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BINUCLEAR ORGANOMETALLIC COMPOUNDS

VIII*. OXIDATIVE ADDITION OF Si—H OR Si—Cl COMPOUNDS TO LOW VALENT Fe, Co, OR Ni COMPLEXES STABILISED BY MONO- OR BIDENTATE PHOSPHINES

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Summary

The reactions of $[(Ph_3P)_4Ni]$, $[(Ph_3P)_3CoN_2]$, $[(dp)_2Ni]$, $[(dp)_2CoH]$, $[(dp)_2Fe(C_2H_4)]$ or $[(dp)_2FeH_2]$ (dp = $Ph_2PCH_2CH_2Ph_2P$) with Ph_nSiCl_{4-n} (n = 1, 2, or 3), Ph_nSiH_{4-n}, X_3SiH (X = Cl or Et), or R_2ClSiH (R = Ph or Me) have been investigated. Solid complexes were isolated which, for the most part, were insoluble in non-polar solvents. Assignments of structures are therefore incomplete, and are based on microanalysis, IR spectra, analogies with established reactions, and (in some cases) chemical degradation. Evidence is presented for the following: *(i)* for Ni^{II}, products from $[(Ph_3P)_4Ni]$ and $HSiXX'X''$ ($XX'X''$ = Ph_3, Ph_2H or PhH_2), the cyclic $[(Ph_3P)_2NiSiCl_2]_2$, and the five-coordinate $[(dp)_2NiX]^+[SiCl_3]^-$ (X = H or Cl_3Si); *(ii)* for Co^{III}, the six-coordinate *cis*-octahedral $[(dp)_2CoH_2]^+[SiXX'X'']^-$ ($XX'X''$ = Cl_3, Cl_2Me, $ClMe_2$, or $ClPh_2$); and for Fe^{II}, the four-coordinate $[(dp)FeH(SiCl_3)]$ and the six-coordinate $[(dp)_2Fe(X)SiCl_3]$ (X = H, Cl, or Cl_3Si).

Introduction

We have considerable interest in the large field of transition organometallic chemistry in which silicon-containing ligands are involved [1]. Our principal concern has been *(a)* compounds having transition metal M—Si bonds [2], *(b)* complexes having Si—C—M bonds, especially the thermally-stable homoleptic alkyls such as $Zr(CH_2SiMe_3)_4$ or $Cr[CH(SiMe_3)_2]_3$ [3], and *(c)* organosilicon reactions in which transition metal complexes have a catalytic role, as in hydrosilylation [4]. The present paper relates mainly to *(a)*, although some of the

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[*] For Part VII, see ref. 2.

reactions and compounds described have relevance to hydrosilylation when catalysed by late first-row transition metal (Fe, Co, or Ni) complexes.

Our previous studies of compounds with M—Si bonds were with d^0 (Zr^{IV} or Hf^{IV}) [5] or d^4 (Cr^{II}, Mo^{II}, or W^{II}) [6] complexes. We also reported on the d^6 Fe^{II} derivatives, with *endo-* [7] or *exo*-cyclic [8] silyl ligands based on strained SiC rings. We now turn to acyclic derivatives of first-row Group VIII transition metals. The systems examined required *(i)* a low valent transition metal substrate (Ni^0, Co^0, Co^I, Fe^0, or Fe^{II}) stabilised with phosphine ligands [the monodentate PPh_3 or the bidentate $Ph_2PCH_2CH_2Ph_2P$(dp)], and *(ii)* a chlorosilane (Ph_nSiCl_{4-n}, $n = 1, 2,$ or 3) or a compound containing an Si—H bond [Ph_nSiH_{4-n}, X_3SiH (X = Cl or Et), or R_2ClSiH (R = Ph or Me)]. Oxidative addition of a silane X_3SiH to a transition metal complex LM to give $LM(H)SiX_3$ or $LM(SiX_3)_2$ is well-established [1]. However, corresponding reactions of chlorosilanes X_3SiCl have not been described, although Ph_3SnCl has been added to $[(Ph_3P)_4Pt]$ [9].

For some of the compounds prepared we suggest ionic structures, in which the anion is a three-coordinate silicon species, e.g., the trichlorosiliconate $[SiCl_3]^-$ anion. Such a proposal is somewhat unusual [10].

A limitation of the present study is the absence of molecular weight, conductivity, or NMR data. The compounds here prepared were, for the most part, insoluble in non-polar solvents and decomposed by water or other polar solvents. Structural assignments depend on stoicheiometry of synthesis, analytical and IR data, and chemical degradation.

Results and discussion

Triphenylphosphine complexes

The results for a Ni^0 and a Co^0 complex are summarised in Figs. 1 and 2.

