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Preliminary communication

ORGANOMETALLOIDAL DERIVATIVES OF THE TRANSITION METALS

VI *. THE POTENTIAL OF ^{29}Si NMR SPECTROSCOPY IN ANALYSIS OF π-ORGANOSILYL COMPLEXES OF THE TRANSITION METALS [1]

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Summary

The ^{29}Si FT NMR characteristics of a number of π organosilyl-transition metal complexes have been determined and their usefulness for characterizing the complexes investigated.

The ability of silicon to stabilize various σ and π complexes of the transition metals is documented [2,3]. The large variety of silylmethyl σ complexes often result in metal—carbon bonds considerably more "stable" than the non silylated analogs, and the direct metal—silicon σ bond often exhibits chemical properties illustrative of a less reactive linkage when compared to the metal—carbon bond. In the area of π complexes, the isolation and characterization of such complexes as $Fe(CO)_4(Me_3SiC{\equiv}CSiMe_3)$ [4] and $Fe(CO)_3(Me_2Si(CH{=}CH_2)_2)$ [5], and the enhanced oxidative and thermal stability of silylallyl complexes [6] illustrate the same idea.

There have recently appeared a few reports on the utilization of ^{29}Si FT NMR for characterizing metal complexes containing σ organosilyl ligands [7,8,9,10], and we have also made a study in this area [11]. However, at the

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* For part V see ref. 1.

TABLE 1

^{29}Si NMR PARAMETERS OF π ORGANOSILYL METAL COMPLEXES [a,b]

	Complex	δ (ppm)		Δδ	J(MSi) (Hz)	—η	
		Complex	(ligand)			Complex	(ligand)
I	AcacRh(CH_2=$CHSiMe_3$)$_2$	—0,62	(—7.6)	6,98	2,3	2,0	(0,2)
II	AcacRh(CH_2=$CHSiMe_2OEt$)$_2$	11,1	(4,12)	6,98	2,4	2,4	(0,3)
III	AcacRh(CH_2=$CHSi(OEt)_3$)$_2$	—53,2	(—59.0)	5,84	2.0	—	—
IV	AcacRh(CH_2=CH—CH_2SiMe_3)$_2$ [c]	—1,39	(0,39)	—1,78	1.9	—	—
V	(η^5-C_5H_5)Rh(CH_2=$CHSiMe_3$)	—0,18	(—7.6)	7,42	2.2	2,2	(0,2)
VI	$(CO)_4Fe(Me_3SiC{\equiv}CSiMe_3)$	—8,54	(—19,25)	10,71	—	—	—
VII	$(CO_6)_2Co_2(Me_3SiC{\equiv}CSiMe_3)$	1,06	(19,25)	20,31	—	—	—
VIII	$(CO)_6Co_2(Me_3SiC_4SiMe_3)$	Si$_\alpha$ 2.45	(—15,99)	18,34	—	1,5	(0,5)
		Si$_\beta$ —16.91	(—15,99)	—0,72	—	1,0	(0,5)
IX	$(CO)_{12}Co_4(Me_3SiC_4SiMe_3)$	1,06	(—15,99)	18,05	—	2,4	(0,5)
X	$(CO)_6Co_2(Me_2ClSiC_2SiMe_2Cl)$	19.17	(—0,61)	19,77	—	—	—

[a] All spectra were measured in a Bruker WP60 FT spectrometer using 5—20% C_6D_6 solutions, with internal standards of TMS or hexamethyldisiloxane. All δ values are referenced to TMS. [b] Complexes prepared using published procedures [4,13]. [c] A second spectrum of this complex was run on a JEOL FX90Q at Bedford College, University of London.

present time there are no data in the literature concerning the ^{29}Si NMR characteristics of π organosilyl complexes. It is the purpose of this communication to report for the first time such data.

We have initially chosen a representative sample of complexes involving different metals (Fe, Rh, Co) with different ligands (vinyl, allyl, acetylenic and diacetylenic silanes), the data being presented in Table 1 along with the data from the appropriate ligand.

Several points of information may be extracted from the data:

1. In each case where the Si atom is bonded directly to a coordinating C atom of the π ligand (Si$_\alpha$), the ^{29}Si resonance exhibits a marked low field shift of 6—11 ppm. This shift appears to be additive such that in the examples where two metals are coordinated to the ligand C atom, e.g. complex VI vs. VII, the shift approximately doubles, from 10.7 to 20.3 ppm.
2. When the Si atom is insulated from the coordinating atom by C atoms (Si$_\beta$), a small high field shift is observed, 0.5—2.0 ppm.
3. Where the metal nucleus has a magnetic spin, M—Si coupling is observed for both Si$_\alpha$ and Si$_\beta$. The one single observation of coupling to Si$_\beta$ is unexpected, especially since the magnitude of the coupling is virtually the same as $J(\mathrm{MSi}_\alpha)$. We have obtained the ^{29}Si NMR spectrum of this complex (IV) on two distinct instruments of 11.9 and 17.9 MHz, to confirm this coupling.
4. Nuclear Overhauser effects (NOE) have been studied on the $-\eta$ values reported in Table 1 are derived from the relationship, $T_1^{\mathrm{DD}} = 2.52\ T_1^{\mathrm{obs}}/\eta$ [12]. Thus a value $-\eta = 2.52$ signifies relaxation of the Si nucleus by a dipole—dipole relaxation while smaller values indicate progressive contributions by spin rotation relaxation. The $-\eta$ values for the silicon nucleus are uniformly increased when the organosilicon ligand becomes coordinated to the transition metal. This suggests a decreased tumbling motion of the now larger assembly of atoms [12]. This decrease in mobility is attenuated as the Si atom is further removed from the site of complexation, as illustrated in complexes VII and IX. This aspect of the ^{29}Si NMR data of silyl metal complexes is dealt with in some detail elsewhere [11].

Overall, the use of ^{29}Si NMR to characterize π organosilyl complexes has been illustrated. The progressive deshielding of α Si atoms upon metal complexation could be explained in terms of simple electron density removal by the metal. However, as no comprehensive interpretation of ^{29}Si chemical shift data for simple organosilicon compounds is available, and since they often exhibit a well known "sagging pattern" of shifts with substituent electronegativity [14] attempts at such analysis must await the collection of further data *.

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* A very recent article [15] records some similar data for (vinyl silane) Fe(CO)$_4$ in keeping with the present chemical shift information.

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