Carbon-13 Chemical Shifts and ^{77}Se-^{13}C Spin-Spin Coupling Constants in Symmetrical Dialkyl Diselenides, Unsymmetrical Alkyl Methyl and Alkyl Phenyl Diselenides, and Related Alkyl Selenols

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Carbon-13 NMR data have been determined for a series of alkyl selenols, symmetrical and unsymmetrical dialkyl diselenides, and alkyl phenyl diselenides. Single-frequency, low-power, off-resonance proton-decoupled ^{13}C-refocused INEPT spectra and ^{13}C-^{1}H chemical shift correlated 2D NMR experiments were useful in assignment of some ^{13}C chemical shifts. In addition, ^{13}C NMR substituent chemical shift additivity parameters for selenium-containing substituents have been determined and are consistent with values found for similar substituent groups. One-bond ^{77}Se-^{13}C spin-spin coupling constants for alkyl selenols are in the range of 45-48 Hz while the same value for diselenides is 68-74 Hz. Two-bond coupling constants of the type ^{77}Se-Se-^{13}C and ^{77}Se-C-^{13}C have also been determined and are reported. In two cases three-bond coupling constants of the type ^{77}Se-C-C-^{13}C were determined. In contrast to the other coupling constants the two-bond ^{77}Se-C-^{13}C coupling constants were found to increase in a consistent, monotonic fashion with successive α-methyl substitution.

Introduction

The diverse chemistry of the chalcogens, group 16 of the periodic table, has been well established.[2] However, multinuclear magnetic resonance spectroscopy has not developed rapidly as a tool to study this group. Oxygen-17 and sulfur-33 are both quadrupolar nuclei and possess low natural abundances and low relative receptivities.[3] Recently, selenium and tellurium, both of which possess spin $^{1}/_{2}$ isotopes (^{77}Se, ^{123}Te, ^{125}Te) in reasonable natural abundance and display a rich organic chemistry, have begun to receive more attention from chemists.[4] Carbon-13 NMR spectroscopy, a technique which has become almost indispensable to the organic chemist, has also been relatively slow to be applied to the various classes of organic compounds containing chalcogen group elements, most notably selenium and tellurium. A few studies have appeared surveying the sign[5] and magnitude[6-9] of $^{n}J_{SeC}$ in selenium compounds with varying numbers of unshared electron pairs on selenium[5] or containing selenium-bound carbon centers in different degrees of hybridization.[6] A study[10] has also appeared on the stereochemical dependence of geminal selenium-carbon coupling constants while different selenium-carbon coupling constants ($^{3}J_{SeC}$) are

found in selenoimidates depending upon the configuration (*E* or *Z*).[11]

Carbon-13 chemical shifts have likewise been largely neglected with most studies focusing on aromatic selenides[12-18] or diselenides[13] with saturated organoselenium compounds[7,9,11,19] having received the least attention. This is most evident in that none of the more recent texts[20] on ^{13}C NMR spectroscopy list any ^{13}C substituent parameters for Se (or Te) compounds. In view of the recent interest in organoselenium chemistry[21-23] and the biochemistry[22-24] of selenium-containing compounds, a study of some of the ^{13}C NMR parameters of alkyl selenols, dialkyl diselenides, and unsymmetrical alkyl methyl and alkyl phenyl diselenides was conducted for the alkyl groups methyl, ethyl, isopropyl, *tert*-butyl, and *n*-butyl and is reported herein.

Experimental Section

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Table I. Aliphatic ^{13}C Chemical Shifts of Alkyl Selenols, Dialkyl Diselenides, and Alkyl Phenyl Diselenides