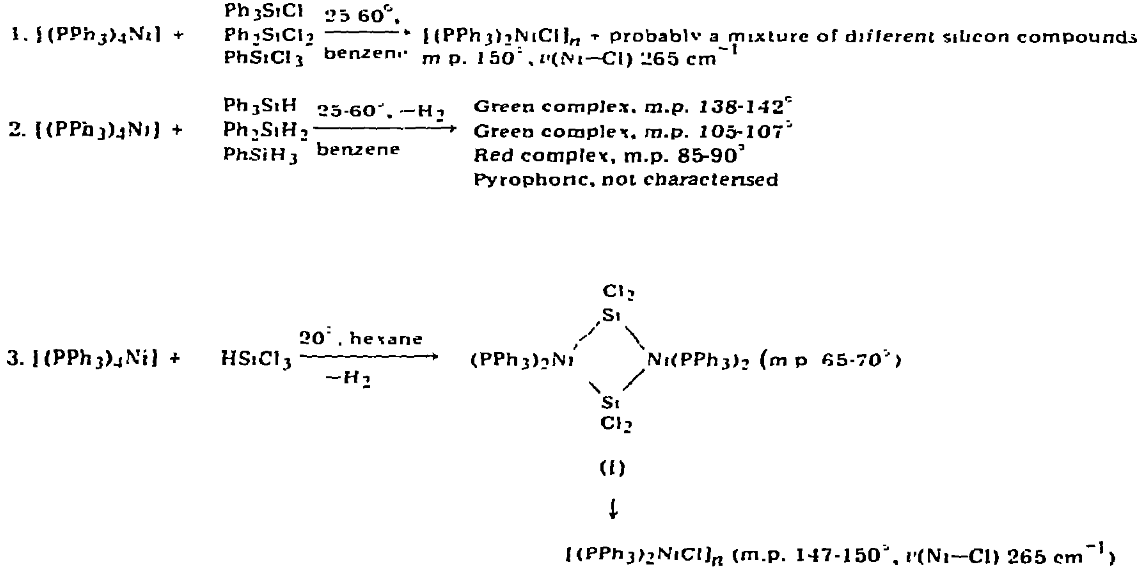


Fig. 1. Ni^0—monodentate ligand substrate reactions

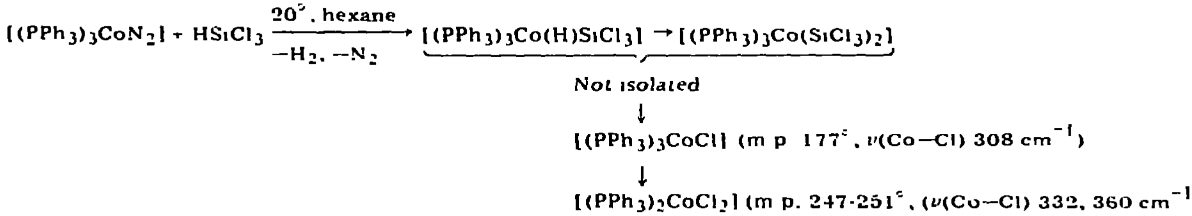


Fig. 2. Co^0—monodentate ligand substrate reactions

Tetrakis(triphenylphosphine)nickel(0) [11] reacted readily with a phenylchlorosilane in benzene. The only compound definitively identified was $[(Ph_3P)_2NiCl]_n$. We suggest that it is produced by chlorine atom abstraction from the chlorosilane and concomitant formation of the appropriate silicon-centred radical, e.g., $Ph_3Si\cdot$, by analogy with the mechanism proposed for the oxidative addition of an alkyl halide (RX, e.g., MeI) to $[(Ph_3P)_3Pt]$ [12]. For the latter, the radical R· was spin-trapped as t-Bu(R)NO and identified by ESR; the highly reactive Pt^IX was converted into $[(Ph_3P)_2Pt(R)X]$, $[(Ph_3P)_2PtX_2]$, or $[(Ph_3P)_2Pt(H)X]$ depending on the nature of R. The oligomeric Ni^I analogue, however, is a stable compound [13]. A bromo analogue has also been obtained from Ph_3BBr and $[(Ph_3P)_2Ni(C_2H_4)]$ [14].

The corresponding reaction with phenylsilicon hydrides instead of chlorides afforded pyrophoric, highly coloured materials which are believed to contain paramagnetic tetrahedral Ni^{II} complexes $[(Ph_3P)_2Ni(SiH_nPh_{3-n})_2]$.

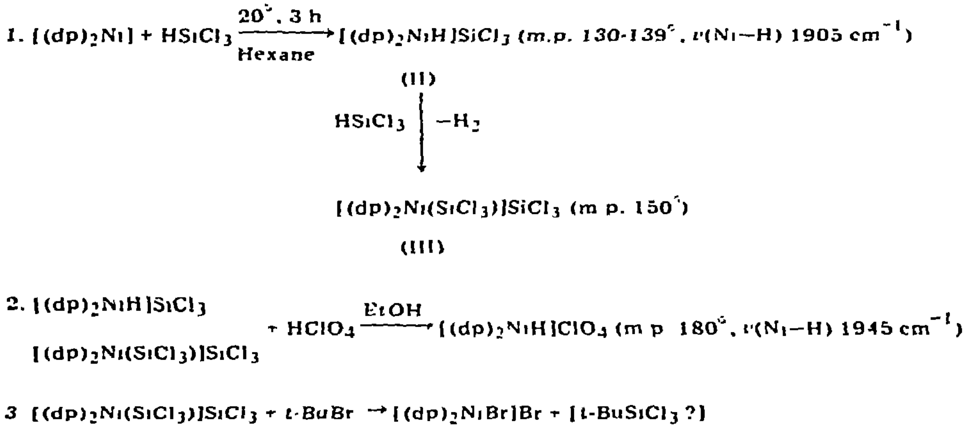
Treatment of red $(Ph_3P)_4Ni$ with Cl_3SiH in hexane produced a yellow precipitate formulated as the ring compound I, which may best be regarded as a Ni^{II} complex. A similar structure has been proposed for $[Cl_2SiFe(CO)_4]_2$ obtained from $Fe(CO)_5$ and Cl_3SiH [15]. Compound I is apparently lattice-stabilised, because dissolution in benzene rapidly caused a colour change and formation of $[(Ph_3P)_2NiCl]_n$.

Trichlorosilane appeared likewise to add oxidatively to $[(Ph_3P)_3CoN_2]$ [16]. However, the postulated Co—Si intermediates were not identified. Both $[(Ph_3P)_3CoCl]$ [17] and $[(Ph_3P)_2CoCl_2]$ [18] are known.

