Kinetically Stabilized *P,Si*-Chelate Metal Complexes: Isolation, Isomerization, and X-ray Structural Analysis

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Received June 23, 2000

*Summary: A series of kinetically stabilized trans bis-chelate metal complexes, trans-(Cab^{P,Si})$_2$M (M = Pt **4**; M = Pd **7a**), bearing bulky o-carboranylphosphine tethers, have been synthesized from the reaction of the phosphinosilanes **2** with d^{10} metal complexes. In the presence of dimethyl acetylenedicarboxylate (DMAD), the trans isomer **4** thermally rearranges to the thermodynamically favored cis isomer, cis-(Cab^{P,Si})$_2$Pt **5**.*

Phosphinoalkylsilanes used as chelate ligands for a wide range of oxidative addition reaction processes with transition metals[1] have been studied in considerable detail, principally for a better understanding of the important metal-catalyzed industrial reactions such as hydrosilylation.[2] Although many examples of bis-chelate metal complexes possessing a *cis*-arrangement of the phosphinoalkylsilyl ligands in a typical square-planar M(II) (M = Pd, Pt) environment have been synthesized[3] and subsequently evaluated in the above context, comparatively few *trans* bis-chelates[3c] have received scrutiny due to their inaccessibility. As an extension of our ongoing investigations of the chemical behavior of the metal silyl complexes based on the *o*-carboranyl ligand systems,[4] we have prepared the unusually stable *trans* bis-chelates. We have discovered that the kinetic stability of *trans* bis-chelates can be greatly enhanced by placing a bulky *o*-carborane unit in the ligand backbone. Here we report the general synthesis of a new class of stable *trans* bis-chelates from the reaction of phosphinoalkylsilanes **2** with d^{10} metal complexes.

The phosphinosilanes **2** have been synthesized according to Scheme 1. The reaction of $(PPh_3)_2Pt(C_2H_4)$ **3** (0.3 mmol) and phosphinosilanes **2a**,**b** (2 equiv) in benzene leads to *trans*-(Cab^{P,Si})$_2$Pt **4a**,**b** in good yield (73−76%). A *trans*-arrangement for the phosphinosilyl ligands in a typical square-planar Pt(II) environment is proposed based on the $^1J_{Pt-P}$ values in the range 2702−4049 Hz for compounds **4a**,**b**.[5] In particular, the ^{1}H NMR chemical shift of δ 1.87 for **4a** as distorted triplets ($^2J_{H-P}$ = 3 Hz) resembles the values reported for the typical virtual coupling in the *trans*-$Pt(PMe_2R)_2X_2$ (R = Me, Ph) complexes.[6] This conclusion was substantiated for complex **4a** based on a single-crystal X-ray study.[7] The reaction proceeds with high stereoselectivity, giving preferential formation of the *trans* isomer. This is unusual, as chelate-assisted oxidative addition of phosphinoalkylsilanes with d^{10} metal complexes regularly occurs with *cis* stereochemistry[3b,d] due to the strong *trans* influence of the silyl group.[8] To the best of our knowledge, this is the first example in which *o*-carboranylphosphine tether is coordinated with a group 10 metal unit, thus improving the kinetic stability of the *trans* product.

Initial attempts to isomerize the *trans* isomer were unsuccessful. The dissolution of *trans*-**4a**,**b** in toluene and heating of the solution for 1 day at 110 °C results in no changes in *trans*-**4a**,**b**. However, in the presence of dimethyl acetylenedicarboxylate (DMAD), the *trans* isomer **4a**,**b** cleanly rearranges to the thermodynamically favored *cis* isomer, *cis*-(Cab^{P,Si})$_2$Pt **5a**,**b**, at 110 °C within 1 h. Interestingly, only activated acetylenes such as DMAD can promote the isomerization to yield the *cis*-product, indicating that electronics influence the

