Journal of Organometallic Chemistry, 365 (1989) 151–161
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 09602

Transition-metal silyl complexes

XXVIII *. Preparation and stereochemistry of phosphite-substituted hydrido silyl complexes of iron and derived anionic complexes **

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(Received July 26th, 1988)

Abstract

$Fe(CO)_3[P(OR')_3](H)SiR_3$ (R′ = Et,Ph) (**1**) and $Fe(CO)_2[P(OEt)_3]_2(H)SiR_3$ (**2**) are obtained by photochemical reaction of $Fe(CO)_4[P(OR')_3]$ or $Fe(CO)_3[P(OEt)_3]_2$ with a number of different silanes. To avoid side reactions, triphenylphosphite derivatives $Fe(CO)_2[P(OPh)_3]_2(H)SiR_3$ (**5**) are better prepared by thermal reaction of the known *ortho*-metallated complex $Fe(CO)_2[P(OPh)_3]_2$ with silanes. Monophosphite substituted complexes **1** have a *mer* arrangement of the CO ligands and a *trans* disposition of the SiR_3 and $P(OR')_3$ ligands. In the bis-phosphite derivatives **2** and **5** the CO ligands are mutually *trans* and the phosphite ligands *cis*. For $Fe(CO)_2[P(OPh)_3]_2(H)SiMeCl_2$ (**5a**) a second isomer, with *cis*-CO ligands and *trans*-$P(OPh)_3$ ligands, is observed at low temperature. The hydrido silyl complexes **1**, **2** and **5** are fluxional at room temperature. Deprotonation of **2** or **5** with KH gives anionic silyl complexes $K[Fe(CO)_2\{P(OPh)_3\}_2SiR_3]$ (**7**). The reactivity of **7** is exemplified by reactions of the $Si(OEt)_3$ derivative **7b** with Me_3SnCl, Me_2SnCl_2 or Ph_3PAuCl (L_nMCl), which gives the corresponding substitution products $Fe(CO)_2[P(OR')_3]_2[Si(OEt)_3]ML_n$ (**9**). The latter compounds have the same geometry as **2** and **5**. While the Ph_3PAu derivative **9c** is fluxional at room temperature, the stannyl derivatives **9a**,**9b** adopt static structures.

Introduction

We have recently shown that silyl-, germyl- or stannyl-substituted anionic metal complexes $[MeCp(CO)_2MnER_3]^-$ (E = Si, Ge, Sn) or $[Fe(CO)_3(PR'_3)SiR_3]^-$, which

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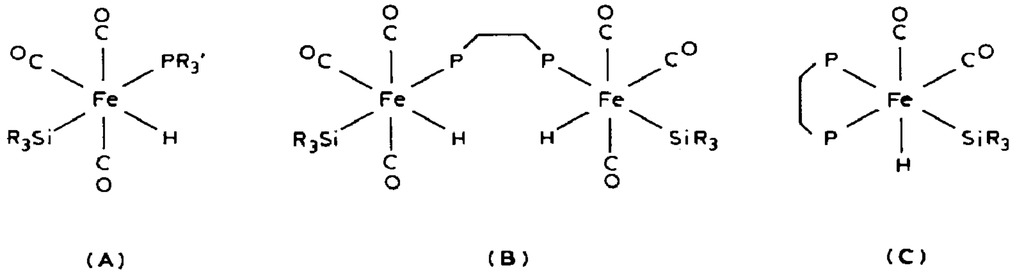
* Part XXVII see ref. 1.

** In memoriam Jerry Zuckermann.

are obtaind by deprotonation of the corresponding hydrido silyl complexes, are interesting precursors for polynuclear complexes [1–3] or complexes containing metal–carbon double bonds [4]. Since the reactivity of the anionic complexes is of course influenced by the electronic and steric properties of the other ligands at the metal, we are interested in obtaining derivatives having different ligand environments. In the iron series, we have already reported on PR_3- and dppe-substituted complexes (dppe = $Ph_2PCH_2CH_2PPh_2$), the preferred geometries of which are given in Scheme 1 [5,6].