1,2-Bis(diphenylphosphino)ethane (dp) complexes

The results for a Ni^0, Co^I, Fe^0, and Fe^{II} complexes are summarised in Figs. 3-5.

Under mild conditions, addition of trichlorosilane to $[(dp)_2Ni]$ [19], obtained from di-1,5-cyclooctadienenickel(0) [11], yielded complexes formulated as the trichlorosiliconates II or III. The cation $[(dp)_2NiH]^+$ is known [e.g., for the tetrachloroaluminate ν(Ni—H) is at 1950 cm^{-1}] [19]. Compounds II or III were each converted into $[(dp)_2NiH]ClO_4$ (IV) by treatment with $HClO_4$/EtOH at 20°; IV was independently obtained from the latter and $[(dp)_2Ni]$. Compound III and t-BuBr gave the known [20] $[(dp)_2NiBr]Br$, but silicon-containing products were not identified; this type of reaction warrants further examination. Although Cl_3Si^- is well-known as a ligand in transition metal chemistry [1], its existence as an uncomplexed anion is unusual (vide supra). It might be expected to be a convenient source of dichlorosilylene $SiCl_2$ by loss of Cl^-.



1. $[(dp)_2Ni] + HSiCl_3 \xrightarrow[\text{Hexane}]{20°,\ 3\ h} [(dp)_2NiH]SiCl_3$ (m.p. 130-139°, ν(Ni—H) 1905 cm^{-1})

(II)

$\downarrow$ $HSiCl_3$, $-H_2$

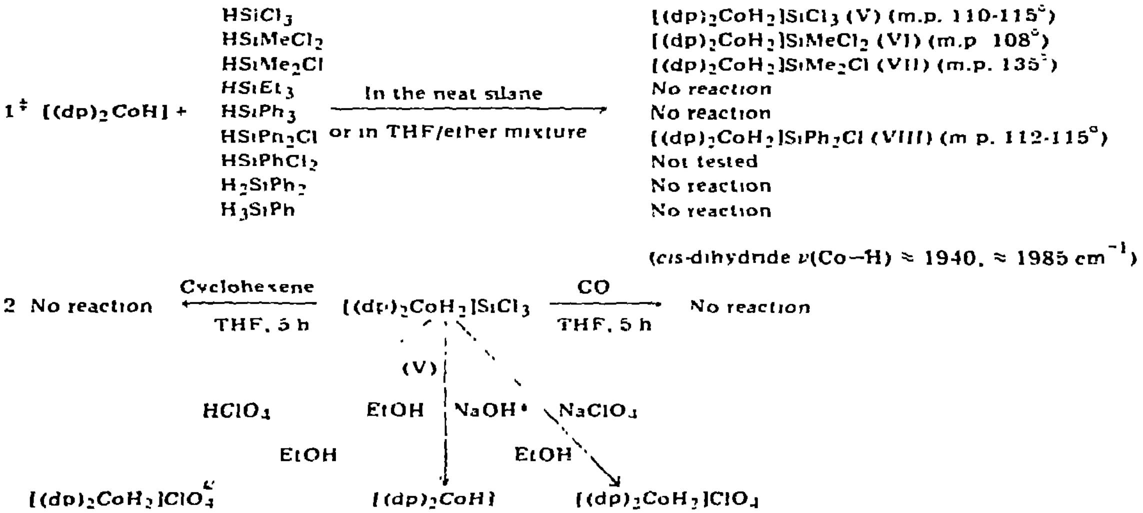
$[(dp)_2Ni(SiCl_3)]SiCl_3$ (m p. 150°)

(III)

2. $\left.\begin{array}{l}[(dp)_2NiH]SiCl_3\\ [(dp)_2Ni(SiCl_3)]SiCl_3\end{array}\right\} + HClO_4 \xrightarrow{EtOH} [(dp)_2NiH]ClO_4$ (m p 180°, ν(Ni—H) 1945 cm^{-1})

3 $[(dp)_2Ni(SiCl_3)]SiCl_3 + t\text{-}BuBr \rightarrow [(dp)_2NiBr]Br + [t\text{-}BuSiCl_3\ ?]$

Fig. 3. Ni^0—bidentate ligand substrate reactions.



1‡ $[(dp)_2CoH]$ + silane $\xrightarrow[\text{or in THF/ether mixture}]{\text{In the neat silane}}$

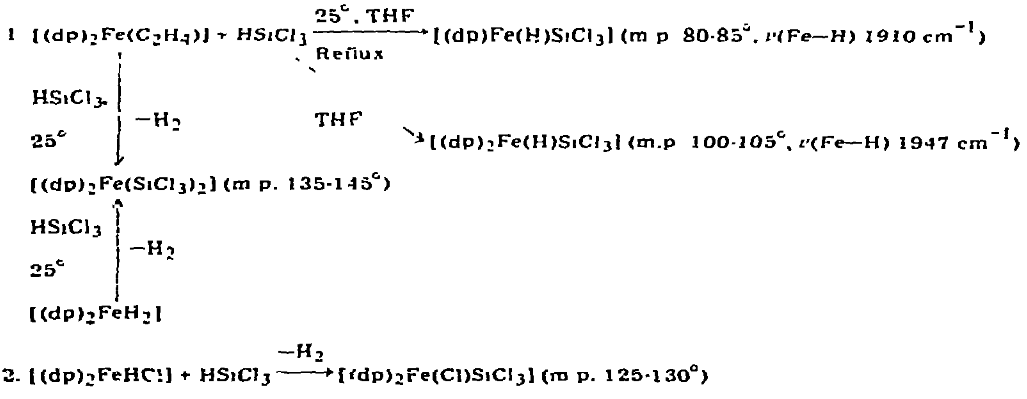
$HSiCl_3$	$[(dp)_2CoH_2]SiCl_3$ (V) (m.p. 110-115°)
$HSiMeCl_2$	$[(dp)_2CoH_2]SiMeCl_2$ (VI) (m.p 108°)
$HSiMe_2Cl$	$[(dp)_2CoH_2]SiMe_2Cl$ (VII) (m.p. 135°)
$HSiEt_3$	No reaction
$HSiPh_3$	No reaction
$HSiPh_2Cl$	$[(dp)_2CoH_2]SiPh_2Cl$ (VIII) (m p. 112-115°)
$HSiPhCl_2$	Not tested
H_2SiPh_2	No reaction
H_3SiPh	No reaction

