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Silicon–Transition Metal Chemistry. V. Photochemical Reactions of Monofunctional Silanes with Rhenium Carbonyl[1]

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Rhenium carbonyl reacts with trichlorosilane and RCl_2SiH (R = CH_3, C_6H_5) under ultraviolet irradiation to form the silyl hydride complexes $Cl_3SiHRe_2(CO)_9$ and $RCl_2SiHRe_2(CO)_9$. Infrared, mass, and nmr spectroscopic evidence suggests a Re–H–Re bridge in these molecules, with the silyl substituent in a radial position. Irradiation of rhenium carbonyl with triphenylsilane provides an attractive one-step synthesis for $HRe_3(CO)_{14}$.

Introduction

The preceding paper of this series[1] described the photochemical reaction of difunctional silanes (R_2SiH_2) with rhenium carbonyl to form three types of silyl hydrides: $R_2SiH_2Re_2(CO)_8$, $(R_2SiH_2)_2Re_2(CO)_6$, and $(R_2Si)_2H_2Re_2(CO)_7$. A most interesting and still unresolved aspect of these complexes is the exact location of the rhenium-bonded hydrogens, in particular their distance from the silicon atoms and whether they can be described as bridging between rhenium and silicon, as can the hydrogen in π-$C_5H_5Mn(CO)_2HSi(C_6H_5)_3$.[2]

In order to extend our knowledge of silyl hydrides of transition metals, we have investigated the photochemical reactions of monofunctional silanes of the series of $Cl_{3-n}R_nSiH$ (n = 0–3; R = C_6H_5, CH_3) with rhenium carbonyl. Spectroscopic studies have enabled us to deduce the probable structures of the products, which have an interesting relation to those of some previously known polynuclear carbonyl hydrides of transition metals.

Results and Discussion

Synthesis.—The products obtained from the ultraviolet irradiation of the monofunctional silanes $Cl_{3-n}R_nSiH$ (R = C_6H_5, CH_3; n = 0–3) with rhenium carbonyl varied with the number of chlorines. This variation is shown in the following scheme, which summarizes the reactions studied

$$\mathrm{Re_2(CO)_{10}} + \begin{cases} \mathrm{Cl_3SiH} \xrightarrow{h\nu} \mathrm{Cl_3SiHRe_2(CO)_9} + \mathrm{CO} \\ \mathrm{RCl_2SiH} \xrightarrow{h\nu} \mathrm{RCl_2SiHRe_2(CO)_9} + \mathrm{CO} \\ \mathrm{R_2ClSiH} \xrightarrow{h\nu} \mathrm{HRe_3(CO)_{14}} \\ \mathrm{R_3SiH} \xrightarrow{h\nu} \mathrm{HRe_3(CO)_{14}} \end{cases}$$

where R = C_6H_5, CH_3.

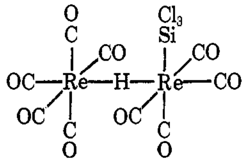
Irradiations were carried out in n-hexane, cyclohexane, or benzene solutions using excess silane; the products precipitate as reaction proceeds.[3] Both types of silicon compound are white, crystalline solids; the trichlorosilicon derivative is air stable, but the RCl_2Si derivatives are only moderately so.

With the silanes R_2ClSiH and R_3SiH, the corresponding silicon derivatives $R_2ClSiHRe_2(CO)_9$ and $R_3SiHRe_2(CO)_9$ are unstable and decompose to yield the known[4] complex $HRe_3(CO)_{14}$ as the only isolable product. During the irradiation of $(CH_3)_2ClSiH$ with $Re_2(CO)_{10}$, infrared evidence for $(CH_3)_2ClSiHRe_2(CO)_9$ was obtained but rapid decomposition to $HRe_3(CO)_{14}$ occurred on attempted purification. Even during the irradiations of RCl_2SiH with $Re_2(CO)_{10}$, small amounts of $HRe_3(CO)_{14}$ were always detected in the reaction mixtures.

When $(C_6H_5)_3SiH$ and $Re_2(CO)_{10}$ were irradiated at a temperature of about 60°, appreciable amounts of $(C_6H_5)_3SiRe(CO)_5$ were obtained.[5] However, when the irradiation was carried out maintaining the reaction solution below 20°, no $(C_6H_5)_3SiRe(CO)_5$ was detected; $HRe_3(CO)_{14}$ was the only carbonyl compound obtained. The fate of the $(C_6H_5)_3Si$ moiety in this reaction remains unresolved.