no.	compd	$\delta(^{13}C)^a$				
		C_1	C_2	C_3	C_4	C_{Me}
1	CH_3SeH	-4.8				
2	C_2H_5SeH	10.9	19.5			
3	i-C_3H_7SeH	25.5	28.0			
4	t-C_4H_9SeH	39.3	36.0			
5	n-C_4H_9SeH	17.1	35.8^b	22.4^b	13.1	
6	$(CH_3)_2Se_2$	10.1^c				
7	$(C_2H_5)_2Se_2$	22.8^d	16.2^e			
8	$(i$-$C_3H_7)_2Se_2$	33.3	24.5			
9	$(t$-$C_4H_9)_2Se_2$	40.8^f	32.2^g			
10	$(n$-$C_4H_9)_2Se_2$	29.6	32.9^h	22.4^h	13.3	
11	$C_2H_5Se_2CH_3$	22.5	16.3			11.0
12	i-$C_3H_7Se_2CH_3$	33.3	24.4			11.5
13	t-$C_4H_9Se_2CH_3$	42.1	31.5			11.8
14	n-$C_4H_9Se_2CH_3$	29.4	32.9^i	22.4^i	13.3	10.8
15	$CH_3Se_2C_6H_5$	11.3				
16	$C_2H_5Se_2C_6H_5$	23.6	16.1			
17	i-$C_3H_7Se_2C_6H_5$	34.5	24.3			
18	t-$C_4H_9Se_2C_6H_5$	43.7	31.5			
19	n-$C_4H_9Se_2C_6H_5$	30.4	32.5^i	22.3^i	13.3	

^{a} In ppm. Obtained on ca. 10–20% solutions of pure compounds in $CDCl_3$ at 20.11 MHz. Measured from the central resonance of the $CDCl_3$ solvent triplet at 76.9 ppm from TMS (δ 0.0). A positive chemical shift denotes a shift to higher frequency (lower shielding). ^{b} Unambiguous ^{13}C assignments based on 400.13-MHz $^1H\{^1H\}$ spectra and a 20.11-MHz ^{13}C-^1H shift correlated 2D NMR experiment. $^c J_{CH} = 142.64 \pm 0.06$ Hz, $^4J_{CH} = 0.22 \pm 0.06$ Hz. $^d J_{C_1H} = 142.18 \pm 0.07$ Hz, $^2J_{C_1H} = 4.99 \pm 0.07$ Hz, measured from first-order ^{13}C spectrum at 100.62 Hz. $^e J_{C_2H} = 127.42 \pm 0.07$ Hz, $^2J_{C_2H} = 2.97 \pm 0.07$ Hz, measured from first-order ^{13}C spectrum at 100.62 Hz. $^f J_{C_1C_2} = 36.93 \pm 0.13$ Hz. $^g J_{C_2C_1} = 36.95 \pm 0.13$ Hz. ^{h} Unambiguous ^{13}C assignments based on 400.13 MHz ^{1}H assignments and a 20.11-MHz ^{13}C-^1H shift correlated 2D NMR experiment. ^{i} Assignments based on the similarity of the chemical shifts found for the n-Bu_2Se_2 and n-$BuSeH$ C-2 and C-3 resonances.

shift correlated two-dimensional NMR experiments were acquired as 128 × 2K spectra (32 scans each) with "negative" (N) type peak selection. The pulse sequence was a standard sequence[25] with $^1J_{CH} = 130$ Hz, $\tau_2 = 1.9$ ms, and t_2 acquisition time = 1.28 s.

Materials. All selenols,[26,27] symmetrical diselenides,[27b,c,28,29] and unsymmetrical diselenides[30] used in this study were prepared by known methods or were obtained commercially (dimethyl diselenide: Strem Chemicals, Inc.). In the preparation of unsymmetrical diselenides, volatile selenols were removed from the reaction mixtures before NMR samples were prepared. The thermally labile,[30] unsymmetrical diselenide NMR samples were in all cases determined to be mixtures of the two symmetrical diselenides and the unsymmetrical diselenide. All sample tubes were freeze–pump–thaw degassed and sealed under dynamic vacuum. Other spectral conditions are given in Tables I–V.

Results and Discussion

The aliphatic ^{13}C chemical shift data for alkyl selenols, dialkyl diselenides, and alkyl phenyl diselenides are presented in Table I. Aromatic ^{13}C chemical shift data for alkyl phenyl diselenides and diphenyl diselenide are reported in Table II. Since the unsymmetrical, aliphatic diselenides contained substantial concentrations of both