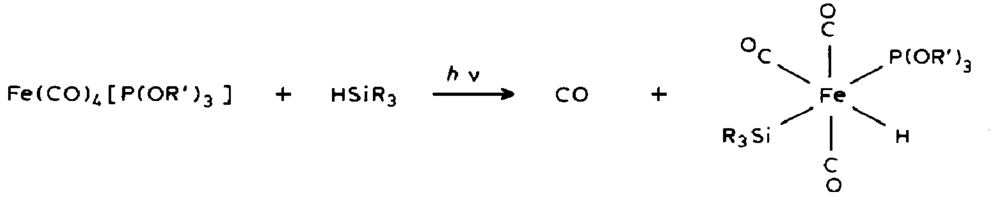
Scheme 1. ($\overline{\text{P}\quad\text{P}}$ = dppe)

This paper deals with the preparation, dynamic behaviour, structural features and reactivity of phosphite-substituted derivatives.

Monosubstituted complexes

For the preparation of the phosphine-substituted complexes **A** UV-irradiation of $Fe(CO)_4PR'_3$ with $HSiR_3$ in hydrocarbon or aromatic solvents is the method of choice [5]. The phosphite-substituted complexes **1** can be correspondingly obtained without difficulties (eq. 1).

Despite the somewhat different electronic and steric properties of $P(OR')_3$ and PR'_3 ligands, complexes **1** adopt the same geometry as their PR'_3-substituted counterparts **A**. The IR spectra are consistent with a *mer* arrangement of the three



(1)

(1)

	R'	SiR_3
a	Ph	$SiMePh_2$
b	Ph	$Si(OEt)_3$
c	Et	$SiPh_3$

Table 1

IR and NMR data of **1**–**3**, **5**, **7** and **9** (+25 °C)

	ν(CO) (cm^{-1})	δ(P) (ppm)	δ(Si) (ppm)	J(PFeSi) (Hz)	δ(FeH) (ppm)	J(PFeH) (Hz) [b]
1a	2062(w),1995(s,sh),1990(vs) [a]	169.9 [b]			−9.4(d)	37
1b	2063(w),2004(s,sh),1998(vs) [a]	169.6 [b]			−9.7(d)	34
1c	2056(w),2000(s,sh),1984(vs) [a]	168.2 [b]	26.8	27.0	−9.2(d)	36
2a	2009(w),1971(s) [c]	164.1 [b]			−10.1(t)	30.0
2b [d]	– [e],1952(s) [a]	170.4 [o]			−10.0(t)	25.1
2c [d]	– [g],1953(s) [h]	173.4 [b]			−10.5(t)	26.9
3 [d]	1996 [a]	179.5 [i,o]			−12.3(t)	18.1
cis-**5a**	2036(m),1985(vs) [h]	157.1 [j]			−9.9(t)	19.4 [n,k]
5b	2016(w),1977(vs) [c]	162.0 [b]	−86.1(t)	81.4	−10.2(t)	17.0
5c [p]	2009(w),1970(vs) [b]	158.6 [j]			−9.9(t)	14.0
5d	2004(w),1963(vs) [h]	160.6 [j]	19.6(t)	7.4	−10.2(t)	15.0
5e	2004(w),1959(vs) [c]	162.8 [b]			−10.5(t)	13.5
5f [d]	2000(w),1955(vs) [a]	163.5 [b]			−10.6(t)	16.5
7a	1920(m),1865(s,sh),1846(vs) [l]					
7b	1914(s),1852(vs),1829(s) [l]	168.8 [m]				
7c	1902(s),1845(s),1812(vs) [o]					
7d	1903(s),1842(vs),1815(s) [l]	168.0 [m]				
7e	1897(m),1841(s),1814(vs) [l]	169.4 [m]				
7f	1884(m),1820(vs),1795(m) [l]					
9a	1943 [c]	155.2(J(AB) 55.1 Hz) [o]				
9b	1960 [a]	152.4(J(AB) 56.6 Hz) [o]				
9c	1952(w),1900(vs) [b]	see text [o]				

