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# Hydrido-Silyl Complexes, Part VIII*. Photochemical Reaction of $[Fe(CO)_3H(PR'_3)SiR_3]$ with Silanes, $HSiR_3$: Influence of $PR'_3$ and $SiR_3$ on Formation and Structures of Bis-silyl Complexes $[Fe(CO)_3(PR'_3)(SiR_3)_2]$

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## Summary

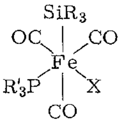
Upon u.v. irradiation of $[Fe(CO)_4(PR'_3)]$ with $HSiR_3$ ($HSiR_3 = HSiMePh_2$, $PR'_3 = PPh_3$; $HSiR_3 = HSiMe_2Cl$, $PR'_3 = PPh_3$ or $PMe_2Ph$; $HSiR_3 = HSiMeCl_2$, $PR'_3 = PPh_3$, $PMePh_2$, $PMe_2Ph$ or $PMe_3$; $HSiR_3 = HSiCl_3$, $PR'_3 = PPh_3$, $PMePh_2$, $PMe_2Ph$, $PMe_3$ or $PBu^n_3$) the corresponding hydrido-silyl complexes $[Fe(CO)_3H(PR'_3)SiR_3]$ are formed. The complexes have the *mer* configuration with a *cis* disposition of the hydride and the silyl ligands. Prolonged irradiation with an excess of silane results in the formation of bis-silyl complexes $[Fe(CO)_3(PR'_3)(SiR_3)_2]$, if electron density at the metal is not too high. Thus, $[Fe(CO)_3H(PPh_3)SiMePh_2]$ and $[Fe(CO)_3H(PMe_2Ph)SiMe_2Cl]$ can be obtained but not the corresponding bis-silyl complexes. Most bis-silyl complexes are obtained as *mer*-isomers with a *cis*-arrangement of the silyl ligands. Only for $[Fe(CO)_3(PR'_3)(SiCl_3)_2]$ with small phosphine ligands ($PR'_3 = PMe_3$ or $PMe_2Ph$) is the *fac*-isomer formed.

## Introduction

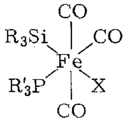
Preparation of hydrido-silyl complexes *cis*-$[Fe(CO)_4(H)SiR_3]$ by oxidative addition of $H\text{-}SiR_3$ to photochemically or thermally generated $[Fe(CO)_4]$ is well established for a variety of silanes(2–4). Since $[Fe(CO)_4(H)SiR_3]$ reacts with an excess of $HSiR_3$ under ultraviolet irradiation, particularly if R is electronegative, bis-silyl complexes *cis*- or *trans*-$[Fe(CO)_4(SiR_3)_2]$ may also be formed in the photochemical reaction of $[Fe(CO)_5]$ with silanes(2, 4, 5).

Phosphine-substituted hydrido-silyl complexes $[Fe(CO)_3H(PR'_3)SiR_3]$ have been prepared by two different routes. The first involves $CO/PR'_3$ exchange of $[Fe(CO)_4(H)SiR_3]$(6). However, this reaction is complicated by the fact that, with basic phosphines, $[Fe(CO)_4(H)SiR_3]$ is deprotonated(6) and, with less basic phosphines, elimination of $HSiR_3$ may occur(2, 6). In a second approach Wrighton *et al.*(7) have prepared $[Fe(CO)_3H(PPh_3)SiR_3]$ by photochemical reaction of $[Fe(CO)_4PPh_3]$ with $HSiR_3$ (R = Et, Ph, OMe or OEt).

