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Silicon-29 NMR Investigation of Silyl Derivatives of the Iron-Group Transition Metals

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Received October 16, 1984

The ^{29}Si NMR spectra of $M(CO)_4(SiMe_{3-n}Cl_n)(H)$ (M = Fe, n = 0–3; M = Ru, Os, n = 3), $M(CO)_4(SiMe_{3-n}Cl_n)_2$ (M = Fe, Ru, Os, n = 0–3 (cis and trans isomers)), $(C_5H_5)Fe(CO)_2(SiMe_{3-n}Cl_n)$ (n = 1–3), $[M(CO)_4(SiMe_{3-n}Cl_n)]_2$ (M = Ru, n = 0–3; M = Os, n = 2, 3), $(Cl_nMe_{3-n}Si)Os_3(CO)_{12}(SiMe_{3-n}Cl_n)$ (n = 2, 3), $M_3(\mu\text{-H})_3(CO)_9(SiCl_3)_3$ (M = Ru, Os), and (arene)$Ru(CO)(SiCl_3)_2$ (arene = C_6H_5Cl, C_6H_6, $C_6H_3Me_3$, C_6Me_6, $C_6H_4\text{-}t\text{-}Bu_2$) have been recorded. Several empirical relationships were found: (1) for a series of $M(SiMe_{3-n}Cl_n)$ (n = 0–3) compounds, the $SiMeCl_2$ derivative usually gave the ^{29}Si NMR resonance to lowest field; (2) for $M(SiMe_{3-n}Cl_n)$ complexes the ^{29}Si NMR resonance shifted upfield on going to the transition metal (M) lower in the periodic table; (3) for $M(CO)_4(SiMe_{3-n}Cl_n)_2$ the resonance of the trans isomer came to lower field than that of the cis isomer; (4) for (arene)$Ru(CO)(SiCl_3)_2$ there was a linear correlation between the ^{29}Si chemical shift and the CO stretching frequency of the compounds. The ^{29}Si NMR spectra of $M'(CO)_m(SiCl_3)$ (M′ = Mn, Re, m = 5; M′ = Co, m = 4) were also obtained.

Introduction

The availability of high-field NMR instruments equipped with variable-frequency probes has allowed the routine study of nuclei of spin $^1/_2$ other than the traditional ones of ^{1}H, ^{13}C, ^{19}F, and ^{31}P. One such nucleus is ^{29}Si,[1-5] present in 4.7% natural abundance and having an NMR receptivity compared to ^{13}C of 2.09.[6] However, besides the usual difficulties of low natural abundance and low sensitivity, the ^{29}Si NMR experiment suffers two further problems. The first is that the ^{29}Si nucleus has a negative gyromagnetic ratio so that under the conditions of broad-band proton decoupling the ^{29}Si resonance will suffer a negative nuclear Overhauser effect if the ^{29}Si nucleus is in close proximity ($\lesssim$3 Å) to any protons. This can diminish the intensity of the signal such that it can be depressed completely to the base line. The second drawback is the long relaxation times of the silicon nucleus, especially when bonded to transition metals. Both of these problems can be overcome by addition of a relaxing agent, such as $Cr(acac)_3$ (acacH = acetylacetone), to the solution. In spite of this, ^{29}Si NMR spectra of transition-metal–silicon derivatives have received little attention. For example, a recent review listed the ^{29}Si NMR chemical shifts of some 2300 compounds of which only 46 contained a transition or heavy non-transition metal.[3] Furthermore, many of the chemical shifts of this group of compounds were determined by the indirect INDOR technique[7] or by the selective population transfer (SPT) method.[8]

Herein we report the ^{29}Si NMR spectra of over 40 transition-metal–silicon complexes. The spectra were determined directly without too much difficulty. The study indicates that ^{29}Si NMR spectroscopy is potentially a valuable technique in the characterization of transition-metal–silicon compounds.

Experimental Section

Unless otherwise stated, manipulations of starting materials and products were carried out under a nitrogen atmosphere with use of standard Schlenk techniques. Solvents were scrupulously dried, distilled, and stored under nitrogen before use. Reactions that required CO pressure were carried out in a 200-mL general-purpose bomb from Parr Instrument Co. Infrared spectra were recorded on a Perkin-Elmer 983 spectrometer; mass spectra on a Hewlett-Packard 5985 GC-MS instrument.

The preparations of virtually all the compounds studied here have appeared before: $Fe(CO)_4(SiMe_{3-n}Cl_n)(H)$ (n = 0–3),[9,10] $Fe(CO)_4(SiMe_3)_2$,[11] $Fe(CO)_4(SiMe_{3-n}Cl_n)_2$ (n = 0–3),[12] *cis*-$M(CO)_4(SiCl_3)_2$ (M = Fe (cis/trans mixture), Ru, Os),[13] $M(CO)_4(SiMe_{3-n}Cl_n)_2$ (M = Ru, Os; n = 0–3 (cis and trans isomers)),[14] $Os(CO)_4(SiMe_3)_2$,[15] $(C_5H_5)Fe(CO)_2(SiMe_{3-n}Cl_n)$ (n = 0–3),[12,16,17] $Ru(CO)_4(SiCl_3)(X)$ (X = H, Br),[18] $Os(CO)_4(SiCl_3)(H)$,[19] (arene)$Ru(CO)(SiCl_3)_2$,[20] $[Ru(CO)_4(SiMe_{3-n}Cl_n)]_2$ (n = 0, 1, 3),[18,21] $[Os(CO)_4(SiMe_{3-n}Cl_n)]_2$ (n = 2, 3),[19] $(Cl_nMe_{3-n}Si)Os_3(CO)_{12}(SiMe_{3-n}Cl_n)$ (n = 2,3),[22] $M_3(\mu\text{-H}_3)(CO)_9(SiCl_3)_3$ (M = Ru, Os),[23] $M(CO)_5(SiCl_3)$ (M = Mn, Re),[12,16] $Co(CO)_4(SiCl_3)$,[24] and $(C_6H_3Me_3)Re(CO)_2(SiCl_3)$.[25] In each case the identity and purity of the compound were checked by infrared spectroscopy (carbonyl region); in many cases a mass spectrum of the compound was also obtained. In all cases the agreement between the observed and reported CO stretching frequencies was excellent. Since some of the preparations are not in the readily available chemical literature and because some preparations employed here differ significantly from the literature methods, some representative preparations are given below.

