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Transition Metal Silyl Complexes LVIII [1]. Silyl Group Exchange between $(R''_3P)_2Pt(SiR_3)_2$ and $HSiR'_3$

Ulrich Schubert*, **Dominique Kalt,** and **Hilmar Gilges**

Institut für Anorganische Chemie, Technische Universität Wien, A-1060 Wien, Austria

Summary. Reaction of *cis*-$(R_3P)_2Pt(SiPhMe_2)_2$ with an excess of $HSi(OMe)_3$, $HSiPh_3$, HSi_3Ph_7, $HPh_2SiSiMe_3$, or H_2SiPh_2 results in a stepwise exchange of the silyl ligands. Exchange of the first $SiPhMe_2$ ligand is faster than that of the second. The exchange rate depends on the nature of the groups R' in $HSiR'_3$ and decreases in the order $HSi(OMe)_3 \gg H_2SiPh_2 > HPh_2SiSiMe_3 \gg HSi_3Ph_7 > HSiPh_3$. The rate of the exchange reaction of $(R_3P)_2Pt(SiMe_2Ph)_2$ with an excess of $HSi(OMe)_3$ depends on the R_3P ligand and decreases in the order $PPh_2Me > PEt_3 > PPhMe_2$. When the chelated complex $(Ph_3P)(Ph_3Si)\overline{Pt(PPh_2CH_2CH_2Si}Me_2)$ is reacted with $HSi(OMe)_3$ or H_2SiPh_2, only exchange of the non-chelated silyl ligand is observed.

Keywords. Silyl complexes; Platinum complexes; Ligand exchange.

Übergangsmetall-Silyl-Komplexe, 58. Mitt. [1]. Silylgruppenaustausch zwischen $(R''_3P)_2Pt(SiR_3)_2$ und $HSiR'_3$

Zusammenfassung. Umsetzung von *cis*-$(R_3P)_2Pt(SiPhMe_2)_2$ mit einem Überschuß an $HSi(OMe)_3$, $HSiPh_3$, HSi_3Ph_7, $HPh_2SiSiMe_3$ oder H_2SiPh_2 führt zum stufenweisen Austausch der Silylliganden. Der Austausch des ersten $SiPhMe_2$-Liganden erfolgt rascher als der des zweiten. Die Austauschgeschwindigkeit hängt von der Art der Reste R' in $HSiR'_3$ ab und sinkt in der Reihenfolge $HSi(OMe)_3 \gg H_2SiPh_2 > HPh_2SiSiMe_3 \gg HSi_3Ph_7 > HSiPh_3$. Bei der Reaktion von $(R_3P)_2Pt(SiMe_2Ph)_2$ mit einem Überschuß an $HSi(OMe)_3$ wird der Austausch in Abhängigkeit vom R_3P-Liganden in der Reihenfolge $PPh_2Me > PEt_3 > PPhMe_2$ langsamer. Bei der Reaktion des Chelat-Komplexes $(Ph_3P)(Ph_3Si)\overline{Pt(PPh_2CH_2CH_2CH_2Si}Me_2)$ mit $HSi(OMe)_3$ oder H_2SiPh_2 wird nur Austausch des nichtchelatisierten Silylliganden beobachtet.

Introduction

Silyl group exchange by reaction of transition metal silyl complexes with hydrosilanes according to Eq. (1) is an interesting possibility for the preparation of metal complexes with silyl ligands which are otherwise difficult to introduce.

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* Corresponding author

Metal complexes with $SiMe_3$ ligands are particularly interesting for preparative purposes because of the high volatility of the leaving silane $HSiMe_3$ [2–6].

$$L_nM{-}SiR_3 + HSiR'_3 \rightleftharpoons L_nM{-}SiR'_3 + HSiR_3 \tag{1}$$

Exchange reactions in metal catalyzed reactions with hydrosilanes could liberate the organosilicon product and thus regenerate an initial stage of the catalytic cycle. On the other hand, however, they could also lead to the undesirable premature extrusion of the silicon component when the transformation of the silyl group at the metal center involves several steps. An example for the latter case would be the exchange of a growing oligosilyl ligand at the metal center by monomeric hydrosilanes during metal catalyzed dehydrogenative polymerization.