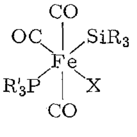
Three of the four possible isomers [(*1–4*), X = H] of $[Fe(CO)_3H(PR'_3)SiR_3]$ have been observed experimentally. Structure *4* (*mer*; H and $PR'_3$ *trans*) was assigned to the products from *thermal* reaction of $PPh_3$ with *cis*-$[Fe(CO)_4(H)SiR_3]$ (R = Ph(6) or Et(7)). Upon *irradiation* of $[Fe(CO)_4(PPh_3)]$ at 100 K in an $HSiEt_3$ matrix or an alkane matrix containing $HSiEt_3$, the *fac*-isomer *(1)* was observed, which rearranges on warming to 298 K to isomer *(3)* (*mer*; $SiR_3$ and $PR'_3$ *trans*). The latter isomer results upon irradiating $[Fe(CO)_4(PPh_3)]$ at 298 K in the presence of $HSiR_3$ (R = Et, Ph, OMe or OEt)(7).



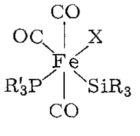
*(1)*



*(2)*



*(3)*



*(4)*

(X = H,$SiR_3$)

To the best of our knowledge, there are only two reports on phosphine-substituted bis-silyl complexes $[Fe(CO)_3(PR'_3)(SiR_3)_2]$(5, 8); both compounds were prepared by $CO/PR'_3$ exchange from the corresponding tetracarbonyl bis-silyl complexes. Three isomers (*1, 2, 3 = 4*; X = $SiR_3$) are possible; $[Fe(CO)_3(PPh_3)(SiCl_3)_2]$ is obtained as isomer *(3 = 4)* from the reaction of $[Fe(CO)_4(SiCl_3)_2]$ with $PPh_3$ at 110–120 °C(5). Recently however, we found that reaction of $[Fe(CO)_4(SiMe_{3-n}Cl_n)_2]$ (n = 0–3) with phosphines is complicated by formation of the *hydrido*-silyl complexes $[Fe(CO)_3H(PR'_3)SiMe_{3-n}Cl_n]$ and *disiloxanes*, $(Me_{3-n}Cl_nSi)_2O$, the extent of these reactions side depending on n and on the reaction conditions(9).

In this paper we report the preparation and stereochemistry of phosphine-substituted bis-silyl complexes by photochemical reaction of $HSiR_3$ with various iron carbonyl phosphine derivatives *via* the corresponding hydrido-silyl complexes.

## Results

The hydrido-silyl complexes *(5–9)* were obtained according to Equation (1) by irradiation of hexane or benzene solutions of $[Fe(CO)_4PR'_3]$ ($PR'_3 = PPh_3$, $PMePh_2$, $PMe_2Ph$, $PMe_3$ or $PBu^n_3$) and a slight excess of $HSiMePh_2$, $HSiMe_2Cl$, $HSiMeCl_2$ or $HSiCl_3$ with ultraviolet light at 0–10 °C.

$$[Fe(CO)_4PR'_3] + HSiR_3 \xrightarrow{h\nu} \underset{(5\text{–}9)}{[Fe(CO)_3H(PR'_3)SiR_3]} + CO \quad (1)$$

| (5–9) SiR3 | PR'3 | $PPh_3$ | $PMePh_2$ | $PMe_2Ph$ | $PMe_3$ | $PBu^n_3$ |
|---|---|---|---|---|---|---|
| $SiMePh_2$ | | *(5a)* | | | | |
| $SiMe_2Cl$ | | *(5b)* | | *(7b)* | | |
| $SiMeCl_2$ | | *(5c)* | *(6c)* | *(7c)* | *(8c)* | |
| $SiCl_3$ | | *(5d)* | *(6d)* | *(7d)* | *(8d)* | *(9d)* |

All hydrido-silyl complexes *(5–9)* are assigned to configuration (*3*, X = H) on grounds of the following spectroscopic findings (Tables 1 and 2). The i.r. spectra are consistent with a *mer*-arrangement of the three carbonyl ligands *(2–4)*. $^2J(PFeH)$ coupling constants (26–31 Hz, Table 2) indicate a *cis*-disposition of H and $PR'_3$ and therefore rule out isomer *(4)*;

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* Part VII of this series, ref. (1).