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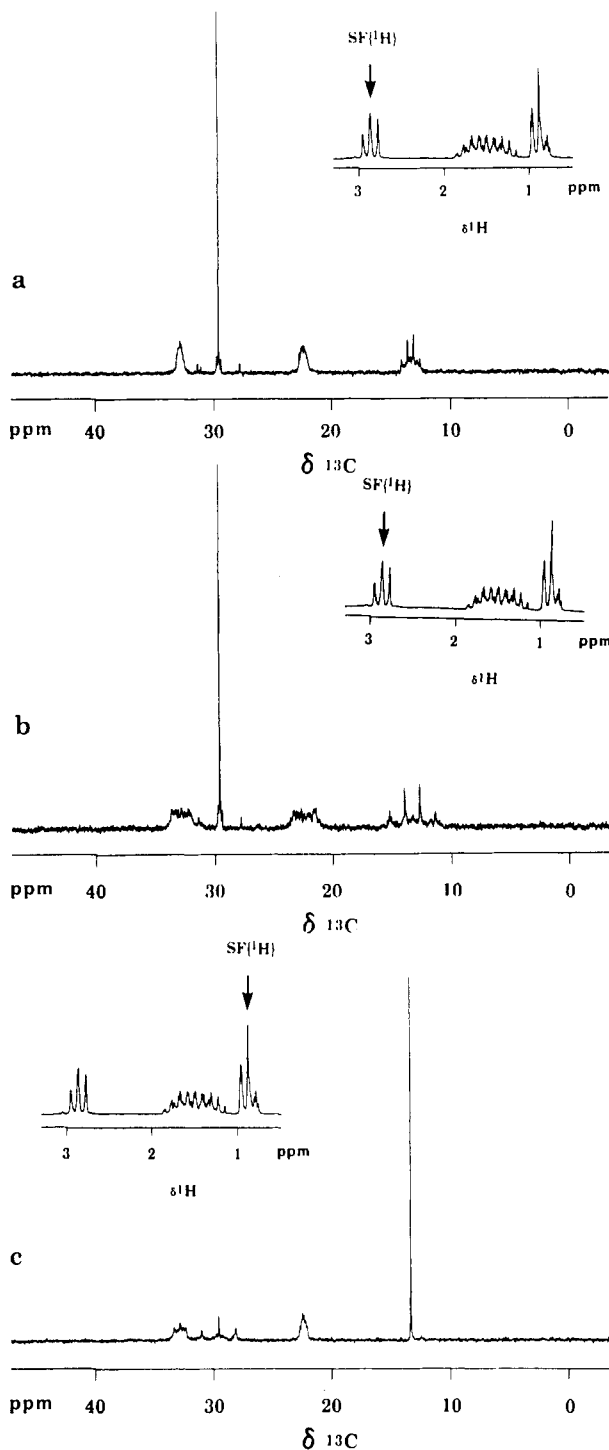
Figure 1. Single-frequency, low-power, proton-decoupled ^{13}C-refocused INEPT spectra of di-n-butyl diselenide, 30% in $CDCl_3$ at ambient temperature (the approximate location of the proton decoupler frequency is shown by an arrow in the inset of the proton spectrum): (a) proton decoupler on-resonance for C-1 protons with decoupler power at 20 H (ca. 0.4 W) in CW mode, 210 scans; (b) Same as (a) except decoupler power at 30 H (ca. 0.04 W), 312 scans; (c) proton decoupler on-resonance for C-4 protons with decoupler power at 30 H, 142 scans. Each plot is ca. 1020-Hz expansion of the 2100-Hz spectrum, acquired with a 3.9-s acquisition time, 15-s proton relaxation delay, 16K/32K data points, and 0.256-Hz line broadening. $\tau/2 = 1.947$ ms for $J_{CH} = 128.4$ Hz, $\Delta_{opt}/2 = 0.974$ ms for two protons with $J_{CH} = 128.4$ Hz, $\pi/2$ (^{13}C) = 5.5 μs, π(^{13}C) = 11.0 μs, $\pi/2$(^{1}H) = 21.1 μs, π(^{1}H) = 42.2 μs.

of the related symmetrical diselenides, chemical shift assignments were made only after assignments were made on the pure, isolated symmetrical diselenides and selenols.

Table II. Aromatic [13]C Chemical Shift Data[a] for Alkyl Phenyl Diselenides and Diphenyl Diselenide and [13]C Substituent Increments Z[b] of Selenium-Containing Substituents -X in Monosubstituted Benzene Derivatives

