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# A $^{125}$Te NMR and Mössbauer Study of Bis(organyltelluro)methanes and Their Halide Derivatives

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The syntheses of the bis(alkyltelluro)methanes are described. The $^{125}$Te NMR chemical shifts measured in $CDCl_3$ solution are reported relative to neat $Me_2Te$ and range from 213.5 ppm for $(MeTe)_2CH_2$ to 713 ppm for $(t\text{-}BuTe)_2CH_2$. The dihalides of the bis(methyltelluro)- and bis(phenyltelluro)methanes have been synthesized and yield chemical shifts in the relatively narrow range of 786 ppm for $CH_2(Te(I)Me)_2$ to 834 ppm for $CH_2(Te(Cl)Me)_2$. The trends in the chemical shifts are compared with those previously reported for the diorganyl tellurides and their dihalides. The $^{125}$Te Mössbauer parameters, measured at 4.2 K, are also compared with those of the diorganyl tellurides and their dihalides.

## Introduction

Recently there have been a number of $^{125}$Te NMR studies of diorganyl tellurides, $R_2Te$, and ditellurides, $R_2Te_2$.[1-4] Another group of compounds closely related to these are the bis(organyltelluro)methanes, $(RTe)_2CH_2$. While the synthesis of the phenyl derivatives of the latter compounds was first reported in 1970,[5] and subsequent synthetic developments reported by Seebach and Beck,[6] Engman and Cava,[7] and Brandt et al.[8] there has been little attempt to spectroscopically characterize these compounds or to prepare their derivatives. DeSilva et al.[9] have recently reported the IR, proton NMR, and $^{125}$Te Mössbauer data for a charge-transfer complex of $(PhTe)_2CH_2$ formed in the reaction of NaTePh with $CH_2Cl_2$. There was also one earlier reference in the literature to the $^{125}$Te NMR chemical shift of $CH_2(TeCl_3)_2$.[10] There has been no previous report in the literature on the synthesis and characterization of the bis(alkyltelluro)methanes.

In this paper we report the synthesis of a series of bis(alkyltelluro) methanes by the reaction of dialkyl ditellurides with diazomethane, the high-resolution (Brüker WM-400) $^{125}$Te NMR spectra of these compounds and the Mössbauer spectra of a selection of them. The proton-coupled and selectively decoupled $^{125}$Te NMR spectra have been studied, although the results of a detailed analysis of these spectra will appear elsewhere. The effect on the $^{125}$Te NMR chemical shift of systematically varying the alkyl ligand has been investigated, and a comparison is drawn with the earlier results of O'Brien et al.[2] on unsymmetrical diorganyl tellurides.

The preparation of the dihalides of the bis(methyltelluro)- and bis(phenyltelluro)methanes, $CH_2(Te(X)_2R)_2$, are described for the first time, and their $^{125}$Te NMR and Mössbauer parameters are reported. The trends in the $^{125}$Te NMR and Mössbauer data are discussed.

**Table I. Tellurium-125 Chemical Shifts for the Bis(organyltelluro)methanes, $(RTe)_2CH_2$**

| R | $\delta^a$ $RTeCH_2TeR$ | $\delta^b$ $RTeCH_2CH_3$ |
|---|---|---|
| Me | 213.5 | 185 |
| *i*-Bu | 282.5 | 254 |
| *n*-Pr | 334.5 | 305 |
| *n*-Bu | 341.9 | 312 |
| Et | 402.2 | 376 |
| *s*-Bu | 498.4 | 469 |
| *i*-Pr | 559.9 | 532 |
| *t*-Bu | 713.0 | 690 |
| Ph | 587.6 | |

[a] Chemical shifts are downfield relative to $Me_2Te$. The spectra were recorded in $CDCl_3$ solution and are referenced to neat $Me_2Te$. [b] Data taken from ref 2.