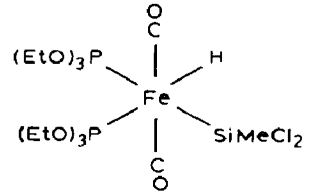
[a] Petroleum ether. [b] Benzene. [c] Cyclohexane. [d] Only spectroscopically identified. [e] Second band hidden by **1c**. [g] Second band hidden by **3**. [h] Et_2O. [i] Off-resonance: quartet. [j] Acetone-d_6. [k] *trans*-**5b**: −9.2 ppm, 62.0 Hz. [l] THF. [m] THF/benzene-d_6. [n] 104 °C in toluene-d_8. [o] Benzene-d_6. [p] ^{13}C NMR (C_6D_6) δ 210.3(t, CO, J(PFeC), 17.1 Hz), 58.3(s, OCH_2), 18.5(s, CH_3).

carbonyl ligands and the magnitude of the ^2J(PFeH) coupling constants indicates a *cis*-disposition of H and $P(OR')_3$ (Table 1).

Disubstituted complexes

While a variety of complexes of the type **A**, **B**, **C** or **1** was prepared by the photochemical route, this method proved to be less efficient for bis-phosphite complexes. On irradiation of $Fe(CO)_3[P(OEt)_3]_2$ with $HSiMeCl_2$, $HSi(OEt)_3$ or $HSiPh_3$, only the $SiMeCl_2$-substituted complex **2a** was obtained without complications (eq. 2).

$$Fe(CO)_3[P(OEt)_3]_2 + HSiMeCl_2 \xrightarrow{h\nu} CO +$$



(2)

(2a)

Reaction with $HSiPh_3$ is extremely slow and gives both the mono-phosphite (**1c**) and the bis-phosphite complex (**2b**) due to competitive phosphite or CO dissociation (eq. 3).

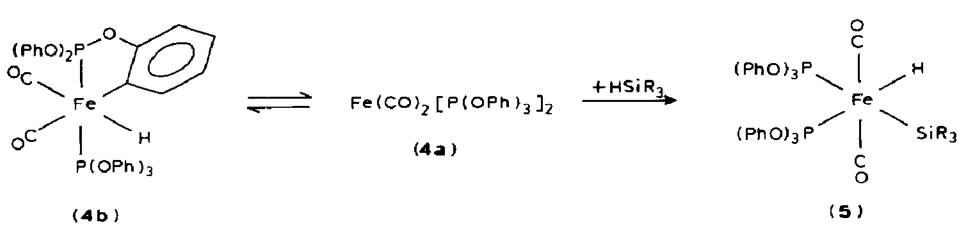
$$\begin{tikzcd} & CO + Fe(CO)_2[P(OEt)_3]_2(H)SiPh_3 \ (\mathbf{2b}) \\ Fe(CO)_3[P(OEt)_3]_2 + HSiPh_3 \arrow[ur, "h\nu"] \arrow[dr] & \\ & P(OEt)_3 + \mathbf{1c} \end{tikzcd} \quad (3)$$

Photochemical reaction of $Fe(CO)_3[P(OEt)_3]_2$ with $HSi(OEt)_3$ is complicated by the formation of $Fe(CO)[P(OEt)_3]_2(H)_3Si(OEt)_3$ (**3**) from **2c** (eq. 4). We were not able to prevent this subsequent reaction or to separate **2c** from **3**.

$$\begin{tikzcd} Fe(CO)_3[P(OEt)_3]_2 + HSi(OEt)_3 \arrow[r, "h\nu", "-CO"'] & Fe(CO)_2[P(OEt)_3]_2(H)Si(OEt)_3 \ (\mathbf{2c}) \arrow[d, "h\nu"', "+HSi(OEt)_3"] \\ & Fe(CO)[P(OEt)_3]_2(H)_3Si(OEt)_3 \ (\mathbf{3}) \end{tikzcd} \quad (4)$$

The spectra of **3** (Table 1) clearly show that this complex is related to the trihydride complexes $Fe(CO)(dppe)(H)_3SiR_3$, which we described recently [7].