(cis-dihydride ν(Co—H) ≈ 1940, ≈ 1985 cm^{-1})

2 No reaction $\xleftarrow[\text{THF, 5 h}]{\text{Cyclohexene}}$ $[(dp)_2CoH_2]SiCl_3$ (V) $\xrightarrow[\text{THF, 5 h}]{CO}$ No reaction

$[(dp)_2CoH_2]ClO_4$ $\quad$ $[(dp)_2CoH]$ $\quad$ $[(dp)_2CoH_2]ClO_4$

Fig. 4. Co^I—bidentate ligand substrate reactions. [* Requires 4 mol NaOH per 1 mol of V.] [‡ Other workers [23] find that $[(dp)_2CoH]$ and either pure (HCl-free) $HSiCl_3$ or $H_2SiMeCl$ yield $[(dp)_2CoCl]$ (vide infra).]



1 $[(dp)_2Fe(C_2H_4)] + HSiCl_3 \xrightarrow[\text{Reflux}]{25°,\ THF} [(dp)Fe(H)SiCl_3]$ (m p 80-85°, ν(Fe—H) 1910 cm^{-1})

$\xrightarrow{THF}$ $[(dp)_2Fe(H)SiCl_3]$ (m.p 100-105°, ν(Fe—H) 1947 cm^{-1})

$\downarrow$ $HSiCl_3$, 25°, $-H_2$

$[(dp)_2Fe(SiCl_3)_2]$ (m p. 135-145°)

$\uparrow$ $HSiCl_3$, 25°, $-H_2$

$[(dp)_2FeH_2]$

2. $[(dp)_2FeHCl] + HSiCl_3 \xrightarrow{-H_2} [(dp)_2Fe(Cl)SiCl_3]$ (m p. 125-130°)

Fig. 5. Fe^0— and Fe^{II}—bidentate ligand substrate reactions.

In a similar way, [(dp)$_2$CoH] [21] was treated with various silanes. Si—H compounds containing one or more electronegative chlorine substituent on the Si atom gave products of oxidative addition (V-VIII). These are formulated as siliconate salts, with *cis*-[(dp)$_2$CoH$_2$]$^+$ as the cation. The corresponding perchlorate [ν(CoH$_2$) 1940 and 1985 cm^{-1}] has been made from [(dp)$_2$CoH] and HClO$_4$ [22]. For the case of Cl$_3$SiH in particular, great care was taken to remove dissolved HCl, because this reacts with [(dp)$_2$CoH], to yield [(dp)$_2$CoH(Cl)]Cl [23]. The structural assignments of V-VIII are supported by *(i)* analogy with other oxidative additions to [(dp)$_2$CoH] and with Cl$_3$SiH addition to (dp)$_2$Ni (see above), *(ii)* distinct m.p.'s and microanalytical data for each of V-VIII, *(iii)* IR comparison with the perchlorate, *(iv)* the quantitative reaction of V with NaOH (4 mol to 1 mol of V), and *(v)* some reactions (Fig. 4) of V*. The treatment of V with cyclohexene was an (unsuccessful) attempt to use the latter as a trap for $\ddot{\mathrm{S}}\mathrm{iCl}_2$.

Reactions in the Fe^0 or Fe^{II}dp system to give octahedral Fe^{II} complexes are unexceptional. Related compounds having two Cl$_3$Si$^-$ ligands, or Cl$_3$Si$^-$/Cl$^-$ or Cl$_3$Si$^-$/H$^-$ combinations, are established; as well as their accessibility by either Fe^0/H—SiCl$_3$ oxidative addition or Fe^{II}—H/H—SiCl$_3$ ligand exchange with loss of H$_2$ [1]. More surprising is the reaction leading to the four-coordinate iron(II) complex IX.

Experimental

General procedures

All reactions were carried out in an atmosphere of dry nitrogen. Hydrocarbon and ether solvents were stored over sodium and were freshly distilled before use from sodium—potassium alloy. IR spectra, for Nujol mulls, were recorded on Perkin—Elmer 337 or 125 grating spectrometers. No NMR spectra were obtained because of the insolubility or extremely sparing solubility of the compounds.

The compounds [(Ph$_3$P)$_4$Ni] [11], [(Ph$_3$P)$_3$CoN$_2$] [16], Ph$_2$PCH$_2$CH$_2$Ph$_2$P [24], [(dp)$_2$FeH$_2$] [25], [(dp)$_2$FeHCl] [25], [(dp)$_2$Fe(C$_2$H$_4$)] [21], [(dp)$_2$CoH] [21], [(1,5-COD)$_2$Ni] [11] were obtained by standard methods. [(dp)$_2$Ni] was prepared from a benzene solution [(1,5-COD)$_2$Ni] by addition of Ph$_2$PCH$_2$CH$_2$PPh$_2$. All the silicon compounds were freshly distilled before use, and were obtained by known procedures [26].

