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Preliminary communication

A novel bidentate silicon containing ligand: cyclopentadienyldimethylsilane

Ernest Colomer *, **Robert J.P. Corriu and Roser Pleixats**

Laboratoire Hétérochimie et Aminoacides, U.A.C.N.R.S. 1097, Institut de Chimie Fine, Université de Montpellier II, Place E.-Bataillon, F-34060-Montpellier-Cédex-01 (France)

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Abstract

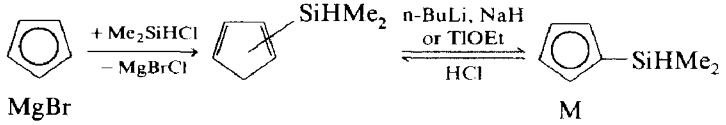
The dimethylsilylcyclopentadienide anion undergoes cleavage of the silicon–cyclopentadienyl bond upon attempted complexation with transition metals. Complexes bearing such ligands can be obtained by metallation of the cyclopentadienyl ligand in tricarbonyl(η^5-cyclopentadienyl)manganese, ferrocene and ruthenocene, followed by reaction with chlorodimethylsilane. The silicon-hydrogen function can react with carbonyl cobalt or carbonyl(hydrido)tris(triphenylphosphine)iridium, to give heterobimetallic complexes in which cyclopentadienyldimethylsilane acts as an assembling ligand.

Similar complexes are obtained starting from tricarbonyl(η^6-benzene)chromium.

Cyclopentadiene, carbon monoxide, and tertiary phosphines are the most widely used ligands in transition metal chemistry. Species containing both cyclopentadiene moiety and phosphine ligands have been used in the synthesis of heterobimetallic complexes with or without direct interaction between the two metallic centers [1].

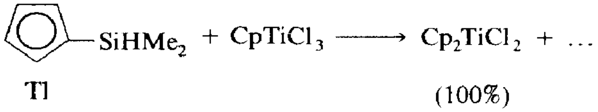
We have examined the possibility of using cyclopentadienyldimethylsilane as a ligand which brings together the cyclopentadiene and a silicon-hydrogen function. Such a compound should allow the complexation of two metals, one through the cyclopentadiene and the other through the silicon. The main point of interest is that, in contrast to that of phosphines, the complexation of the silane can be irreversible [2].

Cyclopentadienyldimethylsilane [3] is conveniently prepared by reaction of a suspension of C_5H_5MgBr in benzene with Me_2SiHCl. Its sodium, lithium or thallium salts are obtained by conventional methods [4,5] (eq. 1). However, treatment of these salts with suitable transition metal complexes leads to a cleavage of the Cp–Si bond; an example of this behaviour is given in eq. 2. Evidently this silicon compound cannot be used directly as a ligand.



(M = Li, Na, Tl)

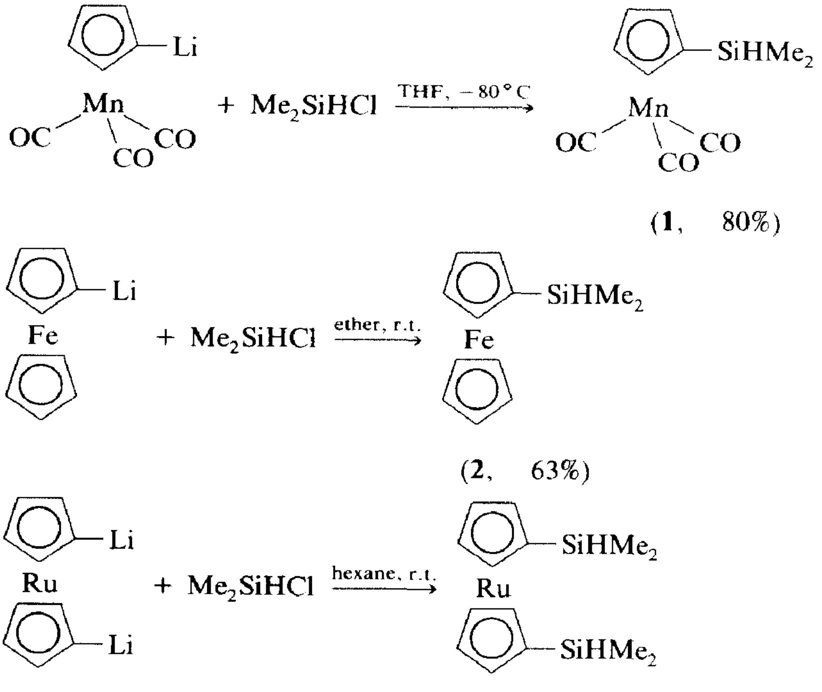
(1)