Under suitable conditions, yields of $HRe_3(CO)_{14}$ in this one-step reaction are quite reasonable (*ca.* 50%). The previous synthesis involved several tedious steps and a lower overall yield.[4] Accordingly, the silane route appears to be the method of choice for the preparation of this interesting compound.

Spectroscopic Properties and Structure.—The spectroscopic properties of $Cl_3SiHRe_2(CO)_9$ and $RCl_2SiHRe_2(CO)_9$ suggest that a probable structure for these complexes would resemble in its gross features that shown in **1**. Such a structure may be derived formally from the known structure[6] of $HMnRe_2(CO)_{14}$ (**2**) by replacing the $Mn(CO)_5$ group with a Cl_3Si fragment. More detailed features of the structure are a matter for conjecture at present. Thus, the Re–H–Re angle is not necessarily 180° as implied by **1**; this angle has been *estimated*[7] to be 164° in **2** and 159° in $HRe_3(CO)_{14}$ (**3**) and may well be similar in the derivatives reported



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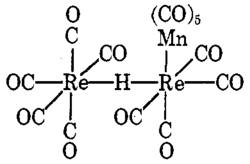

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[1] Part IV: J. K. Hoyano and W. A. G. Graham, submitted for publication in *J. Amer. Chem. Soc.*

[2] M. J. Bennett and W. Hutcheon, to be submitted for publication; *cf. Chem. Eng. News*, **48**, 75 (June 8, 1970).

[3] Only small amounts of $RCl_2SiHRe_2(CO)_9$ precipitate as the compound is more soluble.

[4] W. Fellman and H. D. Kaesz, *Inorg. Nucl. Chem. Lett.*, **2**, 63 (1966).

[5] This compound was first prepared (W. Jetz, P. B. Simons, J. A. J. Thompson, and W. A. G. Graham, *Inorg. Chem.*, **5**, 2217 (1966)) by heating $(C_6H_5)_3SiH$ and $Re_2(CO)_{10}$ at 160–165°. We consider that its formation in a purely thermal reaction at 60° is unlikely.

[6] H. D. Kaesz, R. Bau, and M. R. Churchill, *J. Amer. Chem. Soc.*, **89**, 2775 (1967); M. R. Churchill and R. Bau, *Inorg. Chem.*, **6**, 2086 (1967).

[7] Results of R. P. White, Jr., T. E. Block, and L. F. Dahl, quoted by L. B. Handy, J. K. Ruff, and L. F. Dahl, *J. Amer. Chem. Soc.*, **92**, 7312 (1970); see footnote 84.