Because photochemical preparation of the complexes **2** was less straightforward than anticipated, we looked for another route to prepare bis-phosphite complexes of this type. Grant and Manning showed that the 16-electron species $Fe(CO)_2[P(OPh)_3]_2$ (**4a**), which is generated by irradiation of $Fe(CO)_3[P(OPh)_3]_2$, is stabilized by intramolecular orthometallation. The orthometallated form (**4b**) is in equilibrium with **4a** and can therefore be used for oxidative addition reactions [8].



(5)

	SiR$_3$
cis-a	SiMeCl$_2$
b	Si(OEt)$_3$
c	SiPh$_3$
d	SiMePh$_2$
e	SiMe$_2$Ph
f	SiMe$_3$

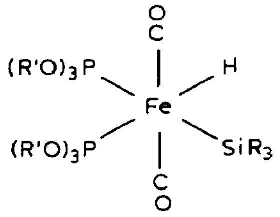
Since the 16-electron species **4a** is thermally generated from the orthometallated complex **4b**, complications arising from photochemical side-reactions can be avoided.

By thermal reaction of **4b** with HSiR$_3$ a number of new hydrido silyl complexes were prepared (eq. 5). The time required for completion of the reaction at room temperature strongly depends on the silane: it increases from 3–4 h for HSiMeCl$_2$ to about 20 h for HSiPh$_3$ and HSiMePh$_2$.

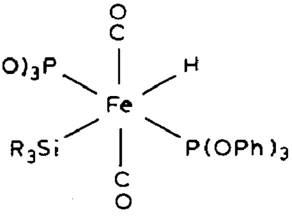
There are two limitations for this reaction: (i) with HSiCl$_3$ not the corresponding hydridosilyl complex but the chloro complex Fe(CO)$_2$[P(OPh)$_3$]$_2$(H)Cl (**6**) is obtained. **6** has previously been prepared by oxidative addition of HCl to **4** [8]. Since we can exclude that the HSiCl$_3$ we used contained HCl, the silane acts as a chlorinating agent in this reaction. Complex **6** is also formed as a byproduct (20%) in the reaction of **4a** with HSiMeCl$_2$. We and others have observed similar reactions before (see e.g. ref. 6,9,10). In **6**, the two P(OPh)$_3$ ligands are *trans* and the two CO ligands *cis* to each other. Melting point and spectroscopic data of **6**, obtained by reaction of **4** with HSiCl$_3$, agree with the values reported in ref. 8 except for δ(Fe*H*), which we observe at -5.9 ppm (instead of -9.9 ppm). (ii) Complexes **5e** and, partially, **5f** with electron-donating silyl ligands are prone to a subsequent reaction, in which (particularly in the presence of excess HSiR$_3$) the silyl group is replaced by a second hydride ligand and the known dihydride complex Fe(CO)$_2$[P(OPh)$_3$]$_2$H$_2$ [8] is formed. This reaction is discussed in more detail in another paper of this series [11].

There are six possible isomers for octahedral complexes of the type Fe(CO)$_2$L$_2$XY. For **2** and **5** the four isomers having *cis*-CO ligands can be excluded on grounds of the ν(CO) bands in the infrared spectra. A very weak absorption between 2000 and 2036 cm^{-1} and a very strong one between 1955 and 1985 cm^{-1} indicate that the two CO ligands are in a distorted *trans* arrangement. Rather strong deviations from an ideal octahedral geometry are not uncommon for transition-metal silyl complexes [6]. Two bands of about equal intensity would be expected for octahedral *cis*-dicarbonyl complexes.

