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ORGANOMETALLOIDAL DERIVATIVES OF THE TRANSITION METALS

III *. σ- AND π-SILYLALLYL COMPLEXES

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Summary

The reaction between 1- and 2-trialkylsilyl-3-chloroprop-1-ene and various metal complexes has led to the preparation of σ- and π-silylallyl complexes of Mn, Fe, Co, Ni, Mo, Pd and W. The general reactions employed involve the use of metal anions in a salt elimination reaction and oxidative addition reactions. The use of in situ silylallyl Grignard reagents with metal halides was also used to prepare silylallyl substituted compounds of Ge, Sn, and Ni. The chemical and physical properties of the new complexes are discussed, as are other attempted synthetic routes that led to metalloid or organic group transfer reactions.

Introduction

In recent years there has developed a considerable interest in silicon substituted organic molecules as potential ligands for transition metals. This interest has been fed by the discovery that such ligands impart a thermal and oxidative stability to the transition metal complexes formed that is not observed with the simple unsubstituted organic ligands. This applies to both σ- and π-complexed ligands. Thus, the recent discoveries by Lappert [2,3] and Wilkinson [4] of many new and novel σ-bonded metal carbon complexes using the silylmethyl ligands R_3SiCH_2 [5]. Various silyl-substituted η^5-cyclopentadienyl- and η^6-benzene-metal

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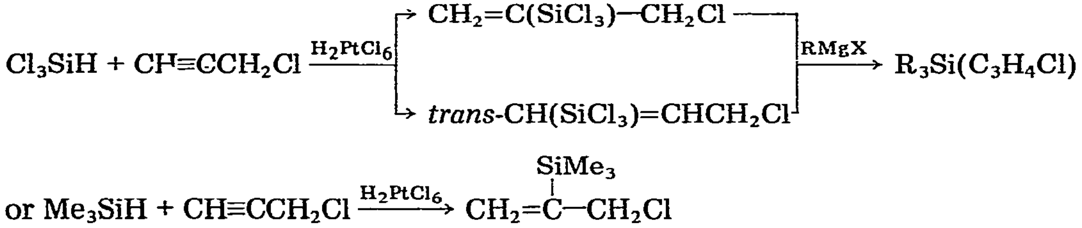
complexes have been described in the literature [6,7,8], and recent results concerning the uses of vinylsilanes and silylacetylenes to produce previously unknown π-complexes of copper and iron have illustrated the potential interest in the formation of silyl-substituted π-metal complexes [9,10].

The study of η^3-allylmetal complexes has long been an active area of research, particularly in view of their homogeneous catalytic properties [11,12]. Substituents on the allyl ligand have included halogens, alkyl and aryl groups as well as various ether groups, but no metalloid-substituted allyl complexes have been reported. Given the enhanced oxidative and thermal stability of the silylalkyl-transition metal complexes compared to the unsubstituted alkyl complexes, the possibility that silyl-substituted allyl-transition metal complexes might possess enhanced stabilities led us to investigate the possible synthesis of such new systems. This paper reports the initial results of such a study.

Experimental

All reactions were performed in an atmosphere of dry nitrogen using dry degassed solvents. The starting 1- and 2-silyl-3-chloroprop-1-enes were prepared by the hydrosilylation of propargyl chloride using either trichlorosilane, producing both isomers, or trimethylsilane producing only the 2-substituted isomer [13].



$$\begin{tikzcd} & CH_2{=}C(SiCl_3){-}CH_2Cl \arrow[dr] & \\ Cl_3SiH + CH{\equiv}CCH_2Cl \arrow[ur, "H_2PtCl_6"] \arrow[dr] & & R_3Si(C_3H_4Cl) \\ & trans\text{-}CH(SiCl_3){=}CHCH_2Cl \arrow[ur, "RMgX"'] & \end{tikzcd}$$

$$\text{or } Me_3SiH + CH{\equiv}CCH_2Cl \xrightarrow{H_2PtCl_6} CH_2{=}\overset{\overset{\displaystyle SiMe_3}{|}}{C}{-}CH_2Cl$$

Starting transition metal complexes were prepared using published procedures or purchased commercially.

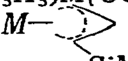
Infrared spectra were recorded on a Perkin—Elmer 421 spectrometer or a Perkin—Elmer 337 spectrometer with expanded scale recorder. The PMR spectra were obtained using a Perkin—Elmer R-12 or Varian A-60 spectrometer. Mass spectra were recorded using either a Hitachi RMU 6E, AEI MS 9 or Du Pont 491 double focusing instrument. Ultraviolet irradiations were performed using a Hanovia 500 watt lamp in conjugation with quartz glassware.

Formation of trans-$(\eta^5\text{-}C_5H_5)M(CO)_n{-}CH_2{-}CH{=}CHSiMe_3$

Typically, a sample of *trans*-1-trimethylsilyl-3-chloroprop-1-ene (6.76 mmol) was added to a dimethoxyethane solution of sodium tricarbonyl(η^5-cyclopentadienyl)tungstate(0) (4.27 mmol) and the mixture stirred at room temperature for 2 h. At this time a precipitate was observed and the solvents were removed under reduced pressure leaving a dark yellow-brown wax. This was extracted with hexane and upon crystallization yielded 1.1 g (2.47 mmol, 58%) of the appropriate title complex, *trans*-$(\eta^5\text{-}C_5H_5)W(CO)_3CH_2CH{=}CHSiMe_3$.

