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Synthesis and Characterization of Aryldihalo(dialkyl dithiophosphato)tellurium(IV) and Diarylbis(dialkyl dithiophosphato)tellurium(IV). Crystal Structures of *p*-$MeOC_6H_4TeBr_2[S_2P(OMe)_2]$ and $Ph_2Te[S_2P(OMe)_2]_2$

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Aryltellurium dithiophosphates of the type $RTeX_2[S_2P(OR')_2]$ and $R_2Te[S_2P(OR')_2]_2$ (R = *p*-$CH_3OC_6H_4$, C_6H_5; R′ = CH_3, C_2H_5, C_3H_7-*i*; X = Cl, Br) have been synthesized in 50–75% yields from the ammonium and sodium salts of the dithiophosphoric acid and the appropriate aryltellurium trihalide or diaryltellurium dichloride in CS_2 and characterized by elemental analyses and ^1H NMR, infrared, and Raman spectroscopy. The crystal structures of *p*-$MeOC_6H_4TeBr_2[S_2P(OMe)_2]$ (1) and $Ph_2Te[S_2P(OMe)_2]_2$ (7) were determined. Both compounds crystallized in the space group $P2_1/c$. The cell parameters for 1 are a = 9.694 (4) Å, b = 13.679 (4) Å, c = 13.879 (6) Å, β = 110.65 (3)°, V = 1722 (1) Å^3, Z = 4, and R = 0.0407 and for 7 are a = 7.820 (4) Å, b = 15.356 (8) Å, c = 20.317 (7) Å, β = 92.84 (3)°, V = 2437 (2) Å^3, Z = 4, and R = 0.0384. In 1, the dithiophosphate group is bidentate, while in 7 it is monodentate. In 1 the geometry around Te is that of a distorted square pyramid whereas in 7 it is that of a distorted saw-horse structure. In both cases a distorted octahedral configuration about tellurium is completed through one Te···Br secondary interaction in 1 and through two Te···S intramolecular interactions in 7.

Introduction

The studies reported here were stimulated by the volume of research into *O,O′*-dialkyl dithiophosphato compounds of the transition and main-group elements.[1,2] Two major reasons for this interest are their potential use as oil additives where they act as antioxidants and improve lubrication properties and the variety of binding modes that the dithiophosphate groups exhibit, i.e. monodentate, bidentate, and bridging. In a recent report on the preparation of alkyltellurium carboxylato compounds, it was suggested that such compounds may act as polymer-stabilizing agents.[3] Surprisingly there are relatively few previous reports of tellurium dithiophosphate and related compounds, exemplified by $Te[S_2P(OMe)_2]_2$,[4] $Te[S_2P(OEt)_2]_2$,[5] and $Te[N(Ph_2PS)_2]_2$.[6] In general, a variety of structures of tellurium compounds have been reported[7-15] that provide many examples of secondary bonding.

In this work we report the synthesis and characterization of two types of tellurium dithiophosphate compounds along with the structures of one example of both types, namely (*p*-methoxyphenyl)dibromo(*O,O′*-dimethyl dithiophosphato)tellurium(IV) and diphenylbis(*O,O′*-dimethyl dithiophosphato)tellurium(IV).

Experimental Section

Materials. $TeCl_4$ was obtained from Alfa Chemicals Ltd. and ammonium *O,O′*-dimethyl and diethyl dithiophosphate were obtained from Aldrich Chemical Co. The sodium isopropyl salt was made from P_4S_{10}, isopropyl alcohol, and sodium hydroxide.[16] $PhTeCl_3$ and Ph_2TeCl_2 were prepared by the reaction of $TeCl_4$ and Ph_3SnCl in toluene at room temperature and under reflux, respectively.[17] *p*-$MeOC_6H_4TeCl_3$ and (*p*-$MeOC_6H_4)_2TeCl_2$ were prepared from the reaction of anisole and $TeCl_4$.[18] $ArTeBr_3$ species were made by reducing the appropriate chloride to the Ar_2Te_2 species with subsequent reoxidation by Br_2 in CCl_4.[18]

Physical Measurements. All solvents were dried and distilled prior to use. The elemental analyses were performed by Guelph Chemical Laboratories, Guelph, Ontarrio, Canada. Density measurements were performed by the flotation method in CCl_4/CH_3I. The infrared spectra were recorded on a Perkin-Elmer 180 double-beam spectrophotometer as Nujol mulls on CsI plates. The Raman spectra of solid samples contained in sealed capillaries were measured on a Spectra-Physics 700 Raman spectrophotometer using the 4880-Å exciting line of an argon ion laser. ^1H NMR spectra were recorded on a Varian EM-360-(60MHz) spectrometer in CS_2 using Me_4Si as internal standard.