no.	compd	$\delta(^{13}C)$				-X	Z_{ipso}	Z_{ortho}	Z_{meta}	Z_{para}
		C_{ipso}	C_{ortho}	C_{meta}	C_{para}					
15	$CH_3Se_2C_6H_5$	130.1	131.1[c]	128.8	127.0	$-Se_2CH_3$	1.6	2.6	0.3	-1.5
16	$C_2H_5Se_2C_6H_5$	130.6	130.9	128.8	126.9	$-Se_2CH_2CH_3$	2.1	2.4	0.3	-1.6
17	$i\text{-}C_3H_7Se_2C_6H_5$	130.7	130.4	128.6	126.6	$-Se_2CH(CH_3)_2$	2.2	1.9	0.1	-1.9
18	$t\text{-}C_4H_9Se_2C_6H_5$	130.7	130.0[d]	128.5	126.4	$-Se_2C(CH_3)_3$	2.2	1.5	0.0	-2.1
19	$n\text{-}C_4H_9Se_2C_6H_5$	130.5	130.9	128.8	126.9	$-Se_2\text{-}(CH_2)_3CH_3$	2.0	2.4	0.3	-1.6
20	$(C_6H_5Se)_2$[e]	130.8	131.4	129.0	127.5	$-Se_2C_6H_5$	2.3	2.9	0.5	-1.0

[a] In ppm. Obtained on ca. 10–20% solutions of compounds in $CDCl_3$ at 20.11 MHz. Measured from the central resonance of the $CDCl_3$ solvent triplet at 76.9 ppm from TMS (δ 0.0). A positive chemical shift denotes a shift to higher frequency (lower shielding). [b] In ppm.

Determined as the difference between the aromatic ^{13}C chemical shifts in the C_6H_5-X compounds and benzene ($\delta_{C_6H_6}$ 128.5). [c] $^2J_{SeC_{ortho}}$ = 11.59 ± 0.17 Hz. [d] $^2J_{SeC_{ortho}}$ = 12.04 ± 0.17 Hz. [e] 20% in $CDCl_3$; lit. values. [f] (In CCl_4): C_{ipso} 130.9; C_{ortho}, 131.4; C_{meta}, 129.0; C_{para}, 127.5 ppm. [f] Kohne, B.; Praefcke, K.; Zeisberg, R. *J. Organomet. Chem.* **1979**, *175*, 49.

Table III. Aliphatic Carbon-13 Chemical Shift Substituent Increments of Selenium-Containing Substituents -X Replacing -H in n-Alkanes[a]

-X	$Z_{\alpha,n}$	$Z_{\beta,n}$	Z_γ	Z_δ
-SeH	4.0	10.9	-2.5	0.0
$-Se_2CH_3$	16.3	8.0	-2.5	0.2
$-Se_2(CH_2)_3CH_3$	16.5	8.0	-2.5	0.2
$-Se_2C_6H_5$	17.3	7.6	-2.6	0.2

[a] In ppm. Determined as the difference between the butyl ^{13}C chemical shifts in the n-butyl X compounds and n-butane.

Table IV. [77]Se–[13]C Spin–Spin Coupling Constant Data for Alkyl Selenols and Dialkyl Diselenides

no.	compd	$^nJ_{^{77}Se-^{13}C}$[a]		
		$^1J_{SeC}$	$^2J_{SeSeC}$	$^2J_{SeCC}$
1	CH_3SeH	48.26 ± 0.26	b	b
2	CH_3CH_2SeH	45.97 ± 0.26	b	4.06 ± 0.26
3	$(CH_3)_2CHSeH$	45.24 ± 0.26	b	7.90 ± 0.26
4	$(CH_3)_3CSeH$	46.71 ± 0.13	b	10.65 ± 0.13
5	$CH_3(CH_2)_3SeH$	47.22 ± 0.26	b	5.06 ± 0.26[c]
6	$(CH_3Se)_2$	73.87 ± 0.26	7.47 ± 0.26	b
7	$(CH_3CH_2Se)_2$	69.93 ± 0.26	7.46 ± 0.26	5.91 ± 0.26
8	$((CH_3)_2CHSe)_2$	67.97 ± 0.26	5.93 ± 0.26	11.38 ± 0.26
9	$((CH_3)_3CSe)_2$	70.52 ± 0.13	5.75 ± 0.13	14.45 ± 0.13
10	$(CH_3(CH_2)_3Se)_2$	71.36 ± 0.26	6.72 ± 0.26	5.06 ± 0.26[d]

[a] In Hz. Obtained on ca. 20–70% solutions in $CDCl_3$ at 20.11 MHz measured at ambient probe temperature, ca. 35 °C. [b] Not applicable. [c] $^3J_{SeCCC}$ = 3.50 ± 0.26 Hz. [d] $^3J_{SeCCC}$ = 3.50 ± 0.26 Hz.