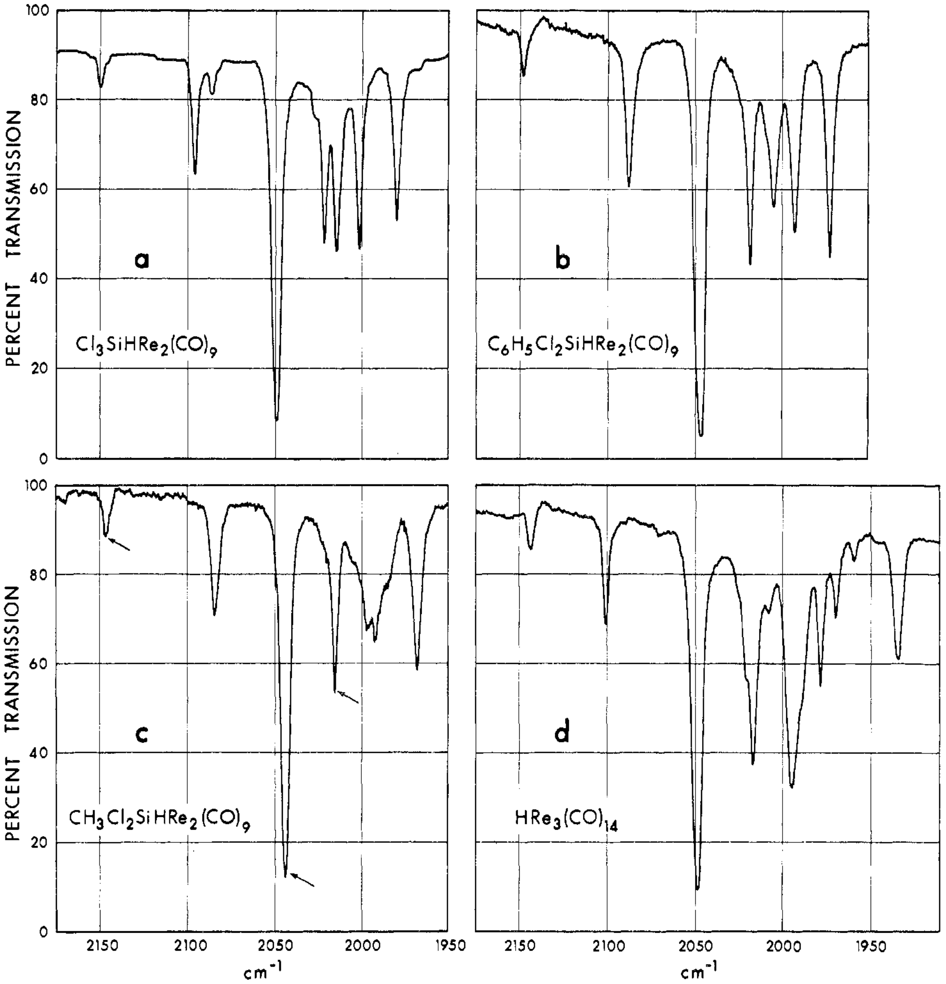

Figure 1.—Infrared spectra in cyclohexane solution of the carbonyl stretching regions of (a) $Cl_3SiHRe_2(CO)_9$, (b) $C_6H_5Cl_2SiHRe_2(CO)_9$, (c) $CH_3Cl_2SiHRe_2(CO)_9$, and (d) $HRe_3(CO)_{14}$. Arrows on spectrum c indicate the three bands (designated A, B, C in the text) common to all spectra which are attributed to the $-Re(CO)_5$ portion of the molecules.

here. The other unknown feature is whether the equatorial ligands of **1** are eclipsed as they are in **2** or staggered as they are in **3**. Both features are related to the Re–Re bond length.[7]

The spectroscopic properties of $Cl_3SiHRe_2(CO)_9$ and $RCl_2SiHRe_2(CO)_9$ will now be discussed and compared with those of $HRe_3(CO)_{14}$ and other carbonyl hydrides of established structure. The **infrared spectra** in the carbonyl stretching region of the complexes $Cl_3SiHRe_2(CO)_9$, $CH_3Cl_2SiHRe_2(CO)_9$, and $C_6H_5Cl_2SiHRe_2(CO)_9$ are shown in Figure 1 and the frequencies are given in Table I. The band patterns for the three compounds are very similar and parallel structures are indicated. The number of carbonyl bands observed is 7 or 8; nine bands are possible for the C_s structure **1** or its staggered form. If the silicon moiety were in an axial position (idealized C_{4v} symmetry), only five carbonyl stretching bands would be expected. The C_{4v} structure can therefore be excluded.

The deuterated complex $Cl_3SiDRe_2(CO)_9$ (prepared from Cl_3SiD) shows a carbonyl stretching band pattern which is almost identical with that of the hydride except for small shifts ($\leqslant 2$ cm^{-1}) in some of the band positions (see Table I). There were no other observable differences in the solution infrared spectra (H *vs.* D) in the region 800–2200 cm^{-1}. As in the hydrides discussed previously,[1] the hydrogen modes appear to be very weak or unobservable in the infrared spectrum. However, weak hydrogen modes have been observed in KBr pellets for $HRe_3(CO)_{14}$ and $DRe_3(CO)_{14}$ at 1035 and 734 cm^{-1}, respectively.[8] The concentration at which the infrared spectrum of $Cl_3SiRe_2(CO)_9$ was observed in our work may well have been insufficient to reveal such weak absorptions.

Detailed examination of the carbonyl stretching band patterns and frequencies of the complexes $Cl_3SiHRe_2(CO)_9$, $RCl_2SiHRe_2(CO)_9$, and $HRe_3(CO)_{14}$ shows some features characteristic of all four complexes which are likely the result of structural similarities. For each complex in Table I, the relative intensities and band frequencies of the highest energy band (A), the most intense band (B), and the band next to the most intense band on the low-frequency side (C) are very similar, as Table II shows. The intensity pattern of these three bands strongly resembles the pattern characteristic of $XM(CO)_5$ complexes, and they may be attributed to the $HRe(CO)_5$ moiety,[9] the common feature of the complexes presuming the Re–H–Re bridge structure.[10]

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[8] R. W. Harrill, Ph.D. Thesis, University of California, Los Angles, Calif., 1967. We thank a referee for calling our attention to this work.

