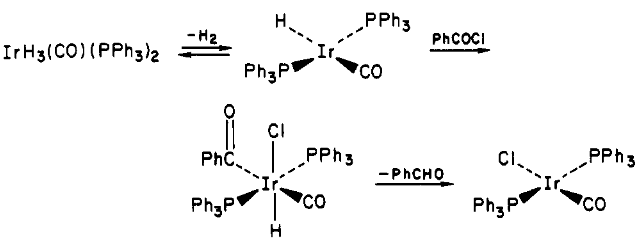

Figure 6. Mechanism proposed for the reaction of $IrH_3(CO)(PPh_3)_2$ with PhCOCl.

facilities of the oxidative additions of PhCHO and PCHO to **1** is not solely due to a kinetic enhancement but is related to the greater thermodynamic stability associated with the cyclometalated product.[36]

Summary

1. The overall effectiveness of simple substrates to add to *trans*-$IrCl(CO)(EPh_3)_2$ (E = P, As) follows the order of their aqueous acidities $PhCO_2H > PhOH \gg PhCHO$.
2. The effectiveness of the chelating substrates toward *trans*-$IrCl(CO)(PPh_3)_2$ follows the order: PCHO > POH $\gtrsim$ PCO_2H. It follows that the intermolecular versions of the oxidative addition reaction do *not* serve as reliable indicators for the corresponding intramolecular processes.
3. The kinetic and thermodynamic facility of the oxidative addition reaction depends heavily on the identity of the ancillary donor component of the bifunctional addend.
4. The differing abilities of PhCHO and PCHO to add to **1** is a consequence of the differing thermodynamic stabilities of the resultant acyl hydrides.

Acknowledgment. This research was supported by the Research Corporation; we also acknowledge the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work. We thank Professor James Ibers and Dr. D. A. Thorne for their help in our attempt to obtain an X-ray structure of the iridium acyl hydride. Dr. Scott Wilson of this department performed the structure determination of the phosphine aldehyde and advised us on the crystallography. We also thank Steve Schmidt for his assistance in preparing AsCHO.

Registry No. **1**, 15318-31-7; **2**, 23954-42-9; **3**, 80062-98-2; **4**, 69721-41-1; **5**, 80062-99-3; **6** isomer 1, 80063-14-5; **6** isomer 2, 80124-62-5; *o*-$Ph_2PC_6H_4CH_2OH$, 53772-42-2; *o*-$Ph_2PC_6H_4CHO$, 50777-76-9; *o*-$Ph_2PC_6H_4CO_2D$, 80049-09-8; *o*-$Ph_2PC_6H_4CO_2H$, 17261-28-8; $\mathrm{r}\overline{\mathrm{IrH(PCO}}\mathrm{_2)Cl(CO)(PPh_3)}$, 80062-96-0; *o*-$Ph_2PC_6H_4OH$, 90254-10-6; $\overline{\mathrm{IrH(PO}}\mathrm{_2)Cl(CO)(PPh_3)}$, 80062-97-1; $IrCl(CO)_2$(*P*-NH_2-$C_6H_4CH_3$), 14243-22-2; *o*-$Ph(P(C_6H_4CHO)_2$, 65654-64-0; *trans*-IrH-[*o*-$Ph_2PC_6H_4C(O)]Cl(CO(AsPh_3)$, 80062-94-8; *trans*-IrH[*o*-$Ph_2A_5C_6H_4C(o)]Cl(CO)(A_5Ph_3)$, 80062-95-9; *o*-$Ph_2AsC_6H_a4CHO$, 80049-10-1; $IrH_3(CO)(PPh_3)_2$, 16971-53-2; $\overline{\mathrm{IrD(PCO}}\mathrm{_2)Cl(CO)(PPh_3)}$, 80062-93-7.

Supplementary Material Available: Tables of bond angles, least-squares planes, analytical data, fractional coordinates, and structure factor amplitudes (20 pages). Ordering information is given on any current masthead page.

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[36] For a discussion of the thermodynamics of *intermolecular* C–H bond activation by platinum(0) see: Luigi, A.; Ayusman, S.; Halpern, J. *J. Am. Chem. Soc.* **1978**, *100*, 2915.

Tellurium-125 Chemical Shifts of Symmetric and Unsymmetric Dialkyl Ditellurides

D. H. O'Brien,* N. Dereu, R. A. Grigsby, and K. J. Irgolic

Department of Chemistry, Texas A&M University, College Station, Texas 77843

F. F. Knapp, Jr.

Nuclear Medicine Technology Group, Health and Safety Research Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37834

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The proton-noise-decoupled tellurium-125 NMR spectra of symmetric dialkyl ditellurides R_2Te_2 [R = Me, Et, *n*-Pr, *i*-Pr, *n*-Bu, *i*-Bu, *s*-Bu, *t*-Bu, *n*-Pent, neo-Pent, *i*-Pent, and *n*-C_nH_{2n+1} (*n* = 6, 7, 8, 9, 11, and 18)] and 36 unsymmetric dialkyl ditellurides (R = all alkyl isomers C_1–C_4 and neopentyl) are reported. The unsymmetric dialkyl ditellurides were prepared in situ by mixing chloroform solutions of two symmetric ditellurides. Equilibration took place but exchange was slow on the tellurium-125 NMR time scale and the spectra contained four Te resonances, one each for the two symmetric ditellurides and two for the unsymmetric ditelluride. The effect of alkyl substitution on tellurium chemical shifts was found to be additive. The magnitude of the effect diminishes as the substitution site moves away from the tellurium atoms and becomes negligible at the fourth atom.