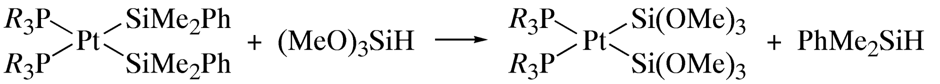
Thermal or photochemical silyl group exchange reactions have not been investigated in detail, although several examples are known [3–15]. Their mechanism is unknown in most cases. It could involve oxidative addition of the entering silane followed by reductive elimination of the leaving silane, but σ-bond metathesis is also possible.

Bis(silyl) complexes are potential intermediates in the conceivable metal catalyzed dehydrogenative silane coupling based on an oxidative addition/reductive elimination mechanism [16]. In the present article we will discuss exchange reactions starting from the *bis*(silyl) complexes *cis*-$(R_3P)_2Pt(SiR_3)_2$ and their chelated analogues $(Ph_3P)\overline{Pt(PPh_2CH_2CH_2Si}Me_2)SiPh_3$. Some exchange reactions involving Pt(II) silyl complexes have already been reported. We have previously prepared the chelated complex (*dppe*)$\overline{PtSiMe_2CH_2CH_2Si}Me_2$ (*dppe* = $Ph_2CH_2CH_2PPh_2$) by thermal reaction of (*dppe*)$Pt(SiMe_3)_2$ with $Me_2HSiCH_2CH_2SiHMe_2$ [3]. $SiMe_3$ group exchange was also observed when *trans*-$(Et_3P)_2Pt(Br)SiMe_3$ was reacted with $HSiMe_2Ph$ or $H_2SiMePh$ [7]. In a detailed study, *Clemmit* and *Glockling* [8, 17] have examined the exchange reactions between (*dppe*)$Pt(EMe_3)_2$ or (*dppe*)$PtCl(EMe_3)$ and $HE'Me_3$ (E, E' = Si, Ge, Sn). They found that a large excess of trimethylsilane was required to partially eliminate $HGeMe_3$, whereas the exchange of $SiMe_3$ by $GeMe_3$ or of $GeMe_3$ by $SnMe_3$ was quantitative with stoichiometric amounts of $HEMe_3$. This reflects the decreasing Pt–E bond strengths in the order $E = Sn \gg Ge > Si$, favouring the formation of the stronger Si–H bond.

Results and Discussion

In this study we intended to simulate conditions of catalytic processes in which an intermediate *bis*(silyl) metal complex would be exposed to a high excess of a hydrosilane. For this reason we employed an excess of the hydrosilane relative to the *bis*(silyl) complexes. The reactions were followed by ^{31}P NMR spectroscopy at room temperature. The different chemical shifts allowed a clear distinction between the starting complexes and the exchange products. Partially exchanged complexes were identified by their typical pattern of two doublets (with ^{195}Pt satellites) due to the chemically inequivalent phosphorus atoms. We observed no side reactions or decomposition.

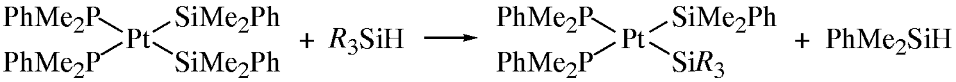
The exchange reactions of both silyl ligands of $(R_3P)_2Pt(SiPhMe_2)_2$ ($R_3P = Me_2PhP$, $MePh_2P$, Et_3P) with $HSi(OMe)_3$ (Eq. (2)) were complete in less than an hour. The ^{31}P NMR spectra of the reaction mixtures then showed only a new singlet with ^{195}Pt satellites.



