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Transition metal silyl complexes.[☆] Part 63. Influence of the phosphane ligands and the metal complex geometry on the silyl group exchange between $L_2Pt(SiMe_2Ph)_2$ ($L_2 = R_2PCH_2CH_2PR_2$ or $2PR_3$) and $HSiR'_3$

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Abstract

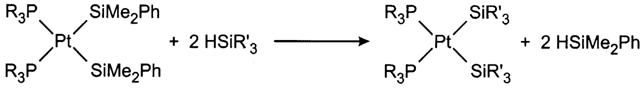
The exchange of the silyl ligands upon reaction of $[(\kappa^2\text{-P,P})\text{-}R_2PCH_2CH_2PR_2]Pt(SiMe_2Ph)_2$ (R = Ph, Me, cyclohexyl) with $HSi(OMe)_3$ or 1,2-bis(dimethylsilyl)benzene was investigated by NMR spectroscopy. The exchange rate is considerably lower than in the complexes *cis*-$(R_3P)_2Pt(SiMe_2Ph)_2$, and decreases in the order R = Ph > Me > cyclohexyl. No exchange was observed in the analogous reactions of *trans*-$(R_3P)_2Pt(SiMe_2Ph)_2$. The isomerization of *cis*-$(PhMe_2P)_2Pt(SiMe_2Ph)_2$ into *trans*-$(PhMe_2P)_2Pt(SiMe_2Ph)_2$ is catalyzed by di- and oligosilanes.

Keywords: Platinum complexes; Silyl complexes; Isomerization

1. Introduction

Silyl group exchange reactions, upon treatment of transition metal silyl complexes with $HSiR_3$, are an interesting option for the synthesis of metal silyl complexes which are otherwise difficult to prepare [2]. Although several exchange reactions are known, little is known about the exchange mechanism and the steric and electronic features that control the exchange reactions.

We have reported recently that reaction of *cis*-$(R_3P)_2Pt(SiPhMe_2)_2$ with an excess of $HSiR'_3$ ($HSiR'_3 = HSi(OMe)_3$, $HSiPh_3$, HSi_3Ph_7, $HPh_2SiSiMe_3$ or H_2SiPh_2) results in the stepwise exchange of both silyl ligands (Eq. (1)) [3]. The exchange rate depends on the nature of the R′ groups and decreases in the order $HSi(OMe)_3 \gg H_2SiPh_2 > HPh_2SiSiMe_3 \gg HSi_3Ph_7 > HSiPh_3$, i.e. rapid exchange is observed if the substituents in the entering silyl group are more electronegative than those of the leaving silane.



(1)

In this article, we discuss the influence of the phosphane ligands and the geometry of the metal complex on the exchange reaction of the complexes $(R_3P)_2Pt(SiMe_2Ph)_2$.

2. Results

In the reaction of *cis*-$(R_3P)_2Pt(SiMe_2Ph)_2$ with an excess of $HSi(OMe)_3$, we had observed previously some influence of the phosphane ligands on the exchange rate [3]. The exchange rate decreased in the order $PPh_2Me > PEt_3 > PPhMe_2$ (complete exchange after 30, 45, or 60 min, respectively), which correlates with the cone angle of PR_3 (PPh_2Me 136° > PEt_3 132° > $PPhMe_2$ 122° [4]). To further test the influence of the

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[☆] For Part 62, see Ref. [1].

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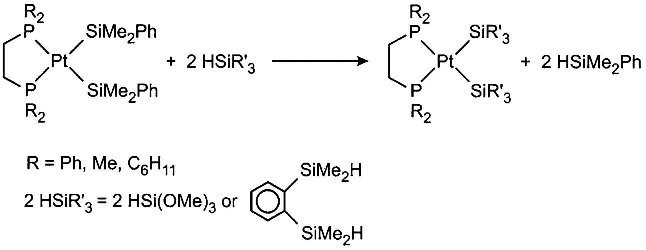
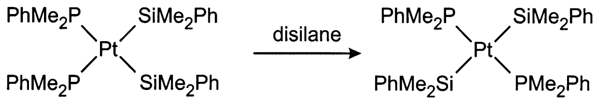
phosphane ligands on the exchange rates and the exchange mechanism, we have employed chelating bis(-phosphane) ligands.