Assignments of the individual ^{13}C resonances in alkyl groups were, in most cases, straightforward and were based primarily on peak intensities in proton-decoupled spectra and on proton-coupled spectra.

The only real difficulty encountered was the assignment of the C-2 and C-3 resonances of the n-butyl groups. This was accomplished by single-frequency (SF), low-power,

off-resonance proton-decoupled ^{13}C-refocused INEPT spectra and [13]C–[1]H chemical shift correlated 2D NMR experiments (Figures 1 and 2). For example, in di-n-butyl diselenide the 400.13-MHz ^{1}H spectrum is first-order and readily analyzed with the C-2 ^{1}H resonance appearing as a quintet with essentially equal coupling to the hydrogens on C_1 and C_3 (7.48 ± 0.28 Hz) and the C-3 ^{1}H resonance appearing as a sextet with approximately equal [1]H–[1]H spin couping (7.48 ± 0.28 Hz). The proton assignments allowed tentative assignments of the ^{13}C resonances based on the INEPT spectra and definitive assignments could be made from the 2D NMR experiments. Similar experiments were performed on 1-butane selenol.

The only compound to exhibit chemical exchange in any of the room-temperature NMR spectra (^{13}C ahd [77]Se) was phenyl isopropyl diselenide when the reaction mixture was *not* treated to an aqueous workup.[30] At -10 °C, the exchange has slowed sufficiently to allow all ^{13}C resonances of the unsymmetrical diselenide and both symmetical diselenides to be sharp and distinct. Raising the temperature to ca. +55 °C increases the rate significantly and causes several of the aromatic ^{13}C resonances and the isopropyl C_β resonances to coalesce to "singlets" with the remainder of the resonances being broad "doublets". A subsequent aqueous workup destroys the chemical exchange as evidenced by a straightforward ambient-temperature ^{13}C NMR spectrum. The reaction between phenyl selenenyl chloride and 2-propaneselenol was used to prepare phenyl isopropyl diselenide,[30] and the effect of an aqueous workup upon the chemical dynamics suggests that the loss of a water-soluble compound, presumably HCl, is successful in stopping a catalytic, reversible reaction causing interconversion between the unsymmetrical diselenide and the symmetrical diselenides. Further work is needed to elucidate the possible reaction pathway(s) in the chemical exchange.

Table V. [77]Se–[13]C Spin–Spin Coupling Constant Data for Alkyl Methyl Diselenides and Alkyl Phenyl Diselenides[a]

no.	compd	$^nJ_{^{77}Se-^{13}C}$				
		$^1J_{SeC_{Me}}$	$^2J_{SeSeC_{Me}}$	$^1J_{SeC_R}$	$^2J_{SeSeC_R}$	$^2J_{SeCC_R}$
11	$CH_3CH_2Se_2CH_3$	73.85 ± 0.13	7.61 ± 0.13	69.88 ± 0.13	b	5.30 ± 0.13
12	$(CH_3)_2CHSe_2CH_3$	73.82 ± 0.13	7.80 ± 0.13	67.84 ± 0.13	6.91 ± 0.13	10.21 ± 0.13
13	$(CH_3)_3CSe_2CH_3$	74.54 ± 0.13	7.79 ± 0.13	68.86 ± 0.13	6.53 ± 0.13	13.92 ± 0.13
14	$CH_3(CH_2)_3Se_2CH_3$	73.92 ± 0.26	7.61 ± 0.26	71.20 ± 0.26	b	b
15	$CH_3Se_2C_6H_5$	c	c	73.74 ± 0.26	7.23 ± 0.26	c
16	$CH_3CH_2Se_2C_6H_5$	c	c	b	7.03 ± 0.26	b
17	$(CH_3)_2CHSe_2C_6H_5$	c	c	67.70 ± 0.13	6.49 ± 0.13	10.47 ± 0.13
18	$(CH_3)_3CSe_2C_6H_5$	c	c	68.61 ± 0.13	6.14 ± 0.13	13.87 ± 0.13
19	$CH_3(CH_2)_3Se_2C_6H_5$	c	c	71.05 ± 0.13	6.76 ± 0.13	4.81 ± 0.13