Introduction

Recent investigations have shown that organic tellurium compounds have considerable potential as agents in nuclear medicine. Telluracarboxylic acids are attractive candidates for myocardial imaging,[1-4] tellurium-containing steroids show preferential uptake by the adrenal gland,[5-7] and alkyltellurobarbiturates show promise as reagents for the determination of regional cerebral blood perfusion.[8,9] Because of the large number of resonances and complex

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[1] F. F. Knapp, Jr., K. R. Ambrose, A. P. Callahan, R. A. Grigsby, and K. J. Irgolic, *Radiopharm.* [*Int. Symp.*], *2nd*, 101 (1979).

[2] F. F. Knapp, Jr. *Radiopharm.* [*Int. Symp.*], in press.

[3] D. R. Elmaleh, F. F. Knapp, Jr., T. Yasuda, J. L. Coffey, S. Kopiwoda, and H. W. Strauss, *J. Nucl. Med.*, in press.

[4] F. F. Knapp, Jr., K. R. Ambrose, A. P. Callahan, L. A. Ferren, R. A. Grigsby, and K. J. Irgolic, *J. Nucl. Med.*, in press.

[5] F. F. Knapp, Jr., K. R. Ambrose, and A. P. Callahan, *J. Labelled Compd. Radiopharm.*, 16, 35 (1979).

[6] F. F. Knapp, Jr., K. R. Ambrose, and A. P. Callahan, *J. Nucl. Med.*, 21, 251 (1980).

[7] F. F. Knapp, Jr., K. R. Ambrose, and A. P. Callahan, *J. Nucl. Med.*, *21*, 258 (1980).

[8] F. F. Knapp, Jr., R. A. Grigsby, and K. J. Irgolic, unpublished results.

[9] R. A. Grigsby, Ph.D. Dissertation, Texas A&M University, 1980.

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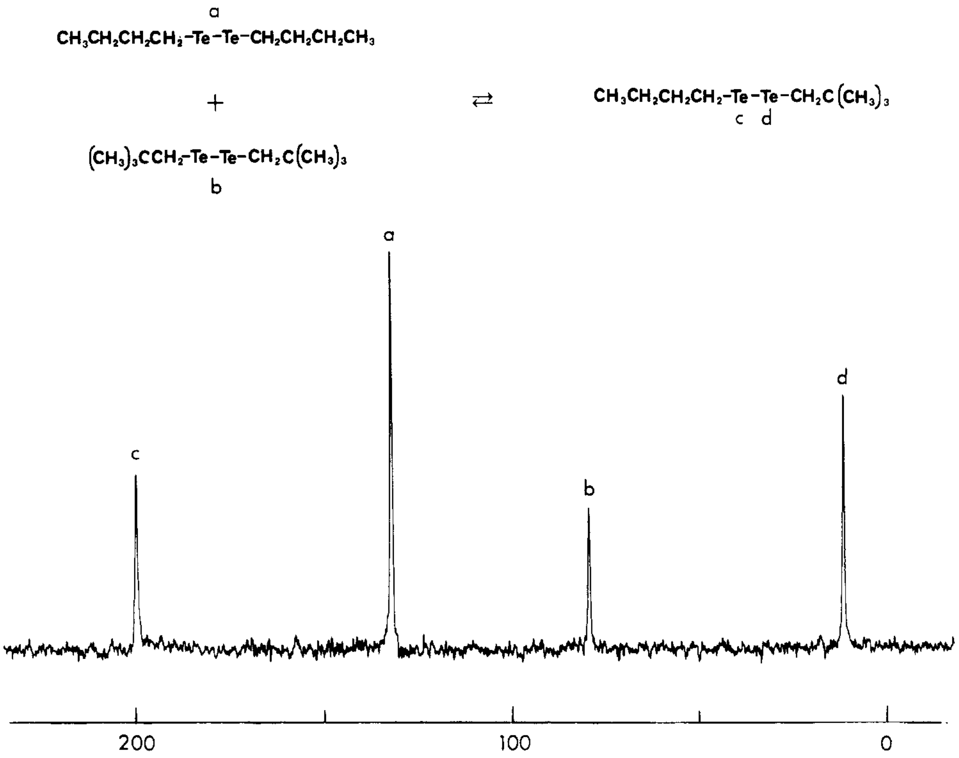

Figure 1. The tellurium-125 NMR spectrum of *n*-butyl neopentyl ditelluride generated by mixing $CDCl_3$ solutions of dibutyl ditelluride and dineopentyl ditelluride.

coupling patterns inherent in proton NMR, ^{125}Te NMR is a more efficient method to assess the purity of reagents and products and to detect and identify byproducts. In addition, ^{125}Te NMR may also be a useful method to investigate the metabolism and fate of the organic tellurium compounds in the biological systems. Tellurium-125 NMR with a chemical shift range of at least 4000 ppm is a much better method for these purposes.