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(5) *trans*-(Cab^{P,Si})$_2$Pt **4a**: ^{1}H NMR (CDCl$_3$, δ) 0.33 (d, $^3J_{Pt-H}$ = 13 Hz, 12H, SiMe_2), 1.87 (dt, $^3J_{Pt-H}$ = 35 Hz, $^2J_{P-H}$ = 3 Hz, 12H, PMe_2); ^{13}C NMR (CDCl$_3$, δ) 6.43 (d, $^2J_{Pt-C}$ = 44 Hz, SiMe_2), 18.09 (d, $^2J_{Pt-C}$ = 39 Hz, PMe_2); ^{31}P NMR (CDCl$_3$, δ) 48.60 (d, $^1J_{Pt-P}$ = 2702 Hz, PMe$_2$). *trans*-(Cab^{P,Si})$_2$Pt **4b**: ^{1}H NMR (CDCl$_3$, δ) 0.40 (d, $^3J_{Pt-H}$ = 13 Hz, 12H, SiMe_2), 1.38 (t, $^3J_{H-H}$ = 7 Hz, 12H, P(OCH$_2$$Me$)$_2$), 4.19 (m, 8H, P(OC$H_2$Me)$_2$); ^{13}C NMR (CDCl$_3$, δ) 6.53 (SiMe_2), 16.29 (P(OCH$_2$$Me$)$_2$), 66.73 (P(O$CH_2$Me)$_2$); ^{31}P NMR (CDCl$_3$, δ) 164.80 (d, $^1J_{Pt-P}$ = 4049 Hz, P(OCH$_2$Me)$_2$).

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(7) Colorless crystals, triclinic $P\bar{1}$ (No. 2), Z = 2, a = 8.6548(3) Å, b = 11.0158(8) Å, c = 11.0685(7) Å, α = 104.516(5)°, β = 106.106(4)°, γ = 98.033(4)°, V = 956.3(1) Å^3, D_{calc} = 1.413 g/cm^3. Of 4060 reflections measured ($2\theta_{max}$ = 52°, empirical absorption correction (psi scans)), 3758 were unique, refined in full-matrix on F^2. All nonhydrogen atoms anisotropic, H atoms in idealized positions. R_1 = 0.0288, wR_2 = 0.0722 ($I > 2\sigma I$); and R_1 = 0.0309 and wR_2 = 0.0732 (all data).

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(9) See Supporting Information.

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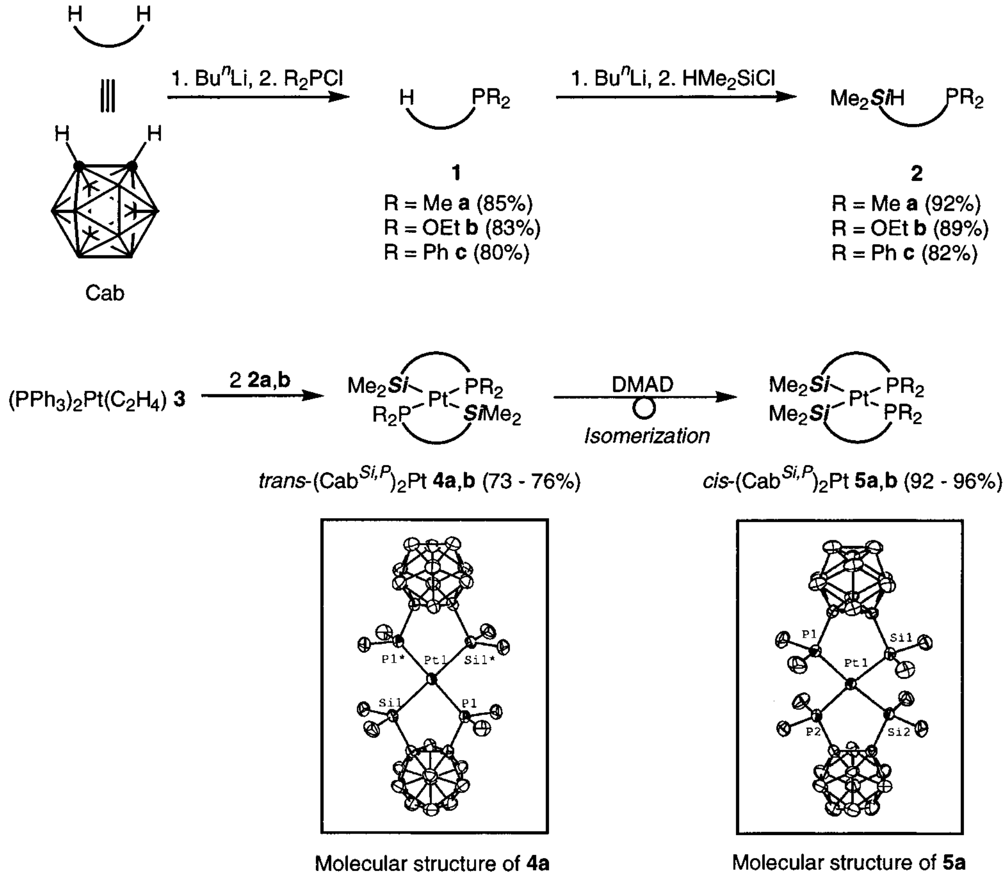
10.1021/om0005405 CCC: $19.00
Publication on Web 11/28/2000