(100%)

(2)

The required complexes can be obtained by an indirect method, involving metallation of the cyclopentadienyl ring in metal complexes, followed by reaction with Me_2SiHCl. Thus the lithium derivatives of tricarbonyl(η^5-cyclopentadienyl)



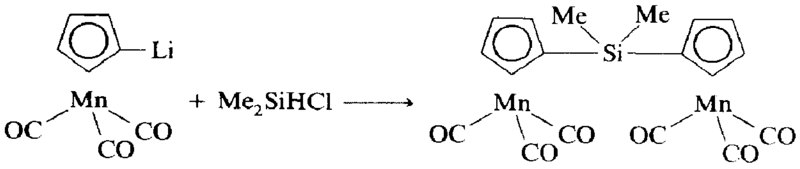
(**1**, 80%)

(**2**, 63%)

(**3**, 84%)

Scheme 1

manganese, ferrocene and ruthenocene [6,7,8] react normally with Me_2SiHCl (Scheme 1). The experimental conditions are important; the lithium compound must be added to the chlorosilane, reverse addition leading to disubstitution (eq. 3).



(3)

Table 1

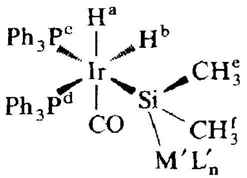
Some physicochemical data of new complexes

Complex	IR (hexane ν((CO) (cm^{-1})	(δ(ppm)) SiH	^{1}H NMR (C_6D_6) C_5H_4 and C_5H_5			CH_3 δ (ppm), J (Hz))	Mass spectrum (molecular peak)	M.p. (°C)
1	2022,1942 2136 (ν(SiH))	4.47 (m, 1H)	4.40 (m, 2H)	4.27 (m, 2H)		0.10 (s, 6H, J 3)	262	oil
2	2118 (ν(SiH))	4.81 (hept, 1H, J 3.6)	4.33 (t, 2H, J 1.8)	4.18 (t, 2H, J 1.8)	4.15 (s, 5H)	0.28 (d, 6H, J 3.6)		oil
3	2110 (ν(SiH))	4.73 (hept, 2H, J 3.6) (partially obscured)	4.72 (t, 4H, J 1.8)	4.58 (t, 4H, J 1.8)		0.20 (d, 12H, J 3.6)	347 ($M^+ - 1$)	oil
4	2090, 2022, 1996, 1945		4.58 (m, 2H)	4.17 (m, 2H)		0.67 (s, 6H)	348 ($M^+ - 3CO$)	90–93
5	2015, 1958, 1915 2070 (ν(IrH))							80–82
6	2093, 2030, 1992		4.04 (t, 2H, J 1.8)	3.96 (t, 2H, J 1.8)	3.80 (s, 5H)	0.53 (s, 6H)	414	90–92
7	1958 2065 (ν(IrH))							121–122
8	2090, 2025, 1992, 1988		4.88 (broad s, 4H)	4.77 (broad s, 4H)		0.75 [a] (s, 12H)	517 ($M^+ - Co(CO)_4$)	63 dec.
9	1980, 1913, 2130 (ν(SiH))		4.83 (m, 3H) (SiH obscured)	4.47 (m, 3H)		0.10 (d, 6H, J 3)	272	34–36
10	2090, 2030, 1998, 1978, 1915		5.70 (m, 3H)	5.28 (m, 2H)		0.93 [a] (s, 6H)	442	145–148 dec.
11	1955, 1875 2070 (ν(IrH))							78–81

[a] In $CDCl_3$.