Among the two isomers having *trans* CO ligands, **D** appears more likely than **E** because a hydride ligand usually avoids being *trans* to a silyl ligand. A distinction



(D)



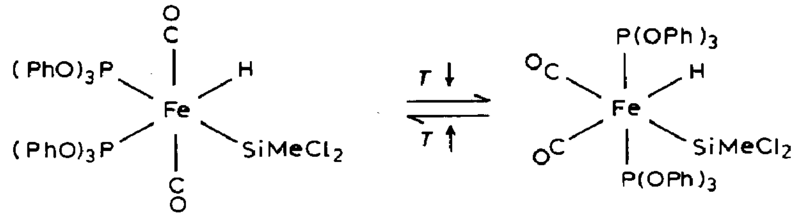
(E)

between both isomers is possible by NMR spectroscopy, because the two phosphorus nuclei are equivalent in **E**, but not in **D**. The room temperature NMR spectra of **2** and **5** show triplets for both the hydride ligand and the silicon nucleus, and a singlet (off-resonance: doublet) for the phosphorus nuclei (Table 1). However, broadening of the phosphorus signal and the center line of the hydride triplet in **2a** and **5b–5d** indicates, that a dynamic process is responsible for the equivalence of the phosphorus atoms rather then a static structure **E**. This is confirmed by low temperature $^{31}P\{^{1}H\}$ and ^{1}H NMR spectra of these compounds. At −60 °C the phosphorus resonance splits into an AB-type signal (**2a**: J(AB) 88 Hz), and in the ^{1}H NMR spectra of **5c**,**5d** a virtual doublet ($J \sim 50$ Hz) is observed at −40 °C for the hydride ligand. Coalescence temperatures are lower for **2b**,**2c** and **5e**,**5f**.

The low-temperature spectra are consistent with structure **D**. Fluxional behaviour is very typical for octahdral hydridosilyl complexes of iron. In fact, all derivatives of type **A**, **B**, **C**, **2** or **5**, which we prepared until the present time [5,6], are dynamic at room temperature.

The $SiMeCl_2$ derivative **5a** exhibits a strucural feature, which is unique among complexes of this type: At +104 °C the hydride signal of **5a** appears as a sharp triplet at −9.9 ppm (J(PFeH) 19.4 Hz) due to the dynamic process discussed above. On cooling, the lines get broader (particularly the low-field signal of the triplet) and coalesce to an unsymmetrical, structureless broad signal at room temperature. However, contrary to the other derivatives, a weak new triplet appears at lower field (−9.3 ppm, J(PFeH) 62 Hz), which becomes stronger and sharper at −50 °C. This phenomenon is reversible. The temperature dependence of the $^{31}P\{^{1}H\}$ NMR spectrum of **5a** provides additional information: The sharp singulet observed at +80 °C at 157.2 ppm gets broad at room temperature. At −70 °C the four lines of the AB spectrum at 159.6 ppm (static structure **D**) are superimposed by a singlet at 157.8 ppm.

Clearly, the additional signals in the low-temperature spectrum of **5a** are due to a second isomer ("*trans*-**5a**"), which is in thermal equilibrium with *cis*-**5a**. The spectroscopic data of *trans*-**5a** are consistent with the structure given in equ. 6. In particular, the high value of J(PFeH), which is similar to J(PFeH) in $Fe(CO)_2[P(OPh)_3]_2HX$ (X = H, Cl; ~ 63 Hz), is indicative for a hydride *cis* to both phosphite ligands [12]. Thus, *trans*-**5a** has the same geometry as $Fe(CO)_2[P(OPh)_3]_2H_2$ ($SiMeCl_2$ replaced by a second hydride) or $Fe(CO)_2[P(OPh)_3]_2(H)Cl$ (**6**, $SiMeCl_2$ replaced by Cl).



(*cis*-**5a**) (*trans*-**5a**)

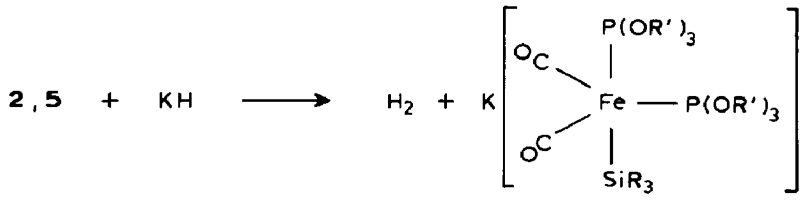
(6)

The isomer with *trans*-P(OPh)$_3$ ligands but *trans*-CO ligands, which would also be in agreement with the observed NMR data for *trans*-**5a**, appears rather unlikely, because a *trans* arrangement of the hydride and the silyl ligand is less favourable in this type of complexes.