The complexes [(κ^2-P,P)-$R_2PCH_2CH_2PR_2$]Pt($SiMe_2$-$Ph)_2$ (R = Ph [dppe], Me [dmpe], Cy [dcpe, Cy = cyclohexyl]) were reacted with $HSi(OMe)_3$ and 1,2-bis-(dimethylsilyl)benzene (Eq. (2)). The ^{31}P NMR spectra allowed a clear distinction between the starting complexes and the exchange products. Partially exchanged complexes were not observed, and there were no side or decomposition reactions, i.e. after complete exchange of the silyl ligands, the ^{31}P NMR spectra of the reaction mixtures only showed one new singlet with ^{195}Pt satellites. The time needed for the complete exchange of the silyl ligands was considerably longer than for the complexes with monodentate PR_3 ligands. While both silyl ligands of $(R_3P)_2Pt(SiPhMe_2)_2$ were exchanged with $HSi(OMe)_3$ in 30–60 min (depending on the PR_3 ligand), 1 day was needed for the dppe complex to completely react with $HSi(OMe)_3$, likewise with 1,2-bis(dimethylsilyl)benzene under the same conditions. Four days were needed for the dmpe complex and 20 days for the dcpe complex. Thus, the order of reactivity was $2PR_3 > > >$ dppe > dmpe > > dcpe.



(2)

We also tested whether the silyl ligands of *cis*-$(PhMe_2P)_2Pt(SiMe_2Ph)_2$ were exchanged when the complex is reacted with di- and oligosilanes instead of hydrosilanes. When benzene solutions of *cis*-$(PhMe_2P)_2Pt(SiMe_2Ph)_2$ were treated with a 20-fold excess of Si_5Ph_{10}, $(PhMe_2Si)_2$ or $(Ph_2MeSi)_2$, various new signals, which could not be assigned, developed in the ^{31}P NMR spectra. However, in every case, all signals eventually merged into the signal of *trans*-$(PhMe_2P)_2Pt(SiMe_2Ph)_2$ (Eq. (3)). For example, intermediate signals at 0.25 ppm ($^1J_{PtP} = 2870$ Hz) and -2.01 ppm ($^1J_{PtP} = 940$ Hz) were observed in the presence of $(Ph_2MeSi)_2$, and signals at 0.25 ppm ($^1J_{PtP} =$ 2870 Hz) and -18.87 ppm ($^1J_{PtP} = 3597$ Hz) in the presence of Si_5Ph_{10}. The disilanes thus promote isomerization, and the isomerization rate depends on the nature of the silane. Complete isomerization occurred within 9 days in the presence of Si_5Ph_{10}, within 13 days with $(Ph_2MeSi)_2$ and within 18 days with $(PhMe_2Si)_2$. The bis(silyl) complex also isomerizes in the absence of a disilane but at a distinctly lower rate.



(3)

Surprisingly, there was no indication of a silyl group exchange within 9 days when *trans*-$(PhMe_2P)_2Pt$-$(SiMe_2Ph)_2$ was treated with an excess of $HSi(OMe)_3$ or $HSiMe_2SiPh_3$ under the same conditions as employed for *cis*-$(PhMe_2P)_2Pt(SiMe_2Ph)_2$.

Although *trans*-$(PhMe_2P)_2Pt(SiMe_2Ph)_2$ does not exchange the silyl groups, phosphane exchange reactions are possible. When *cis*- or *trans*-$(PhMe_2P)_2$Ptz $(SiMe_2Ph)_2$ was reacted with a 20-fold excess of the slightly less basic $PMePh_2$ phosphane, slow exchange was observed in both cases and *cis*- or *trans*-$(Ph_2MeP)_2Pt(SiMe_2Ph)_2$ was formed. Reaction of the *cis* complex was complete in 18 days, and that of the *trans* complex in 6 days under the same conditions.