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**Table 1.** ν(CO) absorptions ($cm^{-1}$) of compounds (*5–14*).

| Complex | | I.r. |
|---|---|---|
| (*5a*) | *mer*-$[Fe(CO)_3H(PPh_3)SiMePh_2]$[c] | 2032w, 1982s, sh, 1965vs |
| (*5b*) | *mer*-$[Fe(CO)_3H(PPh_3)SiMe_2Cl]$[b] | 2025w, 1991s, sh, 1974vs |
| (*5c*) | *mer*-$[Fe(CO)_3H(PPh_3)SiMeCl_2]$[b] | 2052w, 2001s, sh, 1991vs |
| (*5d*) | *mer*-$[Fe(CO)_3H(PPh_3)SiCl_3]$[a] | 2066w, 2016s, sh, 2004vs |
| (*6c*) | *mer*-$[Fe(CO)_3H(PMePh_2)SiMeCl_2]$[a] | 2055w, 2004s, sh, 1993vs |
| (*6d*) | *mer*-$[Fe(CO)_3H(PMePh_2)SiCl_3]$[a, d] | 2073w, 2015s, sh, 2006vs |
| (*7b*) | *mer*-$[Fe(CO)_3H(PMe_2Ph)SiMe_2Cl]$[b] | 2025w, 1990s, sh, 1973vs |
| (*7c*) | *mer*-$[Fe(CO)_3H(PMe_2Ph)SiMeCl_2]$[b] | 2059w, 2002s, sh, 1992vs |
| (*7d*) | *mer*-$[Fe(CO)_3H(PMe_2Ph)SiCl_3]$[a] | 2068w, 2013s, sh, 2003vs |
| (*9d*) | *mer*-$[Fe(CO)_3H(PBu^n_3)SiCl_3]$[a, d] | 2068w, 2010s, 1999vs |
| (*10b*) | *mer*-$[Fe(CO)_3(PPh_3)(SiMe_2Cl)_2]$[a, d] | 2025m, 1991s, sh, 1974vs |
| (*10c*) | *mer*-$[Fe(CO)_3(PPh_3)(SiMeCl_2)_2]$[a] | 2053m, 2004s, sh, 1989vs |
| (*10d*) | *mer*-$[Fe(CO)_3(PPh_3)(SiCl_3)_2]$[b, e] | 2075m, 2031s, 2011vs |
| (*11c*) | *mer*-$[Fe(CO)_3(PMePh_2)(SiMeCl_2)_2]$[b] | 2056m, 2004s, sh, 1987vs |
| (*11d*) | *mer*-$[Fe(CO)_3(PMePh_2)(SiCl_3)_2]$[b] | 2075m, 2032s, 2011vs |
| (*12c*) | *mer*-$[Fe(CO)_3(PMe_2Ph)(SiMeCl_2)_2]$[b] | 2058m, 2004s, sh, 1992vs |
| (*12d*) | *fac*-$[Fe(CO)_3(PMe_2Ph)(SiCl_3)_2]$[b] | 2086vs, 2034s, 1998vw |
| (*13c*) | *mer*-$[Fe(CO)_3(PMe_3)(SiMeCl_2)_2]$[b] | 2065m, 2005s, sh, 1987vs |
| (*13d*) | *fac*-$[Fe(CO)_3(PMe_3)(SiCl_3)_2]$[b] | 2083vs, 2030vs |
| (*14d*) | *mer*-$[Fe(CO)_3(PBu^n_3)(SiCl_3)_2]$[b] | 2072m, 2021s, sh, 2009vs |

[a] petrol ether; [b] $C_6H_6$; [c] $CH_2Cl_2$; [d] not isolated, only spectroscopically observed; [e] see also ref.(5).

a value of 47 Hz was previously reported for an isomer of $[Fe(CO)_3H(PPh_3)SiEt_3]$, in which H and $PPh_3$ are mutually *trans*(7). The close similarity with the i.r. spectra of some of the corresponding bis-silyl complexes, for which configuration (*3* = *4*) (X = $SiR_3$) are proved by $^{29}Si$ n.m.r. (*vide infra*), is decisive in favour of (*3*, X = H).