At this point a comparison between the structures of Fe(CO)$_2$[P(OR')$_3$]$_2$(H)SiR$_3$ (**2**, **5**) and Fe(CO)$_2$(dppe)(H)SiR$_3$ seems appropriate. While a geometry of that of *trans*-**5a** is not possible for dppe-substituted complexes, a structure corresponding to **D** would be. In fact, the latter geometry is adopted by bis-silyl complexes Fe(CO)$_2$(dppe)(SiR$_3$)$_2$ (a second SiR$_3$ being in place of H) [6]. For Fe(CO)$_2$(dppe)(H)SiR$_3$ only structure **C** is observed. The hydride ligand obviously avoids being *trans* to a phosphine ligand in Fe(CO)$_2$(dppe)(H)SiR$_3$, while it tolerates a less electron-donating phosphite ligand in a *trans* position. By this, the sterically more favourable arrangement of ligands in isomer **D** (the smaller hydride being in the same plane as the bulky phosphite and silyl ligands) becomes possible.

Anionic complexes

The bis-phosphite substituted complexes **2** and **5** are easily deprotonated by KH in THF (eq. 7). Although the derived anionic silyl complexes **7** can be crystallized



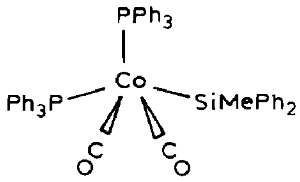
(7)

(**7**)

	R'	SiR$_3$
a	Ph	SiMeCl$_2$
b	Ph	Si(OEt)$_3$
c	Ph	SiPh$_3$
d	Ph	SiMePh$_2$
e	Ph	SiMe$_2$Ph
f	Et	Si(OEt)$_3$

from the solution at low temperatures, their isolation is not necessary if they are used for subsequent reactions.

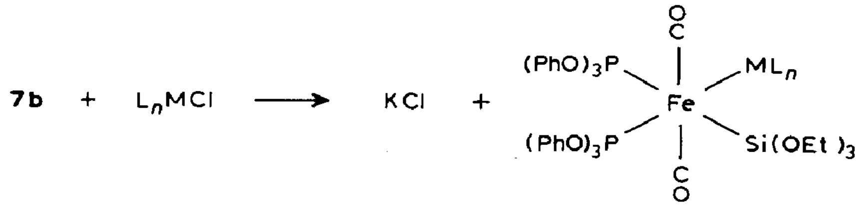
The presence of contact ion pairs is indicated by the number of ν(CO) absorptions in the IR spectra of THF solutions of 7 (Table 1). This behaviour is typical for metal carbonylates [13] and has also been observed for $[Fe(CO)_3(PR'_3)SiR_3]^-$ [3]. On addition of an equimolar amount of 18-crown-6 or $[Ph_3P{-}N{-}PPh_3]^+$ to THF solutions of 7, only the two bands at higher wavenumbers remain, which therefore correspond to the undisturbed anionic metal complex. Their intensity ratio of about 1/2 excludes a trigonal-bipyramidal structure with the CO ligands in an axial/axial or axial/equatorial arrangement and a square-pyramidal structure with *cis*-CO ligands. At room temperature, complexes 7 are fluxional and, therefore, one singulet is observed in the $^{31}P\{^1H\}$ NMR spectra (Table 1). However, the low-temperature ^{31}P NMR spectrum of **7b** ($-85\,^\circ C$) shows an AX pattern (δ 182.9 and 159.0 ppm, *J*(PFeP) 52 Hz) due to chemically non-equivalent phosphorus nuclei. A recent X-ray structure determination of isoelectronic $Co(CO)_2(PPh_3)_2SiMePh_2$ (**8**) shows that this complex, which is also fluxional at room temperature, is square pyramidal in the solid state [14]:



(**8**)

This geometry appears sterically more favourable than a trigonal bipyramid with two of the bulky ligands in axial positions. It is therefore not unreasonable to assume that the structures of the undisturbed anionic metal complexes 7 are similar to **8**.

