6 H), 6.63 (d, J = 7.6 Hz, 2 H), 6.73 (dd, J = 7.6 Hz, 1 H); δ_C (100 MHz, THF-d_8) 1.1, 1.4, 1.6, 1.7 (SiCH_3), 17.7 ($C_{Ar}CH_3$), 18.5, 18.7 ($C(CH_3)_3$), 25.4 ($PCHCH_2CH_2CH_2$), 26.7 (d, $^2J_{P-C}$ = 10 Hz, PCHCH_2), 28.2, 28.3 ($C(CH_3)_3$), 30.0 ($PCHCH_2CH_2$), 33.0 (d, $^1J_{P-C}$ = 6 Hz, PCH), 126.8 (C_{ipso}), 127.2 ($C_{Ar(m)}$), 127.3 ($C_{Ar(p)}$), 132.6 ($C_{Ar(o)}$), 164.1 (C≡N); δ_{Si} (79 MHz, C_6D_6) −60.4 (d, $^2J_{P(cis)-Si}$ = 15 Hz), −39.4 (d, $^2J_{P(trans)-Si}$ = 48 Hz), +4.97, +4.99, 5.8, 5.9; δ_P (161 MHz, C_6D_6) +30.9.

[η²-Tetrakis(*tert*-butyldimethylsilyl)disilene]bis(2,6-dimethylphenyl isocyanide)palladium 9

To a mixture of disilene complex **4** (7.0 mg, 7.7 × 10⁻³ mmol) and isocyanide **7** (2.0 mg, 1.5 × 10⁻² mmol) in a degassed NMR tube (5 mm ϕ) was introduced dry benzene-d_6 (0.4 cm³) through a vacuum line at −50 °C. Quantitative formation of bis(isocyanide) complex **9** was confirmed by ¹H, ²⁹Si and ³¹P NMR spectroscopies. Evaporation of benzene-d_6 and recrystallization from toluene at −20 °C gave **9** as orange plates. **9**: mp 136 °C (decomp.); δ_H (400 MHz, C_6D_6) 0.56 (s, 12 H), 0.59 (s, 12 H), 1.30 (s, 36 H), 2.28 (s, 12 H), 6.65 (d, J = 7.6 Hz, 4 H), 6.77 (dd, J = 7.6 Hz, 2 H); δ_C (100 MHz, THF-d_8) 1.4, 1.6 (SiCH_3), 17.5 ($C_{Ar}CH_3$), 18.1 ($C(CH_3)_3$), 28.3 ($C(CH_3)_3$), 126.3 (C_{ipso}), 127.1 ($C_{Ar(m)}$), 127.7 ($C_{Ar(p)}$), 133.3 ($C_{Ar(o)}$), 161.6 (C≡N); δ_{Si} (79 MHz, C_6D_6) −41.2, +6.6.

[η²-Tetrakis(*tert*-butyldimethylsilyl)disilene](2,6-dimethylphenyl isocyanide)(trimethylphosphine)palladium 11

To a mixture of 16-electron disilene complex **2** (0.100 g, 0.129 mmol) and isocyanide **7** (0.017 g, 0.130 mmol) in a degassed Schlenk flask (50 cm³) was introduced dry toluene (5 cm³) through a vacuum line. Stirring the resulting light orange solution for 16 h at rt, distilling off the solvent, and recrystallization from hexane at −20 °C gave **11** (0.089 g, 0.107 mmol) as orange prisms in 83% yield. **11**: δ_H (400 MHz, C_6D_6) 0.46 (s, 6 H), 0.47 (s, 6 H), 0.51 (s, 6 H), 0.56 (s, 6 H), 1.23 (d, $^2J_{P-H}$ = 6 Hz, 9 H), 1.25 (s, 18 H), 1.27 (s, 18 H), 2.27 (s, 6 H), 6.67 (d, J = 7.0 Hz, 2 H), 6.76 (dd, J = 7.0 Hz, 1 H); δ_C (100 MHz, THF-d_8) 1.2 (br), 1.3, 1.4 (SiCH_3), 17.6 ($C_{Ar}CH_3$), 18.3 (d, $^1J_{P-C}$ = 3 Hz, PCH_3), 18.4, 18.5 ($C(CH_3)_3$), 28.2, 28.3 ($C(CH_3)_3$), 126.7 (C_{ipso}), 127.2 ($C_{Ar(m)}$), 127.4 ($C_{Ar(p)}$), 132.9 ($C_{Ar(o)}$), 163.1 (C≡N); δ_{Si} (79 MHz, C_6D_6) −48.0 (d, $^2J_{P(cis)-Si}$ = 17 Hz), −44.7 (d, $^2J_{P(trans)-Si}$ = 60 Hz), 5.8, 5.9, 6.0, 6.1; δ_P (161 MHz, C_6D_6) −31.4 (m).