(2)

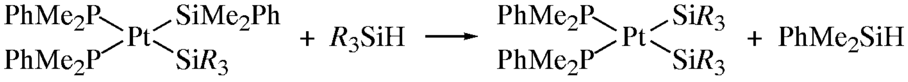
$R_3P = PhMe_2P, Ph_2MeP, Et_3P$

The exchange reactions of *cis*-$(Me_2PhP)_2Pt(SiPhMe_2)_2$ with $HSiPh_3$, HSi_3Ph_7, $HPh_2SiSiMe_3$ and H_2SiPh_2 were much slower under the same conditions, and the rates showed a clear dependence on the nature of the entering silyl group. In each case, the unsymmetrically substituted complex $(Me_2PhP)_2Pt(SiPhMe_2)(SiR_3)$ was observed (Eq. (3)), although the NMR signals could not always be assigned unequivocally due to overlap with the signals of the starting and fully exchanged complexes. The time for the disappearance of the starting complex increased in the order H_2SiPh_2 (~1 h) < $HPh_2SiSiMe_3$ (~3 h) < HSi_3Ph_7 (~1 d) < $HSiPh_3$ (~4 d). Exchange of the second silyl ligand, *i.e.* formation of the symmetrically substituted complexes *cis*-$(Me_2PhP)_2Pt(SiR_3)_2$ (Eq. (4)), was even slower. Formation of these complexes with the more reactive silanes H_2SiPh_2 and $HPh_2SiSiMe_3$ took place within hours. The doubly exchanged products were not observed with HSi_3Ph_7 and $HSiPh_3$ during several days at room temperature. However, when a *THF* solution of $(Me_2PhP)_2Pt(SiPhMe_2)_2$ and $HSiPh_3$ was heated to 60°C for 10 d, the fully exchanged product $(Me_2PhP)_2Pt(SiPh_3)_2$ was formed.



(3)

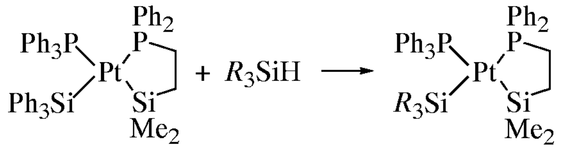
$R_3SiH = Ph_3SiH, Ph_2SiH_2, Me_3SiSiPh_2H, Ph_7Si_3H$



(4)

$R_3SiH = Ph_2SiH_2, Me_3SiSiPh_2H$

Chelation is known to stabilize transition metal complexes towards reductive eliminations. Thus, when the *bis*(silyl) complex $(Ph_3P)(Ph_3Si)\overline{Pt(PPh_2CH_2CH_2Si}Me_2)$ [18] was treated with $HSi(OMe)_3$ or H_2SiPh_2, only products resulting from the exchange of the non-chelated silyl group were obtained, even with the highly reactive $HSi(OMe)_3$ (Eq. (5)).



(5)

$R_3SiH = (MeO)_3SiH, Ph_2SiH_2$

Only the reaction of $(R_3P)_2Pt(SiMe_2Ph)_2$ with an excess of $(MeO)_3SiH$ results in the rapid exchange of both silyl ligands (Eq. (2)). Although the reaction is fast compared to the reactions with other silanes, there is a significant influence of the phosphine ligands on the exchange rate. It increases in the order $PPh_2Me > PEt_3 > PPhMe_2$. This trend can be correlated with the cone angle of the phosphine ligands [19, 20]: PPh_2Me (136°) > PEt_3 (132°) > $PPhMe_2$ (122°). Since PEt_3 is the most basic phosphine ligand in this series, the steric influence of the PR_3 ligands appears to play a more important role than their electronic influence. This indicates that (reversible) elimination of a PR_3 ligands is the initial step of the reaction which is easier for bulky substituents. Phosphine dissociation is often the preliminary step in reaction of d^8 systems.

Exchange of the first SiR_3 ligand was always more rapid than that of the second. The exchange reaction rates for the exchange of both the first and second silyl ligand depend on the entering silane and decrease in the order $HSi(OMe)_3 \gg H_2SiPh_2 > HPh_2SiSiMe_3 \gg HSi_3Ph_7 > HSiPh_3$, *i.e.* the reaction rate mainly depends on the electronic properties of the entering silane. Electron withdrawing substituents increase the reaction rate. The slow reaction of HSi_3Ph_7 indicates that the steric properties also play a role. Exchange of the second $SiMe_2Ph$ ligand with HSi_3Ph_7 or $HSiPh_3$ is so slow at room temperature that no significant concentration of the *bis*-exchanged complexes was observed within days. These complexes were only obtained at higher temperatures.

