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²⁹Si NMR SPECTRA OF METAL CARBONYL SILANES BY THE SELECTIVE POPULATION TRANSFER METHOD

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Summary

Utilization of the novel Selective Population Transfer (SPT) technique for the first NMR observation of ²⁹Si nuclei directly bound to transition metals is reported. Four metal carbonyl trimethylsilanes ((CH₃)₃SiMn(CO)₅, (CH₃)₃SiRe(CO)₅, (CH₃)₃SiCo(CO)₄, and (CH₃)₃SiFe(CO)₂(C₅H₅)) have been studied and their chemical shifts and coupling constants obtained. These data are compared with existing ²⁹Si NMR spectra of more conventional (CH₃)₃Si—X compounds and ¹¹⁹Sn NMR spectra of homologous (CH₃)₃Sn—metal complexes.

Introduction

The increasing availability of Fourier transform (FT) NMR and the rapidly growing interest in organo- and transition metal-silicon chemistry has resulted in a number of studies entailing the direct observation of naturally abundant (4.7%) ²⁹Si nuclei [1]. However, various nuclear properties of ²⁹Si have impeded the widespread use of ²⁹Si NMR. These include its low sensitivity, negative gyromagnetic ratio, and long relaxation times [2]. Additional difficulties include the high multiplicity of many uncoupled spectra (e.g., polyalkylsilanes), reactions with relaxation agents such as Cr(acac)₃ *, and quadrupole broadening by substituents such as chlorine.

Metal-catalyzed reactions of silicon compounds such as olefin hydrosilylation are presently under intense investigation [4]. In the course of studying silylmetalation reactions of organic compounds [4d], we encountered situations where ²⁹Si NMR would constitute a valuable means of characterizing transition metal

* For example, Cr(acac)₃ has been observed to cause the decomposition of several perhalosilanes [3].

trimethylsilanes. We report in this paper the utilization of the novel Selective Population Transfer (SPT) method for the first direct NMR observation of ^{29}Si nuclei bound to transition metals. Together with earlier experiments by Jakobsen and coworkers on $^{13}\text{C}\{^1\text{H}\}$, [5], $^{29}\text{Si}\{^1\text{H}\}$ [6] and $^{13}\text{C}\{^{14}\text{N}\}$ systems [7] and our own recent work [8] on $^{29}\text{Si}\{^{19}\text{F}\}$ systems, this study demonstrates the utility of the SPT technique for the simultaneous acquisition of marked sensitivity enhancements and coupling constant information. Furthermore, comparisons of the information provided herein with previously reported ^{29}Si and ^{119}Sn NMR data [9,10] may aid in the understanding of silicon—metal interactions.

The SPT experiment for metal-silanes entails the application of a weak irradiating field, H_2 , to a ^1H transition for a length of time τ . If this is done so as to satisfy the condition $\gamma_{\text{H}}(H_2)\tau = \eta$, where γ_{H} = gyromagnetic ratio of ^1H , then complete inversion of corresponding energy level populations occurs. There are two primary consequences of this experiment: (a) population inversion may occur between levels separated by several units of the magnetic quantum number, and (b) the line intensities in the ^{29}Si spectra will be affected by a factor which is the absolute value of the ratio of gyromagnetic ratios, $|\gamma_{\text{H}}/\gamma_{\text{Si}}| = 5$, thus circumventing negative NOE factors.

Results and discussion

Figure 1 depicts the $^{29}\text{Si}\{^1\text{H}\}$ spectrum of $(\text{CH}_3)_3\text{SiMn}(\text{CO})_5$ [11] after 1760 transients (ca. 6 h) obtained using a gated decoupling sequence to eliminate NOE effects. Figure 2 shows the undecoupled spectrum of the same region after 300 transients. The spectrum obtained after 300 transients and SPT irradiation of the high frequency ^1H transition is illustrated in Fig. 3. This series of experiments clearly demonstrates the dramatic sensitivity enhancement possible