Although there has been an increasing use of direct ^{125}Te NMR measurements with broad-band probes in the characterization of tellurium compounds,[10–24] few data have been reported for dialkyl ditellurides.[25] Earlier shift measurements were obtained with double-resonance techniques.[25–27] The chemical shift range for tellurium is quite large, from the highly deshielded tellurium–selenium dications (δ ~2600–3300)[21,22] to the much more shielded dialkyl ditellurides and dialkyl tellurides (δ ~0 to 700).[16,18,25–27] It has been noted that changing the halogen in tellurium halides results in the expected deshielding of the tellurium as the halogen becomes more electronegative. However, the limited data so far reported have been for compounds of such widely different structures that little is known concerning the response of tellurium chemical shifts to structural changes in the organic moiety of similar tellurium compounds.

Results and Discussion

We report the ^{125}Te chemical shifts for a large number of symmetric and unsymmetric dialkyl ditellurides. The only previously reported chemical shifts for symmetric dialkyl ditellurides were for dimethyl ditelluride (δ 63), diethyl ditelluride (δ 188), and diisopropyl ditelluride (δ 303).[25] These large changes in shift upon α-alkyl substitution have not been explained. No chemical shifts have been reported for unsymmetric dialkyl ditellurides. Unsymmetric diorganyl ditellurides have not yet been isolated although mass spectral evidence[28,29] and proton NMR data point to their existence.[29] The presence of unsymmetric dialkyl ditellurides in solution has now been established on the basis of their ^{125}Te NMR spectra.

For dialkyl ditellurides with Me, Et, Pr, Bu, and neoPent groups, nine symmetric dialkyl ditellurides and 36 unsymmetric dialkyl ditellurides can be prepared. Only one ^{125}Te resonance is observed for the equivalent telluriums in the symmetric ditellurides and two separate ^{125}Te resonances are observed for the nonequivalent telluriums in the unsymmetric ditellurides. The unsymmetric dialkyl

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(10) D. B. Denney, D. Z. Denney, P. J. Hammond, and Y. F. Hsu, *J. Am. Chem. Soc.*, **103**, 2340 (1981).

(11) P. Granger, S. Chapelle, and C. Brevard, *J. Magn. Reson.*, **42**, 203 (1981).

(12) H. J. Gysling, N. Zumbulyadis, and J. A. Robertson, *J. Organomet. Chem.*, **209**, C41 (1981).

(13) W. Lohner and K. Praefcke, *J. Organomet. Chem.*, **208**, 43 (1981).

(14) W. Lohner and K. Praefcke, *J. Organomet. Chem.*, **208**, 39 (1981).

(15) N. Zumbulyadis and H. J. Gysling, *J. Organomet. Chem.*, **192**, 183 (1980).

(16) P. Granger and S. Chapelle, *J. Magn. Reson.*, **39**, 329 (1980).

(17) B. Kohne, W. Lohner, K. Praefcke, H. J. Jakobsen, and B. Villadsen, *J. Organomet. Chem.*, **166**, 373 (1979).

(18) G. V. Fazakerley and M. Celotti, *J. Magn. Reson.*, **33**, 219 (1979).

(19) T. Drakenberg, A.-B. Hornfeldt, S. Gronowitz, J.-M. Talbot, and J.-L. Piette, *Chem. Scr.* **13**, 152 (1978–1979).

(20) W. Koch, O. Lutz, and A. Nolle, *Z. Phys. A*, **289**, 17 (1978).

(21) C. R. Lassigne and E. J. Wells, *J. Chem. Soc., Chem. Commun.*, 956 (1978).

(22) G. J. Schrobiligen, R. C. Burns, and P. Granger, *J. Chem. Soc., Chem. Commun.*, 957 (1978).

(23) K. U. Buckler, J. Kronenbitter, O. Lutz, and A. Nolle, *Z. Naturforsch., A*, **32A**, 1263 (1977).

(24) P. L. Goggin, R. J. Goodfellow, and S. R. Haddock, *J. Chem. Soc., Chem. Commun.*, 176 (1975).

(25) H. C. E. McFarlane and W. McFarlane, *J. Chem. Soc., Dalton Trans.*, 2416 (1973).

(26) C. Rodger, N. Sheppard, C. McFarlane, and W. McFarlane, "Group VI-Oxygen Sulphur, Selenium and Tellurium" in "NMR and the Periodic Table", R. K. Harris and B. E. Mann, Eds., Academic Press, New York, 1978, p 383–419.

(27) W. McFarlane, F. J. Berry, and B. C. Smith, *J. Organomet. Chem.*, **113**, 139 (1976).

(28) C. D. Desjardins, H. L. Paige, J. Passmore, and P. Taylor, *J. Chem. Soc., Dalton Trans.*, 488 (1975).

(29) N. S. Dance and W. R. McWhinnie, *Chem. Scr.*, **8A**, 112 (1975).