Each of the new complexes has the same stereochemistry (*3*, X = H) as the products obtained by photochemical reaction of $[Fe(CO)_4PPh_3]$ with other silanes(7). Thus, reaction (1) is quite insensitive to influences of both the silane, $HSiR_3$, and $PR'_3$.

**Table 2.** N.m.r. data of compounds (*5–14*) ($^1H$, $^{31}P\{^1H\}$, $^{29}Si\{^1H\}$; δ [ppm], J [Hz]).

| Compound | $\delta_P$[a] | $\delta_{Fe\text{-}\underline{H}}$[b] | $^2J_{PFeH}$ | $\delta_{Si}$[b] | $^2J_{PFeSi}$ | $\delta_{SiC\underline{H}_3}$ | $\delta_{PC\underline{H}_3}$ |
|---|---|---|---|---|---|---|---|
| (*5a*) | 60.86 | −9.02[c] | 26 | 25.89 | 10.3 | 1.22 | |
| (*5b*) | 58.25 | −8.94 | 26 | | | 1.06 | |
| (*5c*) | 56.74 | −8.63 | 28 | | | 1.38 | |
| (*5d*) | 56.04 | −8.46 | 28 | | | | |
| (*6c*) | 37.06 | −9.12 | 28 | | | 1.38 | 1.48 |
| (*6d*)[d] | 36.93 | −8.95 | 28 | | | | 1.38 |
| (*7b*) | 20.59 | −9.80 | 30 | | | 1.08 | 1.10 |
| (*7c*) | 19.77 | −9.58 | 30 | | | 1.11 | 1.21 |
| (*7d*) | 19.89 | −9.30 | 31 | | | | 1.05 |
| (*9d*)[d] | 37.74 | −9.25 | 30 | | | | |
| (*10b*)[d] | 51.60 | | | | | 0.95 | |
| | | | | | | 1.39 | |
| (*10c*) | 47.58 | | | 73.75 | 16.2 | 1.39 | |
| | | | | 79.34 | 18.4 | 1.52 | |
| (*10d*) | 44.69 | | | | | | |
| (*11c*) | 27.84 | | | | | 1.40 | 1.81 |
| | | | | | | 1.38 | |
| (*11d*) | 25.36 | | | | | | 1.82 |
| (*12c*) | 12.21 | | | 78.51 | 14.0 | 1.36 | 1.38 |
| | | | | 77.56 | 19.9 | | |
| (*12d*) | 9.56 | | | 75.89 | 47.1 | | 1.60 |
| (*13c*) | 3.59 | | | | | 1.38 | 0.85 |
| (*13d*) | 0.98 | | | | | | 1.14 |
| (*14d*) | 25.94 | | | 51.57 | 8.8 | | |
| | | | | 50.15 | 9.6 | | |

[a] $C_6D_6$, rel. ext. $H_3PO_4$; [b] $C_6D_6$, rel. int. TMS; [c] $CDCl_3$, rel. int. TMS; [d] not isolated, only observed spectroscopically.

By contrast, both formation and structures of the bis-silyl complexes (Equation 2) depend on the nature of $HSiR_3$ and $PR'_3$. Formation of $[Fe(CO)_3(PR'_3)(SiR_3)_2]$ is favoured by an increasing number of chlorine substituents at silicon and is suppressed by increasing basicity of the phosphine ligand. The influence of the silyl group is in accordance with the order of reactivity established earlier for the formation of other bis-silyl complexes(10, 11). Thus, if $[Fe(CO)_4PR'_3]$ are irradiated with an excess of $HSiMeCl_2$ or $HSiCl_3$ for prolonged periods (Equations 1 and 2), or if the isolated hydrido-silyl complexes (*5c–8c*) or (*5d–9d*) react with the corresponding silane under the same conditions, the bis-silyl complexes (*10c–13c*) or (*10d–14d*) are obtained without difficulty.

