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Exclusive C−Si Bond Formation upon Reaction of a Platinum(II) Alkyl with Silanes

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An unusual, highly selective C−Si coupling reaction takes place upon treating the platinum(II) alkyl complex *cis*-(DIPPIDH)(DIPPID)PtMe (**2**) (DIPPIDH = α^2-(*di*iso*p*ropyl*p*hosphino)*isod*urene, **1**) with $HSiR_3$ (R_3 = Et_3, $EtMe_2$, Me_2Ph), leading to formation of $MeSiR_3$ and the hydrido complex *trans*-(DIPPIDH)(DIPPID)PtH (**5**). The overall process involves activation of a Si−H bond, reverse-cyclometalation of the phosphine ligand DIPPIDH (**1**), and C−Si elimination. The resulting thermally stable platinum(II) hydride complex **5** was independently prepared by thermolysis of a platinum(II) dihydride, *trans*-$(DIPPIDH)_2PtH_2$ (**6**), which was obtained by reaction of **2** with H_2. In the absence of silane, the cis complex **2** isomerizes thermally to *trans*-(DIPPIDH)(DIPPID)PtMe (**3**), which does not react productively with silanes. Our results indicate that opening of the metallacycle of **2** by benzylic C−H formation is kinetically preferred over formation of CH_4 or CH_3SiR_3.

Introduction

Hydrosilylation processes of olefins and acetylenes,[1] which are frequently catalyzed by Pt complexes,[2] are thought to proceed by the Chalk−Harrod mechanism which invokes C−Si bond formation as the product-forming step.[3] Reactions of metal alkyl complexes with primary silanes can lead to products of both C−H and C−Si reductive elimination.[4,5,6] For instance, reaction of (dmpe)Pt(Me)(OTf) (dmpe = $Me_2PCH_2CH_2PMe_2$) with Et_3SiH led to formation of CH_4 and CH_3SiEt_3.[5a] Methane was formed in the reaction of $MeRh(PMe_3)_4$ with $HSiPh_3$,[5b] while, in the analogous reaction with $HSiEt_3$, both methane and CH_3SiEt_3 were formed. A theoretical study showed that CH_3−H reductive elimination from Pt(II) is 26.8 kcal/mol more favorable than that of CH_3−SiH_3.[7]

Few detailed studies on selective metal-mediated C−Si formation have been reported.[6,8] Gladysz et al. observed this key step directly by thermolysis of $Fe(CO)_4(SiMe_3)(Me)$.[8a] Kinetic data were obtained for C−Si reductive elimination from *cis*-$Pt(Me)(SiPh_3)(PMePh_2)_2$,[8b,c] and a reversible C−Si addition to Pt and to binuclear Ru complexes was observed recently.[8d,e] We demonstrated that C−H and C−Si reductive elimination from isolated Ir(III) complexes can occur competitively at comparable rates (Scheme 1).[6]

We report here that reaction of the cyclometalated *cis*-Pt(II) alkyl complex **2** with H−SiR_3 (R_3 = Et_3, $EtMe_2$, Me_2Ph), results in *exclusive* C−Si bond formation and generation of the new Pt(II) hydride complex **5** (Scheme 2). Interestingly, the trans isomer **3** exhibits totally different reactivity.

Results and Discussion

We reported recently that reaction of $(COD)Pt(CH_3)_2$ (COD = 1,5-cyclooctadiene) with α^2-(diisopropylphosphino)isodurene (**1**) in C_6H_6 at room temperature resulted in cyclometalation to form complex **2** and CH_4 quantitatively.[9] Thermolysis of **2** in C_6H_6 resulted in the competitive formation of the trans isomer **3** and complex **4** with liberation of CH_4 (Scheme 2). Continuous heating of complex **3** resulted also in the quantitative formation of CH_4 and **4**, which was fully characterized by X-ray analysis.