Table I. Tellurium-125 Chemical Shifts for Dialkyl Ditellurides[a]

	δ_{Me}	$\delta_{\text{neo-Pent}}$	$\delta_{i\text{-Bu}}$	$\delta_{n\text{-Pr}}$	$\delta_{n\text{-Bu}}$	δ_{Et}	$\delta_{s\text{-Bu}}$	$\delta_{i\text{-Pr}}$	$\delta_{t\text{-Bu}}$
Me	69	92	150	205	213	284	390	455	617
neo-Pent	62	80	142	192	201	269	373	435	597
i-Bu	16	37	99	151	158	228	335	398	565
n-Pr	−11	11	73	124	132	202	311	374	540
n-Bu	−11	12	73	125	133	203	312	375	542
Et	−28	−5	57	108	117	186	296	357	523
t-Bu	−48	−25	36	83	91	155	269	325	497
i-Pr	−74	−45	14	64	71	138	256	313	490
s-Bu	−88	−59	1	50	57	125	243	301	480

[a] Shifts are relative to dimethyl telluride; negative shifts are upfield from dimethyl telluride.

ditellurides were prepared in situ by dissolving approximately equal molar amounts of the symmetric ditellurides in deuteriochloroform. Equilibration took place but exchange was slow on the ^{125}Te NMR time scale. Four tellurium resonances were observed in the spectra of solutions initially containing two symmetric dialkyl ditellurides, one resonance corresponding to the Te in each symmetric ditelluride and two resonances representing the nonequivalent tellurium atoms of the unsymmetric ditelluride (Figure 1).

In the spectra of 33 of the unsymmetric ditellurides, the two resonances of the unsymmetric ditellurides appeared outside the range bounded by the resonance of the parent symmetric ditellurides. In the spectra of the other three compounds, the Te resonances for isopropyl *sec*-butyl ditelluride, isopropyl *tert*-butyl ditelluride, and *n*-propyl *n*-butyl ditelluride were located between the resonances of the symmetric ditellurides. The principle that the effect of a structural change on the chemical shift of an atom decreases as the site of the change is moved away from the atom has been used to assign the tellurium resonances of the unsymmetric ditellurides (Table I). For example, the resonances for ethyl methyl ditelluride, $\mathrm{CH_3CH_2{-}Te_a{-}Te_b{-}CH_3}$ are δ 284 for $\mathrm{Te_a}$ and δ −28 for $\mathrm{Te_b}$. Compared to dimethyl ditelluride (δ 69), the effect of methyl substitution is a larger, downfield shift change for the close tellurium, $\mathrm{Te_a}$ (+215 ppm), and a smaller, upfield shift change for the remote tellurium, $\mathrm{Te_b}$ (−97 ppm).

In Table I, the ^{125}Te chemical shifts of the symmetric dialkyl ditellurides are underlined. Each of the two shifts for an unsymmetric ditelluride may be located in Table I by proceeding down the column headed by the appropriate alkyl group and finding the shift opposite the other alkyl group. As an example, the chemical shifts for *n*-butyl isopropyl ditelluride are δ 71 for the tellurium attached to the *n*-Bu group (*n*-butyl column opposite isopropyl) and δ 375 for the tellurium attached to the *i*-Pr group (isopropyl column opposite *n*-butyl). Table I is arranged so that the chemical shifts increase in the horizontal rows from left to right. In this manner, the effect of changing alkyl group structure on the chemical shift of the directly attached tellurium is illustrated. The vertical columns have been arranged with the chemical shifts decreasing from top to bottom. This arrangement clearly illustrates the effect of a change in the alkyl group on the chemical shift of the tellurium not bonded to this alkyl group.

Several features of the tellurium chemical shifts for dialkyl ditellurides are apparent. The range of shifts is quite large, ~705 ppm (*t*-Bu–Te of *t*-Bu–Te–Te–Me, δ 617; Me–Te of Me–Te–Te–*s*-Bu, δ −88). The large effect caused by α-methyl substitution of $\mathrm{R_a}$ on $\mathrm{Te_a}$ may be seen by comparing the values listed in the chemical shift columns (Table I) for Me to Et, Et to *i*-Pr, and *i*-Pr to *t*-Bu. The effect of alkyl substitution on tellurium chemical shifts diminishes as the site of substitution moves away from the tellurium atoms. For example, γ-methyl substitution of $\mathrm{R_a}$ in dialkyl ditellurides (*n*-Pr to *n*-Bu, Table I) results in a downfield shift change of 7–9 ppm for the close tellurium atom $\mathrm{Te_a}$ and no change at the remote tellurium $\mathrm{Te_b}$. In contrast, γ substitution in the symmetric dibutyl ditelluride to form diisopentyl ditelluride results in a downfield shift change of 7 ppm (Table II) for both tellurium atoms. In Table II the tellurium chemical shifts for long-chain symmetric dialkyl ditellurides are summarized. These shifts vary between δ 133 and 140, indicating that alkyl substitutions on the δ-carbon or further down the chain have a very small influence on the ^{125}Te chemical shift.