Preparation of $Fe(CO)_4(SiMe_3)(H)$ and $Fe(CO)_4(SiMe_3)_2$. To a quartz Carius tube (fitted with a Teflon valve) were added $Fe(CO)_5$ (0.60 g, 3.1 mmol) and hexane (30 mL). The tube was cooled to −196 °C and evacuated; the solution was degassed with a freeze–thaw cycle. With the temperature maintained at −196 °C, Me_3SiH (1.91 g, 25.7 mmol) was condensed into the vessel, which was then allowed to warm slightly and pressurized with CO (~1 atm). The tube was warmed to room temperature and subjected to ultraviolet irradiation (200-W source, 5 cm from source to edge of solution) for 60 h. (The solution was stirred during the irradition.) After this treatment the CO and excess Me_3SiH were released, and the solution was transferred to a Schlenk flask. An infrared spectrum of the reaction mixture indicated approximately equal quantities of $Fe(CO)_4(SiMe_3)(H)$ and $Fe(CO)_4(SiMe_3)_2$ (very little decomposition had occurred). The hexane was removed at 0 °C on the vacuum line, and with the flask maintained at 0 °C the $Fe(CO)_4(SiMe_3)(H)$ was distilled to a second Schlenk flask maintained at −78 °C. The product, a white solid that melted to a yellow liquid at room temperature, was pure $Fe(CO)_4(SiMe_3)(H)$ by infrared and ^{29}Si NMR

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spectroscopy, although it probably contained traces of hexane. An infrared spectrum of the solid that remained after the distillation revealed it was mainly $Fe(CO)_4(SiMe_3)_2$ (no $Fe(CO)_4(SiMe_3)(H)$ remained). It was sublimed at 30 °C to a probe at −78 °C (<0.02 mm). Although the product was green (perhaps due to traces of $Fe_3(CO)_{12}$), the infrared and ^{29}Si NMR spectra showed it was esentially pure $Fe(CO)_4(SiMe_3)_2$.

Preparation of $Fe(CO)_4(SiCl_3)(H)$. A Carius tube with $Fe_2(CO)_9$ (0.50 g, 1.4 mmol) and Cl_3SiH (3 mL) in hexane (15 mL) was cooled to −196 °C and evacuated; the solution was degassed with a freeze–thaw cycle. After warming to room temperature, the tube was placed in an oil bath at 60 °C and the solution stirred for 45 min, during which time all the gold-colored $Fe_2(CO)_9$ was consumed. The solution was then filtered through Celite to a Schlenk flask, which served to remove a gray-green precipitate that had formed during the reaction. Removal of the solvent, $Fe(CO)_5$, and excess Cl_3SiH on the vacuum line gave $Fe(CO)_4(SiCl_3)(H)$ (0.42 g, 50%). The compound (a colorless liquid) was pure by infrared spectroscopy. It may, however, be purified by distillation at room temperature and <0.02 mm to a collection flask at −196 °C. For this purification a system of two interconnecting Schlenk flasks was used. The first flask, which contained the crude material, had an inner rim that prevented the hydride from flowing directly into the second flask when the flasks were inverted. The second flask was cooled to −196 °C and the system evacuated through the side arm of the second Schlenk tube to effect the distillation. The other hydrides $Fe(CO)_4(SiMe_{3-n}Cl_n)(H)$ (n = 0–2) were prepared similarly. $Fe(CO)_4(SiMe_3)(H)$: ν(CO) (hexane) 2093 m, 2028 m–s, 2018 s, 2007 s cm^{-1}. $Fe(CO)_4(SiMe_2Cl)(H)$: ν(CO) (hexane) 2106 m, 2044 m–s, 2038 s, 2022 vs cm^{-1}. $Fe(CO)(SiMeCl_2)(H)$: ν(CO) (hexane) 2115 m, 2058 m–s, 2050 s, 2037 vs cm^{-1}. (Prolonged accumulation times for the ^{29}Si NMR spectrum of $Fe(CO)_4(SiMe_3)(H)$ resulted in the appearance of new resonances (at 6.9 and −16.4 ppm) indicative of decomposition products.)

Preparation of $Fe(CO)_4(SiMeCl_2)_2$. A sealed, evacuated Carius tube with $Fe_2(CO)_9$ (4.0 g, 11 mmol) and Cl_2MeSiH (4 mL) in hexane (20 mL) was heated at 85 °C for 19 h. (The solution was stirred during this treatment.) The tube was cooled and the solution transferred to a Schlenk tube. The solvent, $Fe(CO)_5$ (a coproduct in the reaction), and excess Cl_2MeSiH were removed on the vacuum line. Vacuum distillation as previously described gave the pure product, $Fe(CO)_4(SiMeCl_2)_2$ (2.2 g, 50%), as a pale yellow liquid: ν(CO) (hexane) 2111 s, 2061 sh, 2058.5 s, 2048 m, 2036 vs, 2030.5 m, sh cm^{-1}. The extra CO absorptions have been attributed to conformation effects.[12,16] The compound prepared in this manner was pure by ^{13}C[26] and ^{29}Si NMR spectroscopy. The $SiMe_2Cl$ analogue, $Fe(CO)_4(SiMe_2Cl)_2$, was prepared similarly: ν(CO) (hexane) 2093 s, 2040 m, 2024 m, 2010 vs cm^{-1}.