Also produced using this general technique were the following metal complexes: *trans*-(η^5-C_5H_5)Fe(CO)$_2$CH$_2$CH=CHSiMe$_3$, 65%, wax purified by chromatography; *trans*-(η^5-C_5H_5)Mo(CO)$_3$CH$_2$CH=CHSiMe$_3$, 44%, m.p. 40—41°C; *trans*-Mn(CO)$_5$CH$_2$CH=CHSiMe$_3$, 38%, liquid purified by distillation/sublimation.

Formation of (η^5-C_5H_5)M(CO)$_{n-1}$(η^3-$Me_3SiC_3H_4$)

Method A (for LM—  *)*

SiMe$_3$

A solution of 1-trimethylsilyl-3-η^1-allyl(tricarbonyl)(η^5-cyclopentadienyl)-tungsten(II) (1.0 g, 2.24 mmol) in 200 ml of hexane was irradiated for 2.5 h under nitrogen. At this time a considerable amount of decomposition was observed. The solvent was removed under reduced pressure subsequent to filtration. This yielded a yellow semi-solid that was purified by recrystallization from hexane to yield 0.44 g (1.05 mmol. 47%) of the appropriate title complex, (η^5-C_5H_5)W(CO)$_2$(η^3-$Me_3SiC_3H_4$). Also prepared by this technique:

(η^5-C_5H_5)Fe(CO)(η^3-$Me_3SiC_3H_4$), 30%, oil purified by chromatography.
(η^5-C_5H_5)Mo(CO)$_2$(η^3-$Me_3SiC_3H_4$), 50%, wax purified by chromatography.

Method B (for LM—  *SiMe$_3$)*

To a solution containing 2-trimethylsilyl-3-chloroprop-1-ene (6.0 mmol) in 100 ml of THF was added an equivalent of NaCo(CO)$_4$. The solution was stirred for 1 h and the solvent removed under reduced pressure. The product, Co(CO)$_3$-(η^3-$Me_3SiC_3H_4$), was purified by repeated trap to trap distillation, yield 55%, m.p. 5°C. Analytical samples were prepared by recrystallization from pentane at —80°C. Also prepared by this general route: (η^5-C_5H_5)Mo(CO)$_2$(η^3-$Me_3SiC_3H_4$), 15%.

trans-1-Trimethylsilyl-3-η^1-allyl(trimethyl)tin

To a magnetically stirred mixture of trimethyltin chloride (1.34 g, 6.76 mmol) and magnesium (0.16 g, 6.76 mmol) in 4 ml of dry THF was added dropwise over a 30 min period 1.0 g (6.76 mmol) of 1-trimethylsilyl-3-chloroprop-1-ene in 10 ml of the same solvent. During the addition time the solution darkened appreciably and the precipitate formed. After stirring the mixture for 1 h the reaction system was quenched on ice and extracted with diethyl ether. Subsequent to drying the solvents with anhydrous magnesium sulphate, the solvents were removed under reduced pressure. The resulting oil was purified by column chromatography on Grade H alumina eluting with hexane to yield 0.92 g (3.3 mmol, 49%) of the title compound. Also prepared by the same general method: *trans*-Ph$_3$Ge-CH$_2$CH=CHSiMe$_3$, 50%, recrystallized from hexane.

Bis(η^3-2-trimethylsilylallyl)nickel

To a magnetically stirred mixture of magnesium (0.16 g, 6.75 mmol), nickel(II) chloride (0.4 g, 3.09 mmol) and a trace of mercury(II) chloride in 5 ml of THF at —10°C was added dropwise 2-trimethylsilyl-3-chloroprop-1-ene in 10 ml of the same solvent. Almost immediately a colour change was observed and after all the silylallyl halide had been added, 30 min, a dirty yellow solution was obtained. This was stirred for a further 30 min and the solvent removed under reduced pressure at the same low temperature, to leave a brown residue. This was extracted with hexane to produce a clear yellow solution. Slow evaporation of this solution failed to yield any crystalline product even upon cooling to —70°C. Finally, all the solvent was removed to yield a red-yellow oil. In the freezer this solidified to orange needles, thermally stable at room temperature for a period of hours, yield 36%.

(η^3-2-triethylsilylallyl)chloropalladium(II) dimer

Carbon monoxide was bubbled into a 5% aqueous methanol solution of 1.0 g (3.41 mmol) Na_2PdCl_4 and 1.0 g (5.26 mmol) of 2-triethylsilyl-3-chloroprop-1-ene. After 30 min, the red solution had turned yellow with no observed decomposition. The solution was poured onto 150 ml of water and extracted with chloroform. Removal of the solvent from the extracts yielded a bright yellow solid that was recrystallized from petroleum ether, 0.25 g (0.49 mmol, 15%), m.p. 90°C. Also prepared by this route: (η^3-1-trimethylsilylallyl)chloropalladium(II) dimer, 17%, m.p. 47°C; and (η^3-2-trimethylsilylallyl)chloropalladium(II) dimer, 21%, m.p. 72°C.