[a] In Hz. Obtained on ca. 20–70% solutions in $CDCl_3$ at 20.11 MHz measured at ambient probe temperature, ca. 35 °C. R = alkyl. [b] Not observed. [c] Not applicable.
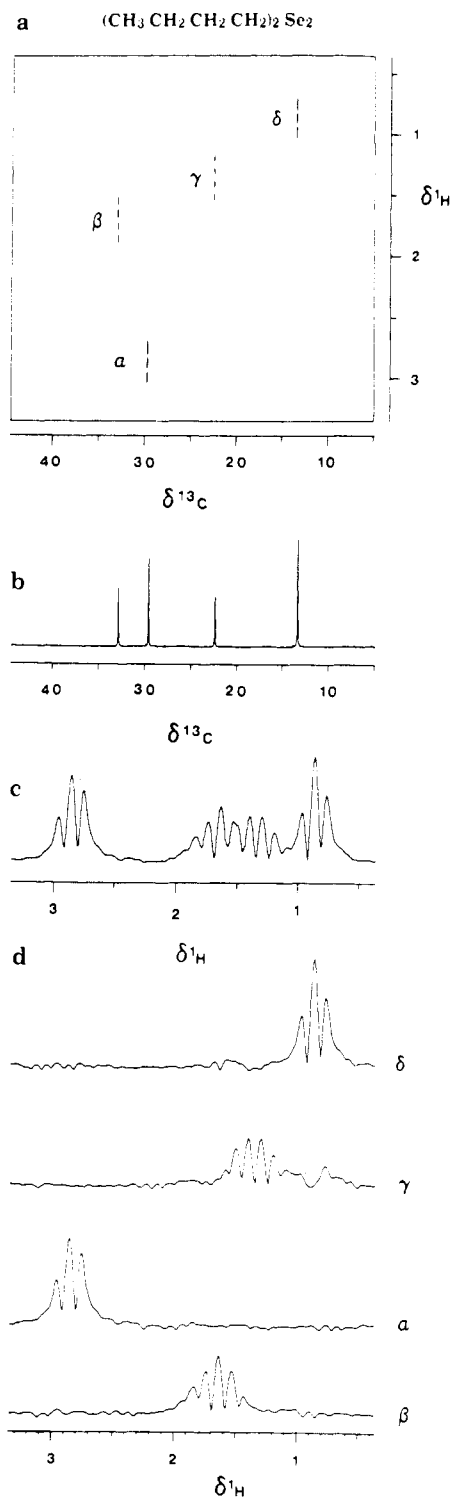
a   (CH₃ CH₂ CH₂ CH₂)₂ Se₂

Figure 2. 20.13-MHz ^{13}C–^{1}H shift-correlated two-dimensional NMR experiment on di-*n*-butyl diselenide, 30% in CDCl₃ (the shift correlation was accomplished by polarization transfer via the $^{1}J_{CH}$ couplings): (a) contour plot, each multiplet corresponds to one CH$_n$ group; (b) horizontal projection onto the F2 (^{13}C) axis; (c) vertical projection onto the F1 (^{1}H) axis; (d) vertical cross sections through the indicated carbon resonances yielding the ^{1}H-coupled proton resonances associated with that carbon. Parameters: 128 ^{13}C {^{1}H} FID's of 32 scans each with an 800-Hz sweep width were acquired with a acquisition time of 1.28 s, 2K data points in t_2, and a relaxation delay of 4.0 s. The t_1 dimension had a sweep width of 240 Hz and was zero-filled once prior to the Fourier transform in t_1. $\Delta t_1/2$ = 2.08 ms, τ_1 = 3.846 ms, and τ_2 = 1.923 ms, with phase cycling for quadruture detection in F1. Total acquisition = ca. 6.4 h and transform = ca. 26 min, with sine-bell shifted $\pi/9$ in t_2 and Lorentz–Gauss (LB = –2.0 Hz, GB = 0.10) in t_1.

The paucity of ^{13}C chemical shift data for diorganyl diselenides and the relative difficulty encountered in making the ^{13}C assignments in the *n*-butyl compounds point to the desirability of having ^{13}C NMR substituent chemical shift additivity parameters[20a] for selenium-containing substituents. The ^{13}C $Z_{\alpha(\beta,\gamma,\delta)}$ substituent increments[31] for *n*-alkyl compounds for several Se-containing substituents (–SeH, –Se₂Me, –Se₂-*n*-Bu, and –Se₂Ph) are listed in Table III as determined from the ^{13}C data of the corresponding *n*-butyl compounds and the shieldings in *n*-butane.[32] These values of substituent increments are in line with values found for similar substituent groups. The decreasing Z_α values in the series of substituents –OH, –SH, and –SeH (49, 10.5, and 4.0 pm, respectively) follow the decreasing electronegativity difference between the heteroatom in the substituent –X and the α-carbon in the *n*-butyl group, while the Z_β values in the same series (10, 11.5, and 10.9 ppm, respectively) appear to be independent of the substituent's electronegativity. As expected, Z_γ and Z_β are essentially constant with Z_γ being the only increment to display a shielding effect.