3. Discussion

Phosphane dissociation or displacement is often the first step in reactions of d^8 complexes. Even the reductive elimination of Me–EPh_3 (E = Si, Ge) from *cis*-$[(PhMe_2P)_2Pt(EPh_3)Me]$ in the presence of diphenylacetylene is initiated by such a process [5]. All experimental evidence shows that this is also the rate-determining step in the silyl group exchange reactions of $L_2Pt(SiMe_2Ph)_2$ complexes ($L_2 = R_2PCH_2CH_2PR_2$ or $2PR_3$). Decoordination of one phosphorus centers of a chelating bisphosphane ligand is less favored than elimination of one monodentate PR_3. Therefore, the silyl exchange reactions of [(κ^2-P,P)-$R_2PCH_2CH_2PR_2$]Ptz $(SiMe_2Ph)_2$ are strongly retarded relative to the corresponding $(R_3P)_2Pt(SiMe_2Ph)_2$ complexes. The notion that the reversible decoordination of one phosphorus donor is the initial step of the reaction is also supported by our recent finding that platinum complexes containing hemilabile P,N-chelating ligands are considerably more reactive towards silanes than their bis(phosphane) counterparts due to the reversible de-coordination of the nitrogen center [1,6].

In the series of $(R_3P)_2Pt(SiMe_2Ph)_2$ complexes with monodentate PR_3 ligands, the reactivity order was determined by the size of the PR_3 ligands, with bulkier ligands resulting in faster reactions. This is in line with the proposed mechanism as bulkier ligands are more easily eliminated. The reactivity order within the series of complexes with chelating bisphosphane ligands appears to be more dependent on the basicity of the phosphorus centers rather than by their steric properties; more basic phosphorus atoms retard the exchange reaction. The strongly retarding chelate effect appears to override the steric influence of the phosphane substituents.

Once the three-coordinate complex $(R_3P)Pt(SiMe_2Ph)_2$ is formed, the exchange reaction probably proceeds by adding the entering silane to the metal center, i.e. formation of an intermediate five-coordinate Pt(IV) complex $(R_3P)PtH(SiR_3)_3$. If one assumes a square-pyramidal geometry with the hydrogen in the axial position (this requires the least movement of atoms around the metal) then elimination of the silyl group *transoid* to another silyl ligand is more favorable than elimination of the silyl group *transoid* to the PR_3 ligand, due to the strong *trans* effect of silyl ligands (see Ref. [1] for an example on the magnitude of the *trans* effect of silyl ligands). Thus, the complex retains the *cis* geometry once the leaving silane is eliminated and PR_3 ligand re-coordinates (the assumption of any other geometry for the intermediate species would lead to the same result, particularly because they would interconvert by Berry pseudorotation).

The failure of a silyl group exchange for the complexes *trans*-$(PhMe_2P)_2Pt(SiMe_2Ph)_2$ parallels the observation that *cis*-$L_2Pt(SiPh_3)Me$ ($L = PMe_2Ph$, $PMePh_2$) readily reacts with phenylacetylene to give the insertion products *cis*-$L_2Pt[CPh{=}CH(SiPh_3)]Me$, while *trans*-$L_2Pt(SiPh_3)Me$ is totally unreactive towards insertion under the same conditions [7]. Kinetic data indicated that the displacement of a PR_3 ligand by phenylacetylene was the rate-determining step. It was assumed that *cis*-$L_2Pt(SiPh_3)Me$ is more reactive toward PR_3 displacement than the *trans* isomer due to the greater *trans* effect of the SiR_3 ligand. The inhibited elimination of a PR_3 ligand is also the only reasonable explanation for the failure of the silyl group exchange reaction of *trans*-$(PhMe_2P)_2Pt(SiMe_2Ph)_2$.