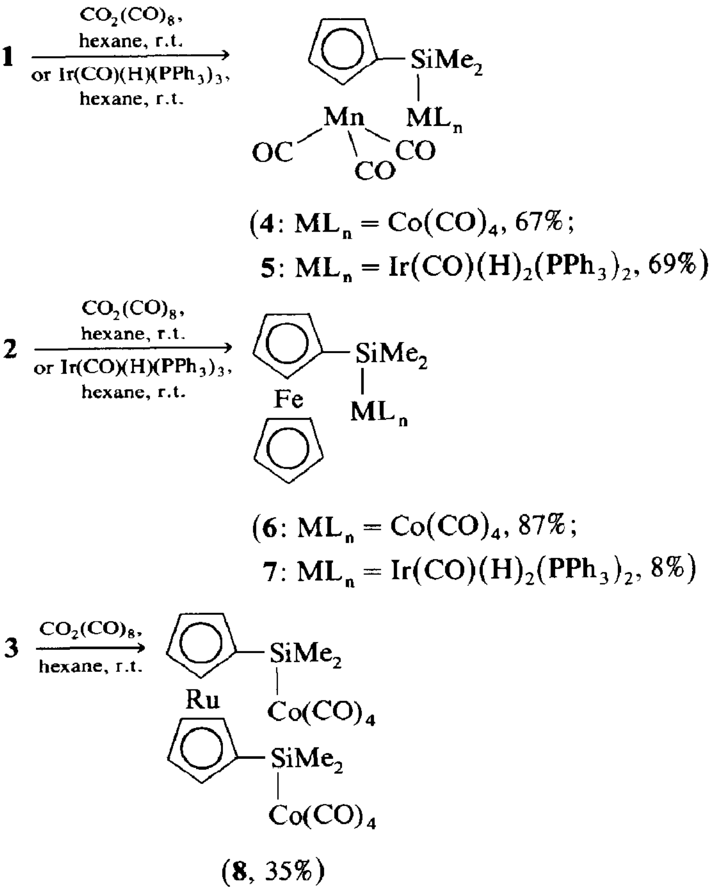
Table 2

^1H NMR spectra of complexes [a]



Complex	^1H NMR (C_6D_6) (δ(ppm), J(Hz))							
	Ar	C_5H_4 and C_5H_5			CH_3		H^a	H^b
5	7.80–6.70 (m, 30H)	4.70 (m, 2H)	4.38 (m, 1H)	4.27 (m, 1H)	0.80 (d, 3H)	0.38 (d, 3H)	−9.70 (d, d, d, 1H)	−11.03 (d, d, d, 1H)
7	7.70–6.90 (m, 30H)	4.45 (broad s, 4H)	4.33 (s, 5H)		1.05 (d, 3H)	0.70 (d, 3H)	−9.32 (d, d, d, 1H)	−10.12 (d, d, d, 1H)
11	8.10–6.70 (m, 30H)	5.50 (d, 2H, J 6)	4.93 (t, 1H, J 6)	4.57 (q, 2H, J 6)	0.88 (d, 3H)	0.48 (d, 3H)	−8.47 (d, d, d, 1H)	−9.87 (d, d, d, 1H)

[a] The structures and attributions can be given by comparison with previously reported complexes [9,10].