[9] P. S. Braterman, R. W. Harrill, and H. D. Kaesz, *J. Amer. Chem. Soc.*, **89**, 2851 (1967).

[10] Such an assignment is necessarily very approximate in so complex a molecule and implies that the coupling of vibrations between the $HRe(CO)_5$ and $Re(CO)_4X$ parts is quite small.

TABLE I

INFRARED CARBONYL STRETCHING FREQUENCIES AND INTENSITIES

Compd	Freq,[a] cm^{-1}				
$Cl_3SiHRe_2(CO)_9$	2150 (1.4)	2095 (3.6)	2085 (1.6)	2047 (10.0)	2019 (5.4)
	2012 (5.6)	1999 (5.6)	1978 (4.8)		
$Cl_3SiDRe_2(CO)_9$	2151 (0.8)	2095 (2.4)	2086 (0.8)	2048 (10.0)	2020 (3.5)
	2012 (4.9)	2000 (4.4)	1979 (3.6)		
$C_6H_5Cl_2SiHRe_2(CO)_9$	2149 (1.0)	2087 (3.9)	2046 (10.0)	2017 (5.8)	2004 (4.3)
	2004 (4.3)	1991 (5.0)	1971 (5.6)		
$CH_3Cl_2SiHRe_2(CO)_9$	2148 (1.0)	2086 (3.2)	2044 (10.0)	2016 (5.0)	1998 (3.5)
	1992 (3.6)	1985 (2.3)	1968 (4.6)		
$HRe_3(CO)_{14}$[b]	2145 (1.2)	2101 (2.5)	2048 (10.0)	2015 (5.6)	1992 (7.0)
	1975 (4.2)	1966 (2.3)	1956 (1.5)	1933 (4.0)	

[a] Cyclohexane solutions. Figures in parentheses are relative band heights on a transmittance scale. [b] In good agreement with reported values.[4]

TABLE II

Compd	ν(CO), cm^{-1} (rel intens)		
	A	B	C
$Cl_3SiHRe_2(CO)_9$	2150 (1.4)	2047 (10.0)	2019 (5.4)
$C_6H_5Cl_2SiHRe_2(CO)_9$	2149 (1.0)	2046 (10.0)	2017 (5.8)
$CH_3Cl_2SiHRe_2(CO)_9$	2148 (1.0)	2044 (10.0)	2016 (5.0)
$HRe_3(CO)_{14}$	2145 (1.2)	2048 (10.0)	2014 (5.6)
$HRe(CO)_5$[9]	2131 (vw)	2014 (s)	2005 (m)

If the $HRe(CO)_5$ portion of the $HRe_3(CO)_{14}$ molecule can be regarded as a two-electron donor as has been suggested,[6] one would expect a flow of electrons away from the $HRe(CO)_5$ moiety

$$(CO)_5ReH \rightarrow Re_2(CO)_9 \longrightarrow (CO)_5\overset{\delta^+}{Re}-H-\overset{\delta^-}{Re}(CO)_4Re(CO)_5$$

In this case, as well as for the silicon compounds, the carbonyl bands due to the $HRe(CO)_5$ moieties should be at higher energy than the corresponding bands in $HRe(CO)_5$ itself; the trend is in agreement with this expectation.

TABLE III

PERCENTAGE HYDROGEN LOSS IN MASS SPECTRA OF RHENIUM CARBONYL HYDRIDES

Compd	Ion	*n*									
		0	1	2	3	4	5	6	7	8	9
$Cl_3SiHRe_2(CO)_9$	$[Cl_3SiHRe_2(CO)_n]^+$	25	10	5	0	0	0	0	0	*a*	0
	$[Cl_2SiHRe_2(CO)_n]^+$	70	60	*b*	*b*	35	*b*	15	0	*b*	0
	$[HRe_2(CO)_n]^+$	95	75	*b*	60	70	70	80	75	65	*b*
	$[HRe(CO)_n]^+$	95	85	60	75	65	60				
$CH_3Cl_2SiHRe_2(CO)_9$	$[HRe(CO)_n]^+$	90	75	*b*	65	70	55				
$C_6H_5Cl_2SiHRe(CO)_9$	$[HRe(CO)_n]^+$	90	75	45	65	60	40				
$HRe(CO)_5$[c]	$[HRe(CO)_n]^+$	95	70	35	50	25	15				
$HRe_3(CO)_{14}$	$[HRe(CO)_n]^+$	90	80	35	50	45	20				

[a] Not observed. [b] Very weak; overlap with other fragments made calculation of hydrogen loss impossible. [c] Estimated from the figure given by J. Lewis and B. F. G. Johnson, *Accounts Chem. Res.*, **1**, 245 (1968).