Triphenylphosphine-(η^3-2-triethylsilylallyl)chloropalladium(II)

To a solution of 42 mg (7.08×10^{-5} mol) of η^3-(2-triethylsilylallyl)chloropalladium(II) dimer were added 0.18 g (0.71 mmol) of triphenylphosphine. The solution was stirred for 2 h and the solvent removed under reduced pressure. The solid residue was recrystallized from hexane to yield 43 mg (0.077 mmol, 54%) of the title complex.

Formation of Me_3Si—ML via oxidative addition reactions

A mixture containing 4 g (24×10^{-3} mol) $Ni(CO)_4$ and 3.2 g (21×10^{-3} mol) 2-trimethylsilyl-3-chloroprop-1-ene dissolved in 40 ml of hexane was refluxed until the evolution of carbon monoxide ceased. The resulting dark red solution was cooled to —78°C and a crop of orange crystals isolated. Material for spectral analysis was obtained by three successive recrystallizations from pentane, and the complex identified as $[Me_3SiC_3H_4NiCl]_2$.

Also prepared by the same general method (from $2\text{-}(Me_3Si)C_3H_4I$ * and $Fe(CO)_5$): (η^3-$Me_3SiC_3H_4$)$Fe(CO)_3I$, 60%, m.p. 103°C.

Reaction between [Me_3Si— $NiCl]_2$ and allyl Grignard reagent

To 1 g $[(\eta^3\text{-}2\text{-}Me_3SiC_3H_4)NiCl]_2$ was added an excess of C_3H_5MgCl in ether at —20°C under N_2. After stirring for 1 h, the solution was warmed to room temperature and the ether removed in vacuo. Extraction with pentane yielded a yellow solution. The pentane was removed in vacuo at —80°C. The products were distilled into the trapping network at —50°C. Repeated distillation at 0.1 mm Hg separated a very volatile component (which was identified as $(\eta^3\text{-}C_3H_5)_2Ni$ by PMR and mass spectra) from the less volatile product. The latter compound was a yellow solid which melted at 45°C and was moderately air-stable. Conventional analysis was not possible due to partial decomposition to a white powder after one or two days under vacuum. A high resolution mass spectrum of the

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* Prepared by stirring a slurry of $2\text{-}Me_3SiC_3H_4Cl$ and NaI in acetone for one week.

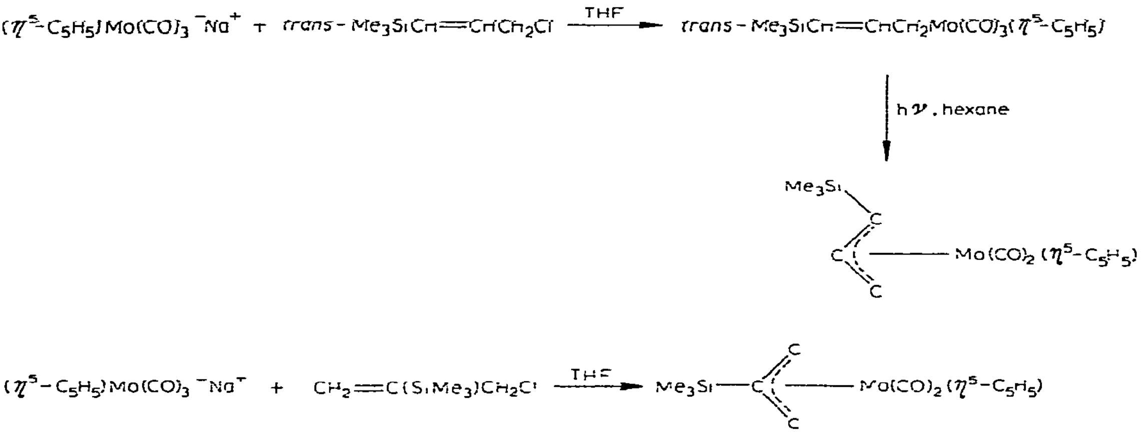
molecular ion *m/e* 284 showed elemental composition $C_{12}H_{26}Si_2Ni$, (found *m/e* 284.0912, calcd. *m/e* 284.0919), yield 15%.

Results and discussion: synthesis and reactivity

Reactions between various transition metal complexes and the *trans*-1- and -2-trialkylsilyl-3-chloroprop-1-enes yield the corresponding σ- and π-metal complexes in general accord with the published reactions of such complexes with the related unsubstituted allyl chlorides. Tables 1 and 2 list the infrared and PMR spectral data for the new complexes along with representative analytical data.