Synthesis of Compounds. The compounds synthesized and isolated are listed in Table I along with the analytical data and melting points. Moisture was carefully excluded from the reactions because products 1–5 were found to be very moisture-sensitive. The procedures given below provide representative examples of the preparative method. Other pertinent details of reactions are included in Table I.

1. (*p*-Methoxyphenyl)dibromo(*O,O′*-dimethyl dithiophosphato)tellurium(IV) (1), (*p*-$CH_3OC_6H_4)Br_2Te[S_2P(OCH_3)_2]$. Dry ammonium *O,O′*-dimethyl dithiophosphate (0.042 g, 0.22 mmol) was added to a stirred slurry of (*p*-methoxy-

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Table I. Reaction Conditions, Physical Appearance, and Analytical Data for the Tellurium Dithiophosphates

							analyses			
							calcd		found	
	no.	reactn time, h	yield, (%)	recrystn solv	colr	mp, °C	C	H	C	H
p-$CH_3OC_6H_4TeBr_2[S_2P(OMe)_2]$	1	2	74	$CHCl_3$/n-hexane	lemon yellow	121	19.57	2.36	19.74	2.60
p-$CH_3OC_6H_4TeBr_2[S_2P(OEt)_2]$	2	3	62	$CHCl_3$/n-hexane	lemon yellow	102	22.87	2.93	23.17	3.19
p-$CH_3OC_6H_4TeBr_2[S_2P(O$-i-$Pr)_2]$	3	3	46	$CHCl_3$/n-hexane	lemon yellow	134	25.67	3.46	26.02	3.70
p-$CH_3OC_6H_4TeCl_2[S_2P(OEt)_2]$	4	1/2	49	$CHCl_3$/n-hexane	yellow	97	26.91	3.46	26.90	3.66
$PhTeBr_2[S_2P(OEt)_2]$	5	4	66	$CHCl_3$/n-hexane	lemon yellow	123	21.83	2.73	22.12	2.97
$(p$-$CH_3OC_6H_4)_2Te[S_2P(OMe)_2]_2$	6	4	66	CS_2	pale yellow	109	32.95	3.99	33.20	4.31
$Ph_2Te[S_2P(OMe)_2]_2$	7	4	62	CS_2	pale yellow	116	32.24	3.72	31.99	3.56
$(p$-$CH_3OC_6H_4)_2Te[S_2P(OEt)_2]_2$	8	4	72	CS_2/n-hexane	pale yellow	61	37.10	4.78	37.08	4.56
$Ph_2Te[S_2P(OEt)_2]_2$	9	4	67	CS_2/n-hexane	pale yellow	93	36.83	4.60	36.78	4.72
$(p$-$CH_3OC_6H_4)_2Te[S_2P(O$-i-$Pr)_2]_2$	10	6	42	CS_2/n-hexane	colorless	95	40.64	5.47	40.61	5.76
$Ph_2Te[S_2P(O$-i-$Pr)_2]_2$	11	6	57	n-hexane	colorless	113	40.70	5.37	40.51	5.69

phenyl)tellurium tribromide (0.103 g, 0.22 mmol) in CS_2 (5 mL). The mixture was stirred at room temperature for 30 min and then filtered. The solvent was evaporated at 0 °C under vacuum, leaving a gummy yellow residue. The residue was recrystallized from 1:1 chloroform/n-hexane at −4 °C and dried under vacuum; yield 0.09 g (74%). One more recrystallization yielded crystals suitable for X-ray analysis.

2. Diphenylbis(*O*,*O*′-dimethyl dithiophosphato)tellurium(IV) (7), $(C_6H_5)_2Te[S_2P(OCH_3)_2]_2$. Dry ammonium *O*,*O*′-dimethyl dithiophosphate (0.25 g, 1.2 mmol) was added to diphenyltellurium dichloride (0.20 g, 0.57 mmol) in CS_2 (5 mL) while stirring. The mixture was refluxed for 3 h, cooled, and filtered. The filtrate was concentrated to approximately 1 mL under vacuum. n-Hexane (1 mL) was added, and the product was crystallized out by cooling to −4 °C; yield 0.27 g (72%).