$$\begin{array}{l} [Fe(CO)_3H(PR'_3)SiR_3] + HSiR_3 \\ \qquad\qquad \downarrow h\nu \\ [Fe(CO)_3(PR'_3)(SiR_3)_2] + H_2 \qquad\qquad (2) \\ \qquad (10\text{–}14) \end{array}$$

| (*10–14*) | $PR'_3$<br>$SiR_3$ | $PPh_3$ | $PMePh_2$ | $PMe_2Ph$ | $PMe_3$ | $PBu^n_3$ |
|---|---|---|---|---|---|---|
| | $SiMe_2Cl$ | (*10b*) | | | | |
| | $SiMeCl_2$ | (*10c*) | (*11c*) | (*12c*) | (*13c*) | |
| | $SiCl_3$ | (*10d*) | (*11d*) | (*12d*) | (*13d*) | (*14d*) |

If the number of chlorine atoms at silicon is further decreased, the analogous reaction becomes more difficult: In the photochemical reaction of (*5b*) with an excess of $HSiMe_2Cl$ the conversion to (*10b*) is incomplete even after several days. If the more basic $PMe_2Ph$ ligand is used instead of $PPh_3$, *i.e.* if (*7b*) is irradiated with $HSiMe_2Cl$, the corresponding bis-silyl complex, $[Fe(CO)_3(PMe_2Ph)(SiMe_2Cl)_2]$, is not formed at all. Note that $[Fe(CO)_4(H)SiMe_2Cl]$ (containing the less basic CO instead of $PR'_3$) cleanly reacts with an excess of $HSiMe_2Cl$ under these conditions to give $[Fe(CO)_4(SiMe_2Cl)_2]$(9). Extrapolating these results, it is not unexpected that *5a* does not react with an excess of $HSiMePh_2$.

The stereochemical outcome of Reaction (2) depends on the $PR'_3$ and $SiR_3$ ligands. All bis-silyl complexes containing *$SiMe_2Cl$* or *$SiMeCl_2$* ligands (*10b*, *10c–13c*) have the same configuration as judged by the infrared ν(CO) absorptions and the $^{31}P$-n.m.r chemical shifts (Tables 1 and 2). $^{29}Si$-n.m.r. spectra of two representatives from this series (*10c* and *12c*) show two different signals. Since only (*3* = *4*, X = $SiR_3$) has non-equivalent silyl groups, this structure is unambiguously proved by the $^{29}Si$-n.m.r. spectra.

In the case of *trichloro*silyl-substituted bis-silyl complexes, $[Fe(CO)_3(PR'_3)(SiCl_3)_2]$, two different isomers are obtained from reaction (2), depending on the nature of the phosphine ligand. Whereas (*10d*) and (*11d*) have the *mer*-configuration as in (*10b*) and (*10c–13c*) (thermal reaction of $[Fe(CO)_4(SiCl_3)_2]$ with $PPh_3$ also yields isomer (*3* = *4*) of (*10d*)(5)), i.r. and n.m.r. spectra of (*12d*) and (*13d*) are different. In particular, there is only one signal in the $^{29}Si$-n.m.r. spectrum of (*12d*). Only isomers (*1*) and (*2*) have equivalent silyl ligands, but they can easily be distinguished by their i.r. spectra. The ν(CO) absorptions suggest a *fac*-arrangement of the three carbonyls [isomer (*1*), X = $SiCl_3$]. $^{31}P$-n.m.r.-spectroscopic investigation of a solution in which reaction of (*7d*) with $HSiCl_3$ had been prematurely stopped, showed a small additional signal at $\delta_P$ = 10.66 ppm. In addition, a doublet at 1.31 ppm (J(PCH) = 10 Hz) was observed in the $^1$H-n.m.r. spectrum of this solution. These signals disappear, if irradiation is continued. For *(12d)* and *(13d)* we therefore cannot exclude that *mer*-isomer *(3 = 4)* is originally formed (as for the other bis-silyl complexes), and it then isomerizes to the *fac*-isomer *(1*, X = $SiCl_3$)*.