Reaction of [(Ph$_3$P)$_4$Ni] with Ph$_3$SiCl

Tetrakis(triphenylphosphine)nickel(0) (2.0 g, 1.8 mmol) and chlorotriphenylsilane (0.54 g, 1.8 mmol) were dissolved in benzene (20 ml) and heated (60°) with stirring for 3-4 h. The red solution slowly turned to brown. Excess of solvent was evaporated and the oily residue was washed with n-hexane (3 × 10 ml). The yellow product was recrystallised (C$_6$H$_6$/C$_6$H$_{14}$), washed with hexane, and dried in vacuo to give the yellow complex [(Ph$_3$P)$_2$NiCl]$_n$ [13] (0.5 g, 40.3%), m.p. 148-150°, ν(Ni—Cl) 265 cm^{-1} (Found: C, 71.2; H, 5.4. C$_{72}$H$_{60}$Cl$_2$Ni$_2$P$_4$ calcd.: C, 69.9; H, 4.9; Cl, 5.7%.)

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* However, Archer, Haszeldine and Parish find [23] that [(dp)$_2$CoH] does not react with HSiCl$_3$ or HSiMeCl$_2$ in this way but affords [(dp)$_2$CoCl] and presumably H$_2$SiCl$_2$ or H$_2$SiMeCl, respectively.

Reaction of [(Ph$_3$P)$_4$Ni] with Ph$_2$SiCl$_2$

A similar reaction was carried out between tetrakis(triphenylphosphine)nickel(0) (2.0 g, 1.8 mmol) and dichlorodiphenylsilane (0.46 g, 1.8 mmol) for 3 h in benzene (20 ml) at 40°. The colour of the reaction changed from red to brown. Work-up as before gave [(Ph$_3$P)$_2$NiCl]$_n$ (0.4 g, 36.0%), m.p. 142°, ν(Ni—Cl) 265 cm^{-1} (Found: C, 71.1; H, 5.8%).

Reaction of [(Ph$_3$P)$_4$Ni] with PhSiCl$_3$

Similarly, tetrakis(triphenylphosphine)nickel(0) (2.0 g, 1.8 mmol) and trichlorophenylsilane (0.38 g, 1.8 mmol) in benzene (20 ml) were stirred at room temperature for 5 h, and the same colour change was noted. Work-up as before likewise gave [(Ph$_3$P)$_2$NiCl]$_n$ (0.5 g, 40%), m.p. 148°, ν(Ni—Cl) 265 cm^{-1} (Found: C, 71.1; H, 5.3%).

Reactions of [(Ph$_3$P)$_4$Ni] with severally Ph$_3$SiH, Ph$_2$SiH$_2$, and PhSiH$_3$

To tetrakis(triphenylphosphine)nickel(0) (2.0 g, 1.8 mmol) in benzene (20 ml) an excess of Ph$_3$SiH was added. The solution was heated at 60° for 5 h. The intense red colour changed to brown. Solvent was evaporated off. The oily residue was washed with several portions of n-hexane. The solid was filtered off and dried in vacuo to give the green bis(triphenylsilyl)bis(triphenylphosphine)nickel(II), m.p. 138-142°.

Similarly, Ph$_2$SiH$_2$ and PhSiH$_3$ gave respectively the green bis(diphenylsilyl)bis(triphenylphosphine)nickel(II), m.p. 105-107°, and the red bis(phenylsilyl)bis(triphenylphosphine)nickel(II), m.p. 85-90°. These compounds are all pyrophoric. Consequently, satisfactory analyses were not obtained, and their probable paramagnetism prevented NMR signals from being recorded.

Reaction of [(Ph$_3$P)$_4$Ni] with HSiCl$_3$

Tetrakis(triphenylphosphine)nickel(0) (1.6 g, 1.4 mmol) was dissolved in n-hexane (15 ml) and the solution was cooled to —196°. An excess of trichlorosilane was distilled into the mixture, which was then allowed to warm to room temperature with stirring. During the reaction a gas was evolved and the red colour of the starting material turned yellow after reaching room temperature (1 h). The product was filtered off under nitrogen, washed with n-hexane, and dried in vacuo to give the complex [(Ph$_3$P)$_2$Ni(SiCl$_2$)]$_2$ (0.9 g, 94.0%), m.p. 65-70° (Found: C, 63.2; H, 4.8; Cl, 9.8. $C_{72}H_{60}Cl_4Ni_2P_4Si_2$ calcd.: C, 63.4; H, 4.4; Cl, 10.4%.)

Decomposition of [(Ph$_3$P)$_2$Ni(SiCl$_2$)]$_2$ in benzene solution

[(Ph$_3$P)$_2$Ni(SiCl$_2$)]$_2$ (1.0 g, 0.73 mmol) was dissolved in benzene (30 ml). The yellow solution became green within 5 min. A portion (ca. 15 ml) of the solvent was evaporated. Addition of n-hexane to the solution furnished yellow crystals. These were filtered off under nitrogen, washed with hexane, and dried in vacuo to give the complex [(Ph$_3$P)$_2$NiCl]$_n$ (0.6 g, 66.3%), m.p. 147-150°, ν(Ni—Cl) 265 cm^{-1}. (Found: C, 70.5; H, 5.3; Cl, 4.7%.)