Structure Determination. X-ray diffraction data for 1 and 7 were collected on a Syntex $P2_1$ diffractometer by the procedures already described.[19] A prismatic crystal of 1 was sealed in a capillary because of the moisture-sensitive nature of the compound, while that of 7 was mounted on a glass fiber. For both 1 and 7, the space group $P2_1/c$ was established from systematic absences ($h0l$, $l = 2n + 1$; $0k0$, $k = 2n + 1$). The least-squares refinement of the setting angles of 15 and 32 high angle reflections $15 < 2\theta < 30°$ for 1 and $15 < 2\theta < 35°$ for 7, respectively, leads to the cell dimensions given in Table II. During data collection, the intensities of three monitor reflections measured after 60 reflections decreased by approximately 3 and 1%, respectively, for 1 and 7, and so the appropriate scaling factors were applied. Each set of data was corrected for Lorentz and polarization effects, and analytical absorption corrections were applied. A summary of crystal and refinement data is given in Table II.

The position of the tellurium atom was determined by a sharpened Patterson synthesis using SHELX, and difference maps revealed the remaining atoms. Complete anisotropic refinement by full-matrix least-squares methods minimizing the function $\sum w(|F_o| - |F_c|)^2$ converged at $R = 0.0407$ (1) and 0.0384 (7) and $R_w = 0.0417$ (1) and 0.0430 (7). Hydrogen atoms were included at the idealized positions (C–H = 0.95 Å; CCH = 109.5°; HCH = 120°) with isotropic U's set at 0.01 Å^2 greater than that of the corresponding carbon atom. A weighting scheme of the form $w = 1/[\sigma^2(F) + pF^2]$ was employed with final p values of 0.000 01 for 1 and 0.001 37 for 7. A peak of the order of 1.1 e Å^{-3} (at 0.162, 0.240, 0.193) was found in the final difference map of 7 at 1.51 Å from C(1), suggesting some disorder around that methoxy group. However, no evidence of secondary extinction was found in either of the two data sets.

The final atomic coordinates and isotropic thermal parameters for non-hydrogen atoms are listed in Tables III and IV, with the important bond lengths and angles in Tables V and VI. The molecular structures of the two compounds are displayed in Figures 1 and 2.

Results and Discussion

The tellurium dithiophosphate compounds were made by simple metathetical reactions between the appropriate ammonium or sodium *O*,*O*′-dialkyl dithiophosphate and the organotellurium halides.

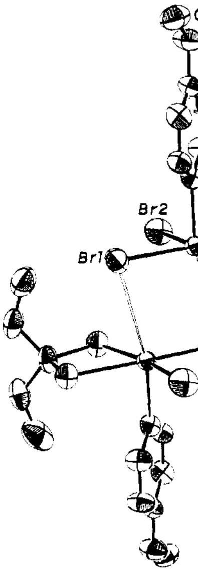

Figure 1. ORTEP plot of the molecule p-$MeOC_6H_4TeBr_2[S_2P(OMe)_2]$ (1). The atoms are drawn with 50% probability ellipsoids. Hydrogen atoms are omitted for clarity. Secondary bonds are shown as open bonds.

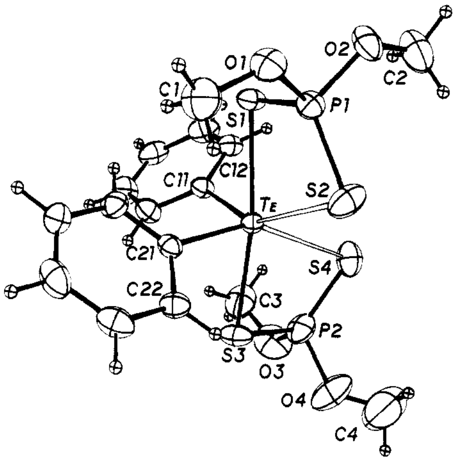

Figure 2. ORTEP plot of $Ph_2Te[S_2P(OMe)_2]_2$ (7).