**Table II. Tellurium-125 Chemical Shift Changes Due to Methyl Substitution for the Bis(alkyltelluro)methanes**

| substn$^a$ | $\Delta\delta$ $RTeCH_2TeR$ | comparison | $\Delta\delta^b$ $RTeCH_2CH_3$ |
|---|---|---|---|
| $\alpha_1$ | +188 | Me to Et | +191 |
| $\alpha_{2\text{-}1}$ | +158 | Et to *i*-Pr | +156 |
| $\alpha_{2\text{-}2}$ | +163 | *n*-Pr to *s*-Bu | +164 |
| $\alpha_3$ | +153 | *i*-Pr to *t*-Bu | +158 |
| $\beta_1$ | −67 | Et to *n*-Pr | −71 |
| $\beta_{2\text{-}1}$ | −53 | *n*-Pr to *s*-Bu | −63 |
| $\gamma$ | +15.0 | *n*-Pr to *n*-Bu | +7.0 |

[a] The substitution nomenclature is taken from ref 1. [b] Data taken from ref 2.

## Results and Discussion

**NMR Data.** Sample high-resolution $^{125}$Te NMR spectra for $MeTeCH_2TeMe$ are shown in Figure 1. The proton-coupled spectrum shows the presence of a quartet split into triplets. On decoupling the methyl protons the spectrum reduces to a simple triplet while decoupling the Te–C-$H_2$–Te methylene protons produces a quartet. The proton-coupled $^{125}$Te spectra of the other bis(alkyltelluro)methanes are generally more complex. By selective decoupling it was possible to abstract detailed information on the tellurium–proton couplings, and as noted above the results of such a study will be published separately. The $^{125}$Te chemical shifts, which are directly abstracted from the data, are important for the present discussion and are given in Table I.

The $^{125}$Te chemical shifts span a range from +213.5 ppm ($(Me_2Te)_2CH_2$) to +713 ppm ($(t\text{-}BuTe)_2CH_2$) with respect to $Me_2Te$; positive chemical shifts are downfield from $Me_2Te$. With the assumption that the chemical shifts are dominated by the paramagnetic shielding term,[11] more

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(1) O'Brien, D. H.; Dereu, N.; Grigsby, R. A.; Irgolic, K. J. *Organometallics* **1982**, *1*, 513.

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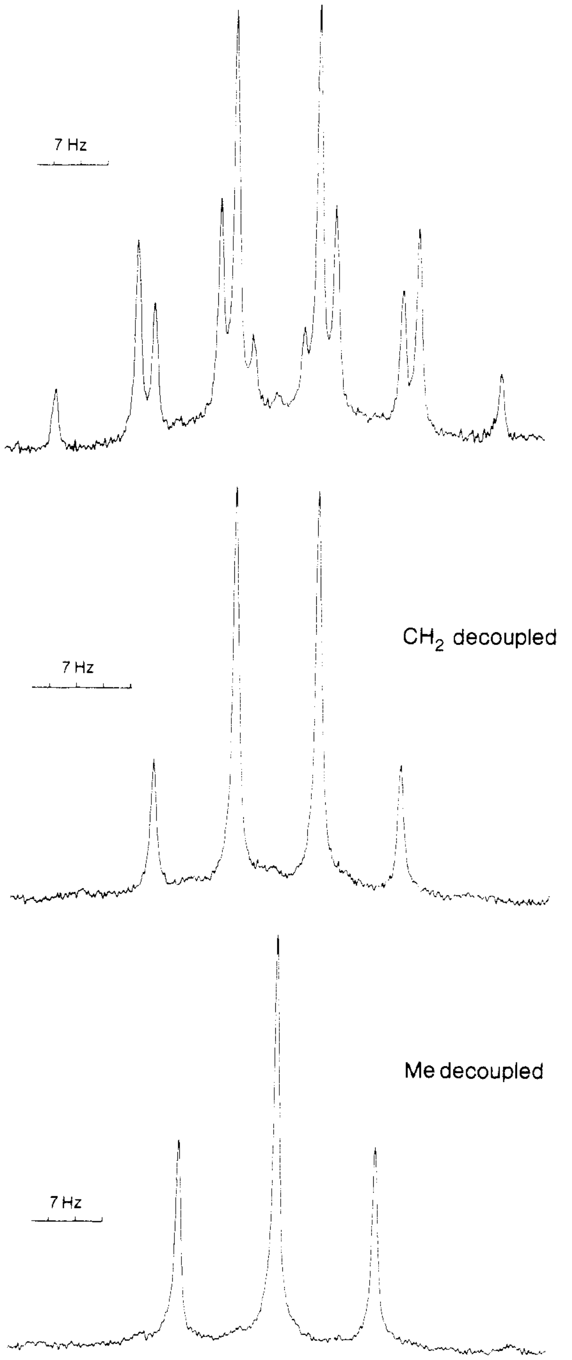