Preparation of *cis*-$Os(CO)_4(SiCl_3)(H)$. A sealed, evacuated Carius tube with $Os(CO)_5$[27] (ca. 0.21 g, 0.64 mmol) and Cl_3SiH (6 mL) in hexane (35 mL) was heated at 80 °C for 18 h. (The solution was stirred during the reaction.) The cloudy, yellow solution was then transferred to a Schlenk flask, and the hexane and excess Cl_3SiH were removed on the vacuum line to yield an orange liquid. An infrared spectrum of the crude material revealed no carbonyl compounds except the desired product, *cis*-$Os(CO)_4(SiCl_3)(H)$: ν(CO) (hexane) 2150 w, 2087 m, 2069 s cm^{-1}. This sample was considered of sufficient purity for the ^{29}Si NMR spectrum; the compound may, however, be purified by sublimation.[19]

Preparation of $[Os(CO)_4(SiMeCl_2)]_2$. To a Carius tube (fitted with a Teflon valve) were added $Os_3(CO)_{12}$ (0.30 g, 0.33 mmol), Cl_2MeSiH (~0.20 mL, ~2.0 mmol), and hexane (20 mL). The tube was evacuated at −196 °C and the solution degassed with two freeze–thaw cycles. The tube was warmed to room temperature, pressurized with CO (2 atm), and heated at 140 °C for 24 h. An infrared spectrum of the red reaction solution at this stage indicated only *cis-*/*trans*-$Os(CO)_4(SiMeCl_2)_2$ and $[Os(CO)_4(SiMeCl_2)]_2$ were present. The solvent and excess Cl_2MeSiH were removed on the vacuum line. The remaining solid was subjected to sublimation at 80 °C and <0.02 mm to a probe at −78 °C. This separated both the monomer and the dimer from traces of impurities. The sublimate was then carefully resublimed at 40 °C (<0.02 mm) to a probe at −78 °C. This removed $Os(CO)_4(SiMeCl_2)_2$ from the pale yellow $[Os(CO)_4(SiMeCl_2)]_2$, which did not sublime appreciably under the latter conditions. The product had an IR spectrum (CO region) identical with that reported in the literature.[19] Although not actually prepared in this manner, it is probable that the $SiCl_3$ analogue can be made by this method, which is superior to the previous literature method.[19] The latter compound, $[Os(CO)_4(SiCl_3)]_2$, has also been prepared by the treatment of a hexane solution of $Os_3(CO)_{12}$ with excess Cl_3SiH under CO (80 atm) at 145 °C for 40 h. The coproduct *trans*-$Os(CO)_4(SiCl_3)_2$ was removed from the desired product by sublimation.

Table I. ^{29}Si NMR Chemical Shifts for $M(CO)_4(SiMe_{3-n}Cl_n)_2$ and $M(CO)_4(SiMe_{3-n}Cl_n)(H)$ Derivatives[a]

	δ	
compd	cis Isomer	trans Isomer
$Fe(CO)_4(SiMe_3)_2$	26.6[b,c]	
$Fe(CO)_4(SiMe_2Cl)_2$	61.3 (5.1)[d]	
$Fe(CO)_4(SiMeCl_2)_2$	68.5 (6.2)[d]	
$Fe(CO)_4(SiCl_3)_2$	41.8	46.0
$Ru(CO)_4(SiMe_3)_2$	2.1[c]	
$Ru(CO)_4(SiMe_2Cl)_2$	47.9 (5.7)[d]	
$RuCO)_4(SiMeCl_2)_2$	56.2 (6.2)[d]	57.4 (6.2)[d]
$Ru(CO)_4(SiCl_3)_2$	28.3	30.7
$Os(CO)_4(SiMe_3)_2$	−22.8[c]	−19.3[c]
$Os(CO)_4(SiMe_2Cl)_2$	19.2 (5.5)[d]	21.6 (4.8)[d]
$Os(CO)_4(SiMeCl_2)_2$	24.4 (6.1)[d]	25.3 (5.2)[d]
$Os(CO)_4(SiCl_3)_2$	−7.0	−6.6
$Fe(CO)_4(SiMe_3)(H)$	27.4[c] 27.3[c,e]	
$Fe(CO)_4(SiMe_2Cl)(H)$	63.2[c,e]	
$Fe(CO)_4(SiMeCl_2)(H)$	70.7[e]	
$Fe(CO)_4(SiCl_3)(H)$[e]	46.5 (21.7)[d,e]	
$Ru(CO)_4(SiCl_3)(H)$[e]	30.8[f] 30.4[e,f]	
$Os(CO)_4(SiCl_3)(H)$[e]	−7.1 (7)[d] −6.5 (8.0)[d,e]	

[a] Chemical shifts (ppm) relative to Me_4Si; CH_2Cl_2 solution except as noted. [b] May contain some of the trans isomer in rapid equilibrium with cis form: Vancea, L.; Bennett, M. J.; Jones, C. E.; Smith, R. A.; Graham, W. A. G. *Inorg. Chem.* **1977**, *16*, 897. [c] Broad-band proton decoupled. [d] ^2J(Si–H). [e] Hexane/C_6D_6 (4:1) solution. [f] H coupling not observed.

Preparation of $Re(CO)_5(SiCl_3)$. A 200-mL general-purpose autoclave was charged with $Re_2(CO)_{10}$ (1.0 g, 1.5 mmol), hexane (25 mL), and $HSiCl_3$ (6 mL, ~60 mmol) and pressurized with CO (70 atm). The vessel was heated in an oil bath at 200 °C for 16 h. It was then cooled, the gases were vented, and the solution was transferred to a Schlenk flask to leave white crystals of $Re(CO)_5(SiCl_3)$. The crystals (1.14 g) were washed with hexane and dried with a stream of nitrogen. The solution, on standing at −78 °C for 2 h, afforded further $Re(CO)_5(SiCl_3)$ (0.20 g; total yield 95%). The product in each case was pure enough to be used for most preparations; it can, however, be purified by sublimation at 65 °C to a probe at −78 °C (<0.02 mm). The compound showed no apparent decomposition even after exposure to air for 24 h: ν(CO) (hexane) 2141 w, 2038 vs, 2030 m cm^{-1} (lit.[16] 2139, 2037, 2028 cm^{-1} (cyclohexane)); MS m/e (most abundant peak) calcd 459.81, found 460. The same procedure with the modifications noted was adopted for the preparation (from the respective carbonyls) of the compounds listed below (yields were excellent in all cases). $Mn(CO)_5(SiCl_3)$: reaction temperature 145 °C; isolated product slightly yellow, which suggested traces of $Mn_2(CO)_{10}$ may have remained unreacted; ν(CO) (hexane) 2123 m, 2035 vs cm^{-1} (lit.[16] 2123, 2035 cm^{-1}); MS m/e calcd 329.79, found 330 (vw). $Co(CO)_4(SiCl_3)$: reaction temperature 125 °C; a precipitate formed, which was removed by filtration; product obtained by sublimation at room temperature to probe at −78 °C (<0.02 mm, closed atmosphere); ν(CO) (hexane) 2119 m, 2064 m, 2039 s cm^{-1} (lit.[28] 2121, 2065, 2039 cm^{-1}); MS m/e $(P - CO)^+$ calcd 277.80, found 278, P^+ vw. *trans*-$Ru(CO)_4(SiCl_3)_2$: for this preparation, $Ru_3(CO)_{12}$ (1.28 g, 2.0 mmol) in hexane (30 mL) yielded *trans*-$Ru(CO)_4(SiCl_3)_2$ (1.2, g; 44%) as a crystalline precipitate; ν(CO) (hexane) 2089 vs cm^{-1}. The mother solution contained both *cis*- and *trans*-$Ru(CO)_4(SiCl_3)_2$.[14] $(C_5H_5)Fe(CO)_2(SiCl_3)$: reaction temperature 180 °C; ν(CO) (hexane) 2039 s, 1995 s cm^{-1} (lit.[16,17] 2039, 1995 cm^{-1}). $(C_5H_5)Fe(CO)_2(SiMeCl_2)$: reaction temperature 140 °C; ν(CO) (hexane) 2030 m, 2021 s, 1982 m, 1973 s cm^{-1} (lit.[16] 2031, 2022, 1983, 1973 cm^{-1}). $(C_5H_5)Fe(CO)_2(SiMe_2Cl)$: reaction temperature 145 °C; compound purified by distillation at room temperature to Schlenk flask at −196 °C; ν(CO) (hexane) 2015 w, sh, 2010 s, 1969 w, 1958 s cm^{-1}; MS m/e $(P - CO)^+$ calcd 241.96, found 242, P^+ vw.