$$RTeX_3 + NH_4S_2P(OR')_2 \xrightarrow[CS_2]{23\ °C} RTeX_2[S_2P(OR')_2] + NH_4X$$

$$R_2TeCl_2 + 2NaS_2P(OR')_2 \xrightarrow[CS_2]{reflux} R_2Te[S_2P(OR')_2]_2 + 2NaCl$$

$$R = p\text{-}MeOC_6H_4, Ph;\ R' = Me, Et, i\text{-}Pr;\ X = Cl, Br$$

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Table II. Summary of Crystal Data, Intensity Collection, and Structural Refinement of p-$CH_3OC_6H_4TeBr_2[S_2P(OCH)_3]_2$ (1) and $(C_6H_5)_2Te[S_2P(OCH_3)_2]_2$ (7)

	1	7
formula	$C_9H_{13}S_2PO_3Br_2Te$	$C_{16}H_{22}S_4P_2O_4Te$
cell constants	a = 9.694 (4) Å, b = 13.679 (4) Å, c = 13.879 (6) Å, β = 110.65 (3)°	a = 7.820 (4), b = 15.356 (8) Å, c = 20.317 (7) Å, β = 92.84 (3)°
cell vol, Å^3	1722 (1)	2437 (2)
cryst system	monoclinic	
space group	$P2_1/c$	
mol wt	551.7	596.2
Z	4	
ρ_{obsd}, ρ_{calcd}, g cm^{-3}	2.13, 2.10	1.63, 1.63
cryst dimens, mm	0.10 × 0.12 × 0.25	0.14 × 0.19 × 0.37
abs coeff μ, cm^{-1}	64.62	15.79
min abs corr	2.797	1.238
max abs corr	4.379	1.324
radiatn	Mo Kα, λ = 0.710 69 Å	
monochromator	highly oriented graphite	
temp, °C	17 ± 2	21 ± 1
2θ angle, deg	4–50	3–50
scan type	coupled θ(crystal)/2θ(counter)	
scan width	Kα_1 − 1° to Kα_2 + 1°	
scan speed, deg min^{-1}	variable, 3.91–9.77	variable, 2.02–4.88
bkgd time/scan time	0.5	
total reflcns measd	3535 (+h,+k,±l)	5080
unique data used	1909 [$I > 3\sigma(I)$]	3032
no. of parameters (NP)	163	244
$R = (\sum\lVert F_o\rvert - \lvert F_c\rVert/\sum\lvert F_o\rvert)$	0.0407	0.0384
$R_w = [\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\sum w\lvert F_o\rvert^2]^{1/2}$	0.0417	0.0430
$\Delta\rho_{max}$, e Å^{-3}	0.72	1.08
shift/error (max)	0.005	0.08

Table III. Final Fractional Coordinates and Isotropic Thermal Parameters for Non-Hydrogen Atoms of p-$MeOC_6H_4TeBr_2[S_2P(OMe)_2]$ (1) with Standard Deviations in Parentheses

	x	y	z	10^3U_{eq},^{a} Å^2
Te	0.29945 (6)	−0.04723 (4)	0.42421 (4)	42.3 (3)
Br(1)	0.4265 (1)	0.0335 (1)	0.3007 (1)	66 (1)
Br(2)	0.2419 (1)	0.1222 (1)	0.4890 (1)	74 (1)
S(1)	0.1790 (3)	−0.1446 (2)	0.5379 (2)	55 (2)
S(2)	0.3319 (3)	−0.2387 (2)	0.3815 (2)	63 (2)
P	0.2299 (3)	−0.2685 (2)	0.4802 (2)	59 (2)
O(1)	0.0908 (10)	−0.3353 (5)	0.4336 (6)	79 (4)
O(2)	0.3208 (9)	−0.3386 (5)	0.5696 (5)	75 (4)
O(3)	0.3164 (7)	−0.5481 (5)	0.4288 (5)	71 (4)
C(1)	−0.0295 (15)	−0.3033 (8)	0.3437 (11)	105 (10)
C(2)	0.4614 (14)	−0.3070 (8)	0.6419 (9)	87 (8)
C(3)	0.3328 (13)	−0.5772 (8)	0.5308 (7)	73 (6)
C(11)	0.0940 (10)	−0.0480 (6)	0.2998 (6)	43 (4)
C(12)	−0.0324 (11)	−0.0191 (7)	0.3192 (7)	55 (6)
C(13)	−0.1674 (11)	−0.0194 (7)	0.2400 (7)	61 (7)
C(14)	−0.1784 (10)	−0.0515 (7)	0.1429 (7)	53 (6)
C(15)	−0.0507 (11)	−0.0818 (6)	0.1257 (7)	49 (5)
C(16)	0.0824 (11)	−0.0778 (7)	0.2041 (7)	52 (6)

[a] U_{eq} is calculated from the refined anisotropic thermal parameters ($U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i{}^*a_j{}^*\mathbf{a}_i\cdot\mathbf{a}_j$).