To find out, whether there is a steric or an electronic influence of the phosphine ligand on the stereochemistry of $[Fe(CO)_3(PR'_3)(SiCl_3)_2]$ complexes, we allowed $[Fe(CO)_4PBu^n_3]$ to react with an excess of $HSiCl_3$. $PBu^n_3$ is as basic as $PMe_3$, but has a much larger cone angle$^{(12)}$ ($PPh_3$ 145°, $PMePh_2$ 136°, $PBu^n_3$ 132°, $PMe_2Ph$ 122°, $PMe_3$ 118°). If the stereochemistry of the isomer of *(14d)* formed preferentially is governed by *electronic* factors, the $PBu^n_3$ derivative should have the same structure *(1*, X = $SiCl_3$) as the $PMe_3$-substituted complex. On the other hand, a *steric* influence of the phosphine ligand should result in the same structures for *(11d)* and *(14d)*, $PMePh_2$ and $PBu^n_3$ having about the same cone angles. The latter is found experimentally. On grounds of the i.r. and $^{29}$Si-n.m.r. spectra, the *mer*-configuration *(3 = 4*, X = $SiCl_3$) is unambiguously proved for *(14d)*.

In conclusion, photochemically prepared bis-silyl complexes $[Fe(CO)_3(PR'_3)(SiR_3)_2]$ usually have a *mer*-configuration with a *cis*-disposition of the silyl ligands *(3 = 4*, X = $SiR_3$). Only for $SiR_3$ = $SiCl_3$ and small phosphine ligands ($PMe_3$ or $PMe_2Ph$) is the *fac*-isomer *(1*, X = $SiCl_3$) obtained. We believe that the influence of the silyl groups on the stereochemistry is electronic, because the cone angles of $SiCl_3$ and $SiMeCl_2$ are very similar. We were unable to find any indication of a *mer-fac*-isomerization when we irridiated or heated a solution of *(13c)* for prolonged periods.

Except with *(7d/12d)* and *(8d/13d)*, the progress of reactions (1) and (2) is difficult to monitor, because the ν(CO) absorptions of the hydrido-silyl complexes *(5–9)* and the corresponding *mer*-bis-silyl complexes are very similar. The main difference is a more intense ν(CO) absorption with the highest wavenumber for the bis-silyl complexes. However, formation of the hydrido-silyl complexes is quite rapid (more rapid than photochemical reaction of unsubstituted $[Fe(CO)_5]$ with the same silanes under the same conditions), whereas formation of the bis-silyl complexes is much slower and requires an excess of $HSiR_3$. Therefore the hydrido-silyl complexes *(5–9)* can be obtained free of bis-silyl complexes *(10–14)*, if irradiation is stopped as soon as the i.r. spectra indicate that the $[Fe(CO)_4PR'_3]$ has been consumed. Conversion of the hydrido-silyl complexes to the corresponding bis-silyl complexes (Equation 2) is best monitored by the disappearance of the Fe–H signal in the $^1$H-n.m.r. spectrum of the reaction mixture.

There are some general trends in the spectroscopic data of the complexes *(5–14)*:

(1) ν(CO) are shifted considerably to higher wavenumbers (i.e. the electron density at the metal is decreased), by an increasing number of chlorine atoms at silicon. Simultaneously, $\delta_P$ decreases and $\delta_{Fe\text{-}\underline{H}}$ increases;

(2) Within a series of complexes having the same silyl but different phosphine ligands, ν(CO) and $^2J_{PFeH}$ are hardly affected if $PPh_3$ is replaced by the more basic $PMe_2Ph$. However, $\delta_{Fe\text{-}\underline{H}}$ shifts upfield;

(3) Substitution of the hydride ligand in hydrido-silyl complexes by a second silyl ligand does not greatly influence the ν(CO) absorptions, but causes an upfield shift of the phosphorus resonance;

(4) In *mer*-$[Fe(CO)_3(PR'_3)(SiMe_nCl_{3-n})_2]$, the non-equivalent silyl groups should give rise to two signals for the methyl groups at silicon. However, with increasing basicity of the phosphine ligand the difference in the chemical shifts of the methyl groups becomes smaller. Whereas the signals are separated by 0.13 ppm in *(10c)* and 0.02 ppm in *(11c)*, they coincide in *(12c)* and *(13c)*.