The fact that both *cis*- and *trans*-$(PhMe_2P)_2Pt(SiMe_2Ph)_2$ slowly exchange the PR_3 ligands is no contradiction to the observed trends in the silane exchange reactions, because the former reactions probably proceed via a five-coordinate intermediate (i.e. an associative mechanism) rather than a three-coordinate intermediate [8].

The *cis*/*trans* isomerization of $(R_3P)_2PtMe_2$ is an equilibrium reaction which varies with the basicity of the PR_3 ligands. With less basic ligands the equilibrium is on the side of the *cis* form, and with more basic ligands on the *trans* side [9]. *Cis*/*trans* equilibration was also observed for the complexes $(R_3P)_2Pt(SiHaryl_2)_2$ (R = Me, Et) [10]. The equilibria were slightly dependent on the solvent and the PR_3 ligands. Less polar solvents and the use of PMe_3 as the auxiliary ligand increased the portion of the *trans* isomer. Most other known Pd(II) and Pt(II) bis(silyl) complexes were obtained as the *cis* isomers, although steric effects appear to play an important role [11]. The results reported in this paper show that the preferred occurrence of the *cis* isomer may also be a kinetic phenomenon. The *cis* isomer of $(PhMe_2P)_2Pt(SiMe_2Ph)_2$ converts in solution to the *trans* isomers on a time-scale of many days to weeks. This very slow isomerization could be the reason why *cis*/*trans* isomerization was not observed more often.

It is known that the *cis*/*trans* isomerization of Pt(II) complexes L_2PtX_2 is catalyzed by nucleophiles [12]. They allow the intermediate formation of five-coordinate compounds and Berry-type rearrangements. The results presented in this paper suggest that di- and oligosilanes can act as rearrangement-promoting nucleophiles. Although no stable oxidative addition product is observed, the Si–Si bonds may weakly coordinate (via a three-center bond) and thus facilitate isomerization.

4. Conclusions

The rate of the exchange of the silyl ligands in the complexes $(R_3P)_2Pt(SiR_3)_2$ upon treatment with hydrosilanes $HSiR'_3$ not only depends on the relative strengths of the involved Pt–Si bonds, but also on the ability of the metal complex to form three-coordinate intermediates $(R_3P)Pt(SiR_3)_2$. While these intermediates easily form from the starting complex *cis*-$(R_3P)_2Pt(SiR_3)_2$ by dissociation of one PR_3 ligand, the use of chelating phosphane ligands in $[(\kappa^2\text{-}P,P)\text{-}R_2PCH_2CH_2PR_2]Pt(SiR_3)_2$ renders dissociation of one phosphorus center more difficult due to the chelate effect and thus retards the silyl group exchange reaction. In the *cis*-$(R_3P)_2Pt(SiR_3)_2$ complexes both PR_3 ligands are *trans* to the strongly activating silyl ligands. Contrary to that, dissociation of a PR_3 ligand in *trans*-$(R_3P)_2Pt(SiR_3)_2$ is inhibited by the much weaker *trans*-effect of the PR_3 ligand.

Promotion of the *cis*/*trans*-isomerization of $(R_3P)_2Pt(SiR_3)_2$ in the presence of di- and oligosilanes indicates that weak coordination of the Si–Si group to the metal center takes place which facilitates isomerization via a five-coordinate intermediate.

5. 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. All reported chemical shift data refer to ^{31}P NMR spectra recorded on Bruker AC250 spectrometer (101.25 MHz) in benzene-d_6 solutions. The solvent was dried over molecular sieve (4 Å) and was stored under argon.

$(dppe)Pt(SiMe_2Ph)_2$ ($\delta = 56.54$ ppm, $^1J_{PtP} = 1308$ Hz) was prepared as reported [13]. $(dcpe)Pt(SiMe_2Ph)_2$ ($\delta = 69.83$ ppm, $^1J_{PtP} = 1398$ Hz) and $(dmpe)Pt(SiMe_2Ph)_2$ ($\delta = 34.23$ ppm, $^1J_{PtP} = 1237$ Hz) were prepared analogously.