Table II. Tellurium-125 Chemical Shifts for Long-Chain Symmetric Dialkyl Ditellurides, $\mathrm{R_2Te_2}$

R	δ	R	δ
n-$\mathrm{C_4H_9}$	133	*n*-$\mathrm{C_8H_{17}}$	138
i-$\mathrm{C_5H_{11}}$	140	*n*-$\mathrm{C_9H_{19}}$	134
n-$\mathrm{C_5H_{11}}$	135	*n*-$\mathrm{C_{10}H_{21}}$	133
n-$\mathrm{C_6H_{13}}$	137	*n*-$\mathrm{C_{11}H_{23}}$	137
n-$\mathrm{C_7H_{15}}$	140	*n*-$\mathrm{C_{18}H_{37}}$	134

Table III. Tellurium-125 Chemical Shift Changes Caused by α-Methyl Substitution, α_1, in Dialkyl Ditellurides, $\mathrm{R_a{-}Te_aTe_b{-}R_b}$

$\mathrm{R_a}$	$\mathrm{R_b}$	$\delta_{\mathrm{Te_a}}$	$\Delta\delta_{\mathrm{Te_a}}$	$\delta_{\mathrm{Te_b}}$	$\Delta\delta_{\mathrm{Te_b}}$
Me	Me	69	+215	69	−97
Et	Me	284		−28	
Me	neo-Pent	62	+207	92	−97
Et	neo-Pent	269		−5	
Me	*i*-Bu	16	+212	150	−94
Et	*i*-Bu	228		56	
Me	*n*-Pr	−11	+213	205	−97
Et	*n*-Pr	202		108	
Me	*n*-Bu	−11	+214	213	−98
Et	*n*-Bu	203		115	
Me	Et	−28	+214	284	−98
Et	Et	186		186	
Me	*t*-Bu	−48	+203	617	−94
Et	*t*-Bu	155		523	
Me	*i*-Pr	−74	+212	454	−98
Et	*i*-Pr	138		357	
Me	*s*-Bu	−88	+213	390	−94
Et	*s*-Bu	125		296	
		av	+211 ± 3		−96 ± 2

The consistency of the differences in shifts among columns or rows of Table I strongly suggests that the effect of alkyl substitution on ^{125}Te chemical shifts obeys simple additive rules similar to those developed for the empirical calculation of carbon-13 shifts of alkanes.[30] These data may be useful in assigning substitution patterns to ditellurides of unknown structure. In Figure 2 the desig-

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(30) J. B. Strothers, "Carbon-13 NMR Spectroscopy", Academic Press, New York 1972, pp 55–60.

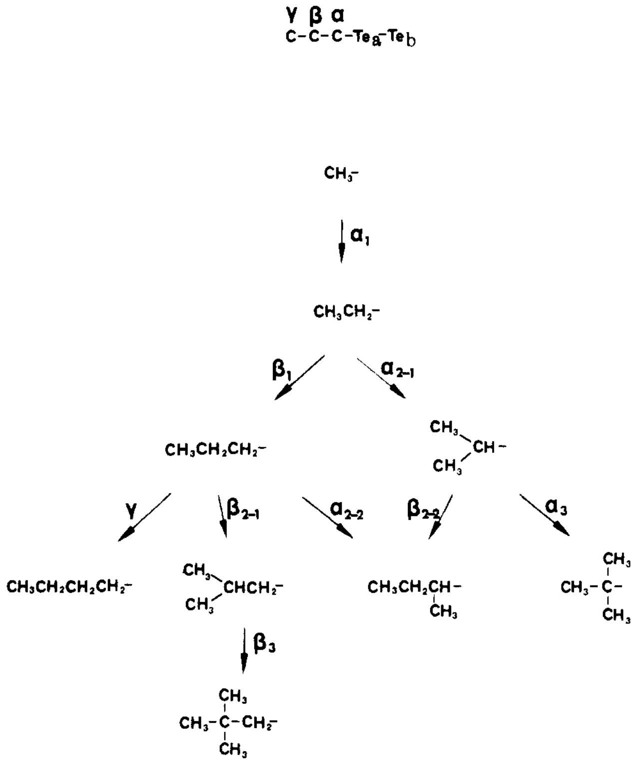

Figure 2. Scheme of methyl substitutions generating all C_1 through C_4 alkyl isomers and neopentyl.

Table IV. Tellurium-125 Chemical Shift Changes Caused by Methyl Substitutions in Dialkyl Ditellurides, R_a-Te_aTe_b-R_b

substitutn[a]	$\Delta\delta_{Te_a}$	$\Delta\delta_{Te_b}$	comparison
α_1	+211 ± 3	−96 ± 2	Me to Et
α_{2-1}	+171 ± 2	−42 ± 3	Et to *i*-Pr
α_{2-2}	+187 ± 3	−72 ± 4	*n*-Pr to *s*-Bu
α_3	+170 ± 4	+17 ± 5	*i*-Pr to *t*-Bu
β_1	−77 ± 2	+17 ± 0	Et to *n*-Pr
β_{2-1}	−51 ± 2	+25 ± 1	*n*-Pr to *i*-Bu
β_{2-2}	−61 ± 3	−13 ± 1	*i*-Pr to *s*-Bu
β_3	−61 ± 3	+40 ± 3	*i*-Bu to neo-Pent
γ	+7 ± 1	0 ± 0	*n*-Pr to *n*-Bu