## Conclusions

Phosphine-substituted hydrido-silyl complexes $[Fe(CO)_3H(PR'_3)SiR_3]$ can be prepared easily by photochemical reaction of $[Fe(CO)_4PR'_3]$ with the corresponding silane. A single isomer *(3*, X = H; $SiR_3$ and $PR'_3$ trans) is obtained for a variety of silanes and a number of different phosphines. Upon prolonged irradiation with an excess of silane, the corresponding phosphine-substituted bis-silyl complexes are obtained, if electron density at the metal is not too high. Therefore, electron-withdrawing silyl ligands (*i.e.* silyl groups having electronegative substituents) and phosphine ligands of low basicity favour formation of bis-silyl complexes.

In most cases the geometry of the complexes is preserved upon H/$SiR_3$-exchange and *mer*-$[Fe(CO)_3(PR'_3)(SiR_3)_2]$ *(3 = 4*, X = $SiR_3$) are obtained. Only for $SiCl_3$-substituted complexes containing small phosphine ligands is the *fac*-isomer *(1)* formed, probably by isomerization of the *mer*-isomer.

## Experimental

All reactions were carried out under $N_2$ in dried and $N_2$-saturated solvents. Photochemical reactions were performed in an irradiation vessel using a cooled (0–10 °C) high pressure mercury lamp (TQ 150, Heraeus). $^{31}$P- and $^{29}$Si-n.m.r. measurements were carried out on a Bruker WH 90 spectrometer.

### *Preparation of* $[Fe(CO)_3H(PR'_3)SiR_3]$ *(5–9)*

In a typical experiment $[Fe(CO)_4PR'_3]$ (2–3 mmol) and $HSiR_3$ (4–5 mmol) were dissolved in petrol, $Et_2O$ or $C_6H_6$ (250 cm$^3$). The stirred solution was irradiated with u.v. light for 2–3 h at 0–10 °C. The progress of the reaction was moni-

**Table 3.** Analytical data, melting points and yields.

| Compound | Found (Calcd.) %<br>C | <br>H | M.p.<br>(°C) | Yield<br>(%) |
|---|---|---|---|---|
| *(5a)* | 68.2 (68.01) | 4.9 (4.87) | 88 (dec.) | 80 |
| *(5b)* | 56.2 (56.36) | 4.7 (4.49) | 83 (dec.) | 24 |
| *(5c)* | 50.2 (51.08) | 4.2 (3.68) | 147 (dec.) | 25 |
| *(5d)* | 46.7 (46.90) | 2.9 (2.99) | 69 (dec.) | 35 |
| *(6c)* | 44.6 (44.88) | 3.8 (3.77) | 54 | 55 |
| *(7b)* | 41.5 (41.68) | 5.0 (5.38) | 31 | 25 |
| *(7c)* | 36.4 (36.62) | 3.8 (3.85) | 60 | 40 |
| *(7d)* | 31.7 (31.92) | 2.8 (2.90) | 40 | 45 |
| *(10c)* | 43.6 (43.83) | 3.2 (3.36) | 208 (dec.) | 58 |
| *(11c)* | 38.4 (38.05) | 3.6 (3.37) | 154 | 65 |
| *(11d)* | 31.7 (31.55) | 1.9 (2.15) | 182 | 60 |
| *(12c)* | 31.3 (30.86) | 3.5 (3.39) | 76 | 55 |
| *(12d)* | 24.5 (24.13) | 1.8 (2.01) | 60 | 60 |
| *(13c)* | 21.4 (21.64) | 3.1 (3.38) | 64 | 50 |
| *(13d)* | 15.1 (14.87) | 1.8 (1.87) | 65 | 60 |
| *(14d)* | 29.4 (29.78) | 4.4 (4.50) | 104 | 75 |

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* Note added on proof: On heating a toluene solution of *fac-(12d)* to 115 °C *mer-(12d)* is formed quantitatively. *mer*-(12d) re-isomerizes upon u.v. irradiation to give *fac-(12d)*. *(13d)* behaves analogously.