In $Cl_3SiHRe_2(CO)_9$ the four bands at 2095, 2012, 1999, and 1978 cm^{-1} are presumably due to the *cis*-$(CO)_4Re{<}^{SiCl_3}$ moiety; for $C_6H_5Cl_2SiHRe_2(CO)_9$ these four bands are shifted to 2087, 2004, 1991, and 1971 cm^{-1}, respectively. These shifts are much greater than the shifts of the bands which were assigned to the $HRe(CO)_5$ groups. This observation is in agreement with the proposed structure; the frequencies due to the $Re(CO)_4$ group should be more sensitive to the silyl ligand than are the farther removed carbonyl groups on the $HRe(CO)_5$ moiety.

Mass spectrometry proved again an almost indispensable tool in determining the exact molecular formulas of these volatile hydrido complexes. Moreover, the mass spectral fragmentation patterns give convincing support for the bridging Re–H–Re formulation in the silicon compounds. Table III summarizes the hydrogen loss percentages of the various fragmentation series in the spectrum of $Cl_3SiHRe_2(CO)_9$. The complexes $RCl_2SiHRe_2(CO)_9$ exhibited fragmentation series very similar to that of $Cl_3SiHRe_2(CO)_9$. The long series beginning with the parent ion $[Cl_3SiHRe_2(CO)_9]^+$ shows hydrogen loss only after seven carbonyls have been lost. The only other polynuclear metal carbonyl hydrides which have been reported to show similar fragmentations are the complexes $HRe_3(CO)_{14}$,[11] $HMnRe_2(CO)_{14}$,[11] $HFeCo_3(CO)_{12}$,[12] and $HRuCo_3(CO)_{12}$.[12] The first two complexes have a Re–H–Re bridge system as previously discussed; the structure of the latter two complexes is less certain but a structure with the hydrogen located in the center of a tetrahedral cage of metal atoms has been proposed.[12] Other compounds with bent hydrogen bridges between two transition metals such as $H_2Re_2(CO)_8$,[1] $H_3Mn_3(CO)_{12}$,[11] and $HMn_3(CO)_{10}(BH_3)_2$[11] show the molecular ion with no hydrogen loss but hydrogen loss is observed after the loss of one to three carbonyl groups. The degree to which hydrogen loss is competitive with CO loss is no doubt determined by several factors. One would hope for some correlation with the M–H–M angle in simple bridged systems, but at present too few examples are known to permit such fine distinctions to be made.

Other fragmentation series observed in the mass spectrum of $Cl_3SiHRe_2(CO)_9$ are the ones beginning with $[Cl_2SiHRe_2(CO)_9]^+$, $[HRe_2(CO)_9]^+$, and $[HRe(CO)_5]^+$. The latter two series display competitive hydrogen loss in all fragments (see Table III); this is similar to the fragmentation observed in $HRe_3(CO)_{14}$.[11] The fact that $[HRe(CO)_5]^+$ is observed at all strongly suggests that the $HRe(CO)_5$ moiety is present in the molecule, although one cannot completely discount the possibility of CO transfer during fragmentation;[11–13] however, the

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(11) J. M. Smith, K. Mehner, and H. D. Kaesz, *J. Amer. Chem. Soc.*, **89**, 1759 (1967).

(12) M. J. Mays and R. N. F. Simpson, *J. Chem. Soc. A*, 1444 (1968).

(13) H. J. Svec and G. A. Junk, *J. Amer. Chem. Soc.*, **89**, 2836 (1967).

relative intensities within the $[HRe(CO)_n]^+$ series suggest that $[HRe(CO)_5]^+$ is not due to CO transfer. Table III compares the $[HRe(CO)_n]^+$ series among the various complexes, including $HRe(CO)_5$. The silicon compounds show a less intense spectrum for this series than does $HRe_3(CO)_{14}$, in which the $[HRe(CO)_n]^+$ series is the most intense in the spectrum.[11] This is reflected in the fact that donor ligands react with $HRe_3(CO)_{14}$ under mild conditions to displace $HRe(CO)_5$ while the silicon compounds are much less reactive (see below). However, Table III shows that the hydrogen loss percentages for the $[HRe(CO)_n]^+$ series are all similar.