Stepwise ligand exchange of disilene complex 2 with isocyanide 7 followed by NMR spectroscopy

When disilene complex **2** (10 mg, 1.5 × 10⁻⁵ mol) and isocyanide **7** (2.0 mg, 1.5 × 10⁻⁵ mol) were dissolved in benzene-d_6 in an NMR tube, ¹H NMR spectrum of the mixture showed the existence of **2** and mono(isocyanide) complex **11** in 1 : 4 ratio. Addition of isocyanide **7** (2.0 mg, 1.5 × 10⁻⁵ mol) to the resulting solution afforded bis(isocyanide) complex **9** almost quantitatively as observed by ¹H NMR spectroscopy.

cis-Bis(dimethylphenylphosphine)dichloropalladium 14

To a benzene (10 cm³) solution of *cis*-bis(phenyl isocyanide)-dichloropalladium[17] (0.472 g, 1.23 mmol) in a Schlenk flask (50 cm³) was added dimethylphenylphosphine (0.4 cm³, 2.8 mmol). The red solution was stirred for 40 min and then the solvent was distilled off. Recrystallization of the resulted sticky solid from benzene afforded **14** as orange needles in the yield of 0.540 g (1.19 mmol, 97%).

[η²-Tetrakis(*tert*-butyldimethylsilyl)disilene]bis-(dimethylphenylphosphine)palladium 13

To a mixture of palladium dichloride **14** (0.102 g, 0.293 mmol) and 1,2-dilithiodisilane **5** (0.157 g, 0.296 mmol) in a degassed Schlenk flask (50 cm³) was introduced THF (5 ml) dried over K mirror through a vacuum line. The mixture was stirred for 2 h at rt and then THF was distilled off. Addition of toluene (40 cm³) to the yellow–brown residue and then the resulting precipitate was filtered off. Removal of toluene *in vacuo* and then recrystallization from toluene at −20 °C gave **13** (0.035 g, 0.04 mmol) in 20% yield. **13**: mp 148 °C (decomp.); δ_H (400 MHz, C_6D_6) 0.49 (s, 12 H), 0.54 (s, 12 H), 1.25 (s, 36 H), 1.38 (d, $^2J_{P-H}$ 4.8 Hz, 12 H), 7.00 (dd, 4 H), 7.07 (d, 2 H), 7.47 (dd, 4 H); δ_C (100 MHz, THF-d_8) 3.1, 3.3 (SiCH_3), 20.1 (Si$C(CH_3)_3$), 20.8 (dd, $^1J_{P-C}$ 11 Hz, P(CH_3)₃), 30.2 (C(CH_3)₃), 128.9 (dd, $^3J_{P-C}$ = 4 Hz, $^5J_{P-C}$ = 2 Hz, $C_{Ar(m)}$), 129.4 ($C_{Ar(p)}$), 131.5 (dd, $^2J_{P-C}$ = 6 Hz, $^4J_{P-C}$ = 4 Hz, $C_{Ar(o)}$), 141.9 (dd, $^1J_{P-C}$ = 12 Hz, $^2J_{P-C}$ = 5 Hz, C_{ipso}); δ_{Si} (79 MHz, C_6D_6) −44.8 (dd, $^2J_{P(cis)-Si}$ = 21 Hz, $^2J_{P(trans)-Si}$ = 80 Hz), +4.8; δ_P (161 MHz, C_6D_6) −19.0.

Crystallography

Single crystals of complexes **8**, **9** and **13** were obtained by recrystallization from toluene, mounted in Apiezon grease and transferred to the cold gas stream of the diffractometer. X-Ray data were collected on a Rigaku/MSC Mercury CCD diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). The data were corrected for Lorentz and polarization effects. The structures were solved by direct methods and refined by full-matrix least squares against F^2 using all data (SHELXL-97).[19]

In the single crystal of complex **8**, two crystallographically independent molecules (molecule 1 and molecule 2) exists in an asymmetric unit. In molecule 1, one *t*-BuMe₂Si group on Si(2) is disordered over two sites with occupancies 0.862(3) [central silicon atom: Si(6)] and 0.138(3) [central silicon atom: Si(13)]. All *tert*-butyl and methyl carbon atoms on minor Si(13) were refined with isotropic displacement parameters.

Acknowledgements

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