5.1. Reactions of $[(\kappa^2\text{-}P,P)\text{-}R_2PCH_2CH_2PR_2]Pt(SiMe_2Ph)_2$ with hydrosilanes

A 20-fold excess of $HSi(OMe)_3$ or 1,2-bis(dimethylsilyl)benzene was added to a benzene-d_6 solution of $[(\kappa^2\text{-}P,P)\text{-}R_2PCH_2CH_2PR_2]Pt(SiMe_2Ph)_2$ in an NMR tube. The NMR tube was sealed under argon, and ^{31}P NMR spectra were recorded at regular intervals to monitor the progress of the reaction.

5.1.1. $(dppe)Pt(SiMe_2Ph)_2$

After 24 h at room temperature, only $(dppe)Pt[Si(OMe)_3]_2$ ($\delta = 60.14$ ppm, $^1J_{PtP} = 1354$ Hz) or $(dppe)Pt(SiMe_2C_6H_4SiMe_2)$ was observed ($\delta = 58.95$ ppm, $^1J_{PtP} = 1394$ Hz).

5.1.2. $(dcpe)Pt(SiMe_2Ph)_2$

After 20 days at room temperature, only $(dcpe)Pt[Si(OMe)_3]_2$ ($\delta = 75.11$ ppm, $^1J_{PtP} = 1405$ Hz) or $(dcpe)Pt(SiMe_2C_6H_4SiMe_2)$ was observed ($\delta = 73.42$ ppm, $^1J_{PtP} = 1429$ Hz).

5.1.3. $(dmpe)Pt(SiMe_2Ph)_2$

After 5 days at room temperature, only $(dmpe)Pt[Si(OMe)_3]_2$ ($\delta = 41.67$ ppm, $^1J_{PtP} = 1310$ Hz) or $(dmpe)Pt(SiMe_2C_6H_4SiMe_2)$ was observed ($\delta = 37.89$ ppm, $^1J_{PtP} = 1323$ Hz).

5.2. Isomerization of *cis*-$[(Me_2PhP)_2Pt(SiMe_2Ph)_2]$ in the presence of di- and oligosilanes

A 20-fold excess of $Si_2Me_4Ph_2$, $Si_2Me_2Ph_4$ or Si_5Ph_{10} was added to a benzene-d_6 solution of *cis*-$[(Me_2PhP)_2Pt(SiMe_2Ph)_2]$ in a NMR tube. The NMR tube was sealed under argon, and ^{31}P NMR spectra were recorded at regular intervals to monitor the progress of the reaction. The signals of several intermediate compounds were observed which eventually disappear after 18, 13 and 9 days, respectively. After this period, only *trans*-$[(PhMe_2P)_2Pt(SiMe_2Ph)_2]$ ($\delta = -5.24$ ppm, $^1J_{PtP} = 2860$ Hz) was observed.

5.3. Phosphane exchange reactions of *cis*-$(PhMe_2P)_2Pt(SiMe_2Ph)_2$

A 20-fold excess of $PMePh_2$ was added to a benzene-d_6 solution of *cis*- or *trans*-$[(PhMe_2P)_2Pt(SiMe_2Ph)_2]$ in an NMR tube. The NMR tube was sealed under argon. ^{31}P NMR spectra were recorded at regular intervals to monitor the progress of the reaction. After 18 (*cis* complex) or 6 days (*trans* complex) at room temperature, *cis*-$(Ph_2MeP)_2Pt(SiMe_2Ph)_2$ ($\delta = 7.59$ ppm, $^1J_{PtP} = 1629$ Hz) or *trans*-$(Ph_2MeP)_2Pt(SiMe_2Ph)_2$ ($\delta = -0.38$ ppm, $^1J_{PtP} = 2613$ Hz) was obtained quantitatively.

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