Nmr results are presented in Table IV. The high τ values are consistent with a bridging position for the rhenium-bonded hydrogen.[1] If, as the other evidence suggests, the structures are similar in all four compounds, then the chemical shift of the hydride ligand should depend mainly on the electronegativity of the group attached (Cl_3Si, RCl_2Si, $Re(CO)_5$). The observed chemical shifts are consistent with this supposition, shifting to lower field with increased electronegativity.

TABLE IV

NMR DATA FOR $XHRe_2(CO)_9$ DERIVATIVES

Compd	τ value of high-field proton
$Cl_3SiHRe_2(CO)_9$	22.45 ($CDCl_3$)
$CH_3Cl_2SiHRe_2(CO)_9$[a]	24.44 ($CDCl_3$)
$C_6H_5Cl_2SiHRe_2(CO)_9$[b]	24.60 ($CDCl_3$)
$HRe_3(CO)_{14}$	26.25[4]

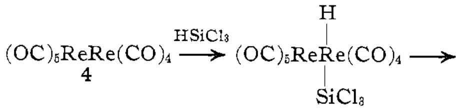
[a] Methyl resonance a sharp singlet at τ 8.78. [b] Phenyl region is a complex multiplet.

The nmr spectrum of $CH_3Cl_2SiHRe_2(CO)_9$ shows a sharp singlet for the methyl protons; this appears to rule out formulations in which the hydride ligand is proximate to the silicon moiety, as it is in $(CH_3)_2SiH_2Re_2(CO)_8$,[1,14] where proton–silicon coupling is observed.

An X-ray structure determination of one of these compounds is desirable to establish conclusively the correct structure. However, numerous attempts to grow crystals of $Cl_3SiHRe_2(CO)_9$ have thus far failed to give samples suitable for X-ray analysis; although physically attractive, the crystals were found to be twinned on close examination.

Chemical Properties and Mode of Formation.—The complexes $Cl_3SiHRe_2(CO)_9$ and $RCl_2SiHRe_2(CO)_9$ were much less reactive than $HRe_3(CO)_{14}$. A stirred hexane solution of $Cl_3SiHRe_2(CO)_9$ under 1000 psi CO pressure showed no observable reaction after 4 days. The complex $HRe_3(CO)_{14}$ has been shown to react with CO at atmospheric pressure to give $HRe(CO)_5$ and $Re_2(CO)_{10}$ after 2 days.[15] With triphenylphosphine, $Cl_3SiHRe_2(CO)_9$ reacted only slowly at 120°; there was much decomposition and the only compound identified (by infrared and mass spectroscopy) was $[(C_6H_5)_3P]_2(CO)_3ReH$.[16] Because of the high temperature needed for reaction, any $HRe(CO)_5$ formed would probably react with the phosphine to form the observed product.[17]

It seems reasonable to assume here, as in related reactions,[18] that ultraviolet irradiation produces a reactive, coordinatively unsaturated intermediate such as $Re_2(CO)_9$ (**4**). Oxidative addition of the silicon–hydrogen bond to the unsaturated rhenium atom of **4** might proceed *via* an intermediate such as **5**,[19,20] which could undergo a shift of hydrogen into the rhenium–rhenium bond to form the presumed structure **1**.



$$\underset{\mathbf{4}}{(OC)_5ReRe(CO)_4} \xrightarrow{HSiCl_3} \underset{\mathbf{5}}{(OC)_5Re\overset{H}{\underset{SiCl_3}{Re}}(CO)_4} \longrightarrow \mathbf{1}$$

Experimental Section

A nitrogen atmosphere was maintained during all reactions and during work-up procedures by the use of Schlenk apparatus. Irradiations were usually carried out using a Hanovia utility lamp (Model 30620, 140 W) at a distance of about 10 cm from a quartz flask containing the reaction mixture; the solution was maintained below room temperature during irradiation by means of a water-cooled cold finger. A more powerful Hanovia lamp (No. L679A, 450 W) was occasionally used. Reactions using methyldichlorosilane were carried out in Pyrex Carius tubes (approximate volume 70 ml) equipped with a threaded Teflon valve (Fischer and Porter Co.) for intermittent pressure release.