Reaction of the *cis*-Pt(II)CH_3 complex **2** with 5 equiv of various primary silanes in C_6D_6 at 100 °C (120 h in a sealed vessel) quantitatively afforded the new *trans*-

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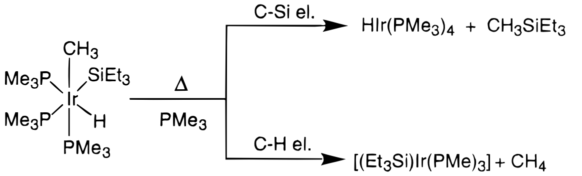
Scheme 1



Pt(II)H complex **5** and CH_3SiR_3 ($R_3 = Et_3$, $EtMe_2$, Me_2Ph) as judged by $^{31}P\{^1H\}$, ^1H, $^1H\{^{31}P\}$, $^1H-^1H$ COSY NMR, IR, FD-MS, and GC-MS analysis of the product solution and by comparison with authentic samples (vide infra). Surprisingly, only traces of CH_4 (<4%) were detected by quantitative GC analysis of the gas phase. When deuterated solvents were used, no deuterium incorporation into the products was observed.[10] The $^{31}P\{^1H\}$ NMR spectrum of **5** exhibits two sharp doublets of equal intensity at δ 89.2 and 45.1 ppm, flanked by ^{195}Pt satellites. The large $^{31}P-^{31}P$ coupling ($^2J_{PP} = 392.8$ Hz) shows that both nuclei are mutually trans, in agreement with the observed $^{195}Pt-^{31}P$ coupling constants ($^1J_{PtP} = 3193.5$ and 2992.1 Hz, respectively). The low-field shift of δ 89.2 reflects a deshielding effect of this phosphorus atom due to the six-membered ring.[9,11] The signal at δ 45.1 is in a range normally observed for (η^1-phosphine)platinum(II) complexes.[9] The Pt−H ligand appears in the IR at $\nu = 1964$ cm^{-1} and in the ^1H NMR as a virtual triplet at δ −7.00 (cis $^2J_{PH} = 18.4$ Hz, flanked by ^{195}Pt satellites ($^1J_{PtH} = 773.2$ Hz). These values are typical for a hydride trans to a σ-bonded alkyl.[12] FD-MS analysis shows the molecular ion (M^+, *m*/*e* 695) and an expected logical isotope pattern.

By contrast, heating of the thermally more stable *trans*-Pt(II)CH_3 complex **3** with 5 equiv of $HSiR_3$ ($R_3 = Et_3$, Me_2Ph) in C_6D_6 at 100 °C (120 h in a sealed vessel) resulted in quantitave formation of complex **4** and CH_4. Surprisingly, formation of **5** and CH_3SiR_3 was not observed by NMR, IR, and GC-MS analysis of the product solution. Complex **5** is stable under the reaction conditions and would have been easily detected spectroscopically had it been formed. Thus, as opposed to the reactivity of the cis isomer **2**, in the case of the trans isomer **3** formation of complex **4** and CH_4 is kinetically (and probably thermodynamically) preferred over C−Si bond generation. Significantly, complex **4** is thermally stable under the reaction conditions and was recovered unchanged even after heating with 5 equiv of $HSiMe_2Ph$ in C_6H_6 at 150 °C for 48 h. Thus, it cannot be an intermediate in the formation of complex **5**. These experiments indicate that *for the selective C−Si bond formation the cis geometry of the metal complex is required*.

While reactions of various silanes with (dmpe)Pt(Me)(OTf) and with $MeRh(PMe_3)_4$ as well as the competitive C−H and C−Si reductive elimination from Ir(III) complexes are strongly influenced by the electronic properties of the substituents on silicon (Scheme 1),[5a,b,6] no such an influence was observed here.