The strength of metal-silicon bonds is influenced by the substituents on silicon. Electronegative substituents such as halogens strengthen and electron donating moieties such as methyl groups weaken the M–Si bond. Since the substituents at silicon in the starting *bis*(silyl) complex ($SiMe_2Ph$) are more electron donating than those of the employed hydrosilanes, the formation of the exchange products is thermodynamically favoured in each case. Due to the large excess of the silane, the original silyl groups should therefore exchange completely.

The electronic situation at the metal center is somewhat different for the exchange of the first and the second silyl ligand. The electronic properties of the starting metal complex are determined by the two $SiMe_2Ph$ groups and the spectator ligands. After replacement of the first $SiMe_2Ph$ ligand, the electron density at the metal is decreased because the new silyl ligand is less electron donating than $SiMe_2Ph$. Thus, oxidative addition of the second silyl ligand and/or initial dissoziation of the PR_3 ligand is somewhat disfavoured relative to the first step. The degree of this effect depends on the difference in the electronic properties of the silyl groups involved in the exchange reaction.

This might explain why the exchange of the second silyl ligand is slower than that of the first one. Rapid exchange was only observed with $HSi(OMe)_3$. However, the order of reactivity with regard to the employed hydrosilanes is still the same as in the first step. Thus, the effect that a lower electron density at the silicon atom promotes the addition of hydrosilanes to the metal overrides the effect that the same substituents in a silyl ligand lower the reactivity of the metal center.

Conclusions

Exchange of the silyl ligands upon reaction of Pt(II) *bis*(silyl) complexes with hydrosilanes is slow unless there is a large difference in the electronic properties of the involved silyl groups. Rapid exchange is only observed if the substituents in the entering silyl group are much more electronegative than those of the leaving silane. The exchange rates for a given silyl complex depend both on the properties of the spectator ligands and the substituents at the hydrosilane.

The incorporation of a silyl group in a chelate system impairs their exchange, *i.e.* opening of the chelate ring of $(Ph_3P)\overline{Pt(PPh_2CH_2CH_2Si}Me_2)SiPh_3$ by the hydrosilane and formation of $(Ph_3P)Pt(PPh_2CH_2CH_2SiMe_2H)(SiPh_3)(SiR'_3)$ was not observed even for the highly reactive $HSi(OMe)_3$. This is another proof for the stabilizing influence of chelation compared to complexes with electronically equivalent non-chelated ligands.

Experimental

All operations were performed in an atmosphere of dry and oxygen-free argon with standard *Schlenk* tube techniques using dried and argon saturated solvents. ^1H and ^{31}P NMR spectra were recorded on a Bruker AC250 spectrometer (^1H: 250.13 MHz, δ rel. to internal *TMS*; ^{31}P: 101.25 MHz, δ rel. to external 85% H_3PO_4). All NMR spectroscopic investigations were carried out in benzene-d_6. The solvent was dried with molecular sieve (4 Å) and stored under argon. The starting complexes and the hydrosilanes were prepared according to the literature [18, 21].

Reactions of platinum(II) complexes with hydrosilanes, general procedure

20 molar equivalents of the hydrosilane were added to a benzene-d_6 solution of *cis*-$(R_3P)_2Pt(SiPhMe_2)_2$ in an NMR tube, or 4 molar equivalents of the hydrosilane to a solution of $(Ph_3P)(Ph_3Si)\overline{Pt(PPh_2CH_2CH_2Si}Me_2)$. The NMR tube was sealed under argon. ^{31}P NMR spectra were recorded in regular intervals to monitor the progress of the reaction.

Reactions of $(PhMe_2P)_2Pt(SiMe_2Ph)_2$ (^{31}P NMR: -6.48 ppm ($^1J_{PtP} = 1514$ Hz))

(a) With $(MeO)_3SiH$: after 1 h at room temperature, only $(PhMe_2P)_2Pt[Si(OPh)_3]_2$ was observed; ^{31}P NMR: -37.22 ppm ($^1J_{PtP} = 1201$ Hz).