**Figure 1.** The $^{125}$Te NMR spectrum of $MeTeCH_2TeMe$ showing the proton-coupled and the selectively decoupled spectra.

positive shifts correspond to a decrease in shielding at the tellurium nucleus. The trends in the chemical shifts observed here are similar to those reported earlier by O'Brien et al. for the diorganyl tellurides[2] and ditellurides.[1] Thus as methyl substitution occurs at the $\alpha$-carbon of the alkyl group, the chemical shift becomes more positive. On the other hand, substitution at the $\beta$-carbon, for example, in $EtTeCH_2TeEt$, decreases the chemical shift. These effects are illustrated in Table II where the $\alpha$ and $\beta$ substitution nomenclature has been taken from ref 1.

The compounds $RTeCH_2TeR$ can be viewed as unsymmetrical tellurides containing the linkage $R{-}Te{-}CH_2{-}$. The two tellurium sites are of course exactly equivalent when R is the same alkyl group attached to each tellurium. A comparison of the effects on the NMR chemical shifts of $\alpha$ and $\beta$ substitution in the alkyl group of the bis(alkyltelluro)methanes is then probably best made with the unsymmetrical tellurides $RTeCH_2CH_3$ again containing the $R{-}Te{-}CH_2{-}$linkage and where the ethyl ligand is kept constant and R is systematically varied. This comparison is made in Table II where the data for the appropriate $CH_3CH_2TeR$ compounds have been taken from ref 2. It can be seen that there is very good agreement between the $\Delta\delta$ values for $RTeCH_2TeR$ and $RTeCH_2CH_3$. Thus the first $\alpha$ substitution, on going from Me to Et, produces a large downfield shift change of +188 ppm, and subsequent $\alpha$-methyl substitutions produce somewhat smaller downfield changes that are roughly constant in magnitude. Alkyl substitution $\beta$ to the tellurium produces a smaller upfield change, while $\gamma$ substitution causes only a very small downfield change.

From Table I it is also apparent that the second tellurium atom in the $RTeCH_2(TeR)$ molecule produces a fairly constant downfield shift change of +30 ppm in comparison with that observed in $RTeCH_2(CH_3)$ regardless of R, i.e., $\alpha$ substitution by TeR rather than by Me produces a decrease in shielding equivalent to a change in shift of 30 ppm.

While the chemical shifts of the (alkyltelluro)methanes appear to be roughly an additive property of the number of $\alpha$-methyl groups in the alkyl ligand, the chemical shift for $(PhTe)_2CH_2$ of 587 ppm also appears to be roughly an additive property of the ligands. Thus from the chemical shift for $MeTe(CH_2TeMe)$ (214 ppm), the $CH_2TeR$ ligand may be assigned a partial shift of 214 ppm, that for Me being zero by definition, while $Ph_2Te$ (688 ppm) leads to a partial shift for Ph of 344 ppm with respect to $Me_2Te$. On this basis it would be expected that $PhTeCH_2TePh$ would have a chemical shift of ca. 558 ppm, in reasonable agreement with the observed value of 587 ppm.

The trend in chemical shifts observed for the bis(alkyltelluro)methanes on $\alpha$-methyl substitution not only parallels that observed in the dialkyl tellurides and ditellurides but also that for $^{77}$Se in the dialkyl selenides and diselenides. It was noted[11] some time ago that the trends for the latter compounds also parallel those of $^{31}$P in the trialkylphosphines. All of these trends appear to run counter to that expected on the basis of simple electronegativity considerations. A decrease in the electronegativity of the alkyl ligand would have been expected to result in an increase in the paramagnetic shielding at the tellurium and an upfield shift. However, the reverse trend is observed. In the Ramsey formulation the paramagnetic shielding is dependent on the mean electronic excitation energy, $\Delta E^{-1}$, the expectation value of the cube of the radius, $\langle r^{-3} \rangle$, of the valence p and d orbitals, and the unbalance, $Q$, in the valence p and d orbital populations. The relative importance of these three terms in influencing the NMR chemical shifts of $^{125}$Te and $^{77}$Se is not clearly understood. Gombler[14] was unable to establish any simple relationship between $\Delta E^{-1}$ and $\delta(^{77}Se)$ for a wide range of organoselenides, $CF_3SeX$, although for some a linear correlation of $\delta(^{77}Se)$ with the electronegativity of the ligand X was observed pointing to the importance of the $\langle r^{-3} \rangle$ and $Q$ terms discussed above. A more detailed interpretation of the $^{125}$Te NMR chemical shift data and of the subtle effects of $\alpha$, $\beta$, and $\gamma$ methyl substitution must await further experimental results.