[a] See Figure 2 for definitions.

nation for methyl substitutions on the C_1 through C_4 alkyl isomers are illustrated. In Table III, the chemical shift changes for nine α-methyl substitutions, α_1, are calculated from the chemical shifts of dialkyl ditellurides, R_a–Te_aTe_b–R_b, in which one alkyl group (R_a) is changed from methyl to ethyl. The chemical shift change for the close tellurium, Te_a, is large and downfield while the change for the remote tellurium, Te_b, is smaller and upfield. These opposite effects explain why chemical shift data on *symmetrical* dialkyl ditellurides alone do not lead to recognizable patterns of shift changes with substitution. Simply by comparison of the ^{125}Te chemical shifts in symmetric dialkyl ditellurides, it is not possible to predict the chemical shifts observed in the unsymmetric ditellurides. As shown in Table III, the chemical shift change at each tellurium of diethyl ditelluride compared to dimethyl ditelluride is the sum of the contribution of the close α-methyl substitution (+211 ppm) and the remote α-methyl substitution (−96 ppm).

Table IV summarizes the tellurium chemical shift changes caused by the nine structural changes (methyl substitutions) outlined in Figure 2. These tellurium shift changes are analogous to the additive carbon-13 shift changes for methyl substitution in linear and branched alkanes.[30] Methyl substitution α and β to Te_a are equivalent to β- and γ-methyl substitutions in alkanes. For carbon-13, the shift change parameters are +9.4 ppm for β-methyl and −2.5 ppm for γ-methyl substitutions. The ratio is approximately 3:1 and the sign changes, as has been observed for the corresponding tellurium shift changes. However, the magnitude of the shift changes for tellurium are approximately 20 times larger than for carbon. This is to be expected when one compares the shift range for tellurium in dialkyl ditellurides (~700 ppm) to the shift range for alkane carbons (~30–40 ppm). Unlike carbon-13 shift changes, this larger shift range leads to observable shift changes (~7 ppm) for tellurium when the methyl substitution is three atoms away from the tellurium (γ for Te_a and β for Te_b).

Table V. Tellurium-125 Chemical Shift Changes Caused by Larger-Than-Methyl Group or Multiple Substitutions

	$\Delta\delta_{Te_a}$		$\Delta\delta_{Te_b}$		calculatn[a]
substitutn	calcd	obsd	calcd	obsd	group modification
α-ethyl	+135	+134	−79	−79	$\alpha_1 + \beta_1$ Me to *n*-Pr
2 α-methyl	+383	+382	−138	−138	$\alpha_1 + \beta_{2-1}$ Me to *i*-Pr
α-propyl	+142	+141	−78	−79	$\alpha_1 + \beta_1 + \gamma$ Me to *n*-Bu
α-isopropyl	+84	+83	−54	−54	$\alpha_1 + \beta_1 + \beta_{2-1}$ Me to *i*-Bu
α-methyl, α-ethyl	+322	+321	−151	−151	$\alpha_1 + \beta_1 + \alpha_{2-2}$ Me to *s*-Bu
3 α-methyl	+551	+552	−121	−121	$\alpha_1 + \alpha_{2-1} + \alpha_3$ Me to *t*-Bu
α-*tert*-butyl	+23	+22	−13	−14	$\alpha_1 + \beta_1 + \beta_{2-1} + \beta_3$ Me to neo-Pent

[a] The overall shift change was calculated as the sum of the shift changes corresponding to the pertinent structural modifications of the alkyl group (Figure 2).

The shift parameters for methyl substitution allow the calculation of shift changes that occur upon larger group or multigroup substitutions. Table V shows shift changes that are observed for α-ethyl, α-propyl, α-isopropyl, and α-*tert*-butyl and for multiple group substitutions. These observed shift changes agree well with those calculated by summing the appropriate methyl shift changes from Table IV.

The shift parameters found in this work are also useful in predicting tellurium chemical shifts for aryl alkyl ditellurides. Solutions of phenyl methyl ditelluride and phenyl ethyl ditelluride were prepared by mixing diphenyl ditelluride with dimethyl ditelluride or with diethyl ditelluride. The chemical shifts for phenyl methyl ditelluride were δ 404 for the phenyl tellurium and δ 115 for the methyl tellurium. For phenyl ethyl ditelluride, the shifts were δ 309 for the phenyl tellurium and δ 315 for the ethyl tellurium. The shift values predicted from Table IV for phenyl ethyl ditelluride are δ 308 and 326, respectively. Similar additive shift changes are to be expected for tellurium in monotellurides, and these will be reported in a forthcoming publication.

Experimental Section

Symmetric dialkyl ditellurides were synthesized as reported elsewhere.[31] Solutions for NMR measurements were prepared by dissolving approximately 100 mg of the symmetric ditelluride or approximately 100 mg each of two different symmetric di-

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(31) K. J. Irgolic, R. A. Grigsby, N. Dereu, S. W. Lee, and F. F. Knapp, in preparation.