The reactivity of the bis-phosphite substituted anionic complexes 7 is similar to that of $[Fe(CO)_3(PR'_3)SiR_3]^-$ [3], as exemplified by reactions of **7b** with selected metal halides. On reaction with Me_2SnCl_2, Me_3SnCl or Ph_3PAuCl, the substitution products **9** are obtained within a few minutes (eq. 8).



(8)

(**9**)

	ML_n
a	$SnMe_3$
b	$SnMe_2Cl$
c	$AuPPh_3$

9a,**9b** are rather unstable; particularly in THF solution they decompose within a few hours to give **5b**. The structures of the stannyl silyl complexes **9a**,**9b** are unequivocally deduced from their spectra: A single ν(CO) band in the infrared spectra proves a *trans* arrangement of the CO ligands. In the ^{31}P NMR spectra an AB pattern is observed at room temperature. The phosphite ligands are therefore inequivalent and must be *cis* towards each other. Although the stannyl silyl complexes are isostructural to the corresponding hydrido silyl complx **5b**, they are no longer fluxional at room temperature.

Contrary to that, the spectroscopic properties of **9c** are very similar to those of **5b**. A weak second ν(CO) band at hiher wave-numbers in the infrared spectrum suggests that the CO–Fe–CO axis is slightly bent, although the two CO ligands are still in a *trans* arrangement. Bending of carbonyl ligands towards the gold atom is observed in many dinuclear L_nM–$AuPPh_3$ complexes with carbonyl-containing ML_n fragments [3]. Contrary to **9a**,**9b**, but similar to **5b**, the gold complex **9c** is dynamic at room temperature. While the low-temperature **31P** NMR spectrum is already obtained at +5 °C (ABX pattern with 12 lines, δ(AB) 172.2, 171.0, 170.7, 169.5, 163.0, 162.4, 161.6, 160.0 ppm, *J*(AB) 52 Hz; X-part centered around 39.0 ppm, *J*(AX) and *J*(BX) not determined), the AB part of the spectrum coalesces at 25 °C to two broad, unresolved signals. At +95 °C there is one broad signal for the phosphite ligands and a triplet for the PPh_3 ligand.

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 high-pressure mercury lamp (180 Watt, TQ 150, Heraeus). ^{31}P NMR measurements were carried out on a Bruker WM90 (36.44 MHz, δ(P) rel. ext. H_3PO_4), ^{29}Si NMR measurements on a Bruker WM90 (17.6 MHz) or Jeol FX90Q (17.76 MHz) spectrometer (δ(Si) rel. int. TMS). Analytical data, melting points, and yields of all isolated products are given in Table 2.

Preparation of mer-$Fe(CO)_3[P(OR')_3](H)SiR_3$ (1). This preparation was carried out according to the procedure given for the corresponding PR'_3 derivatives [5]. Colorless solids.

Preparation of $Fe(CO)_2[P(OEt)_3]_2(H)SiMeCl_2$ (2a). A solution of 0.75 g (2 mmol) $Fe(CO)_3[P(OEt)_3]_2$ and 0.81 g (7 mmol) $HSiMeCl_2$ in 150 ml methylcyclohexane is irradiated at −5 °C for 4 h. The progress of the reaction is monitored by IR. The solution is then filtered and concentrated in vacuo. The oily residue is extracted with petroleum ether and the extract concentrated to 5 ml. At −20 °C **2a** precipitates as pale yellow crystals.

Preparation of $Fe(CO)_2[P(OPh)_3]_2(H)SiR_3$ (5). A solution of 2–3 mmol $Fe(CO)_3[P(OPh)_3]_2$ in 150 ml toluene is irradiated at 0 °C for about 3 h according to ref. 8. Particularly towards the end of the reaction (monitored by IR), N_2 is bubbled through the solution to expel CO. After the lamp has been switched off, a 3–5 fold excess of silane is added and the temperature is allowed to raise to room temperature. The solution is then stirred at room temperature until the ν(CO) bands of **4b** are no longer observed (3–20 h depending on the silane). Then the solvent is removed in vacuo.