The NMR chemical shifts for the halide derivatives $CH_2(Te(X)_2R)_2$ are given in Table III, and the shifts are more positive than those of the parent telluromethanes. On bonding the halogens to tellurium the shielding at the tellurium nucleus decreases significantly. The deshielding

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[11] Harris, R. K., Mann, B. E., Eds. "NMR and the Periodic Table"; Academic Press: New York, 1978; p 402.

**Table III. Tellurium-125 Chemical Shifts for the Halides $CH_2(Te(X)_2R)_2$**

| | $\delta^a$ | | $\delta^a$ |
|---|---|---|---|
| $CH_2(Te(Cl)_2Me)_2$ | 834 | $CH_2(Te(Cl)_2Ph)_2$ | 858.1 |
| $CH_2(Te(Br)_2Me)_2$ | 791,[b] 808[c] | $CH_2(Te(I)_2Ph)_2$ | 786 |
| $CH_2(Te(I)_2Me)_2$ | 786[c] | $CH_2(TeCl_3)_2$ | 1276.7 (1198[d]) |

[a] Chemical shifts, measured in $CDCl_3$ except where noted, relative to $Me_2Te$ neat. [b] $(CD_3)_2CO$ solution. [c] $(CH_3)_2SO$ solution. [d] From ref 9.

**Table IV. Tellurium-125 Mössbauer Parameters for the Bis(organyltelluro)methanes and Their Halide Derivatives**

| | $\delta^a$ | $\Delta$, mm $s^{-1}$ | $\Gamma_{av}$ |
|---|---|---|---|
| $(PhTe)_2CH_2$ | 0.26 | 11.1 | 6.5 |
| $(MeTe)_2CH_2$ | 0.23 | 10.4 | 6.4 |
| $(EtTe)_2CH_2$ | 0.30 | 10.6 | 6.2 |
| $(i\text{-}PrTe)_2CH_2$ | 0.21 | 10.4 | 6.0 |
| $CH_2(Te(Cl)_2Me)_2$ | 0.66 | 9.3 | 6.3 |
| $CH_2(Te(Br)_2Me)_2$ | 0.68 | 8.1 | 5.7 |
| $CH_2(Te(I)_2Me)_2$ | 0.55 | 6.3 | 5.4 |
| $CH_2(Te(Cl)_2Ph)_2$ | 0.70 | 8.4 | 6.0 |
| $CH_2(Te(Br)_2Ph)_2$ | 0.68 | 7.5 | 5.8 |
| $CH_2(Te(I)_2Ph)_2$ | 0.68 | 6.0 | 5.7 |
| $CH_2(TeCl_3)_2$ | 0.90 | 7.6 | 6.0 |

[a] Isomer shifts relative to I/Cu with source and absorbers at 4.2 K. The error in $\delta$ is ±0.08 mm $s^{-1}$ and in $\Delta$ ±0.10 mm $s^{-1}$. $\Gamma_{av}$ is the average linewidth.

is greatest in the chlorides and least in the iodides although the range of shifts is only small. This trend in the chemical shifts and the range of values observed is similar to that previously reported for the $R_2TeX_2$ halides.[12,13]

While the $^{125}Te$ chemical shift of the bis(methyltelluro)- (213.5 ppm) and bis(phenyltelluro)methanes (587.6 ppm) differ by some 364 ppm, the dihalide derivatives have very similar shifts. Thus, for example, the shifts of $CH_2(Te(Cl)_2Ph)_2$ (858 ppm) and $CH_2(Te(Cl)_2Me)_2$ (834 ppm) differ by only 24 ppm. This behavior is similar to, but more marked than, that of $Me_2Te$ and $Ph_2Te$ and their corresponding dihalides where the parent tellurides have shifts which differ by 688 ppm but the dichlorides by only 232 ppm. For the $CH_2(Te(X)_2R)_2$ compounds the chemical shifts appear to be dominated by the halogen ligands rather than by the $CH_2$ or R groups. However, at the same time within the dihalides the shifts are not strongly dependent on the electronegativity of the halogen.