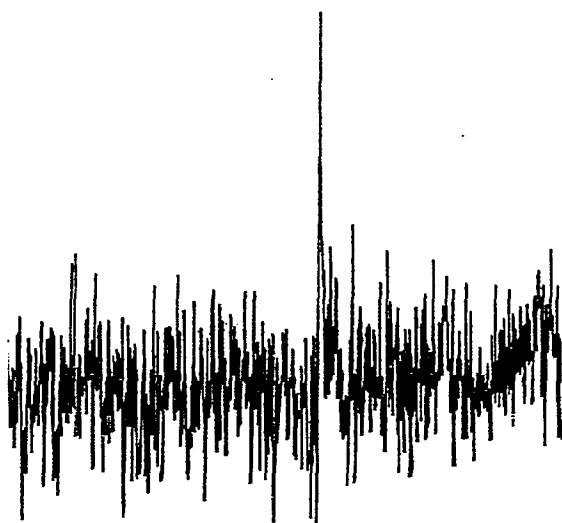


Fig. 1. $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of $(\text{CH}_3)_3\text{SiMn}(\text{CO})_5$ after 1760 transients.



Fig. 2. ^{29}Si NMR spectrum of $(\text{CH}_3)_3\text{SiMn}(\text{CO})_5$ after 300 transients.

via SPT techniques. The ^{29}Si NMR spectra of $(\text{CH}_3)_3\text{SiRe}(\text{CO})_5$ [12], $(\text{CH}_3)_3\text{SiFe}(\text{CO})_2(\text{C}_5\text{H}_5)$ [13], and $(\text{CH}_3)_3\text{SiCo}(\text{CO})_4$ [14] were obtained by similar procedures. Chemical shifts and coupling constants are summarized in Table 1. The corresponding ^{119}Sn NMR data for the homologous metal stannanes [10] are included for comparison.

In a separate experiment, the NOE factor, η , for $(\text{CH}_3)_3\text{SiMn}(\text{CO})_5$ was determined to be -0.05 . This small value suggests that the difficulties in the acquisition of decoupled spectra lie in long T_1 values and perhaps quadrupole effects from the metal.

The calculated relative line intensities for a trimethylsilyl group in a $^{29}\text{Si}\{^1\text{H}\}$ SPT experiment assuming complete inversion of populations are $-44: -306: -864: -1176: -504: 756: 1340: 934: 324: 46$. Although excellent quality spectra were obtained for each metal trimethylsilane after 400 transients, maximum enhancement was not achieved, presumably due to incomplete relaxation between pulse sequences ($\tau \ll T_1$ and 10 sec repetition rate).

The values of $^2J(\text{Si}-\text{H})$ are not unlike those of previously reported $(\text{CH}_3)_3\text{Si}-\text{X}$ derivatives [9]. The phases of the SPT spectra are consistent with $^2J(\text{Si}-\text{H}) > 0$ and the magnitude of the coupling constants fall into the narrow range of 6 to 8 Hz.

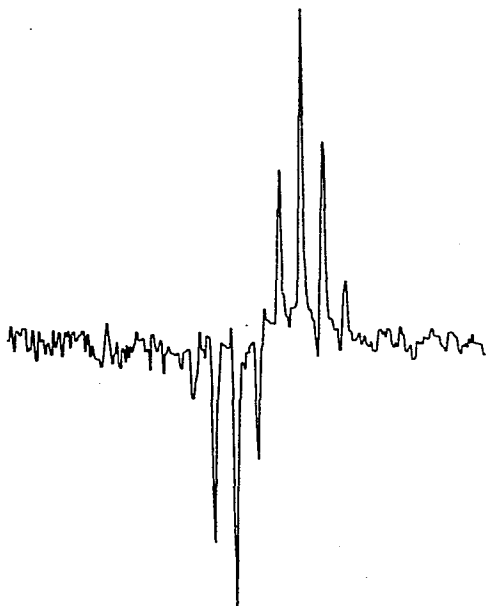


Fig. 3. ^{29}Si NMR spectrum of $(\text{CH}_3)_3\text{SiMn}(\text{CO})_5$ obtained by applying SPT pulse to high frequency ^1H transition for 300 transients.

TABLE 1
SUMMARY OF ^{29}Si AND ^{119}Sn NMR DATA

Compound	$\delta(^{29}\text{Si})$ ^{a,c}	$^2J(\text{Si-H})(\text{Hz})$	$\delta(^{119}\text{Sn})$ ^{b,c,d}	$^2J(\text{Sn-H})(\text{Hz})$ ^d
$(\text{CH}_3)_3\text{M-Re}(\text{CO})_5$	-20.94	6.12	-89	47.0
$(\text{CH}_3)_3\text{M-Mn}(\text{CO})_5$	10.98	6.41	63	48.5
$(\text{CH}_3)_3\text{M-Fe}(\text{CO})_2(\text{C}_5\text{H}_5)$	34.45	6.48	147	49.0
$(\text{CH}_3)_3\text{M-Co}(\text{CO})_4$	37.45	6.73	151	52.8

^a ppm from external $[(\text{CH}_3)_3\text{Si}]_2\text{O}$. ^b ppm from external $(\text{CH}_3)_4\text{Sn}$. ^c Positive δ indicates shifts to higher frequency. ^d Ref. 10.