NMR Spectroscopy. Silicon-29 NMR spectra (Tables I–IV) were obtained on a Bruker WM-400 spectrometer at a frequency of 79.495 MHz. The spectra were recorded unlocked in most cases. The spectral recording parameters varied from spectrum to spectrum. However, a typical set of parameters follows: spectral width 11 900 Hz (149.7 ppm),

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Table II. ^{29}Si NMR Chemical Shifts for Cyclopentadienyl and Arene Derivatives[a]

compd	δ
$(C_5H_5)Fe(CO)_2(SiMe_3)$[b]	41.0 (6.5)[c]
$(C_5H_5)Fe(CO)_2(SiMe_2Cl)$	69.4 (6.2)[c]
$(C_5H_5)Fe(CO)_2(SiMeCl_2)$	61.4 (6.3)[c]
$(C_5H_5)Fe(CO)_2(SiCl_3)$	39.4
$(C_6H_5Cl)Ru(CO)(SiCl_3)_2$	35.3 (2021)[d]
$(C_6H_6)Ru(CO)(SiCl_3)_2$	36.5 (2017)[d]
$(C_6H_3Me_3)Ru(CO)(SiCl_3)_2$	37.6 (2008)[d]
$(C_6Me_6)Ru(CO)(SiCl_3)_2$	40.8 (1995)[d]
$(C_6H_4\text{-}t\text{-}Bu_2)Ru(CO)(SiCl_3)_2$	34.3 (2007)[d]

[a] Chemical shifts (ppm) relative to Me_4Si; CH_2Cl_2 solution. [b] From ref 8 (value converted to Me_4Si standard). [c] ^2J(Si–H). [d] ν(CO) in CH_2Cl_2.

Table III. ^{29}Si NMR Chemical Shifts for *trans*-$(Cl_nMe_{3-n}Si)[M(CO)_4]_m(SiMe_{3-n}Cl_n)$ Derivatives[a]

compd	δ
$Ru(CO)_4(SiMe_3)_2$[b]	2.1[c]
$[Ru(CO)_4(SiMe_3)]_2$	9.8[c]
$Ru(CO)_4(SiMe_2Cl)_2$[b]	47.9 (5.7)[d]
$[Ru(CO)_4(SiMe_2Cl)]_2$	52.9 (7.3)[d]
$Ru(CO)_4(SiMeCl_2)_2$	57.4 (6.2)[d]
$[Ru(CO)_4(SiMeCl_2)]_2$	59.3 (9.8)[d]
$Ru(CO)_4(SiCl_3)_2$	30.7
$[Ru(CO)_4(SiCl_3)]_2$	31.5
$Os(CO)_4(SiMeCl_2)_2$	25.3 (5.2)[d]
$[Os(CO)_4(SiMeCl_2)]_2$	22.0 (6.2)[d]
$Os(CO)_4[Os(CO)_4(SiMeCl_2)]_2$	21.8[c]
$Os(CO)_4(SiCl_3)_2$	-6.6
$[Os(CO)_4(SiCl_3)]_2$	-11.0
$Os(CO)_4[Os(CO)_4(SiCl_3)]_2$	-10.9

[a] Chemical shifts (ppm) relative to Me_4Si; CH_2Cl_2 solution. [b] Cis isomer. [c] Broad-band proton decoupled. [d] ^2J(Si–H).

Table IV. ^{29}Si NMR Chemical Shifts for Miscellaneous Silyl–Transition-Metal Derivatives[a]

compd	δ
trans-$Ru(CO)_4(SiCl_3)(Br)$	25.9
$Ru_3(\mu\text{-}H)_3(CO)_9(SiCl_3)_3$	24.3
$Os_3(\mu\text{-}H)_3(CO)_9(SiCl_3)_3$	-15.8
$Mn(CO)_5(SiCl_3)$	42.2
$Co(CO)_4(SiCl_3)$	36.2
$Re(CO)_5(SiCl_3)$	16.1
$(C_6H_3Me_3)Re(CO)_2(SiCl_3)$	13.0

[a] Chemical shifts (ppm) relative to Me_4Si; CH_2Cl_2 solution.