The ^{13}C chemical shifts for the aromatic carbons are only slightly displaced from the values of diphenyl diselenide. It is interesting to note that the most deshielded resonance in each aromatic ring switches from being C$_{ipso}$ for selenium-containing alkyl groups which contain one β-carbon to being C$_{ortho}$ for those alkyl groups which contain two or three β-carbons. These trends are more apparent when examining the empirical substitutent increments for selenium-containing monosubstituted benzene derivatives (Table II) which have been determined. The small Z$_{ipso}$ values (1.6–2.2 ppm) are indicative of a small α effect[33] in line with the small difference in electronegativity between selenium (2.81; 13.4% s-orbital character,[34] and carbon (2.48; sp³).[36] This has previously been clearly illustrated in the C$_{ipso}$ ^{13}C NMR data for the diphenyl dichalcogenides,[13] (C₆H₅)₂E₂. When E is S, Se, or Te, the chemical shift of C$_{ipso}$ is 137.2, 130.9, or 108.0 ppm, respectively, following the trend of decreasing electronegativity difference between the chalcogenide and carbon. The relatively small values of Z$_{ortho}$ (1.5–2.6 ppm) and Z$_{para}$ (–1.5 to –2.1 ppm) probably indicate that the Se adjacent to the aromatic ring is only weakly, if at all, interacting with the phenyl π system in a mesomeric sense in these diselenides.

The ^{77}Se–^{13}C spin–spin coupling constants determined for the alkyl selenols and the corresponding symmetrical dialkyl diselenides are presented in Table IV with the coupling constant data for the unsymmetrical alkyl methyl and alkyl phenyl diselenides being presented in Table V. The signs of the ^{77}Se–^{13}C spin–spin coupling constants have in all cases been ignored with only the absolute magnitude being reported in Tables I–V. The sign of the one-bond coupling constant is assumed to be negative in all cases following the work of McFarlane,[5] with the signs of longer range ^{77}Se–^{13}C coupling constants being unknown for the selenols and diselenides. The values of the one-bond couplings, $^{1}J_{SeC}$, are in line with the values determined by McFarlane[5] for a limited series of methyl and *tert*-butylselenium compounds. There is a trend of decreasing

(31) Reference 20a, p 208.

(32) Reference 20a, p 131.

(33) Reference 20a, p 212.

(34) On Pauling scale, calculated by the Mulliken–Jaffé method for an estimated hybridization of the bonding orbitals based on the Se–Se–C bond angle of 98.9° in dimethyl diselenide.[35]

(35) Reference 22, p 997.

(36) Huheey, J. E. *Inorganic Chemistry: Principles of Structure and Reactivity*, 3rd ed.; Harper and Row: New York, 1983; p 146.

$^1J_{SeC}$ as the number of α-methyl substitutions increases until *tert*-butyl is reached whereupon the $^1J_{SeC}$ value jumps back up to a value intermediate between the methyl and ethyl compounds. The same kind of "broken" trend is seen for the two-bond $^{77}Se^{-}Se^{-13}C$ coupling constants across the selenium–selenium bond. Unlike these irregular trends, the values of the two-bond $^{77}Se^{-}C^{-13}C$ coupling constants increase in a consistent, monotonic fashion with succesive α-methyl substitution with the values for the selenols being slightly less (4.06–10.65 Hz vs 5.91–14.45 Hz) than the symmetrical and unsymmetrical diselenides. These significant and consistent changes in the two-bond $^{77}Se^{-}C^{-13}C$ coupling constants with increasing α-methyl substitution could be of potential diagnostic use when other techniques fail or give ambiguous results in marked contrast to the one-bond $^{77}Se^{-13}C$ and two-bond $^{77}Se^{-}Se^{-13}C$ coupling constants. Also of interest in this connection is the failure of the two-bond $^{77}Se^{-}C^{-13}C$ coupling constants in alkyl phenyl selenides[6] ($RSeC_6H_5$) to reflect the degree of α-methyl substitution; i.e., ethyl, isopropyl, and *tert*-butyl

phenyl selenide have $^2J_{SeCC}$ values of 12.9, 12.8, and 13.4 Hz, respectively.