Interestingly, it is possible to reverse the cyclometalation of **2** by the use of mild H_2 pressure. Treating complex **2** with H_2 (30 psi) in C_6H_6 at 60 °C (72 h in a Fischer−Porter pressure vessel) resulted in quantitative formation of the new *trans*-dihydride complex **6** and CH_4 (Scheme 2). This complex, which was isolated and fully characterized by ^1H, $^1H\{^{31}P\}$, $^{31}P\{^1H\}$, and $^{31}P-^1H$ HQMC NMR, IR, FD-MS, and elemental analysis, exhibits spectroscopic features similar to those of analogous Pt(II) *trans*-dihydride complexes.[13] No other complexes were detected. In the $^{31}P\{^1H\}$ one sharp singlet appears at δ 53.7 ppm flanked by ^{195}Pt satellites ($^1J_{PtP} = 2882.2$ Hz), indicating that both phosphorus atoms are magnetically equivalent. The hydride ligands appear in the ^1H NMR as a characteristic triplet resonance at δ −3.15 ppm (cis $^2J_{PH} = 17.5$ Hz; $^1J_{PtH} = 796.0$ Hz), which collapses into a singlet upon $^{31}P\{^1H\}$ decoupling. The IR spectrum shows a strong Pt−H band at $\nu = 1744$ cm^{-1}, which is in the region usually observed for ν(Pt−H) of *trans*-dihydrides (1710−1820 cm^{-1}).[13] Formation of 1 equiv of CH_4 was determined by quantitative GC analysis of the gas phase. Thermolysis of **6** in C_6D_6 at 100 °C (120 h in a sealed vessel) resulted in selective formation of complex **5** and presumably H_2 (Scheme 2). Formation of complex **4** was not observed, in contrast to thermolysis of complexes **2** and **3**, which results in quantitative formation of complex **4** and CH_4.[9] Presumably, the σ-bonded Pt−CH_3 group promotes C−H activation. Complex **5** is considerably more stable than complex **2** and was recovered unchanged when treated with H_2 (15 psi) in C_6H_6 at 80 °C for 24 h. The fact that **5** was not detected in the reaction of **2** and H_2 suggests that benzylic C−H reductive elimination is kinetically preferred over CH_4 formation.

While the reason for the surprising, exclusive C−Si bond formation is uncertain, we suggest that the following speculative mechanism can account for the observations. Complex **2** can undergo phosphine dissociation, promoted by the strong trans influence of the σ benzyl ligand and the steric hindrance of the cyclometalated ligand.[14] H−Si or H−H oxidative addition may afford a Pt(IV) species such as **A** (Scheme 3).[15,16] The silyl or hydride ligands can labilize the benzyl group ($ArCH_2$−Pt) trans to it. The strong trans influence of silyl ligands is similar or even higher than that of

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[10] Formation of **5**, **6**, CH_3SiR_3, and disiloxanes was observed at 55 °C. Reaction of **2** with 5 equiv of $HSiPh_3$ in C_6D_6 at 55 °C (24 h in a sealed vessel) resulted also in the formation of **5**, **6**, CH_3SiPh_3, and $Ph_3SiOSiPh_3$. Only traces of CH_4 (<4%) were detected. The formation of **6** and disiloxanes could be suppressed using silanized glassware, suggesting that adventitious water is involved in this process.