Table 2

Analytical data, melting points and yields for **1–3**, **5** and **9**

		(Found (calcd.) (%))		m.p. (°C)	Yield (%)
		C	H		
1a	$C_{34}H_{29}FeO_6PSi$ (648.5)	63.24 (62.96)	4.51 (4.72)	63–66	50
1b	$C_{27}H_{31}FeO_9PSi$ (614.4)	52.10 (52.77)	4.91 (5.09)	72 (dec)	60
1c	$C_{27}H_{31}FeO_6PSi$ (566.5)	56.70 (57.20)	5.83 (5.52)	110(dec)	80
2a	$C_{15}H_{34}Cl_2FeO_8P_2Si$ (559.2)	31.70 (32.23)	5.96 (6.13)	41–43	40
5a	$C_{39}H_{34}Cl_2FeO_8P_2Si$ (847.5)	54.90 (55.27)	3.96 (4.04)	102–103	65
5b	$C_{44}H_{46}FeO_{11}P_2Si$ (896.7)	58.84 (58.94)	5.26 (5.17)	68–70(dec)	70
5c	$C_{56}H_{46}FeO_8P_2Si$ (992.8)	67.96 (67.74)	4.68 (4.67)	110–112	70
5d	$C_{51}H_{44}FeO_8P_2Si$ (930.8)	65.48 (65.81)	4.82 (4.76)	87–88	75
5e	$C_{46}H_{42}FeO_8P_2Si$ (868.7)	63.38 (63.60)	4.78 (4.87)	58–60(dec)	45
9a	$C_{47}H_{54}FeO_{11}P_2SiSn$ (1059.5)	53.16 (53.28)	5.01 (5.13)	65–69(dec)	50
9b	$C_{46}H_{51}ClFeO_{11}P_2SiSn$ (1080.0)	51.38 (51.16)	5.10 (4.76)	89–90(dec)	70
9c	$C_{62}H_{60}AuFeO_{11}P_3Si$ (1355.0)	56.11 (54.96)	4.65 (4.46)	97–99(dec)	50

5b, 5e, 5f. The red, oily residue is extracted with warm petroleum ether (30–50 °C). On concentrating the solutions in vacuo, colourless **5b** and **5e** precipitate. **5f** was not isolated. **5e** is separated from $Fe(CO)_2[P(OPh)_3]_2H_2$ by repeated recrystallization.

5a, 5c, 5d (less soluble derivatives). The oily residue is washed with a small amount of petroleum ether and then extracted with warm Et_2O. On concentrating the Et_2O solutions, colourless **5a**, **5c** and **5d** precipitate. They are recrystallized from Et_2O.

Preparation of $Fe(CO)_2[P(OPh)_3]_2[Si(OEt)_3]SnR_3$ (***9a,9b***). To a suspension of 10–20 mmol KH in 15–20 ml THF 1.0–1.5 mmol **7b** is added. The mixture is stirred for about 1 h at room temperature until H_2 evolution ceases. Excess KH is then filtered off. The filtered solution is poured to a slight excess of Me_3SnCl or Me_2SnCl_2. After 10 min at 0 °C the solvent is removed in vacuo and the solid is extracted with petroleum ether (**9a**) or Et_2O (**9b**). On concentrating the solutions, **9a** and **9b** precipitate as colorless solids.

Preparation of $Fe(CO)_2[P(OPh)_3]_2[Si(OEt)_3]AuPPh_3$ (***9c***). 269 mg (0.3 mmol) **7b** in 10 ml THF is deprotonated as described above. The filtered solution is added to a suspension of 173 mg (0.35 mmol) Ph_3PAuCl in 2 ml THF. The mixture is stirred at 0 °C for 10 min and then filtered. From the solution the solvent is removed in vacuo. The residue is washed with a small quantity of petroleum ether and dissolved in a toluene/methylcyclohexane mixture. On cooling, **9c** precipitates as an ocher solid.

Acknowledgements

We thank the Deutsche Forschungsgemeinschaft for financial support of this work, Dr. W. Buchner for taking the ^{31}P NMR spectra and Wacker-Chemie GmbH for gifts of chemicals.

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