The compound bis(trichlorotelluro)methane, $CH_2(TeCl_3)_2$, was also prepared and its $^{125}Te$ chemical shift in $CDCl_3$ solution found to be 1276.7 ppm in comparison with 834 ppm for $CH_2(Te(Cl)_2Me)_2$. The shielding at tellurium decreases as the number of chlorine ligands bonded to the tellurium increases as is also found for the $R_2TeX_2$ and $RTeX_3$ compounds.[11]

**Mössbauer Data.** The $^{125}Te$ Mössbauer data for the bis(organyltelluro)methanes and their halide derivatives are shown in Table IV. The parent telluromethanes $(PhTe)_2CH_2$ and $(MeTe)_2CH_2$ have large quadrupole splittings of 11.0 and 10.5 mm $s^{-1}$, respectively, and small positive isomer shifts with respect to I/Cu as a reference standard. These parameters are very similar to those of $Ph_2Te$ and $Me_2Te$.[15] There is no evidence from the Mössbauer parameters that the presence of a second tellurium in the Te–$CH_2$–Te linkage has any significant effect on the electronic environment at tellurium. The Mössbauer parameters are dominated by the fact that each tellurium is bonded to two carbon atoms. Indeed, even on changing the alkyl group from Me to *i*-Pr the Mössbauer parameters show no measurable change, in contrast with the NMR chemical shifts where relatively large changes were observed.

For the halide derivatives the Mössbauer isomer shifts are more positive than those in the parent telluromethanes, corresponding to an increase in the s electron density $|\Psi_s(0)|^2$ at the tellurium nucleus. This is consistent with the tellurium–halogen bonds being predominately p in character, the removal of 5p electron density from tellurium leading to a deshielding of the 5s electrons from the nucleus and an increase in $|\Psi_s(0)|^2$.

The quadrupole splittings for the halide derivatives reflect the p orbital imbalance resulting from the Te–C bonds on the one hand and the Te–halogen bonds on the other. As the electronegativity of the halogen decreases, the covalency of the tellurium–halogen bond increases and the quadrupole splittings decrease. The splittings for the $CH_2(Te(X)_2Me)_2$ compounds are very similar indeed to those previously reported for the corresponding $R_2TeX_2$ halides.[15] However, the quadrupole splittings for the phenyl compounds $CH_2(Te(X)_2Ph)_2$ are significantly smaller, at least for the chloride and bromide. The origin of this difference may lie in the stereochemical requirements of accommodating the bulky phenyl group and the halogen ligands about the two tellurium atoms in these molecules. In the $R_2TeX_2$ halides the environment about tellurium can be described as distorted trigonal bipyramidal with the organic ligands and a nonbonding pair of electrons in the equatorial plane and the halogen atoms in trans axial positions. However, there are invariably distant intermolecular tellurium-halogen bridging contacts in the equatorial plane. The solid-state packing may be significantly different in the $CH_2(Te(X)_2Ph)_2$ halides particularly when X = Cl or Br, leading to the somewhat smaller quadrupole splittings.

For $CH_2(TeCl_3)_2$ the difference is even more marked. The organotellurium trichlorides generally have isomer shifts of ca. 0.9 mm $s^{-1}$ and quadrupole splittings of ca. 9.0 mm $s^{-1}$. However, for $CH_2(TeCl_3)_2$ while $\delta$ is +0.90 mm $s^{-1}$, $\Delta$ is only 7.6 mm $s^{-1}$. The X-ray crystal structure of the $RTeCl_3$ compounds shows them to be polymeric with bridging Cl–Te bonds and the tellurium bonded to four chlorines roughly in a plane with the Te–R bond directed out of the plane. This coordination about tellurium may be difficult to achieve in $CH_2(TeCl_3)_2$ given the presence of two tellurium atoms separated only by a methylene group.

The $^{125}Te$ Mössbauer data suggests that it would be of interest to determine the X-ray crystal structures of both $CH_2(Te(Cl)_2Ph)_2$ and $CH_2(TeCl_3)_2$ since they may show rather different coordinations about tellurium than those observed in $Ph_2TeCl_2$ and $PhTeCl_3$, respectively.