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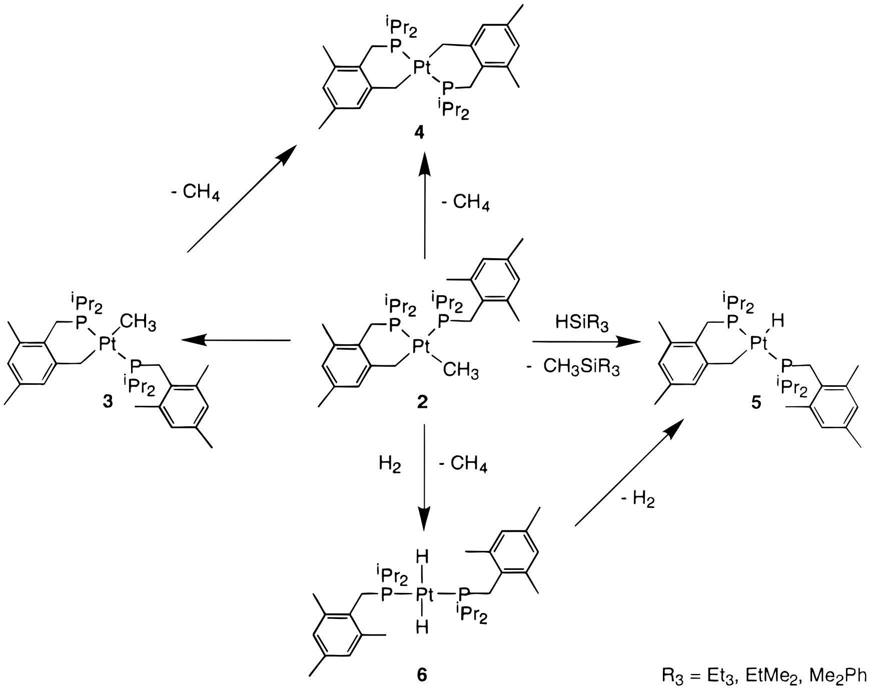
[14] Bubbling CO through a benzene solution of **2** at room temperature for 1 h results in displacement of the η^1-phosphine: Van der Boom, M. E.; Milstein, D. Unpublished results.

[15] An analogous Pt species with $R' = CH_3$ was postulated to be an intermediate in the selective formation of complex **2** and CH_4 (Scheme 2).[9.]

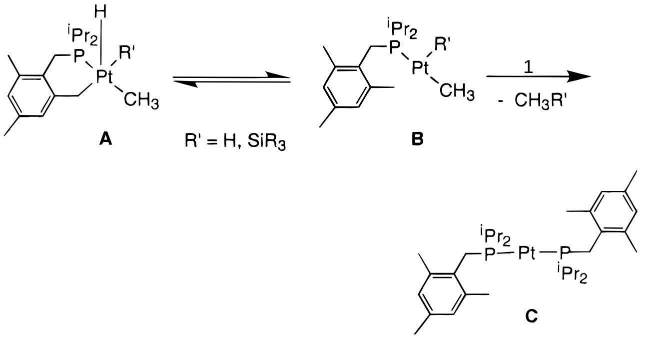
[16] As pointed out by a reviewer, direct H−Si oxidative addition to give a hexacoordinate Pt(IV) species, followed by a selective C−Si reductive elimination, cannot be excluded.

Scheme 2



R$_3$ = Et$_3$, EtMe$_2$, Me$_2$Ph

Scheme 3



hydride ligands.[6,17] Thus, ArCH$_2$−H formation might be preferred over that of CH$_4$ or CH$_3$SiR$_3$ elimination.[18] Since both C−H and C−Si reductive elimination processes are possible,[4−6,19,20] it can be suggested that the overall process is kinetically controlled by electronic factors in the (unobserved) Pt(IV) intermediate **A**. Consequently, CH$_3$−R′ (R′ = H, SiR$_3$) elimination occurs from **B**,[15] to afford a Pt(0) species **C**.[10,21] As is well documented, *cis*-alkyl(hydrido)Pt(II) and Pt(IV) species are very unstable toward C−H reductive elimination.[19] *cis*-Alkyl(silyl)Pt(II) species are postulated intermediates in the hydrosilylation processes of olefins.[1,2] Ozawa et al. showed that C−Si reductive elimination from *cis*-Pt(Me)(SiPh$_3$)(PMePh$_2$)$_2$ is a facile process and proceeds by dissociation of a phosphine.[8b,c] Selective C−H reductive elimination from PtMe$_2$(H)(bis(2-pyridylmethyl)amine)Cl was recently observed by Puddephat et al.[19a]

Complex **C** can undergo cyclometalation to yield **5** or may be trapped by H$_2$ to give **6**,[10,13] thermolysis of which gives **5**. Activation of benzylic C−H bonds by Pt(0) and Pt(II) complexes was reported.[9,22] While intermediacy of an isomer of **A** in which the silane is in the apical position and the hydride in the basal one is also possible, it seems less likely on steric grounds.[23]