The reactions of the carbonyl(η^5-cyclopentadienyl) metallates of Fe, Mo and W and of pentacarbonylmanganate(—1) with *trans*-1-trimethylsilyl-3-chloroprop-1-ene led to moderate yields of the expected *trans*-σ-bonded complex. No evidence was obtained for the production of any other complex from these reactions. The related reaction between the molybdate and 2-trimethylsilyl-3-chloroprop-1-ene led directly to the formation of the π-silylallyl complex, no intermediate σ-complex being observed. A similar result was observed using the tetracarbonylcobaltate(—1) *. This difference in behavior is not clear at this time; however, it can probably be explained in terms of a steric interaction between the bulky trimethylsilyl group and the central transition metal system. This interaction will be the greatest for the unobserved tricarbonyl(η^5-cyclopentadienyl)(2-trimethylsilyl-1-η^1-allyl)molybdenum and would be relieved by formation of the π-complex. This release of steric strain will not be a factor for the related 1-silyl substituted molybdenum complex, where the metal system and the trimethylsilyl group are better separated.

The σ- to π-transformation of the 1-silyl-substituted complexes may, however, be readily achieved by photochemical treatment of the σ-complex in inert hydrocarbon solvents. These results are summarized in the reaction sequences below for molybdenum.



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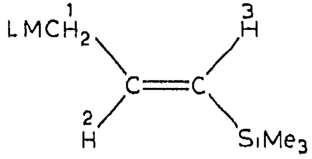
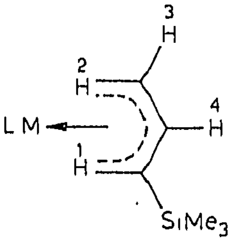
* Small amounts of the σ-complex were observed by PMR spectroscopy on the crude products from the reactions of the Fe and W anions. No pure products were, however, isolated.

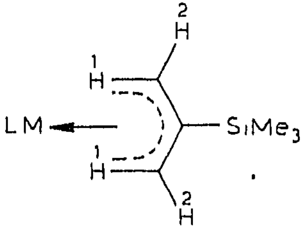
TABLE 1[a]

INFRARED AND PMR DATA FOR THE COMPLEXES:


(a)


(b)

and


(c)

LM	ν(C≡O) (cm^{-1})	τ(H(1)) (ppm)	τ(H(2)) (ppm)	τ(H(3)) (ppm)	τ(H(4)) (ppm)	τ(SiMe$_3$) (ppm)	τ(C$_5$H$_5$) (ppm)	$J_{1,2}$ (Hz)	$J_{1,3}$ (Hz)	$J_{1,4}$ (Hz)	$J_{2,3}$ (Hz)	$J_{2,4}$ (Hz)	$J_{3,4}$ (Hz)
Complexes a													
(η^5-C_5H_5)W(CO)$_3$	2020, 1935, 1930	7.46 ^{b}	3.60 ^{c}	4.72 ^{c}		9.79 ^{d}	4.60 ^{d}	8	1		18		
(η^5-C_5H_5)Mo(CO)$_3$	2020, 1945, 1937	7.56 ^{b}	3.67 ^{c}	4.68 ^{c}		9.98 ^{d}	4.82 ^{d}	8	1		18		
(η^5-C_5H_5)Fe(CO)$_2$	2010, 1961	7.70 ^{b}	3.60 ^{c}	4.56 ^{c}		9.77 ^{d}	5.20 ^{d}	8	<0.5		18		
Mn(CO)$_5$	2112, 2030, 2000	7.94 ^{b}	3.50 ^{c}	4.51 ^{c}		9.75 ^{d}		8	1		18		
SnMe$_3$ ^{i}		7.97 ^{b}	3.70 ^{c}	4.58 ^{c}		9.89 ^{d}		8	<0.5		18		
Ph$_3$Ge ^{j}		7.97 ^{b}	3.75 ^{c}	4.22 ^{c}		9.90 ^{d}		7	<0.5		18		
Complexes b													
(η^5-C_5H_5)W(CO)$_2$	1959, 1880	9.48 ^{c}	8.92 ^{e}	7.54 ^{b}	6.94 ^{f}	9.90 ^{d}	5.28 ^{d}	0.3		12.0	2.0	10.0	6.0
(η^5-C_5H_5)Mo(CO)$_2$	1964, 1882	9.63 ^{c}	9.66 ^{e}	7.42 ^{b}	6.40 ^{f}	9.86 ^{d}	5.27 ^{d}	0.3		12.4	1.4	10.0	6.0
(η^5-C_5H_5)Fe(CO)		9.45 ^{c}	9.15 ^{e}	7.40 ^{b}	6.38 ^{f}	9.83 ^{d}	5.89 ^{d}	^{h}					
(η^3-Me$_3$SiC$_3$H$_4$)$_2$Pd$_2$Cl$_2$		7.14 ^{c}	7.05 ^{e}	6.05 ^{b}	4.82 ^{f}	9.73 ^{d}				11.1		13.4	5.7
Complexes c													
Co(CO)$_3$	2067, 2002, 2000	7.81 ^{d}	6.99 ^{d}			9.79 ^{d}							
(η^5-C_5H_5)Mo(CO)$_2$	1938, 1897	8.27 ^{d}	7.31 ^{g}			9.85 ^{d}	4.77						
(η^3-Me$_3$SiC$_3$H$_4$)$_2$Ni		8.29 ^{d}	6.30 ^{d}			9.88 ^{d}							
(η^3-Et$_3$SiC$_3$H$_4$)$_2$Pd$_2$Cl$_2$ ^{k}		6.90 ^{d}	5.92 ^{d}										
(η^3-Me$_3$SiC$_3$H$_4$)$_2$Pd$_2$Cl$_2$		7.02 ^{d}	6.00 ^{d}			9.53 ^{d}							
Fe(CO)$_3$I	2074, 2028, 1993	6.43 ^{d}	6.08 ^{d}			10.08 ^{d}							
(η^3-Me$_3$SiC$_3$H$_4$)$_2$Ni$_2$Cl$_2$		7.90 ^{d}	7.02 ^{d}			9.55 ^{d}							