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tored by i.r. spectroscopy. When the ν(CO) absorptions of $[Fe(CO)_4PR'_3]$ had disappeared, irradiation was stopped. Reaction time decreases with an increasing number of chlorine substituents at silicon. The reaction mixture was then filtered. From the clear yellow filtrate, all volatile components were removed *in vacuo*. The remaining pale yellow-to-brown residue was extracted several times with hot hexane or hexane/benzene 2:1. On cooling the combined solutions to 0 °C the hydrido-silyl complexes precipitated as pale yellow solids. If necessary, they were recrystallized from hexane or hexane/benzene. Elemental analyses, melting points and yields are given in Table 3. Yields were not optimized.

### *Preparation of $[Fe(CO)_3(PR'_2)(SiR_3)_2]$ (10–14)*

Reactions were carried out as decribed above using benzene as a solvent. A 20-fold excess of $HSiR_3$ was used and irradiation times were increased to 1–2 days. Irradiation was stopped when the hydride signal in the $^1H$-n.m.r. spectrum of a sample disappeared. The bis-silyl complexes were isolated as described above; if necessary, the complexes were recrystallized from heptane/benzene or heptane/methylene chloride. Elemental analyses, melting points and yields are given in Table 3 . Yields were not optimized.

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# Reactions of Bis(2,4-pentanedionato)diaquacobalt(II). Part 1. Formation of Dioxygen and Carbonato-complexes

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## Summary

Oxygenation of $[Co(pd)_2(H_2O)_2]$ (Hpd = 2,4-pentanedione) in the presence of triphenylphosphine forms $[Co(pd)_3]$ and a peroxo-complex that shows strong ν(O–O) at 865 $cm^{-1}$. The mechanism of Co-pd cleavage and the concomitant formation of $[Co(pd)_3]$ are discussed. With guanidine carbonate the title compound forms a carbonato-complex, $(CH_5N_3H)_2[Co(CH_5N_3)(CO_3)_2] \cdot H_2O$, which is the violet component of the so-called blue-violet pair of the complexes of the general formula $[CoA_2(CO_3)_2]^{2-}$ ($A_2$ = ethylenediamine or $2\,NH_3$). The carbonato-complex is assigned either a square-pyramidal geometry with monodentate $CH_5N_3$ or a polymeric octahedral structure with a bridging $CH_5N_3$ group.

## Introduction

Molecular oxygen reversibly forms adducts with certain complexes [Equation (1), n = 1 or 2] in biological systems and in a variety of compounds under laboratory conditions, generally when the metal ions are in low oxidation states(1). Dioxygen binding can often be induced (Equation (2), (B = Lewis base) by suitable neutral ligands.

$$n\,[ML] + O_2 = [(ML)_nO_2] \qquad (1)$$

$$n\,[ML] + n\,B + O_2 = [(MLB)_nO_2] \qquad (2)$$

The added ligand ensures extra negative charge on the metal through σ-donation and thereby aiding π-back-donation to the dioxygen.

## Experimental

Bis(2,4-pentanedionato)diaquacobalt(II) was prepared according to the standard method(2) and its i.r. spectrum compared with that of anhydrous $[Co(pd)_2]$(3). The two spectra are essentially similar except that the dihydrate shows a strong absorption at 3400 $cm^{-1}$. The i.r. spectra were recorded on a Perkin-Elmer 283 spectrophotometer. The microanalysis was performed in the Microanalytical Laboratory of the Institute of Inorganic Chemistry, Stuttgart University.

### *Reaction of bis(2,4-pentanedionato)diaquacobalt(II) with molecular oxygen*

A solution of $[Co(Pd)_2(H_2O)_2]$ (0.5 g; 1.7 mmol) in 1:1 PhH:EtOH (50 $cm^3$) was treated with $PPh_3$ (0.45 g; 1.7 mmol) for 4 h at 25 °C. The resultant green solution was filtered, dried in rotary evaporator and then chromatographed

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