(b) With Ph_2SiH_2: when the starting complex had disappeared after 1 h at room temperature, a mixture of $(PhMe_2P)_2Pt(SiMe_2Ph)(SiHPh_2)$ (major product) and $(PhMe_2P)_2Pt(SiHPh_2)_2$ (minor product) was spectroscopically observed. Due to signal overlap, the resonances of $(PhMe_2P)_2Pt(SiMe_2Ph)(SiHPh_2)$ could not be unequivocally assigned. ^{31}P NMR of $(PhMe_2P)_2Pt(SiHPh_2)_2$: -58.58 ppm ($^1J_{PtP} = 1135$ Hz).

(c) With Ph_7Si_3H: when the starting complex had disappeared after 1 d at room temperature, only $(PhMe_2P)_2Pt(SiMe_2Ph)(Si_3Ph_7)$ was observed. ^{31}P NMR: -2.48 ($^1J_{PtP} = 3202$, $^2J_{PPtP} = 17$ Hz), -6.46 ($^1J_{PtP} = 2256$ Hz) ppm.

(d) With $Me_3SiSiPh_2H$: when the starting complex had disappeared after 3 h at room temperature, a mixture of $(PhMe_2P)_2Pt(SiMe_2Ph)(SiPh_2SiMe_3)$ (major product) and $(PhMe_2P)_2Pt(SiPh_2SiMe_3)_2$ (minor product) was spectroscopically observed. Due to signal overlap, the resonances of $(PhMe_2P)_2Pt(SiMe_2Ph)(SiPh_2SiMe_3)$ could not be unequivocally assigned. ^{31}P NMR of $(PhMe_2P)_2Pt(SiPh_2SiMe_3)_2$: -4.37 ppm ($^1J_{PtP} = 1665$ Hz).

(e) With Ph_3SiH: when the starting complex had disappeared after 4 d at room temperature, only $(PhMe_2P)_2Pt(SiMe_2Ph)(SiPh_3)$ was observed. ^{31}P NMR: -3.11 ($^1J_{PtP} = 1544$, $^2J_{PPtP} = 18$ Hz), -5.81 ($^1J_{PtP} = 2272$ Hz) ppm. $(PhMe_2P)_2Pt(SiPh_3)_2$ was obtained after heating a *THF* solution to 60°C for 4 d; ^{31}P NMR: -10.11 ppm ($^1J_{PtP} = 1487$ Hz).

Reaction of $(Ph_2MeP)_2Pt(SiMe_2Ph)_2$ (^{31}P NMR: -0.12 ppm ($^1J_{PtP} = 3582$ Hz)) *with* $(MeO)_3SiH$

After 30 min at room temperature, only $(Ph_2MeP)_2Pt[Si(OMe)_3]_2$ was observed; ^{31}P NMR: 15.14 ppm ($^1J_{PtP} = 2818$ Hz).

Reaction of $(Et_3P)_2Pt(SiMe_2Ph)_2$ (^{31}P NMR: 10.49 ppm ($^1J_{PtP} = 2560$ Hz)) *with* $(MeO)_3SiH$

After 45 min at room temperature, only $(Et_3P)_2Pt[Si(OMe)_3]_2$ was observed; ^{31}P NMR: 19.55 ppm ($^1J_{PtP} = 2024$ Hz).

Reaction of $(Ph_3P)(Ph_3Si)\overline{Pt(PPh_2CH_2CH_2Si}Me_2)$ (^{31}P NMR: 57.80 ($^1J_{PtP} = 1648$, $^2J_{PPtP} = 17$ Hz), 29.30 ($^1J_{PtP} = 1762$ Hz) ppm)

(a) With $(MeO)_3SiH$: after 15 min at room temperature, only $(Ph_3P)[(MeO)_3Si]\overline{Pt(PPh_2CH_2CH_2Si}Me_2)$ was observed; ^{31}P NMR: 61.81 ($^1J_{PtP} = 1651$, $^2J_{PPtP} = 21$ Hz), 33.50 ($^1J_{PtP} = 1542$ Hz) ppm.

(b) With Ph_2SiH_2: after 15 min at room temperature, only $(Ph_3P)(Ph_2HSi)\overline{Pt(PPh_2CH_2CH_2Si}Me_2)$ was observed; ^{31}P NMR: 61.33 ($^1J_{PtP} = 1795$, $^2J_{PPtP} = 21$ Hz), 31.60 ($^1J_{PtP} = 1546$ Hz) ppm.

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