Conclusions

Addition of H−SiR$_3$ (R$_3$ = Et$_3$, EtMe$_2$, Me$_2$Ph) to the Pt(II) alkyl complex **2** results in kinetically preferred *exclusive* alkyl−SiR$_3$ bond formation to yield complex **5**. Interestingly, the cis geometry and the presence of the metallacycle, which readily opens up, play a key role in the selective product formation. The overall process involves a series of reactions that are influenced by electronic and steric factors. The C−Si coupling is probably directed by the strong trans influence of the ligands, while formation of the *trans*-Pt(II)H complex **5** is sterically influenced by the bulky phosphine ligand **1**.

Experimental Section

The procedures and spectroscopic analysis are similar to those previously reported.[9] All reactions were carried out

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(20) Levi, C. J.; Puddephatt, R. J. *Organometallics* **1995**, *14*, 5019.

(21) Formation of **C** was observed upon reacting 2 equiv of **1** and 5 equiv of HSiMe$_2$Ph with (COD)Pt(CH$_3$)$_2$ at room temperature. This reaction is not selective since CH$_4$ and SiMe$_3$Ph were detected. The ^{31}P{^{1}H} NMR of the reaction mixture shows a broadened signal at δ 61.15 ($^1J_{PtP}$ = 4220 Hz; compare (^{i}Pr$_3$P)$_2$Pt, $^1J_{PtP}$ = 4202 Hz (Mann, B. E.; Musco, A. *J. Chem. Soc., Dalton Trans.* **1980**, 776)). Thermolysis results in quantitative formation of complex **5**. Apparently, the metallacycle of **2** plays a key role in the selective C−Si formation.

(22) Hackett, M.; Whitesides, G. M. *J. Am. Chem. Soc.* **1988**, *110*, 1449.

(23) Oxidative addition of silanes to Ir(I) has been found to proceed with 98% stereoselectivity: Johnson, C. E.; Eisenberg, R. *J. Am. Chem. Soc.* **1985**, *107*, 6531.

under an inert atmosphere. Solvents were dried, distilled, and degassed before use. Complexes **2**−**4** and (COD)Pt(CH$_3$)$_2$ were prepared according to published procedures.[9,24]

Reaction of Complex 2 with HSiR$_3$ (R$_3$ = Et$_3$, Me$_2$Et, Me$_2$Ph) at 100 °C.[10] A colorless solution of complex **2** (36 mg, 0.050 mmol) and a 5-fold excess of HSiR$_3$ in C$_6$D$_6$ (1.5 mL) was heated using a pressure flask at 100 °C for 5 days. Quantitative analysis of the gas phase by GC showed only traces of CH$_4$ (<4%). The product solution was analyzed by ^{1}H, ^{1}H{^{31}P}, ^{31}P{^{1}H} NMR, IR, GC-MS, and FD-MS showing the quantitative formation of complex **5** (vide infra) and MeSiR$_3$. ^{1}H NMR and GC-MS analysis showed traces of Et$_4$Si, HSiMe$_3$, Me$_2$SiPh$_2$, Me$_3$SiPh, and disiloxanes; formation of the latter could be suppressed using silanized glassware.