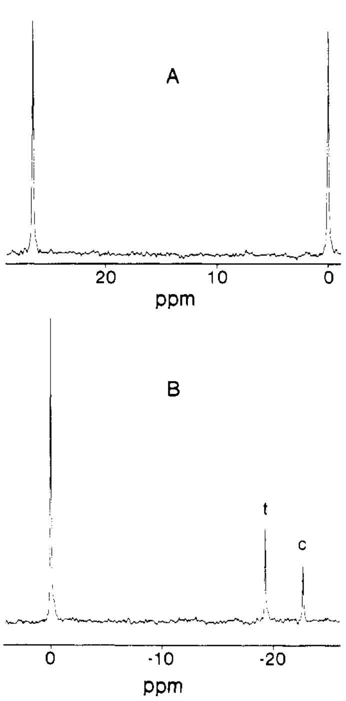

Figure 1. $^{29}Si\{^1H\}$ NMR spectra: (A) $Fe(CO)_4(SiMe_3)_2$; (B) *cis*- and *trans*-$Os(CO)_4(SiMe_3)_2$. In each case there was about 0.4 g of sample in 3.0 mL of CH_2Cl_2 (with Me_4Si); $Cr(acac)_3$ was added as a relaxing agent. Each spectrum represents the result of 3000 scans.

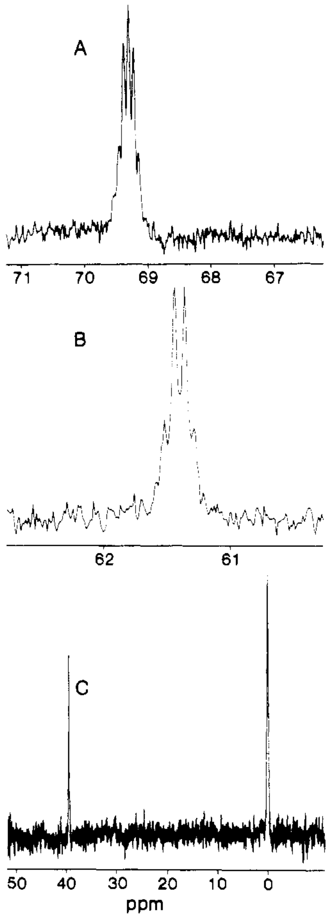

Figure 2. ^{29}Si NMR spectra: (a) $(\eta\text{-}C_5H_5)Fe(CO)_2(SiMe_2Cl)$ (spectrum after 8899 scans); (B) $(\eta\text{-}C_5H_5)Fe(CO)_2(SiMeCl_2)$; (C) $(\eta\text{-}C_5H_5)Fe(CO)_2(SiCl_3)$ (0.32 g in 3.0 mL; spectrum after 5300 scans). All spectra: CH_2Cl_2 solvent with Me_4Si as internal reference. (The ^{29}Si chemical shift of $(\eta\text{-}C_5H_5)Fe(CO)_2(SiMe_3)$ has been reported at 41.0 ppm.[8])

16K memory size, 1.45 Hz/data point, acquisition time 0.688 s, with a ~10° pulse of 5 μs. Smaller sweep widths (e.g., 5000.0 Hz, 62.90 ppm) were used for the osmium compounds. The number of scans varied dramatically (e.g., Figures 1 and 2). For samples that contained $Cr(acac)_3$ (e.g., $Fe(CO)_4(SiMe_3)_2$) or that had a high concentration of a species with a single resonance (e.g., $(C_5H_5)Fe(CO)_2(SiCl_3)$), spectra of acceptable quality could be obtained after ~3000 scans (<60-min accumulation time). On the other hand, for samples that were quadrupole broadened (e.g., $Mn(CO)_5(SiCl_3)$ and $Re(CO)_5(SiCl_3)$, but not $Co(CO)_4(SiCl_3)$), that contained more than one type of silicon coupled to protons (e.g., the cis and trans mixture of $Ru(CO)_4(SiMeCl_2)_2$), or that were in very low concentration (e.g., $[Os(CO)_4(SiCl_3)]_2$), up to 125 000 scans were required in order to obtain spectra of suitable quality. This represented an overnight accumulation of transients. Spectra were recorded in CH_2Cl_2 that contained 5–10% Me_4Si except those for the hydrides, where hexane was employed (with ~20% C_6D_6 to provide a lock signal). Samples were prepared in the drybox; they were contained in 10-mm NMR tubes that had between 0.1 and 0.7 g of sample in 2.5–4 mL of solvent (molar concentration of Si ~0.05–1.0 M). The signal to noise ratios of the spectra were dramatically improved by addition of the relaxation agent $Cr(acac)_3$ (5–10 mg; acacH = acetylacetone) to the sample. However, since the relaxation agent could not be conveniently removed from the sample, it was only used in those cases where absolutely essential. These were those samples that were broad-band proton decoupled (e.g., complexes with $SiMe_3$ ligands), the hydrides (Table I), those that were in low concentration, and some where the sample gave more than one ^{29}Si NMR resonance. Some of the Os–$SiCl_3$ derivatives had almost identical ^{29}Si NMR chemical shifts, which were also close to that of TMS. In these cases the spectra were repeated in CH_2Cl_2 that did not contain TMS to ensure there were no resonances hidden by the reference signal. The identity of the sample was also checked by infrared spectroscopy before and after the ^{29}Si NMR spectrum was recorded.

Results and Discussion

The ^{29}Si NMR spectra have been recorded of a number of derivatives that contain M–Si(Me$_{3-n}$Cl$_n$) (M = Fe, Ru, Os, n = 0–3) linkages (Tables I–IV). For most samples the relaxation agent Cr(acac)$_3$ (acacH = acetylacetone) was not used in order that they could be recovered uncontaminated. However, in some cases where the concentration of the sample was low and in all cases where broad-band proton decoupling was used to obtain the spectrum, the relaxation agent was added. It was established that addition of varying quantities of Cr(acac)$_3$ to a solution of *cis*-Ru(CO)$_4$(SiCl$_3$)$_2$ caused no significant change in the ^{29}Si NMR chemical shift of the compound. There was, however, a significant improvement in the signal to noise ratio of the signal over that given by the sample with no added Cr(acac)$_3$. The number of transients needed to obtain a spectrum of suitable quality varied enormously with the identity of the sample (see the Experimental Section for details). Some typical spectra are presented in Figures 1 and 2.

For spin $^1/_2$ nuclei other than ^{1}H the contributions to the various terms that give rise to the chemical shift of the nucleus are poorly understood, e.g., ^{13}C and ^{31}P NMR chemical shifts.[29,30] This is especially the case when the nucleus in question is bound to a transition metal or another heavy element. The situation for ^{29}Si NMR spectroscopy is no different.[1-5] In this discussion we make no attempt at a theoretical interpretation of the ^{29}Si NMR chemical shifts but note only empirical correlations that are potentially useful to the synthetic chemist.