Organometallics **1982**, *1*, 517–522

tellurides in 1.5 mL of deuteriochloroform ($\sim$0.2M). All tellurium-125 spectra were obtained with a Varian Associates Model FT80 NMR spectrometer equipped with a broad-band probe tuned to 25.104 MHz. About 1000–3000 average transients were required to obtain satisfactory signal to noise ratios using sweep widths of either 8 KHz ($\sim$318 ppm) or 4 KHz ($\sim$159 ppm) stored in 8K data points. With these spectral parameters, proton-noise-decoupled tellurium resonances were 5–10 Hz wide at half-height. All tellurium-125 shifts are referenced to dimethyl telluride at 25 094 885 Hz and are believed to be precise to at least ±1 ppm. Positive shifts are downfield and negative shifts are upfield from dimethyl ditelluride. The differences between shifts of dialkyl ditellurides reported in the literature and those presented in Table I (Me_2Te, δ 63[25] vs. δ 69; Et_2Te_2, δ 188[25] vs. δ 186; and i-Pr_2Te_2, δ 303[25] vs. δ 313) are probably due to solvent. In the previous work, the spectra were obtained for neat liquids or for solutions in benzene.

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Registry No. Me_2Te_2, 20334-43-4; (*neo*-pent)$_2$Te$_2$, 79971-41-8; (*i*-Bu)$_2$Te$_2$, 79982-95-9; (*n*-Pr)$_2$Te$_2$, 79971-42-9; (*n*-Bu)$_2$Te$_2$, 77129-69-2; Et_2Te_2, 26105-63-5; (*s*-Bu)$_2$Te$_2$, 79971-43-0; (*i*-Pr)$_2$Te$_2$, 51112-73-3; (*t*-Bu)$_2$Te$_2$, 79971-44-1; (Me)(*neo*-pent)Te$_2$, 79971-45-2; (Me)(*i*-Bu)Te$_2$, 79971-46-3; (Me)(*n*-Pr)Te$_2$, 79971-47-4; (Me)(*n*-Bu)Te$_2$, 79971-48-5; (Me)(Et)Te$_2$, 79971-49-6; (Me)(*s*-Bu)Te$_2$, 79971-50-9; (Me)(*i*-Pr)Te$_2$, 79971-51-0; (Me)(*t*-Bu)Te$_2$, 79971-52-1; (*neo*-pent)(*i*-Bu)Te$_2$, 79971-53-2; (*neo*-pent)(*n*-Pr)Te$_2$, 79971-54-3; (*neo*-pent)(*n*-Bu)Te$_2$, 79971-55-4; (*neo*-pent)(Et)Te$_2$, 79971-56-5; (*neo*-pent)(*s*-Bu)Te$_2$, 79971-57-6; (*neo*-pent)(*i*-Pr)Te$_2$, 79971-58-7; (*neo*-pent)(*t*-Bu)Te$_2$, 79971-59-8; (*i*-Bu)(*n*-Pr)Te$_2$, 79971-60-1; (*i*-Bu)(*n*-Bu)Te$_2$, 79971-61-2; (*i*-Bu)(Et)Te$_2$, 79971-62-3; (*i*-Bu)(*s*-Bu)Te$_2$, 79971-63-4; (*i*-Bu)(*i*-Pr)Te$_2$, 79971-64-5; (*i*-Bu)(*t*-Bu)Te$_2$, 79971-65-6; (*n*-Pr)(*n*-Bu)Te$_2$, 79971-66-7; (*n*-Pr)(Et)Te$_2$, 79971-67-8; (*n*-Pr)(*s*-Bu)Te$_2$, 79971-68-9; (*n*-Pr)(*i*-Pr)Te$_2$, 79971-69-0; (*n*-Pr)(*t*-Bu)Te$_2$, 79971-70-3; (*n*-Bu)(Et)Te$_2$, 79971-71-4; (*n*-Bu)(*s*-Bu)Te$_2$, 79971-72-5; (*n*-Bu)(*i*-Pr)Te$_2$, 79971-73-6; (*n*-Bu)(*t*-Bu)Te$_2$, 79971-74-7; (Et)(*s*-Bu)Te$_2$, 79971-75-8; (Et)(*i*-Pr)Te$_2$, 79971-76-9; (Et)(*t*-Bu)Te$_2$, 79971-77-0; (*t*-Bu)(*s*-Bu)Te$_2$, 79971-78-1; (*t*-Bu)(*i*-Pr)Te$_2$, 79971-79-2; (*i*-Pr)(*s*-Bu)Te$_2$, 79971-80-5; (*i*-Pent)$_2$Te$_2$, 79971-81-6; (*n*-Pent)$_2$Te$_2$, 79971-82-7; (n-C_6H_{13})$_2$Te$_2$, 79971-83-8; (n-C_7H_{15})$_2$Te$_2$, 79971-84-9; (n-C_8H_{17})$_2$Te$_2$, 79971-85-0; (n-C_9H_{19})$_2$Te$_2$, 79971-86-1; (n-$C_{10}H_{21}$)$_2$Te$_2$, 79971-87-2; (n-$C_{11}H_{23}$)$_2$Te$_2$, 79971-88-3; (n-$C_{18}H_{37}$)$_2$Te$_2$, 79971-89-4.