Formation of the *trans*-Dihydride 6. A colorless solution of **2** (43 mg, 0.06 mmol) in benzene (10 mL) was loaded in a Fischer−Porter and pressurized with 30 psi of H$_2$. The yellowish solution was stirred at 60 °C for 3 days. Quantitative analysis of the gas phase by GC showed formation of 1 equiv of CH$_4$. Subsequently, the solvent was removed in a vacuum and the resulting brownish solid was recrystallized from pentane to afford complex **6** (33 mg, 80%) as a colorless crystalline powder. FD-MS (*m*/*z*): 697 (calcd M$^+$, 697; correct isotope pattern). Anal. Calcd for C$_{32}$H$_{55}$P$_2$Pt: C, 55.24; H 7.82. Found: C, 54.94; H, 7.42. ^{1}H NMR (400.19 MHz; C$_6$D$_6$): δ −3.15 (t, $^2J_{PH}$ = 17.5 Hz, $^1J_{PtH}$ = 796 Hz, 2 H, Pt*H*), 1.05 (q, $^3J_{HH}$ = 7.5 Hz, 12 H, PCH(C*H*$_3$)$_2$), 1.20 (vq, $^3J_{HH}$ = 7.4 Hz, 12 H, PCH(C*H*$_3$)$_2$), 1.95 (m, 4 H, PC*H*(CH$_3$)$_2$), 2.14 (s, 6 H, *p*-ArC*H*$_3$), 2.48 (s, 12 H, *o*-ArC*H*$_3$), 3.31 (vt, $^2J_{PH}$ = 3.4 Hz, $^3J_{PtH}$ = 36.2 Hz, 4 H, PC*H*$_2$Ar), 6.79 (s, 4 H, Ar*H*). ^{31}P{^{1}H} NMR (161.9 MHz; C$_6$D$_6$): δ 53.7 (s, $^1J_{PtP}$ = 2882.2 Hz). IR (film): ν(Pt−H) = 1744 cm^{-1}.

Formation of 5 from 6. A solution of **6** (14 mg, 0.02 mmol) in C$_6$D$_6$ (1 mL) was transferred to a 5 mm screw cap NMR tube. The sealed NMR tube was placed in an oil bath at 100 °C and monitored by ^{31}P{^{1}H} NMR at room temperature. After 5 days **6** was selectively converted to **5**; removal of the solvent in a vacuum afforded a white powder. Performing the thermolysis of **6** in the presence of a 5-fold excess of HSiMe$_2$Ph resulted also in the selective formation of complex **5**; no influence of the silane on the progress and the product formation was observed by ^{31}P{^{1}H} NMR. FD-MS (*m*/*z*): 695 (calcd M$^+$, 695; correct isotope pattern). Anal. Calcd for C$_{32}$H$_{53}$P$_2$Pt: C, 55.32; H 7.69. Found: C, 55.21; H, 7.41. ^{1}H NMR (400.19 MHz; C$_6$D$_6$): δ −7.00 (br t, $^2J_{PH}$ = 18.4 Hz, $^2J_{PH}$ = 773.2 Hz, 1 H, Pt*H*), 0.86 (dd, $^2J_{PH}$ = 14.2 Hz, $^3J_{PH}$ = 7.0 Hz, 6 H, PCH(C*H*$_3$)$_2$), 1.00−1.10 (m, 12 H, PCH(C*H*$_3$)$_2$), 1.15 (dd, $^2J_{PH}$ = 13.9 Hz, $^3J_{HH}$ = 7.0 Hz, 6 H, PCH(C*H*$_3$)$_2$), 1.66 (m, 1 H, PC*H*(CH$_3$)$_2$), 1.85 (m, 3 H, PC*H*(CH$_3$)$_2$), 2.13 (s, 3 H, ArC*H*$_3$), 2.18 (s, 3 H, ArC*H*$_3$), 2.30 (s, 6 H, *o*-ArC*H*$_3$), 2.44 (m, partly overlapped, 2 H, ArC*H*$_2$Pt), 2.46 (s, 3 H, ArC*H*$_3$), 2.84 (m, $^3J_{PtH}$ = 37.3 Hz, 2 H, ArC*H*$_2$P), 3.26 (dd, $^2J_{PH}$ = 3.2 Hz, $^3J_{PtH}$ = 10.2 Hz, 2 H, ArC*H*$_2$P), 6.70−6.80 (m, 4 H, Ar*H*). ^{31}P-{^{1}H} NMR (161.9 MHz; C$_6$D$_6$): δ 45.1 (d, $^2J_{PP}$ = 392.8 Hz, $^1J_{PPt}$ = 2992.1 Hz, 1 P), 89.2 (d, $^2J_{PP}$ = 392.8 Hz, $^1J_{PtP}$ = 3193.5 Hz, 1 P). IR (film): ν(Pt−H) = 1964 cm^{-1}.

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