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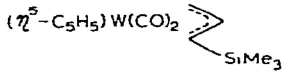
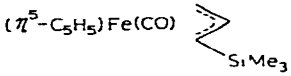
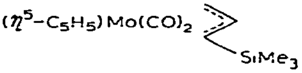
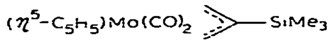
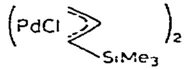
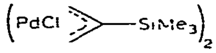
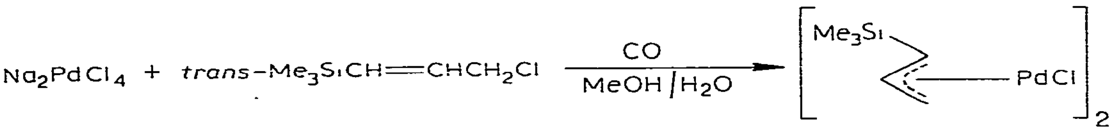
[a] All PMR data recorded in CDCl$_3$. Those J values not recorded = 0. [b] Pair of doublets [c] Pair of triplets. [d] Singlet. [e] Pair of quartets. [f] Octet. [g] Broad singlet. [h] Insufficient resolution for J-values. [i] τ(SnCH$_3$) 9.86, J(Sn—H) 52. [j] τ(Ph$_3$Ge) 2.6m. [k] τ(SiEt$_3$) 9.0m.

TABLE 2

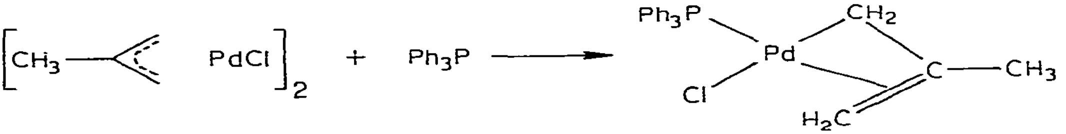
ANALYTICAL DATA FOR NEW COMPLEXES

Complex	Found (calcd.) (%)	
	C	H
$(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_2CH{=}CHSiMe_3$	53.2 (53.8)	5.95 (6.20)
$(\eta^5\text{-}C_5H_5)Mo(CO)_3CH_2CH{=}CHSiMe_3$	46.6 (46.9)	5.23 (5.03)
	37.6 (37.3)	4.74 (4.34)
	54.3 (54.9)	6.81 (6.87)
	47.6 (47.3)	5.75 (5.46)
	47.4 (47.3)	5.78 (5.46)
$Me_3SnCH_2CH{=}CHSiMe_3$	39.96 (39.1)	8.02 (7.94)
$Ph_3GeCH_2CH{=}CHSiMe_3$	69.9 (69.2)	7.09 (6.73)
	36.7 (36.5)	6.70 (6.42)
	28.9 (28.3)	5.10 (5.11)
	28.3 (28.3)*	5.09 (5.11)
$Pd(Ph_3P)Cl(CH_2C(SiEt_3){=}CH_2)$	58.1 (58.1)	6.18 (6.09)

Dent et al. [14], have reported the facile formation of (η^3-allyl)chloropalladium(II) dimers from the reaction between Na_2PdCl_4, 3-haloprop-1-enes and carbon monoxide in a methanolic solution. Using this technique with the various silyl-3-chloroprop-1-enes led to good yields of the appropriate η^3-silylallylchloropalladium(II) dimer. These yellow crystalline complexes are very thermally and oxidatively stable and may be handled in the open without special precautions.



It is important that the reaction medium for this preparative technique contains 5% water. In pure dry methanol reduction of the palladium(II) to metallic palladium(0) occurs rapidly and no allyl complexes are obtained. Such η^3-allylchloropalladium(II) dimers have been shown by Powell and Shaw [15] to readily react with two electron ligands to cause cleavage of the halogen bridge. The resulting complexes formed no longer contain a "normal" η^3-allyl ligand with three equivalent metal carbon interactions. Rather, the new complexes contain a σ-palladium—carbon bond and an η^2-ethylenic palladium bond as illustrated below.



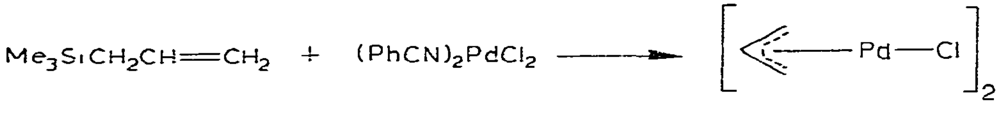
In this regard the new silylallyl complexes proved unexceptional. The reaction between η^3-2-triethylsilylallylchloropalladium(II) dimer and triphenylphosphine led to the related nonsymmetrically bound (silylallyl)chlorotriphenylphosphinepalladium(II) in high yield.