Addition of Electrophiles to the Sulfur Atom of Cobalt Complexes of α,β-Unsaturated Thioaldehydes (Enethials)[1]

Edward Joseph Parker,[2] James Robert Bodwell, Thomas Charles Sedergran, and
Donald Charles Dittmer*

Department of Chemistry, Syracuse University, Syracuse, New York 13210

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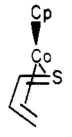
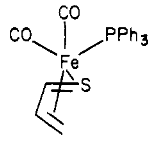
Cyclopentadienylcobalt complexes of α,β-unsaturated thioaldehydes (enethials) can be alkylated on the sulfur atom to give complexes involving the new ligands, formally *S*-alkyl enethial cations or *S*-alkyl allylcarbenium ions. A Hg II complex has been obtained. Silver tetrafluoroborate oxidizes the complexes to fluoroborate salts containing two cobalt atoms.

Introduction

Complexation with transition metals stabilizes a variety of exotic ligands whose existence otherwise would be in jeopardy.[3] Thioaldehydes are extremely rare[4] as are α,β-unsaturated thioaldehydes. Stable examples of the latter involve extensive conjugation of the thiocarbonyl group with a nitrogen[5] or a sulfur[6] atom. The unstable molecule, thioacrolein or propenethial, has been obtained by flash vacuum thermolysis of diallyl sulfide; it decomposes slowly at −196 °C.[7] However, propenethial and other α,β-unsaturated thioaldehydes have been obtained as stable complexes with iron or cobalt (e.g., I, II).[8] An X-ray analysis has been performed on II.[9] These complexes are derived from thietes which are readily prepared.[8b,10]



I



II

Cp = π-C_5H_5

In order to determine how complexation affects the chemical properties of the enethial ligand, we decided at

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[1] Reported in part at the ACS/CSJ Chemical Congress, Honolulu, Hawaii, April, 1979, Abstract ORGN 343.

[2] Taken in part from the Ph.D. Thesis of E. J. Parker, Syracuse University, Dec 1979.

[3] A partial list of examples includes cyclobutadienes [reviewed by A. Efraty, *Chem. Rev.*, **77**, 691 (1977)], pentalene [T. J. Katz and N. Acton, *J. Am. Chem. Soc.*, **94**, 3281 (1972)], carbenium ions $(OC)_9Co_3CCO^+$ [reviewed by D. Seyferth, *Adv. Organomet. Chem.*, **14**, 97 (1976)], carbenes and carbynes [reviewed by E. O. Fischer, *Adv. Organomet. Chem.*, **14**, 1 (1976)], vinyl alcohols [C. H. de Puy, R. N. Greene, and T. E. Schroer, *J. Chem. Soc., Chem. Commun.*, 1225 (1968)], and trimethylenemethane [K. Ehrlich and G. F. Emerson, *J. Am. Chem. Soc.*, **94**, 2464 (1972)].

[4] A. Ohno, "Organic Chemistry of Sulfur", S. Oae, Ed., Plenum Press, New York, 1977, p 196.

[5] R. B. Woodward, W. A. Ayer, J. M. Beaton, F. Bickelhaupt, R. Bonnett, P. Buchschacher, G. L. Closs, H. Dutler, J. Hannah, F. P. Hauck, S. Ito, A. Langemann, E. LeGoff, W. Leimgruber, W. Lwowski, J. Sauer, Z. Valenta, and H. Volz, *J. Am. Chem. Soc.*, **82**, 3800 (1960); S. McKenzie and D. H. Reid, *J. Chem. Soc. C*, 145 (1970); J. Dabrowski and K. Kamienska-Trela, *Org. Magn. Reson.*, **4**, 421 (1972); S. C. Tang, G. N. Weinstein, and R. H. Holm, *J. Am. Chem. Soc.*, **95**, 613 (1973).

[6] H. Davy and J. Vialle, *Bull. Soc. Chim Fr.*, 1435 (1975); D. M. McKennon and J. M. Buchshriber, *Can. J. Chem.*, **49**, 3299 (1971).

[7] W. J. Bailey and M. Isogawa, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, **14**, 300 (1973); [*Chem. Abstr.*, **82**, 74136 (1975)]; H. G. Giles, R. A. Marty, and P. de Mayo, *Can. J. Chem.*, **54**, 537 (1976).

[8] (a) D. C. Dittmer, K. Takahashi, M. Iwanami, A. I. Tsai, P. L. Chang, B. B. Blidner, and I. K. Stamos, *J. Am. Chem. Soc.*, **98**, 2795 (1976); (b) B. H. Patwardhan, E. J. Parker, and D. C. Dittmer, *Phosphorus Sulfur*, **7**, 5 (1979).

[9] R. L. Harlow and C. E. Pfluger, *Acta Crystallogr., Sect B*, **B29**, 2633 (1973).

[10] D. C. Dittmer, P. L. Chang, F. A. Davis, M. Iwanami, I. K. Stamos, and K. Takahashi, *J. Org. Chem.*, **37**, 1111 (1972).

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