Scheme 1



course of the reaction. The solution NMR spectral data[9] of complexes **5a**,**b** are unambiguous and consistent with the *cis*-geometry found in the crystal structure of **5a** (Scheme 1). Similar *trans*–*cis* isomerization has been observed in Kim's work[10] on *trans*-Pt(SiHPh$_2$)$_2$(PMe$_3$)$_2$, which is readily turned, upon dissolution in THF or CD$_2$Cl$_2$, into the thermodynamically more stable *cis* isomer. In contrast, *trans*-**4a**,**b** is robust and does not as readily undergo *trans*–*cis* isomerization in solution. The increased stability of the *trans* product **4a**,**b** is most likely a consequence of the formation of the two bis-chelate rings that is imposed by a bulky *o*-carborane backbone.

Other group 10 metal complexes, such as Pd$_2$(dba)$_3$ **6** and Pt(cod)$_2$ **9**, were tested for the chelate-assisted oxidative addition of **2** as shown in Table 1. The use of **6** in the reaction of **2a** gives bis-chelates *trans*-(Cab^{P,Si})$_2$-Pd **7a** and *cis*-(Cab^{P,Si})$_2$Pd **8a**, in 34% yield with a *trans*:*cis* ratio of 2:1. The reaction of **6** with **2b**,**c**, on the other hand, is *cis*-selective, producing 60–65% yields of the *cis*-(Cab^{P,Si})$_2$Pd **8b**,**c**. Bis(silyl)palladium complexes, which Ito et al.[11] had already reported, have been implicated as key intermediates in the Pd-catalyzed bis-silylation of alkynes.[12] This allowed an investigation of the reactivity of *cis*-(Cab^{P,Si})$_2$Pd **8b**,**c** with alkynes. However, these *cis* isomers are inactive toward bis-silylation, indicating that the bulky *o*-carborane backbone confers some additional strength to the Pd–Si bond.

In contrast, Pt(cod)$_2$ **9** does not have sufficient stereoselectivity in the reactions with the studied phosphinosilanes. The use of **2a** gives **4a** and **5a** with a *trans*:*cis* ratio of 2:1, whereas **2b** yields **4b** and **5b** with a *trans*:*cis* ratio of 1:1. On the other hand, when **9** is reacted with **2c**, the major product formed is the *cis* isomer **5c** along with a minor amount of the *trans* isomer **4c**.

Although a wide range of kinetically stabilized *trans* isomers are obtained under mild conditions, the stereochemistry of the reaction still appears to be dependent on both the silane and the metal complex employed. For example, changing the alkyl substituent on the phosphorus center of the silane to one that is more electron donating and less sterically demanding, as in **2a**, exclusively leads to the *trans* isomer. Increased stereoselectivity is seen in metal complexes such as **3** and **6** to give the *trans* or *cis* isomers depending on the steric bulk of the phosphine substituent.

Of the silanes utilized, **2c** failed to produce an appreciable amount of *trans* bis-chelates. Interestingly, the complex **3** reacted with **2c** by displacement of the ethylene ligand and the oxidative addition of the Si–H bond[13] to generate the chelating phosphinosilane-stabilized *cis* Pt(II) hydrido silyl complex[14] (Cab^{P,Si})Pt(H)(PPh$_3$) **10a**.