All compounds dissolve well in common organic solvents such as CS_2, CCl_4, and $CHCl_3$. The dihalo compounds 1–5 are very moisture sensitive, while the bis compounds 6–11 are air-stable for periods up to at least a week. The diphenyltellurium compounds are stable over an indefinite period of time.

The Crystal Structure of (p-$MeOC_6H_4$)$TeBr_2[S_2P(OMe)_2]$ (1). The singel-crystal X-ray structure (Figure 1) shows the geometry around the tellurium atom as that of a distorted square pyramid with the bromine atoms, cis to one another, and the sulfur atoms of the dithiophosphate ligand in the basal positions. The organo group occupies the apical position. The square plane is slightly distorted with Br(2) and S(2) positioned almost in the plane and Br(1) and S(1) positioned below the plane by 0.0025 (2) Å. The tellurium atom is situated above the plane by 0.0055 (6) Å. Because the bite angle of the dithiophosphate group (STeS = 75.8 (1)°) is considerably less than 90°, the other angles in the square plane are all obtuse (Table V).

Table IV. Final Fractional Coordinates and Isotropic Thermal Parameters for Non-Hydrogen Atoms of $Ph_2Te[S_2P(OMe)_2]_2$ (7) with Standard Deviations in Parentheses

	x	y	z	10^3U_{eq}, Å^2
Te	0.27814 (4)	0.26071 (2)	0.43510 (2)	37.2 (2)
S(1)	−0.0303 (2)	0.2824 (1)	0.3813 (1)	49 (1)
S(2)	0.1935 (3)	0.1312 (1)	0.3028 (1)	76 (1)
S(3)	0.5902 (2)	0.2633 (1)	0.4890 (1)	63 (1)
S(4)	0.3290 (3)	0.1286 (1)	0.5665 (1)	87 (2)
P(1)	−0.0188 (2)	0.1955 (1)	0.3055 (1)	49 (1)
P(2)	0.5523 (3)	0.1815 (1)	0.5649 (1)	77 (1)
O(1)	−0.0740 (6)	0.2444 (3)	0.2399 (2)	64 (3)
O(2)	−0.1882 (6)	0.1390 (3)	0.3070 (2)	72 (3)
O(3)	0.6175 (9)	0.2265 (5)	0.6293 (3)	113 (5)
O(4)	0.7144 (11)	0.1211 (6)	0.5619 (6)	186 (8)
C(1)	0.0355 (1)	0.3086 (6)	0.2119 (4)	89 (6)
C(2)	−0.2106 (12)	0.0791 (5)	0.3593 (4)	100 (6)
C(3)	0.5182 (14)	0.2915 (6)	0.6577 (5)	106 (7)
C(4)	0.7334 (18)	0.0409 (8)	0.5667 (7)	197 (16)
C(11)	0.2020 (7)	0.3525 (4)	0.5069 (3)	43 (3)
C(12)	0.0646 (7)	0.3307 (4)	0.5437 (3)	53 (4)
C(13)	0.0224 (9)	0.3853 (5)	0.5957 (4)	72 (5)
C(14)	0.1154 (9)	0.4603 (5)	0.6074 (3)	69 (5)
C(15)	0.2457 (9)	0.4833 (5)	0.5693 (3)	68 (4)
C(16)	0.2922 (8)	0.4283 (4)	0.5191 (3)	56 (4)
C(21)	0.3747 (7)	0.3502 (3)	0.3655 (3)	42 (3)
C(22)	0.5132 (7)	0.3223 (4)	0.3302 (3)	51 (3)
C(23)	0.5705 (9)	0.3795 (5)	0.2828 (3)	66 (4)
C(24)	0.4933 (10)	0.4584 (5)	0.2698 (3)	75 (5)
C(25)	0.3537 (9)	0.4825 (4)	0.3053 (4)	66 (4)
C(26)	0.2969 (8)	0.4292 (4)	0.3538 (3)	53 (4)