The formation of π-allyl complexes via the oxidative addition of allyl halides to various metal complexes is a well-documented procedure [16]. We have utilized this route for the formation of silyl-substituted π-allyl complexes of Fe and Ni. Thus $Fe(CO)_5$ and $Ni(CO)_4$ react with 2-trimethylsilyl-3-haloprop-1-ene to form $(\eta^3\text{-}Me_3SiC_3H_4)Fe(CO)_3I$ and $[(\eta^3\text{-}Me_3SiC_3H_4)NiCl]_2$ respectively. Attempts to use the silylallylchloronickel(II) dimer to form mixed π-allyl complexes via reaction with allyl Grignard reagents failed. Such reactions led to the isolation of only the homoleptic η^3-allyl nickel(II) complexes, $(\eta^3\text{-}C_3H_5)_2Ni$ and $(\eta^3\text{-}Me_3SiC_3H_4)_2Ni$. This result indicates the occurrence of a disproportionation of the initially formed but unobserved heteroleptic η^3-allylnickel(II) complex, i.e.

$$2(\eta^3\text{-}Me_3SiC_3H_4)Ni(\eta^3\text{-}C_3H_5) \rightarrow (\eta^3\text{-}Me_3SiC_3H_4)_2Ni + (\eta^3\text{-}C_3H_5)_2Ni$$

The same bis(η^3-silylallyl)nickel(II) complex was also formed by the direct reaction of the Grignard reagent derived from 2-trimethylsilyl-3-chloroprop-1-ene with nickel(II) chloride. Initial attempts to produce a silylallyl Grignard reagent and subsequently react it with metal halides led to no new metal complexes but produced viscous oils which were not identified but probably contained some dimer derived from the silylallyl radical. In view of this lack of success we attempted to produce the sought after Grignard in situ, at low temperatures, with the appropriate metal halide, hoping to trap the transient Grignard species. This method worked well on the examples attempted; namely, Ph_3GeCl, Me_3SnCl, Cl_4Sn, $NiCl_2$ and $CrCl_3$. The last reaction product, orange yellow crystals, was not fully characterized, but in general this technique looks very promising for further study of many and varied transition metal silylallyl complexes.

Two other methods for forming the desired Group IV-substituted allylmetal complexes were attempted. As outlined below neither was successful.



$$Me_3SnCH{=}C{=}CH_2 + HMo(CO)_3(\eta^5\text{-}C_5H_5) \longrightarrow Me_3SnMo(CO)_3(\eta^5\text{-}C_5H_5)$$

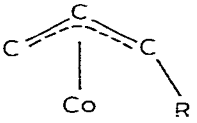
The reaction of the allylsilane with $(PhCN)_2PdCl_2$ led to high yields of the corresponding unsubstituted η^3-allylchloropalladium(II) dimer. Although Abel and Morehouse have reported many examples of such organic group transfer from tin compounds to transition metals, this appears to be one of the few such reactions involving transfer from silicon to a transition metal.

In the second reaction between tricarbonyl(η^5-cyclopentadienyl) hydridomolybdenum(II) and trimethylstannylallene, performed in the hope of obtaining an addition type complex, only the transfer of the trimethyltin group was observed to yield the known complex, $(\eta^5\text{-}C_5H_5)Mo(CO)_3SnMe_3$.

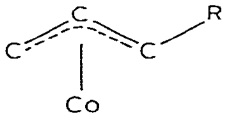
Spectral data

Structural considerations

The infrared and PMR data for the new complexes detailed in Table 1 are in most respects straightforward and simply confirm the various proposed structures. However, a few points of interest are apparent, stemming from the bulky nature of the trimethylsilyl group. The existence of stereochemical isomers for various allyl transition metal complexes has been reported. Thus η^3-methallyltricarbonylcobalt(II) can exist as either structure A or B below, R = CH_3, [17].



(A)

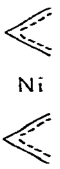


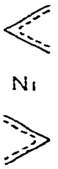
(B)

The corresponding silylallyl complexes reported here, where the silyl substituent is on the terminal allyl carbon atom, appear to exist only in the form of isomer B. This is determined by inspection of their PMR spectra where $J_{1,4}$ is 11 Hz as expected for such a structure. Structure A would exhibit a coupling of 6 Hz, [17]. The exclusive formation of these complexes as the isomer B is hardly surprising based upon the bulky nature of the silyl group which would cause steric problems in isomer A.

The $(\eta^1\text{-}1\text{-}Me_3SiCH{=}CH\text{-}CH_2)$ complexes exist as the *trans*-isomer (as the starting silyl-3-chloroprop-1-ene) as determined by the *trans*-proton coupling constant $\simeq$18 Hz.

Two forms of $(\eta^3\text{-}C_3H_5)Fe(CO)_3I$ have been reported [18] and both $[(\eta^3\text{-}C_3H_5)NiCl]_2$ and $(\eta^3\text{-}C_3H_5)_2Ni$ have been shown to exist as both *cis* and *trans* isomers, [19], e.g.