Reaction of [(Ph$_3$P)$_3$CoN$_2$] with HSiCl$_3$

Dinitrogentris(triphenylphosphine)cobalt(0) (1.0 g, 1.3 mmol) was suspended in n-hexane (10 ml) and cooled to —196° and an excess of trichlorosilane was distilled in. The mixture was allowed to warm to room temperature. The red colour slowly changed to yellow, and gas evolution (H_2/N_2) was observed. The product was rapidly filtered off, washed with n-hexane, and dried in vacuo to give a product of m.p. 80°. Satisfactory analyses were not obtained. In the IR spectrum, absorption at 308 cm^{-1} (Co—Cl) indicated the presence of $(Ph_3P)_3CoCl$ [17]. No ν(Co—H) absorption was seen. When the compound was treated with further $HSiCl_3$ in n-hexane, the colour turned to blue and gave the complex [$(Ph_3P)_2CoCl_2$] [18], m.p. 247-251°, $\nu(CoCl_2)$ 732 and 360 cm^{-1}.

Hydridobis[1,2-bis(diphenylphosphino)ethane]nickel(II) trichlorosiliconate

An excess of trichlorosilane was distilled into bis[1,2-bis(diphenylphosphino)-ethane]nickel(0) (2.0 g, 2.3 mmol) at room temperature. No evolution of hydrogen was observed. The reaction mixture was stirred (3 h) at room temperature. The yellow colour slowly changed to orange. The excess of trichlorosilane was removed under nitrogen. The residue was washed with n-hexane and dried in vacuo to afford the brick-red hydridobis[1,2-bis(diphenylphosphino)ethane]-nickel(II) trichlorosiliconate (2.1 g, 92.0%), m.p. 130-134°, ν(Ni—H) 1905 cm^{-1}. (Found: C, 63.8; H, 5.3; Cl, 9.0. $C_{52}H_{49}Cl_3NiP_4Si$ calcd.: C, 63.1; H, 5.0; Cl, 10.7%.)

Alternatively, an excess of trichlorosilane and bis[1,2-bis(diphenylphosphino)-ethane]nickel(0) (2.0 g, 2.3 mmol) were heated under reflux in n-hexane (20 ml) for 2 h. The yellow colour disappeared, and the residue obtained was orange. Work-up as above gave yellow [$(dp)_2NiH$]$SiCl_3$ (2.2 g, 96.5%), m.p. 130-135°. (Found: C, 63.8; H, 5.2%.)

Trichlorosilylbis[1,2-bis(diphenylphosphino)ethane]nickel(II) trichlorosiliconate

An excess of trichlorosilane was distilled into bis[1,2-bis(diphenylphosphino)-ethane]nickel(0) (2.0 g, 2.3 mmol) at room temperature. The mixture was heated under reflux (35°) for 5 h. The yellow colour of the starting material slowly changed to orange. After ca. 3 h the trichlorosilane was removed under nitrogen and the residue was washed with n-hexane and dried in vacuo to give the yellow trichlorosilylbis[1,2-bis(diphenylphosphino)ethane]nickel(II) siliconate (2.1 g, 81.0%), m.p. 150°. (Found: C, 55.0; H, 4.6. $C_{52}H_{48}Cl_6NiP_4Si_2$ calcd.: C, 55.5; H, 4.3%.)

Hydridobis[1,2-bis(diphenylphosphino)ethane]nickel(II) perchlorate

A suspension of bis[1,2-bis(diphenylphosphino)ethane]nickel(0) (1.0 g, 1.15 mmol) was treated with a solution (10 ml) of 1*M* perchloric acid in ethanol, and the mixture was stirred for 6 h. The yellow precipitate was filtered off, washed with ethanol, and dried in vacuo to give yellow hydridobis[1,2-bis-(diphenylphosphino)ethane]nickel(II) perchlorate (0.9 g, 82%), m.p. 180°, ν(Ni—H) 1945 cm^{-1}. (Found: C, 65.2; H, 5.5. $C_{52}H_{49}ClNiO_4P_4$ calcd. C, 65.3; H, 5.2%.)

Reaction of [$(dp)_2NiH$]$SiCl_3$ or [$(dp)_2NiSiCl_3$]$SiCl_3$ with $HClO_4$

[$(dp)_2NiH$]$SiCl_3$ (0.61 g, 0.62 mmol) or [$(dp)_2NiSiCl_3$]$SiCl_3$ (0.57 g, 0.51 mmol) was added to absolute ethanol containing a slight excess of $HClO_4$. The mixture was stirred for 2 h. The precipitate was filtered off, washed with ethanol, and dried in vacuo to give in both cases [$(dp)_2NiH$]ClO_4 (authentic IR spectra) (0.35 g, 59%, or 0.25 g, 51%, respectively).

Reaction of [(dp)$_2$NiSiCl$_3$]SiCl$_3$ with t-BuBr

[(dp)$_2$NiSiCl$_3$]SiCl$_3$ (0.5 g, 0.45 mmol) was added to t-butyl bromide (10 ml) and the mixture was stirred for 3 h. The yellow colour slowly changed to orange. The precipitate was filtered off, washed with hexane, and dried in vacuo to give the complex [(dp)$_2$NiBr]Br [20] (0.3 g, 66.0%). (Found: C, 60.5; H, 5.0. $C_{52}H_{48}Br_2NiP_4$ calcd.: C, 61.5; H, 4.8%.)

cis-Dihydridobis[1,2-bis(diphenylphosphino)ethane]cobalt (III) trichlorosiliconate

An excess of trichlorosilane was distilled onto hydridobis[1,2-bis(diphenylphosphino)ethane]cobalt(I) (1.0 g, 1.17 mmol) at −78°. The mixture was stirred (2 h) and then allowed to warm to room temperature. Evolution of gas (H_2) was not observed; the red colour of the starting material slowly changed to greenish-yellow. Excess of trichlorosilane was removed under nitrogen and the residue was washed with n-hexane and dried in vacuo to give white *cis*-dihydrido[1,2-bis-(diphenylphosphino)ethane]cobalt(III) trichlorosiliconate (1.1 g, 95.0%), m.p. 110-115°, $\nu(CoH_2)$ 1943 and 1985 cm^{-1}. (Found: C, 62.1; H, 5.2. $C_{52}H_{50}Cl_3CoP_4Si$ calcd.: C, 62.9; H, 5.0; Cl, 12.3; Co, 6.8%.)