The iron and cobalt complexes exhibit two of the highest frequency ^{29}Si resonances observed to date. Only the silicons in $[(\text{CH}_3)_3\text{Si}]_2\text{Hg}$ are known to be more deshielded ($\delta(^{29}\text{Si})$ 56.8 ppm vs. $[(\text{CH}_3)_3\text{Si}]_2\text{O}$) [15]. Other ^{29}Si chemical shifts include 23.44 for $(\text{CH}_3)_3\text{SiCl}$, 7.71 for $(\text{CH}_3)_3\text{SiOC}_2\text{H}_5$, and -4.61 for $[(\text{CH}_3)_3\text{Si}]_2\text{NH}$ [9]. Thus the downfield shifts of $(\text{CH}_3)_3\text{SiFe}(\text{CO})_2(\text{C}_5\text{H}_5)$ and $(\text{CH}_3)_3\text{SiCo}(\text{CO})_4$ and the upfield shift of $(\text{CH}_3)_3\text{SiRe}(\text{CO})_5$ clearly indicate that more is involved in the determination of $\delta(^{29}\text{Si})$ values than simple electronegativity and bond length considerations. Although some success has been reported in the use of the paramagnetic term alone as the major contribution to the ^{29}Si chemical shift of some organosilanes [16], the treatment is not general and does not allow for π -bonding effects. Uncertainty over the relative importance of the diamagnetic term and silicon d orbital involvement further complicates the situation.

Lappert and McFarlane [10] have suggested that ^{119}Sn chemical shifts of transition metal stannanes are influenced primarily by the effects of $(d \rightarrow d)\pi$ interactions, and these effects in turn are dominated by the presence of third row atoms (e.g., rhenium) which cause upfield shifts. As is evident from the data in Table 1, similar trends in chemical shift are exhibited by the silicon and tin complexes.

Metal-silicon bonding has been the focus of many previous discussions. Particularly, the existence and/or extent of silicon d orbital involvement has been a point of controversy both in the theoretical literature * and in the interpretation of experimental observables such as IR [18], NQR [19], and mass spectra [20]. Typical examples of where d orbital effects may be operating are provided by the solid state structures of $(\text{CH}_3)_3\text{SiMn}(\text{CO})_5$ [11c] and $(\text{CH}_3)_3\text{-SiRe}(\text{CO})_5$ [12b], which show significant displacements of the *cis*-carbonyls toward the bulky $(\text{CH}_3)_3\text{Si}$ groups. While it would be attractive to utilize the chemical shift data in Table 1 as a measure of $(d \rightarrow d)\pi$ interaction, such an analysis must await the study of a wider range of compounds and refinements in the theoretical treatment of ^{29}Si chemical shifts.

In conclusion, this study has established the SPT method as a valuable and practical technique for acquiring ^{29}Si NMR spectra of transition metal silanes which would be difficult to obtain (if at all) via conventional methodology. In light of the current interest in hydrosilylation and other reactions involving metal silanes, we anticipate that ^{29}Si SPT NMR will see increased use for the

* For MO calculations and a discussion of experimental data, see ref. 17.

characterization of silicon-containing complexes and intermediates among inorganic and organometallic chemists.

Experimental

All metal carbonyl silanes were prepared according to the procedures cited or by slight modifications thereof [21].

All spectra were obtained using a Varian XL-100-15 spectrometer in the Fourier transform mode. Samples were run in 12 mm tubes with C_6D_6 serving as solvent and lock. Although H_2 was not measured directly, it was set (with constant τ) to provide maximum signal enhancement. The attainment of the precise 1H transition frequency and the correct relative values of τ and H_2 are critical to the success of the SPT experiment. Typical parameters employed were: τ 0.09 sec, pulse width 25 μ sec, AT 8 sec, and H_2 65 db (XL-100 setting).

Acknowledgements

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