The corresponding silylallyl-iron(II) and -nickel(II) complexes exhibit infrared and PMR spectra that provide no evidence for more than one species of each complex. Variable temperature PMR studies on the nickel(II) complexes from —65 to +50°C cause no change in the spectra recorded. This indicates that the bulky silyl group prevents isomerization by raising the activation energy for such a process and it can reasonably be assumed that, for example, $(\eta^3\text{-Me}_3\text{SiC}_3\text{H}_4)_2\text{Ni}$ exists in the *trans*-conformation.

The infrared spectrum of $(\eta^3\text{-Me}_3\text{SiC}_3\text{H}_4)\text{Co(CO)}_3$ exhibits three carbonyl stretching frequencies, 2067, 2002 and 2000 cm^{-1}, contrasting to the spectrum of the related complex $(\eta^3\text{-C}_3\text{H}_5)\text{Co(CO)}_3$, 2056 and 2001 cm^{-1} [20]. Apparently, the trimethylsilyl substituent reduces the local symmetry of the Co(CO)_3 group and causes a splitting of the E mode band. This appears to be the only example of such splitting for substituted η^3-allyltricarbonylcobalt complexes, and also contrasts the lack of splitting observed for the related π-complexes $(\eta^3\text{-R}_3\text{SiC}_5\text{H}_4)\text{Mn(CO)}_3$ and $(\eta^3\text{-R}_3\text{SnC}_6\text{H}_5)\text{Mo(CO)}_3$. The silylallyl complexes of molybdenum and tungsten, $(\eta^5\text{-C}_5\text{H}_5)\text{M(CO)}_3\text{CH}_2\text{CHCHSiMe}_3$ exhibit a low frequency band split, as has been observed for several other such complexes $(\eta^5\text{-C}_5\text{H}_5)\text{M(CO)}_3\text{R}$ [21].

Mass spectra representative of the new complexes were recorded and the data are presented in Table 3. All spectra exhibit parent ions and the carbonyl containing complexes exhibit the ions expected for stepwise loss of the carbonyl

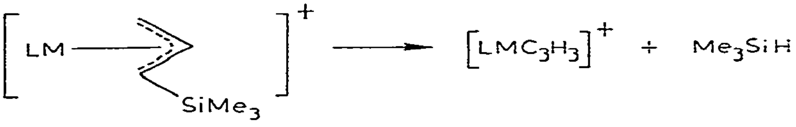
TABLE 3

MASS SPECTRAL DATA FOR SILYLALLYL COMPLEXES

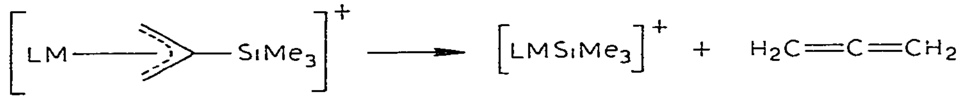
m/e	Intensity	Ion fragment	*m/e*	Intensity	Ion fragment
(a) $(\eta^3\text{-2-Me}_3\text{SiC}_3\text{H}_4)\text{Fe(CO)}_3\text{I}$			*(c)* $(\eta^3\text{-1-Me}_3\text{SiC}_3\text{H}_4)\text{W(CO)}_2\text{Cp}$		
380	0.3	$\text{Me}_3\text{SiC}_3\text{H}_4\text{Fe(CO)}_3\text{I}$	418	36.0	$\text{Me}_3\text{SiC}_3\text{H}_4\text{W(CO)}_2\text{C}_5\text{H}_5$
252	0.1	$\text{Me}_3\text{SiC}_3\text{H}_4\text{Fe(CO)}_2\text{I}$	390	13.0	$\text{Me}_3\text{SiC}_3\text{H}_4\text{W(CO)C}_5\text{H}_5$
324	3.7	$\text{Me}_3\text{SiC}_3\text{H}_4\text{Fe(CO)I}$	362	38.0	$\text{Me}_3\text{SiC}_3\text{H}_4\text{WC}_5\text{H}_5$
309	0.3	$\text{Me}_2\text{SiC}_3\text{H}_4\text{Fe(CO)I}$	344	100.0	$\text{C}_3\text{H}_3\text{W(CO)C}_5\text{H}_5$
296	7.0	$\text{Me}_3\text{SiC}_3\text{H}_4\text{FeI}$	316	20.0	$\text{C}_3\text{H}_3\text{W(CO)C}_5\text{H}_5$
281	0.5	$\text{Me}_2\text{SiC}_3\text{H}_4\text{FeI}$	288	42.0	$\text{C}_3\text{H}_3\text{WC}_5\text{H}_5$
256	5.5	Me_3SiFeI	249	5.0	WC_5H_5
241	0.7	Me_2SiFeI	73	34.0	Me_3Si
225	3.7	CH_2SiFeI			
211	2.3	SiFeI	*(d)* $(\eta^3\text{-2-Me}_3\text{SiC}_3\text{H}_4)\text{Co(CO)}_3$		
197	5.5	$\text{Me}_3\text{SiC}_3\text{H}_4\text{Fe(CO)}$	228	2.69	$\text{Me}_3\text{SiC}_3\text{H}_4\text{Co(CO)}_2$
193	9.3	FeI	200	4.2	$\text{Me}_3\text{SiC}_3\text{H}_4\text{Co(CO)}$
169	17.1	$\text{Me}_3\text{SiC}_3\text{H}_4\text{Fe}$	185	0.9	$\text{Me}_2\text{SiC}_3\text{H}_4\text{Co(CO)}$
73	100.0	Me_3Si	172	9.1	$\text{Me}_3\text{SiC}_3\text{H}_4\text{Co}$
			113	21.0	$\text{Me}_3\text{SiC}_3\text{H}_4$
(b) $(\eta^3\text{-2-Me}_3\text{SiC}_3\text{H}_4)_2\text{Ni}$			73	100.0	Me_3Si
284	10.3	$(\text{Me}_3\text{SiC}_3\text{H}_4)_2\text{Ni}$	59	28.0	Co
244	7.9	$\text{Me}_3\text{SiC}_3\text{H}_4\text{NiSiMe}_3$			
228	3.8	$\text{CH}_2\text{MeSiC}_3\text{H}_4\text{NiSiMe}_3$ [a]	*(e)* $[(\eta^3\text{-2-Me}_3\text{SiC}_3\text{H}_4)\text{NiCl}]_2$		
186	16.4	$\text{Me}_3\text{SiC}_3\text{H}_4\text{Ni-Me}$	412	0.36	$[\text{Me}_3\text{SiC}_3\text{H}_4\text{NiCl}]_2$
170	17.8	$\text{CH}_2\text{MeSiC}_3\text{H}_4\text{Ni-Me}$ [a]	372	0.04	$\text{Me}_3\text{SiC}_3\text{H}_4\text{NiCl}_2\text{NiSiMe}_3$
156	12.3	$\text{MeSiC}_3\text{H}_4\text{NiMe}$ [a]	304	1.0	$\text{Me}_3\text{SiC}_3\text{H}_4\text{NiClNiC}_3\text{H}_4$
130	100.0	$\text{CH}_2\text{MeSiNi-Me}$ [a]	264	5.3	$\text{Me}_3\text{SiC}_3\text{H}_4\text{NiClNi}$
116	24.6	MeSiNiMe [a]	113	20.5	$\text{Me}_3\text{SiC}_3\text{H}_4$
73	43.8	Me_3Si	73	100.0	Me_3Si