For molecules of the type SiMe$_{4-n}$X$_n$ (X = halogen, O or N substituent, n = 0–4) and SiMe$_{3-n}$X$_n$R (R = H, Ph, CH$_2$Ph, etc., n = 0–3) the ^{29}Si NMR chemical shifts do not vary smoothly with a change in n, but rather the most positive (lowest field) chemical shift occurs for the molecule with n = 1 (or occasionally 2).[1-5] (Although this sagging pattern is observed in ^{31}P and ^{119}Sn NMR spectroscopy,[31] it is not observed in the ^{13}C NMR spectra of the carbon analogues.) The pattern has been explained from the semiempirical calculation of the p-orbital "imbalance" and its contribution to the paramagnetic term of nuclear shielding.[1,3,5,31] Arguments based on the sum of the substituent electronegativities[1,3] or pπ–dπ bonding[1] have also been invoked to explain this U-shaped relationship. The present molecules where X = Cl and R = M(CO)$_4$(SiMe$_{3-n}$Cl$_n$) (cis or trans; M = Fe, Ru, Os) (Table I) or Ru$_2$(CO)$_8$(SiMe$_{3-n}$Cl$_n$) (Table III) also showed this sagging pattern. This is illustrated for the *cis*-M(CO)$_4$(SiMe$_{3-n}$Cl$_n$)$_2$ compounds in Figure 3. For R = (η-C$_5$H$_5$)Fe(CO)$_2$, the derivative with the lowest ^{29}Si chemical shift was (η-C$_5$H$_5$)Fe(CO)$_2$-(SiMe$_2$Cl) (Figure 2).

The ^{13}C NMR resonances of the *cis*-M(CO)$_4$(SiMe$_{3-n}$Cl$_n$)$_2$ derivatives, for both the carbonyl and methyl groups, show a smooth shift to higher field with an increase in n.[26] However, besides this important difference between the ^{13}C and ^{29}Si NMR spectra of these derivatives, the spectra do show a number of similarities. Thus, for the M(CO)$_4$(SiMe$_{3-n}$Cl$_n$)$_2$ molecules, the ^{29}Si NMR signal of the cis isomer came to higher field than that of the trans form, e.g., Figure 1, spectrum B. This was what was found for the ^{13}C NMR signals of the carbonyls for these isomers.[26] (Where the cis and trans isomers were in dynamic equilibrium, the cis:trans ratios obtained from the ^{29}Si NMR spectra were in excellent agreement with those previously determined by ^{13}C NMR spectroscopy.[32]) Furthermore, on going to the transition metal lower in the periodic table, for a given M(SiMe$_{3-n}$Cl$_n$) complex there was a shift of the corresponding ^{29}Si NMR resonance to higher field (Tables I, III, and IV and Figure 3). This shift, the cause of which is not understood, has also been observed in the ^{13}C NMR spectra of these[26] and other transition-metal derivatives.[29] A similar shift was found in the ^{119}Sn NMR spectra of some tin–transition-metal derivatives.[33] In this case, a partial rationalization of the shift was presented that was based on a contribution of the transition metal to the diamagnetic term of the tin shielding.[33] This contribution was proportional to Z/r where Z was the atomic number of the transition metal and r the distance of the metal to the tin nucleus.

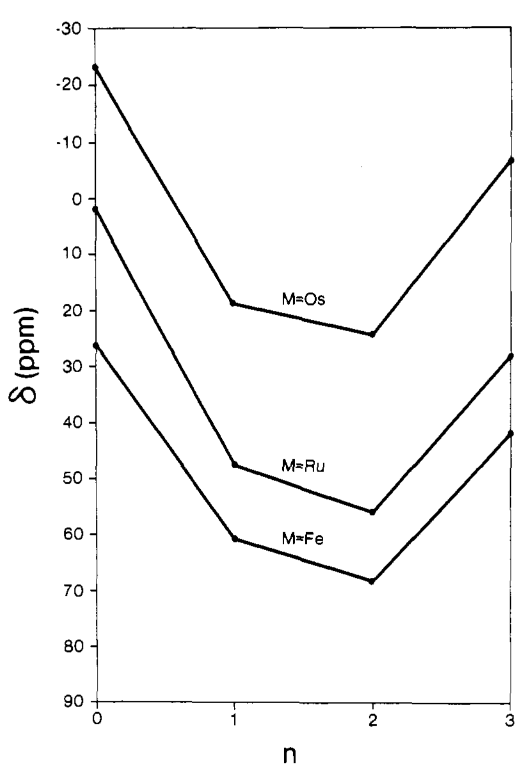

Figure 3. ^{29}Si chemicals shifts for *cis*-M(CO)$_4$(SiMe$_{3-n}$Cl$_n$)$_2$ compounds.

There was an increase in the ^2J(Si–H) value of a given SiMeCl$_2$ derivative when compared to that of its SiMe$_2$Cl analogue. This type of behavior has been seen before in ^{29}Si NMR spectroscopy[3] and, indeed, is a general observation in NMR studies. It is usually explained in terms of Bent's rule[34] that atomic s character concentrates in orbitals directed toward electropositive substituents. That the couplings in the L–SiMe$_n$Cl$_{3-n}$ (L = Fe, Ru, Os, n = 1, 2) derivatives were somewhat smaller than those in compounds where L is an organic group[3] may indicate considerable s character in the metal–silicon bond. Consistent with this view is that the MSiCl(C) bond angles in compounds of this type are invariably greater than the tetrahedral value.[22] (An alternative interpretation has, however, been proposed for the latter result.[22]) The ^2J(Si–H) couplings in the present derivatives were insensitive to the chemical shift of the silicon atom involved. A similar lack of correlation was found in a ^{119}Sn NMR study of tin–transition-metal derivatives, from which it was concluded that the chemical shift of the tin in these derivatives could not be dominated by the inductive effect of its substituents.[33]

In Figure 4 the plot of ν(CO) vs. δ(^{29}Si) is presented for four derivatives of the type (arene)Ru(CO)(SiCl$_3$)$_2$ (see also Table II). As can be seen, there is a linear correlation between the two parameters. (The (C$_6$H$_4$-t-Bu$_2$)Ru(CO)(SiCl$_3$)$_2$ compound is anomalous, but there are severe steric interactions in this molecule[35] that may be responsible for this anomaly.) It is interesting that the slope of the plot is opposite to what would be expected

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[29] Mann, B. E.; Taylor, B. F. "^{13}C NMR Data for Organometallic Compounds"; Academic Press: New York, 1981; p 6.