The above reaction was repeated, taking particular precautions to purify the $HSiCl_3$ to ensure its freedom from HCl. (We have been informed that the hydridocobalt(I) starting complex readily reacts with HCl to form [(dp)$_2$-CoHCl]Cl [23].) The experiment was carried out using a vacuum line for repeated trap-to-trap fractionation of the trichlorosilane, which was ultimately condensed into the hydridocobalt(I) complex in a Schlenk tube. The white trichlorosiliconate, m.p. 115-120° (dec.). (Found: Cl, 13.1; Co, 6.5%.) This white material turns green upon exposure to air; this is attributed to formation of [(diphos)$_2$CoHCl]Cl.

cis-Dihydridobis[1,2-bis(diphenylphosphino)ethane]cobalt(III) dichloro(methyl)-siliconate

Similarly, an excess of methyldichlorosilane was distilled onto hydridobis[1,2-bis(diphenylphosphino)ethane]cobalt(I) (1.0 g, 1.17 mmol) at −78°. The mixture was stirred (3 h) and warmed to room temperature. Gas evolution was not observed and the colour turned from red to greenish-yellow. Work-up as above gave *cis*-dihydrobis[1,2-bis(diphenylphosphino)ethane]cobalt(III) dichloro(methyl)siliconate (1.0 g, 88.0%), m.p. 108°, $\nu(CoH_2)$ 1945 and 1985 cm^{-1}. (Found: C, 65.4; H, 5.5. $C_{53}H_{53}Cl_2CoP_4Si$ calcd.: C, 65.5; H, 5.5%.)

cis-Dihydridobis[1,2-bis(diphenylphosphino)ethane]cobalt(III) chloro(dimethyl)-siliconate

Hydridobis[1,2-bis(diphenylphosphino)ethane]cobalt(I) (1.0 g, 1.17 mmol) was suspended in a mixture (2/1) of ether and THF (15 ml) and chloro(dimethyl)-silane (0.5 ml) was added. The suspension was stirred for 3-4 h. Gas evolution was not observed and the colour changed from red to yellow. The yellow precipitate was filtered off under nitrogen, washed with ether, and dried in vacuo to give *cis*-dihydridobis[1,2-bis(diphenylphosphino)ethane]cobalt(III) chloro(dimethyl)-siliconate (1.0 g, 90.0%), m.p. 135°, $\nu(CoH_2)$ 1940 and 1980 cm^{-1}. (Found: C, 68.0; H, 5.6. $C_{54}H_{56}ClCoP_4Si$ calcd.: C, 68.2; H, 5.9%.)

cis-Dihydrobis[1,2-bis(diphenylphosphino)ethane]cobalt(III) chloro(diphenyl)-siliconate

In a similar manner, the yellow title compound (1.0g, 80%), m.p. 112-115° ν(CoH$_2$) 1942 and 1983 cm^{-1} (Found: C, 71.3; H, 5.5. $C_{64}H_{60}ClCoP_4Si$ calcd.: C, 71.5; H, 5.6%) was obtained from chloro(diphenyl)silane (0.5 ml) and the hydridocobalt(I) complex (1.0 g, 1.17 mmol).

Further experiments with [(dp)$_2$CoH]

In the following systems, using similar procedures to those outlined above, no reaction was observed with any of the following silanes: Et_3SiH, Ph_3SiH, Ph_2SiH_2, or $PhSiH_3$.

Reaction of cis-[(dp)$_2$CoH$_2$]SiCl$_3$ with NaOH

Dihydridobis[1,2-bis(diphenylphosphino)ethane]cobalt(III) trichlorosiliconate was treated with a solution of 1*M* sodium hydroxide in ethanol. The red substance, formed after several hours, was filtered off, washed with ethanol, dried, and identified (authentic IR spectrum, ν(CoH) 1888 cm^{-1}) as [(dp)$_2$CoH] [22].

The trichlorosiliconate (0.1843 g, 0.212 mmol) was suspended in ethanol. Methanolic sodium hydroxide (2 ml, 0.5 *M*) was added and the mixture was stirred at 20° for 48 h. The red precipitate of hydridobis[1,2-bis(diphenylphosphino)ethane]cobalt(I) (authentic IR spectrum) was filtered off. The filtrate was analysed; this established that 0.856 mmol of NaOH had been consumed.

Reaction of cis-[(dp)$_2$CoH$_2$]SiCl$_3$ with HClO$_4$

cis-Dihydridobis[1,2-bis(diphenylphosphino)ethane]cobalt(III) trichlorosiliconate (0.5 g, 0.5 mmol) was added to absolute ethanol containing a slight excess of perchloric acid. The mixture was stirred (2 h); the solid was filtered off, washed with ethanol, and dried in vacuo to give the yellow [(dp)$_2$CoH$_2$]ClO$_4$ [22] (authentic IR spectrum) (0.4 g, 84.0%).