Rhenium carbonyl was purchased from Pressure Chemical Co., Pittsburgh, Pa. Silanes were obtained from Pierce Chemical Co., Rockford, Ill. The deuterated trichlorosilane ($DSiCl_3$) was synthesized by Merck Sharp and Dohme of Canada Ltd., Montreal. Hydrocarbon solvents were of reagent grade and were dried over sodium wire and saturated with dry nitrogen prior to use.

Microanalyses were carried out in the microanalytical laboratory of this department, and the results are given in Table V.

Mass spectra were obtained using Associated Electrical Industries MS-9 and MS-12 instruments. Samples were introduced by direct evaporation of the solid samples at temperatures just sufficient to produce the spectrum (ionizing potential 70 eV). Mass spectra were interpreted with the aid of a computer program which calculated exact masses and isotope combination patterns. As noted previously,[1] an exact knowledge of the theoretical patterns is essential in assessing hydrogen loss. The patterns encountered for the compounds of this paper permitted hydrogen loss to be estimated in a straightforward fashion; it was unnecessary to use the least-squares fitting procedure developed for the more complex isotope patterns of osmium carbonyl hydrides.[21]

Hydrido(trichlorosilyl)nonacarbonyldirhenium, $Cl_3SiHRe_2(CO)_9$.—A magnetically stirred solution of rhenium carbonyl (2.25 g, 3.5 mmol) and trichlorosilane (1.0 ml, 10 mmol) in 50 ml of *n*-hexane was irradiated with the 140-W source for 6 hr while maintaining the reaction solution at *ca.* 15°. Some of the product precipitated as a white powder. Solvent and excess trichlorosilane were evaporated at reduced pressure and the residual solid was sublimed (50°, 0.01 mm) to remove unreacted rhenium carbonyl. Two recrystallizations from *n*-hexane–dichloromethane afforded white crystals of the product (1.40 g). The deuterated analog $Cl_3SiDRe_2(CO)_9$ was prepared by an identical procedure using Cl_3SiD; using quantities similar to the above a 50% yield of the product was obtained.

Hydrido(methyldichlorosilyl)nonacarbonyldirhenium, $CH_3Cl_2SiHRe_2(CO)_9$.—A Carius tube containing rhenium car-

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[14] J. K. Hoyano, M. Elder, and W. A. G. Graham, *J. Amer. Chem. Soc.*, **91**, 4568 (1969).

[15] R. W. Harrill and H. D. Kaesz, *Inorg. Nucl. Chem. Lett.*, **2**, 69 (1966).

[16] M. Freni, D. Giusto, and V. Valenti, *J. Inorg. Nucl. Chem.*, **27**, 755 (1965).

[17] B. L. Booth and R. N. Haszeldine, *J. Chem. Soc. A*, 157 (1966).

[18] W. Jetz and W. A. G. Graham, *Inorg. Chem.*, **10**, 4 (1971).

[19] Such an intermediate was not detected but would be analogous to cases such as π-$C_5H_5Re(CO)_2HSiCl_3$[20] where only a single transition metal is involved.

[20] J. Hoyano and W. A. G. Graham, submitted for publication in *J. Amer. Chem. Soc.*

[21] J. R. Moss and W. A. G. Graham, submitted for publication in *Inorg. Chem.*

TABLE V

MELTING POINTS, YIELDS, COLORS, AND ANALYTICAL RESULTS

Compd	Mp, °C	Yield, %	Color	% calcd C	% calcd H	% calcd Cl	% found C	% found H	% found Cl
$Cl_3SiHRe_2(CO)_9$	155 dec	55	White	14.25	0.13	14.00	14.20	0.16	14.40
$Cl_3SiDRe_2(CO)_9$	154–155 dec	50	White	14.20	0.27	13.97	14.63	0.36	14.47
$C_6H_5Cl_2SiHRe_2(CO)_9$	130–132	50	White	22.49	0.75	8.84	22.67	0.96	8.42
$CH_3Cl_2SiHRe_2(CO)_9$	108–110	35	White	16.25	0.55	9.59	16.48	0.73	9.70
$HRe_3(CO)_{14}$[a]	...	50	Yellow	17.66	0.11	...	17.50	0.25	...