[30] Pregosin, P. S.; Kunz, R. W. *NMR: Basic Princ. Prog.* **1979**, *16*, 47.

[31] Harris, R. K. "Nuclear Magnetic Resonance Spectroscopy"; Pitman: London, 1983; p 192.

[32] The cis:trans ratios determined in this study: Fe(CO)$_4$(SiCl$_3$)$_2$, 76:24 (79:21); Os(CO)$_4$(SiMe$_2$Cl)$_2$, 41:59 (40:60); Os(CO)$_4$(SiMe$_3$)$_2$, 37:63 (37:63). The values in parentheses are the ratios determined by ^{13}C NMR spectroscopy.[26]

[33] Harris, D. H.; Lappert, M. F.; Poland, J. S.; McFarlane, W. *J. Chem. Soc., Dalton Trans.* **1975**, 311.

[34] Bent, H. A. *Chem. Rev.* **1961**, *61*, 275.

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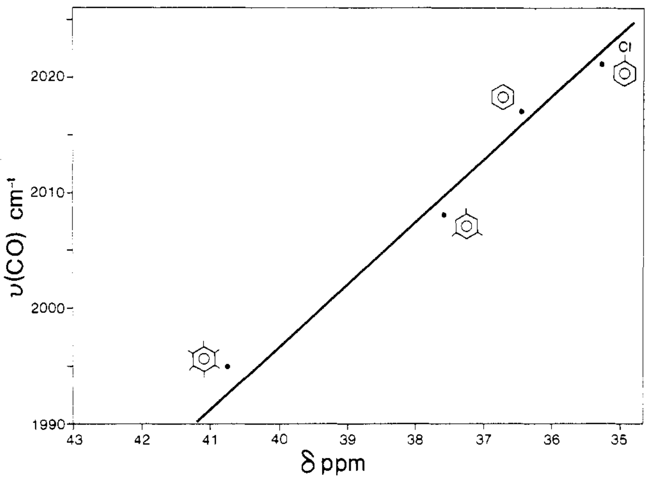

Figure 4. Plot of ^{29}Si chemical shifts vs. CO stretching frequencies for (arene)$Ru(CO)(SiCl_3)_2$ compounds.

from simple bonding arguments. Increasing the electron-releasing substituents on the aromatic ring should increase the electron density at the metal and hence at the silicon atoms. This should cause an upfield shift in the ^{29}Si resonance and not downfield as found. Once again, this observation has its parallel in ^{13}C NMR spectroscopy: there is a linear relationship between the CO stretching force constant and the ^{13}C chemical shift of carbonyls (in most cases), but the slope is opposite to what might initially be expected.[36] This deshielding of the carbonyl carbon atom with an increase in transition metal to carbonyl π back-donation has been attributed to a decrease in the magnitude of the separation between the electronic ground state and the lowest lying excited states.[36]

It is interesting that, for a given $SiMe_{3-n}Cl_n$ ligand, as the identity of the molecule changes the ^{29}Si chemical shift changes in the same manner as the ^{13}C chemical shift of the carbonyls. This may indicate that the bonding in the M–Si bond is similar to that in the M–C bond; i.e., there is significant π bonding in the M–Si bond. This need not involve the 3d orbitals on silicon but rather the σ^* orbitals, as recently pointed out for phosphines.[37]

In Table III the ^{29}Si chemical shifts for *trans*-$(Cl_nMe_{3-n}Si)[M(CO)_4]_m(SiMe_{3-n}Cl_n)$ (M = Ru, Os, m = 1–3, n = 2,3) are presented. For the ruthenium derivatives, *trans*-$Ru(CO)_4(SiMe_{3-n}Cl_n)_2$ and $[Ru(CO)_4(SiMe_{3-n}Cl_n)]_2$, the ^{29}Si chemical shift of the mononuclear compound came to higher field than that of the dinuclear molecule. For the corresponding osmium derivatives the situation was reversed: the resonance of $[Os(CO)_4(SiMe_{3-n}Cl_n)]_2$ was to higher field. The reason for this is not clear. It may be related to the metal–metal bond strength in the dimers. It would be expected that the osmium–osmium bond would be stronger than the ruthenium–ruthenium bond in the $[M(CO)_4(SiMe_{3-n}Cl_n)]_2$ molecules, and this would better transmit the mutual trans influence of the silicon ligands in the osmium case. Also of interest was that the ^{29}Si chemical shifts of $[Os(CO)_4(SiMe_{3-n}Cl_n)]_2$ and $(Cl_nMe_{3-n}Si)Os_3(CO)_{12}(SiMe_{3-n}Cl_n)$ (n = 2, 3) were virtually identical. Consistent with the observations discussed above, the ^{13}C chemical shifts of the carbonyls on terminal osmium atoms in $[Os(CO)_4(SiCl_3)]_2$ and $(Cl_3Si)Os_3(CO)_{12}(SiCl_3)$ had almost the same value.[22]

Collected in Table IV are the ^{29}Si NMR chemical shifts of some miscellaneous silyl-transition-metal derivatives studied here. Considerable difficulty was encountered in the acquisition of the ^{29}Si NMR spectra of the $M'(CO)_5(SiCl_3)$ (M′ = Mn, Re) compounds. Although clearly observable, broad signals of marginal quality were obtained even though more than 70000 scans were accumulated on concentrated solutions. This was undoubtedly due to quadrupolar broadening (^{55}Mn, $^{185,187}Re$: spin = $^5/_2$). (This situation could probably have been improved by recording the spectrum at low temperature,[38] but this was not attempted.) In contrast, a ^{29}Si NMR spectrum of $Co(CO)_4(SiCl_3)$ of acceptable quality was obtained after only 2073 transients even though the Co nucleus is quadrupolar (^{59}Co: spin = $^7/_2$). This suggests that in this molecule coupling of the silicon to the quadrupole cobalt nucleus was small. This may, in turn, be attributed to the small mount of s character in the axial Co–Si bond of this trigonal-bipyramidal molecule. The ^{13}C NMR signal of $Co(CO)_4(SiCl_3)$ exhibited severe quadrupolar broadening at room temperature,[39] which indicates there is a considerable electric field gradient within the molecule.