## Experimental Section

**Preparation and Characterization of Compounds.** The bis(alkyltelluro)methanes were synthesized by adding an excess of diazomethane solution to the appropriate dialkyl ditelluride in anhydrous ether at 0 °C and stirring the reaction mixture at that temperature for 3 h. Excess diazomethane was then removed by bubbling nitrogen through the solution, and finally the ether was removed under vacuum. The resulting maloderous yellow liquids were characterized by the GC mass spectroscopy (HP 5985B) of $CH_2Cl_2$ solutions at 70 EV and in the temperature range 100–200 °C using a 15-m DB1 column. The prepared compounds exhibited the following characteristics, where the *m/e* values refer

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(15) Gruverman, I. J., Seidel, C. W., Eds. "Mössbauer Effect Methodology", Plenum: New York, 1976; Vol. 10, p 227.

to the $^{130}$Te mass peaks and correspond to the parent ion peak in each case: $CH_2(TeMe)_2$, retention time (minutes) 2.38, *m/e* 302; $CH_2(TeEt)_2$, retention time 3.68, *m/e* 330; $CH_2(Te\text{-}i\text{-}Pr)_2$, retention time 6.12, *m/e* 386; $CH_2(Te\text{-}s\text{-}Bu)_2$, retention time 6.05, *m/e* 386; $CH_2(Te\text{-}t\text{-}Bu)_2$, retention time 4.95, *m/e* 386. Bis(phenyltelluro)methane was prepared in the same way from diphenyl ditelluride and diazomethane and characterized by C and H analysis. Anal. Calcd for $C_{13}H_{12}Te_2$: C, 36.79; H, 2.83. Found: C, 36.88; H, 2.88.

The halide derivatives were prepared in essentially quantitative yield by reaction of the bis(methyltelluro)methanes with elemental halogen in $CCl_4$ at room temperature and were characterized by chemical analysis. Anal. Calcd for $C_3H_8Cl_4Te_2$: C, 8.18; H, 1.80. Found: C, 8.24; H, 1.77. Calcd for $C_3H_8Br_4Te_2$: C, 5.80; H, 1.29. Found: C, 5.89; H, 1.10. Calcd for $C_3H_8I_4Te_2$: C, 4.47; H, 0.99. Found: C, 4.46; H, 0.98. The halides of the bis(phenyltelluro)methanes were similarly prepared and characterized. Anal. Calcd for $C_{13}H_{12}Cl_4Te_2$: C, 27.56; H, 212. Found: C, 27.23; H, 2.06. Calcd for $C_{13}H_{12}Br_4Te_2$: C, 20.97; H, 1.61. Found: C, 20.07; H, 1.55. Calcd for $C_{13}H_{12}I_4Te_2$: C, 16.79; H, 1.29. Found: C, 16.68; H, 1.20. The trichloride $CH_2(TeCl_3)_2$ was prepared as previously described. Anal. Calcd for $CH_2Cl_6Te_2$: C, 2.49; H, 0.41. Found: C, 2.53; H, 0.33.

**Spectroscopic Characterization.** The $^{125}$Te NMR spectra were obtained on a Brüker WM 400 spectrometer at 126.24 MHz, operating at ambient temperature.[3,4] The resonances were found by utilizing 166-kHz sweep widths, 10-$\mu$s pulse widths, and a 0.01-s delay between acquisitions. Final spectra were obtained at the appropriate frequency, generally using a 5-kHz sweep width and 90° pulse widths with no delay. No broad-band decoupling was employed. Data acquisition consisted of 16K data points, which were zero filled to 32K data points for the Fourier transform. The line widths were 6–12 Hz. The $^{125}$Te chemical shifts were reported with reference to neat $Me_2Te$.

Mössbauer spectra were recorded by using a Harwell Instruments constant acceleration drive, based on a Harwell 200 series wave form generator and amplifier. A 2-mCi $^{125}$Sb/Cu source (New England Nuclear) was used. The source and absorbers were immersed in liquid helium in a Harwell Instruments Dewar. The 35.5-keV Mössbauer $\gamma$-ray was monitored through the 6-keV escape peak in a $Xe/CO_2$ proportional counter. The spectra were accumulated in a Nuclear Data 66 analyzer as 256-channel spectra and were subsequently computer-fitted to Lorentzians using the N.D. 66 as a computer terminal for transmitting data to, and for computation on, the University IBM 4341 main-frame computer. The spectrometer was routinely calibrated by using a $^{57}$Co/Rh source and an iron foil absorber at room temperature. The $^{125}$Te isomer shifts were reported with respect to $^{125}$I/Cu as a reference standard, and this entailed adding 0.15 mm s$^{-1}$ to the shifts measured against $^{125}$Sb/Cu as the source.