[a] Infrared and mass spectra were in agreement with those reported in ref 4 and 11.

bonyl (1.44 g, 2.20 mmol) and methyldichlorosilane (2.0 g, 18 mmol) was irradiated with the 450-W source for 12 hr. Carbon monoxide pressure was released every 2 hr. Unreacted methyldichlorosilane was distilled off on a vacuum system and the residual solid was sublimed at 55° to remove unreacted rhenium carbonyl. Three recrystallizations from *n*-hexane afforded white crystals (0.60 g) of the pure product.

Hydrido(phenyldichlorosilyl)nonacarbonyldirhenium, $C_6H_5Cl_2SiHRe_2(CO)_9$.—A solution of rhenium carbonyl (1.10 g, 1.70 mmol) and phenyldichlorosilane (1.0 g, 5.6 mmol) in 50 ml of cyclohexane was irradiated for 4.5 hr with the 140-W source. The solution was maintained at *ca.* 15° during the irradiation. Solvent and starting materials were then removed by evaporation at reduced pressure and sublimation at 50°. Unsublimed solid was recrystallized twice from *n*-hexane to yield 0.40 g of the product.

Hydridotetradecacarbonyltrirhenium, $HRe_3(CO)_{14}$.—Eighteen hours of irradiation (140-W source) of a solution of rhenium carbonyl (1.58 g, 2.4 mmol) and triphenylsilane (0.70 g, 2.7 mmol) in 50 ml of benzene gave a yellow solution. Benzene was evaporated at reduced pressure and the residue was sublimed at 60° (0.01 mm) to remove unreacted starting materials. The unsublimed yellow solid was recrystallized from dichloromethane–*n*-hexane to afford yellow crystals of the product (0.70 g).

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Cationic Acetylenic Platinum(II) Compounds and Their Derivatives. IV. Displacement Reactions

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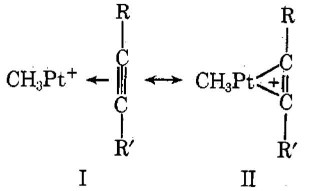
The equilibrium reaction *trans*-$[PtCH_3(L)Q_2]^+PF_6^- + L' \rightleftharpoons$ *trans*-$[PtCH_3(L')Q_2]^+PF_6^- + L$, where $Q = P(CH_3)_2C_6H_5$, has been studied for a variety of neutral ligands, L′, to give a displacement series. The comparison of this series with the trans-influence series, obtained from nmr data, demonstrates the importance of Pt–L π bonding. The dependence of these displacement reactions on the choice of solvent, when L′ is an unsaturated ligand, further indicates the importance of a cationic mechanism in which L′ must occupy the fourth coordination position of the $[CH_3PtQ_2]^+$ plane, before carbonium ion reactivity is achieved.

Introduction

We have previously described[1,2] the preparation and properties of the cationic complexes *trans*-$[PtCH_3(RC{\equiv}CR')Q_2]^+PF_6^-$ (I), where $Q = P(CH_3)_2C_6H_5$ or $As(CH_3)_3$ and R, R′ = alkyl or aryl groups. When R and R′ were other than alkyl or aryl groups, cationic acetylide,[1] alkoxycarbene,[3] or vinyl ether complexes[2] were obtained. These products are believed to be derived from the initial formation of cationic acetylene complexes I which show reactivity characteristic of carbonium ions (II) and hence lead to products interpretable in terms of intramolecular rearrangements and/or nucleophilic addition.[4,5] The addition to the triple bond of the complexed acetylene in the formation of methyl vinyl ether complexes gives[5] only the trans vinylic isomer as predicted from the carbonium ion II. However, depending on the nature of the nucleophile, nucleophilic attack may occur at platinum and thus produce displacement of the acetylene.[4] In this paper we examine the factors influencing the directional course of this nucleophilic attack (attack at platinum *vs.* attack at the triple bond) since this determines the reactivity of an unsaturated ligand when coordinated to the cation $[CH_3PtQ_2]^+$.



I II

Results and Discussion

Values of J(Pt–C–H) for the platinum methyl group and J(Pt–P–C–H) for the phosphine methyl groups for a series of cationic methylplatinum complexes *trans*-$[PtCH_3(L)\{P(CH_3)_2C_6H_5\}_2]^+PF_6^-$ (III) are given in Table I. These platinum–hydrogen coupling con-

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