Conclusions

In this study we have demonstrated that ^{29}Si NMR spectra of silicon derivatives of iron, ruthenium, and osmium may be obtained directly without much difficulty. This was especially the case when the relaxation agent $Cr(acac)_3$ was added to the sample solution. The observed ^{29}Si NMR chemical shifts showed many similarities to the ^{13}C NMR chemical shifts of the carbonyl ligands in these compounds. An important difference, however, was the sagging pattern found for a given series of $M–SiMe_{3-n}Cl_n$ (n = 0–3) molecules: the ^{29}Si chemical shift to lowest field was usually given by the $SiMeCl_2$ derivative. For the ^{13}C NMR resonances of the carbonyls, the lowest field chemical shift occurred for the trimethylsilyl compound.[26] Silicon-29 NMR spectroscopy is potentially a valuable technique for the characterization of transition-metal–silyl derivatives, especially for metals which are nonquadrupolar. This will be illustrated in a second publication for some derivatives of $M(CO)_4(SiCl_3)_2$ (M = Fe, Ru, Os) with phosphorus-donor ligands.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for financial support in the form of an operating grant and an undergraduate research scholarship (to R.K.). We also thank Dr. A. S. Tracey for valuable discussions and M. Tracey for recording the spectra.

Registry No. *cis*-$Fe(CO)_4(SiMe_3)_2$, 53248-31-0; *cis*-$Fe(CO)_4(SiMe_2Cl)_2$, 58894-88-5; *cis*-$Fe(CO)_4(SiMeCl_2)_2$, 58894-89-6; *cis*-$Fe(CO)_4(SiCl_3)_2$, 29660-80-8; *trans*-$Fe(CO)_4(SiCl_3)_2$, 19632-60-1; *cis*-$Ru(CO)_4(SiMe_3)_2$, 53228-31-2; *cis*-$Ru(CO)_4(SiMe_2Cl)_2$, 58894-91-0; *cis*-$Ru(CO)_4(SiMeCl_2)_2$, 58894-92-1; *trans*-$Ru(CO)_4(SiMeCl_2)_2$, 58957-81-6; *cis*-$Ru(CO)_4(SiCl_3)_2$, 36570-60-2; *trans*-$Ru(CO)_4(SiCl_3)_2$, 36570-62-4; *cis*-$Os(CO)_4(SiMe_3)_2$, 29994-24-9; *trans*-$Os(CO)_4(SiMe_3)_2$, 25931-79-7; *cis*-$Os(CO)_4(SiMe_2Cl)_2$, 58957-83-8; *trans*-$Os(CO)_4(SiMe_2Cl)_2$, 58919-93-0; *cis*-$Os(CO)_4(SiMeCl_2)_2$, 58957-84-9; *trans*-$Os(CO)_4(SiMeCl_2)_2$, 58919-94-1; *cis*-$Os(CO)_4(SiCl_3)_2$, 36570-61-3; *trans*-$Os(CO)_4(SiCl_3)_2$, 58957-82-7; *cis*-$Fe(CO)_4(SiMe_3)(H)$, 97465-49-1; *cis*-$Fe(CO)_4(SiMe_2Cl)(H)$, 97374-33-9; *cis*-$Fe(CO)_4(SiMeCl_2)(H)$, 97374-34-0; *cis*-$Fe(CO)_4(SiCl_3)(H)$, 25928-24-9; *cis*-$Ru(CO)_4(SiCl_3)(H)$, 71852-84-1; *cis*-$Os(CO)_4(SiCl_3)(H)$, 81368-50-5; $(C_5H_5)Fe(CO)_2(SiMe_3)$, 31811-63-9; $(C_5H_5)Fe(CO)_2(SiMe_2Cl)$, 33029-76-4; $(C_5H_5)Fe(CO)_2(SiMeCl_2)$, 35744-00-4; $(C_5H_5)Fe(CO)_2(SiCl_3)$, 34742-07-9; $(C_6H_5Cl)Ru(CO)(SiCl_3)_2$, 75752-84-0; $(C_6H_6)Ru(CO)(SiCl_3)_2$, 58369-31-6; $(C_6H_3Me_3)Ru(CO)(SiCl_3)_2$, 71852-81-8; $(C_6Me_6)Ru(CO)(SiCl_3)_2$, 75752-83-9; $(C_6H_4\text{-}t\text{-}Bu_2)Ru(CO)(SiCl_3)_2$, 75752-86-2; *trans*-$Ru(CO)_4(SiMe_3)_2$, 97414-95-4; *trans*-$[Ru(CO)_4(SiMe_3)]_2$, 18745-56-7; *trans*-$Ru(CO)_4(SiMe_2Cl)_2$, 79389-92-7; *trans*-$[Ru(CO)_4(SiMe_2Cl)]_2$, 97374-35-1; *trans*-$[Ru(CO)_4(SiMeCl_2)]_2$, 26024-41-9; *trans*-$[Ru(CO)_4(SiCl_3)]_2$, 25929-57-1; *trans*-$[Os(CO)_4(SiMeCl_2)]_2$, 59423-91-5; *trans*-$Os(CO)_4[Os(CO)_4(SiMeCl_2)]_2$, 97374-36-2; *trans*-$[Os(CO)_4(SiCl_3)]_2$, 81368-54-9; *trans*-$Os(CO)_4[Os(CO)_4(SiCl_3)]_2$, 97374-37-3; *trans*-$Ru(CO)_4(SiCl_3)Br$, 30848-51-2; $Ru_3(\mu\text{-}H)_3(CO)_9(SiCl_3)_2$, 97374-38-4; $Os_3(\mu\text{-}H)_3(CO)_9(SiCl_3)_2$, 97374-39-5; $Mn(CO)_5(SiCl_3)$, 38194-30-8; $Co(CO)_4(SiCl_3)$, 14239-21-5; $Re(CO)_5(SiCl_3)$, 15306-34-0; $(C_6H_3Me_3)Re(CO)_2(SiCl_3)$, 97374-40-8; ^{29}Si, 14304-87-1.

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