In summary, the chemical shifts and $^{77}Se^{-13}C$ spin–spin coupling constants have been determined for a series of alkyl selenols and dialkyl, alkyl methyl, and alkyl phenyl diselenides. Empirical chemical shift substituent effects have been determined for the selenium-containing groups upon the replacement of hydrogen by R (SeH, $-Se_2$ alkyl, $-Se_2$ phenyl) in *n*-alkanes. Also, trends were seen in the $^nJ_{SeC}$ values with the two-bond $^{77}Se^{-}C^{-13}C$ coupling constant promising to be the most diagnostically useful.

Tantalum(I) Alkyne Complexes: Ta(CO)₂(η²-RC≡CR)(I)L₂

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Excess alkyne reacts with $Ta(CO)_3(I)L_3$ to form $Ta(CO)_2(\eta^2\text{-}RC\equiv CR)(I)L_2$ complexes (L = PMe_3 and RCCR = PhCCPh (3), PhCCH (4), HCCH (5), $Ph_2PCCPPh_2$ (6); L = $P(OMe)_3$ and RCCR = PhCCPh (7)). These octahedral d^4 tantalum alkyne adducts have been characterized by ^1H, ^{13}C, and ^{31}P NMR, as well as by infrared and visible spectroscopy. Low-field acetylenic proton and carbon resonances are compatible with a "four-electron donor" alkyne description for these complexes. Variable-temperature ^{13}C NMR studies of ^{13}CO enriched $Ta(CO)_2(PhCCH)(I)(PMe_3)_2$ revealed a ΔG^* of 16 kcal/mol for alkyne rotation about the C–C midpoint of the tantalum–alkyne axis. The X-ray crystal structure of $Ta(CO)_2(PhCCPh)(I)(PMe_3)_2$ has been determined. [Crystal data: monoclinic, $P2_1/c$; a = 12.304 (4) Å, b = 30.971 (8) Å, c = 13.967 (5) Å; β = 96.91 (3)°; Z = 8.] The molecule adopts a distorted octahedral geometry with trans carbonyl ligands and trans PMe_3 ligands. The alkyne is trans to iodide to complete the coordination sphere, and the C–C axis is parallel to the OC–Ta–CO axis. Average metal–ligand bond distances for the two independent molecules in the unit cell are Ta–I, 2.88 (1) Å; Ta–C (alkyne), 2.06 (6) Å; and Ta–CO, 1.98 (9) Å. There is a definite pyramidal distortion of the four equatorial ligands away from the alkyne ligand toward the trans iodide.

Introduction

Reductive coupling of carbon monoxide ligands followed by trapping of the C_2O_2 unit by addition of trimethylsilyl to form tantalum-bound alkynediol products has recently been reported.[1] An important feature of this CO coupling reacton is the stability of the resultant alkyne complex. The net reaction converts $Ta(CO)_2(dmpe)_2Cl$ to $Ta(dmpe)_2(\eta^2\text{-}Me_3SiOC\equiv COSiMe_3)Cl$ (dmpe = 1,2-bis(dimethylphosphino)ethane). An understanding of the stability and reactivity of related tantalum alkyne complexes should be useful in efforts to extend this reductive carbonyl coupling methodology.

A rich chemistry of π-bound alkyne complexes has unfolded for molybdenum and tungsten. The alkyne chemistry of group V metals (V, Nb, Ta) (group 5)[29] is far less developed, particularly for the lower oxidation states. Most of the niobium and tantalum alkyne complexes which have

been reported contain η^5-cyclopentadienyl as a ligand; examples include: (i) metal(I) d^4 derivatives, CpM-(CO)(PhCCPh)L^2; (ii) dimeric metal(II) d^3 derivatives, [CpNb(RCCR)(μ-Cl)]$_2$;[3] (iii) metal(III) d^2 derivatives: $Cp_2M(X)(RC\equiv CR)$ (X = H, halide, SMe, alkyl, O_2CCMe_3),[4] $CpM(X)_2(RCCR)$ (X = halide, OMe).[3,5]

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