[a] These formulae are not necessarily meant to be ion structures but only represent the elemental composition.

groups. Two major fragmentation patterns are observed for the silylallyl ligand: (1) Expulsion of trimethylsilane to form LMC_3H_3 ions, and (2) Expulsion of allene to form $LMSiMe_3$ ions.



(1)



(2)

The expulsion of trimethylsilane is only observed for the tungsten complex $(\eta^3\text{-}1\text{-}Me_3SiC_3H_4)W(CO)_2(\eta^5\text{-}C_5H_5)$ *. The nature of the ion resulting from this expulsion is not clear, but could involve a $\pi \rightarrow \sigma$ rearrangement forming a σ-propargyl system, $[LMCH_2C{\equiv}CH]^+$ or some π-allenic or π-cyclopropenyl species. Only trace amounts of ions indicating the formation of silicon—tungsten bonded species via loss of allene are observed in the spectra of the tungsten complex. The spectra of the other four complexes studied, $(\eta^3\text{-}Me_3SiC_3H_4)Co(CO)_3$, $[(\eta^3\text{-}Me_3SiC_3H_4)NiCl]_2$, $(\eta^3\text{-}Me_3SiC_3H_4)_2Ni$ and $(\eta^3\text{-}Me_3SiC_3H_4)Fe(CO)_3I$ exhibit no ions indicative of Me_3SiH expulsion. All except for the cobalt complex exhibit ions associated with the formation of metal—silicon bonded species, although the ion concentration of the silicon—nickel bonded ions formed from the silylallyl-nickel dimer are extremely small.

Conclusion

From the above data, it is clear that the silyl-substituted allyl complexes are readily available using the standard techniques that have been used for unsubstituted allyl complexes. In the light of the enhanced thermal and oxidative stability of the silylmethyl, silylacetylene and vinylsilane transition metal complexes, we might reasonably expect some enhancement of the stabilities of the silylallyl complexes; cf. the unsubstituted allyl systems. Only the example of the bis-allylnickel complex really affords such a comparison, since this is the most unstable unsubstituted allyl metal complex of which we have made a silyl-substituted analog. Since $(\eta^3\text{-}C_3H_5)_2Ni$ is thermally unstable at room temperature and spontaneously ignites in air, the behavior of the silyl-substituted complex is quite striking, being stable in air at room temperature for quite prolonged periods. None of the other complexes are examples of silyl substitution onto unstable complexes; however, it is noteworthy that none of the silyl complexes reported here are less stable than the unsubstituted systems. This limited observation argues well for the stability of as yet unsynthesized homoleptic silyl-

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* The related Mo and Fe complexes exhibited mass spectra of the corresponding $[(\eta^5\text{-}C_5H_5)M(CO)_n]_2$; thermal decomposition having occurred under the instrument conditions.

allyl complexes, and this may be important considering the great catalytic potential of allylmetal systems.

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