In recording the spectra of the liquid bis(alkyltelluro)methanes, 150 mg of liquid was absorbed onto a glass fiber filter paper mounted in a Teflon holder prior to freezing. This method of sample mounting ensured a more even distribution of the frozen liquid than that obtained simply on freezing the neat liquid in the Teflon absorber holder. Mössbauer parameters obtained on the frozen neat liquid and on the liquid absorbed into the filter paper were identical.

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**Registry No.** $(MeTe)_2CH_2$, 100207-53-2; $(i\text{-}BuTe)_2CH_2$, 100207-54-3; $(n\text{-}PrTe)_2CH_2$, 100207-55-4; $(n\text{-}BuTe)_2CH_2$, 100207-56-5; $(EtTe)_2CH_2$, 100207-57-6; $(s\text{-}BuTe)_2CH_2$, 100207-58-7; $(i\text{-}PrTe)_2CH_2$, 100207-59-8; $(t\text{-}BuTe)_2CH_2$, 100207-60-1; $(PhTe)_2CH_2$, 55136-88-4; $CH_2(Te(Cl)_2Me)_2$, 100207-47-4; $CH_2(Te(Br)_2Me)_2$, 100207-48-5; $CH_2(Te(I)_2Me)_2$, 100207-49-6; $CH_2(Te(Cl)_2Ph)_2$, 100207-50-9; $CH_2(Te(I)_2Ph)_3$, 100207-51-0; $CH_2(TeCl_3)_2$, 61002-75-3; $CH_2(Te(Br)_2Ph)_2$, 100207-52-1; $Me_2Te$, 593-80-6; $i\text{-}Bu_2Te$, 83817-01-0; $n\text{-}Pr_2Te$, 64501-17-3; $n\text{-}BuTe$, 38788-38-4; $Et_2Te$, 627-54-3; $s\text{-}Bu_2Te$, 83817-20-3; $i\text{-}Pr_2Te$, 51112-72-2; $t\text{-}Bu_2Te$, 83817-35-0; $Ph_2Te$, 1202-36-4; diazomethane, 334-88-3.

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# Synthesis and Structure of the Ortho-Metalated Dirhodium(II) Compound $Rh_2(O_2CCH_3)_3[(C_6H_4)P(C_6H_5)(C_6F_4Br)]\cdot P(C_6H_5)_2(C_6F_4Br)$

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Reaction of $Rh_2(O_2CCH_3)_4\cdot 2MeOH$ with the phosphine $P(C_6H_5)_2(C_6F_4Br)$ in $CH_2Cl_2$ leads to the bis(phosphine) adduct $Rh_2(O_2CCH_3)_4[P(C_6H_5)_2(C_6F_4Br)]_2$ (1) which was characterized by spectroscopic and chemical analysis. In refluxing toluene 1 is converted to the ortho-metalated dirhodium complex $Rh_2(O_2CCH_3)_3[P(C_6H_5)_2(C_6F_4Br)][(C_6H_4)P(C_6H_5)(C_6F_4Br)]$ (2) in ca. 50% yield. Molecules of 2 consist of a metal–metal bonded dirhodium unit which is bridged by two cisoid acetate groups as well as by a phosphine ortho metalated at one of the unsubstituted phenyl rings. The fourth equatorial coordination site on one rhodium atom is occupied by a phosphine which also provides the axial ligand by means of the bromine atom. On the other rhodium atom there is a chelating acetate ion that provides both equatorial and axial ligation. The compound crystallizes in the monoclinic space group $P2_1/n$ with cell parameters: $a = 16.656$ (10) Å, $b = 10.522$ (6) Å, $c = 24.978$ (11) Å; $\beta = 103.77$ (2); $V = 4251.6$ Å$^3$; $Z = 4$.

## Introduction

Dinuclear rhodium(II) complexes with a set of homoleptic bridging ligands are known in large numbers, and they have been extensively studied.[1] In contrast, only a limited number of dirhodium(II) complexes with a mixed set of bridging ligands is on record.[2]

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