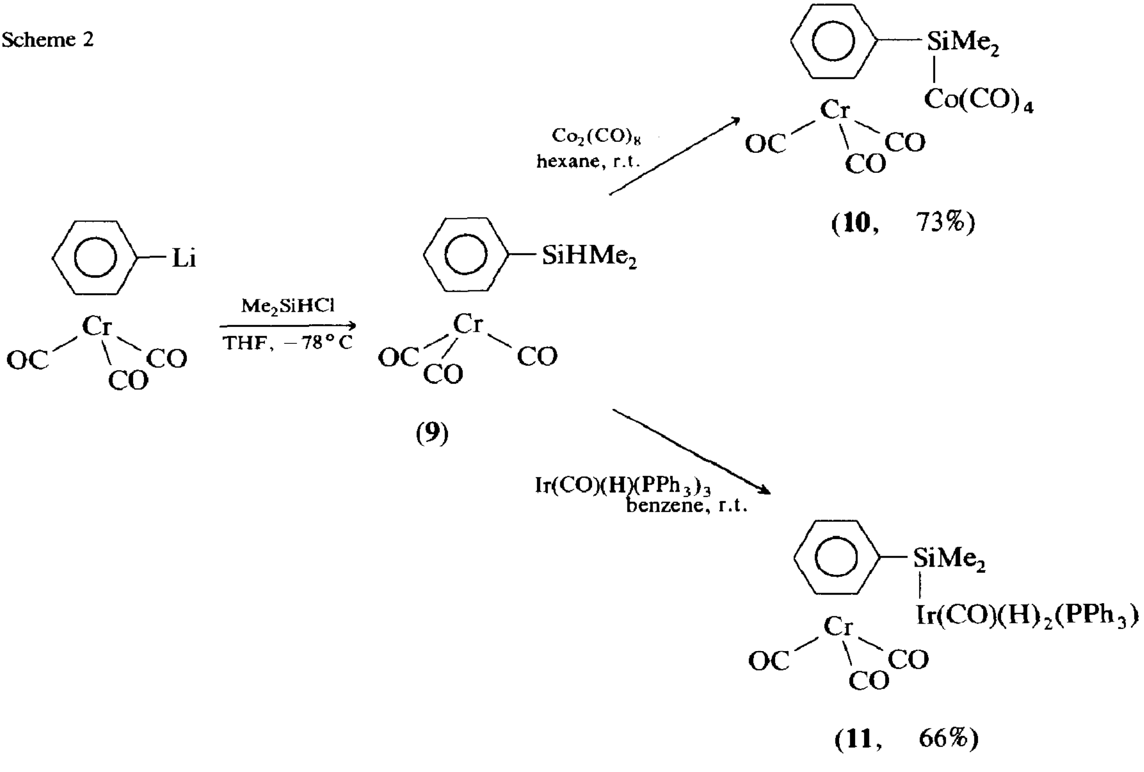


(**4**: ML$_n$ = Co(CO)$_4$, 67%;
5: ML$_n$ = Ir(CO)(H)$_2$(PPh$_3$)$_2$, 69%)

(**6**: ML$_n$ = Co(CO)$_4$, 87%;
7: ML$_n$ = Ir(CO)(H)$_2$(PPh$_3$)$_2$, 8%)

(**8**, 35%)

Scheme 2



(**10**, 73%)

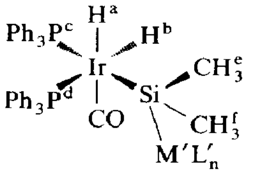
(**9**)

(**11**, 66%)

Scheme 3

Table 3

Coupling constants (Hz) in complexes [a]



Complex	$J_{a,b}$	$J_{a,c}$	$J_{b,c}$	$J_{a,d}$	$J_{b,d}$	$J_{e,c}$	$J_{f,c}$
5	4.5	15	19.5	22.5	118	2.4	2.4
7	4.5	15	19.5	24	118	2.3	2.3
11	4.5	15	19.5	22.5	114	2.3	2.3

[a] The structures and attributions can be given by comparison with previously reported complexes [9,10].

Heterobimetallic complexes have been prepared by reactions of **1**–**3** with $Co_2(CO)_8$ or $Ir(CO)(H)(PPh_3)_3$ (Scheme 2). Some physical data are given in Tables 1–3. The same procedure can be used with tricarbonyl(η^6-benzene)chromium, which is also readily lithiated [11] (Scheme 3).

These results show the potential of silicon-containing compounds as assembling ligands. Further work is directed towards bringing together one early and one late transition metal in the same molecule.

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