Reaction of cis-[(dp)$_2$CoH$_2$]SiCl$_3$ with NaClO$_4$

cis-Dihydridobis[1,2-bis(diphenylphosphino)ethane]cobalt(III) trichlorosiliconate (0.5 g, 0.5 mmol) and sodium perchlorate (0.12 g, 1.0 mmol) in ethanol (10 ml) were stirred for 4 h. The resultant yellow compound was filtered off, washed with ethanol, dried in vacuo, and identified as [(dp)$_2$CoH$_2$]ClO$_4$ [22] (authentic IR spectrum) (0.35 g, 13.0%).

Lack of reaction of cis-[(dp)$_2$CoH$_2$]SiCl$_3$ with severally C_6H_{10} and CO

cis-Dihydridobis[1,2-bis(diphenylphosphino)ethane]cobalt(III) trichlorosiliconate (0.5 g, 0.5 mmol) and cyclohexene (2.0 ml) were mixed in THF (15 ml) and the mixture was set aside at 25° for 5 h. No colour change was observed. The residue was filtered off, washed with n-hexane, and dried in vacuo. Thus, the cobalt starting material (authentic IR spectrum) (0.4 g, 80%) was recovered.

cis-Dihydridobis[1,2-bis(diphenylphosphino)ethane]cobalt(III) trichlorosiliconate (0.5 g, 0.5 mmol) was suspended in THF (15 ml) and carbon monoxide was bubbled through this at 25° for 5 h. Filtration, washing with n-hexane, and drying in vacuo gave authentic (IR) cobalt starting material (0.4 g, 80%).

Hydrido(trichlorosilyl)[1,2-bis(diphenylphosphino)ethane]iron(II)

Bis[1,2-bis(diphenylphosphino)ethane]ethyleneiron(0) (1.5 g, 1.7 mmol) was dissolved in THF (35 ml) and cooled to −78°. An excess of trichlorosilane was distilled into the solution. The mixture was allowed to warm to room temperature, with stirring. The intense red colour of the solution gradually changed during the course of the reaction and a pale yellow compound was deposited. The mixture was set aside for 2 h, whereafter the solid was filtered off, washed with a small amount of anhydrous THF, dried in vacuo, and identified as hydrido(trichlorosilyl)[1,2-bis(diphenylphosphino)ethane]iron(II) (0.8 g, 80.0%), m.p. 80-85°, ν(Fe—H) 1910 cm^{-1}. (Found: C, 52.0; H, 4.7. $C_{20}H_{25}Cl_3FeP_2$ calcd.: C, 52.9; H, 4.3%.)

In another experiment, bis[1,2-bis(diphenylphosphino)ethane]ethyleneiron (0) (1.0 g, 1.13 mmol) was dissolved in THF (20 ml) and an excess of trichlorosilane was distilled into the solution. The mixture was heated (3 h) under reflux. During the course of the reaction a compound, probably [(dp)Fe(H)SiCl$_3$], was deposited but redissolved; at the end of the reaction a deep-purple solution was obtained. The excess of trichlorosilane and some (ca. 10 ml) of the solvent were evaporated. Addition of n-hexane afforded an intense red precipitate. This was filtered off, washed with hexane, and dried in vacuo to give the complex [(dp)$_2$Fe(H)SiCl$_3$] (0.9 g, 80.5%), m.p. 100-105°, ν(Fe—H) 1947 cm^{-1}. (Found: C, 63.4; H, 4.8. $C_{52}H_{49}Cl_3P_4Si$ calcd.: C, 65.2; H, 4.9%.)

Bis(trichlorosilyl)bis[1,2-bis(diphenylphosphino)ethane]iron(II)

An excess of trichlorosilane was distilled into bis[1,2-bis(diphenylphosphino)ethane]ethyleneiron(0) (1.0 g, 1.13 mmol) at −78°. The mixture was stirred (5 h) and then allowed to attain room temperature. Gas (C_2H_4/H_2) evolution was observed and the colour of the original starting material brightened. The pale yellow residue was filtered off, washed with n-hexane, and dried in vacuo to yield bis(trichlorosilyl)bis[1,2-bis(diphenylphosphino)ethane]iron(II) (1.2 g, 95.0%), m.p. 135-145°. (Found: C, 55.7; H, 4.1. $C_{52}H_{48}Cl_6FeP_4Si_2$ calcd.: C, 55.7; H, 4.3%.)

Similarly, an excess of trichlorosilane was distilled into dihydridobis[1,2-bis(diphenylphosphino)ethane]iron(II) (1.0 g, 1.2 mmol) at −78°. The mixture was heated to room temperature and was stirred (2 h). Gas evolution (H_2) was observed. Work-up as above gave the complex [(dp)$_2$ Fe(SiCl$_3$)$_2$] (1.2 g, 89.0%), m.p. 130-144°. (Found: C, 55.7; H, 4.1%.)

Chloro(trichlorosilyl)bis[1,2-bis(diphenylphosphino)ethane]iron(II)

An excess of trichlorosilane was stirred into hydridochlorobis[1,2-bis(diphenylphosphino)ethane]iron(II) (1.0 g, 1.12 mmol) at −78°. The mixture was heated to room temperature and was stirred (2 h). Gas evolution (H_2) was observed. The red colour slowly changed to yellow. The residue was filtered off under nitrogen, then was washed with n-hexane and finally dried in vacuo to give chloro(trichlorosilyl)bis[1,2-bis(diphenylphosphino)ethane]iron(II) (0.9 g, 79.0%), m.p. 125-130°. (Found: C, 61.6; H, 5.0; Cl, 11.2. $C_{52}H_{48}Cl_4FeP_4Si$ calcd.: C, 61.1; H, 4.7; Cl, 13.9%.)

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