In comparison, such a hydrido silyl mono-chelate has not been observed for the oxidative addition of analogous phosphinosilanes.[3] Thus, as can be seen in Scheme 2,

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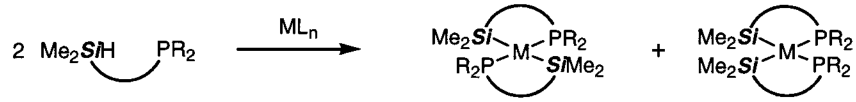
Table 1. Chelate-Assisted Oxidative Addition Reaction of 2



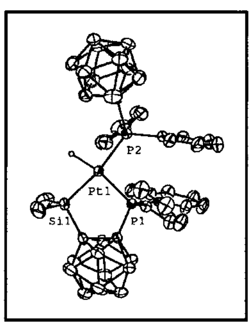
entry	substrate	ML_n	*trans*-$(Cab^{Si,P})_2M$	*cis*-$(Cab^{Si,P})_2M$	yield (%)^b
1	**2a**	$(PPh_3)_2Pt(C_2H_4)$ **3**	**4a**	none	73
2	**2b**	$(PPh_3)_2Pt(C_2H_4)$ **3**	**4b**	none	76
3	**2a**	$Pd_2(dba)_3$ **6**	2 **7a**^{c}	1 **8a**^{c}	34
4	**2b**	$Pd_2(dba)_3$ **6**	none	**8b**	65
5	**2c**	$Pd_2(dba)_3$ **6**	none	**8c**	60
6	**2a**	$Pt(cod)_2$ **9**	2 **4a**^{c}	1 **5a**^{c}	59
7	**2b**	$Pt(cod)_2$ **9**	1 **4b**^{c}	1 **5b**^{c}	51
8	**2c**	$Pt(cod)_2$ **9**	1 **4c**^{c}	6 **5c**^{c}	43

^{a}Conditions: 0.60 mmol **2**, benzene, 25 °C, Ar atm. ^{b}Yields determined after recrystallization or chromatography. ^{c}Stereoisomeric ratios were determined by NMR.

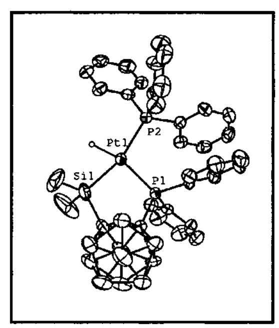
Scheme 2

$(Cab^{Si,P})PtH[(Cab)PPh_2]L$ **10b** (82%)

$(Cab^{Si,P})PtH(PPh_3)$ **10a** (89%)



Molecular structure of **10b**



Molecular structure of **10a**

an increase in the steric bulk of the phosphine substituent appears to retard the second oxidative addition as manifested in the higher yields obtained for **10a**. Given this steric constraint, we next turned to determining whether high yields of the mono-chelate could be obtained if **2c** was reacted with **9** in the presence of the bulky ancillary *o*-carboranylphosphine ligand (Cab)-PPh_2. Indeed, **2c** was found to cleanly react with **9** and (Cab)PPh_2 to provide the sterically encumbered *cis* Pt-(II) hydrido silyl complex $(Cab^{P,Si})Pt(H)[(Cab)PPh_2]$ **10b**, which is stable well above 100 °C.

Thus, our examination of the chelate-assisted oxidative addition reaction of the phosphinosilane may deserve the following comments. The success of demonstrating the formation of kinetically stabilized *trans* bis-chelates has relied on the following two factors: (1) the bulkiness of an alkyl group on the phosphinosilanes, and (2) rapid bis-chelation of the phosphinosilanes with a bulky *o*-carborane backbone. We will use these principles as we continue our studies of the stereoselectivity of the chelate-assisted oxidative addition reactions for the d^{10} metal complexes.

Acknowledgment. We are grateful to the Korea Science and Engineering Foundation (98-0501-02-01-3) for their financial support.

Supporting Information Available: Experimental details and spectroscopic data. Crystallographic data (excluding structure factors) for the structures (**4a**, **5a**, **10a**, and **10b**) reported in this paper. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0005405

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