The structure is clearly related to that of p-$EtOC_6H_4TeBr_3$,[5] which is dimerized through bromine bridges. Substitution of the bridged bromine atoms by the sulfur atoms of the dithiophosphate group leads to the structure of 1. The dithiophosphate ligand is thus bidentate and the tellurium atom is pentacoordinated. Other examples of pentacoordinated tellurium compounds

Table V. Interatomic Distances (Å) and Angles (deg) in $p\text{-MeOC}_6\text{H}_4\text{TeBr}_2[\text{S}_2\text{P(OMe)}_2]^a$ (1)

Te–Br(1)	2.677 (1)	Br(1)–Te–Br(2)	93.3 (1)
Te–Br(2)	2.616 (1)	Br(1)–Te–S(1)	173.9 (1)
Te–S(1)	2.632 (3)	Br(2)–Te–S(1)	92.8 (1)
Te–S(2)	2.728 (2)	Br(1)–Te–S(2)	98.2 (1)
Te–C(11)	2.127 (8)	Br(2)–Te–S(2)	168.5 (1)
S(1)–P	2.009 (3)	S(1)–Te–S(2)	75.8 (1)
S(2)–P	1.993 (4)	Br(1)–Te–C(11)	89.6 (2)
P–O(1)	1.567 (8)	Br(2)–Te–C(11)	91.8 (2)
P–O(2)	1.570 (7)	S(1)–Te–C(11)	89.9 (2)
O(1)–C(1)	1.44 (1)	S(2)–Te–C(11)	88.0 (2)
O(2)–C(2)	1.44 (1)	Te–S(1)–P	88.0 (1)
O(3)–C(3)	1.42 (1)	Te–S(2)–P	85.6 (1)
ring C(11)–C(16)[b]		S(1)–P–S(2)	110.6 (2)
mean C–C	1.38 (2)	S(1)–P–O(1)	111.1 (3)
mean C–C–C	120.0 (8)	S(2)–P–O(1)	113.5 (3)
		S(1)–P–O(2)	110.4 (3)
		S(2)–P–O(2)	113.0 (3)
		O(1)–P–O(2)	97.5 (4)
Te···Br(1)′	3.810 (1)	P–O(1)–C(1)	119.7 (7)
		P–O(2)–C(2)	119.7 (6)
		Te–C(11)–C(12)	118.3 (6)
		Te–C(11)–C(16)	121.8 (7)
		C(11)–Te···Br(1)′	159.4 (2)

[a] Symmetry-equivalent position: the prime indicates $1 - x, -y, 1 - z$. [b] Esd's on mean values have been calculated with the use of the Scatter formula $\sigma = [\sum(d_i - \bar{d})^2/(N - 1)]^{1/2}$, where d_i is the ith and $\bar{d}$ is the mean of N equal measurements.

Table VI. Interatomic Distances (Å) and Angles (deg) in $\text{Ph}_2\text{Te}[\text{S}_2\text{P(OMe)}_2]_2$ (7)

Te–S(1)	2.619 (1)	S(1)–Te–S(3)	171.8 (1)
Te–S(2)	3.383 (2)	S(2)–Te–S(4)	106.7 (1)
Te–S(3)	2.625 (2)	S(1)–Te–S(2)	66.7 (1)
Te–S(4)	3.362 (2)	S(3)–Te–S(4)	66.9 (1)
Te–C(11)	2.133 (5)	S(1)–Te–C(11)	85.3 (1)
Te–C(21)	2.136 (5)	S(3)–Te–C(11)	89.4 (1)
S(1)–P(1)	2.045 (2)	S(1)–Te–C(21)	89.5 (1)
S(2)–P(1)	1.934 (2)	S(3)–Te–C(21)	85.1 (1)
S(3)–P(2)	2.022 (3)	C(11)–Te–C(21)	98.5 (2)
S(4)–P(2)	1.928 (3)	Te–S(3)–P(2)	98.1 (1)
P(1)–O(1)	1.572 (4)	S(1)–P(1)–S(2)	115.1 (1)
P(1)–O(2)	1.585 (5)	S(1)–P(1)–O(1)	107.8 (2)
P(2)–O(3)	1.544 (7)	S(2)–P(1)–O(1)	114.8 (2)
P(2)–O(4)	1.575 (7)	S(1)–P(1)–O(2)	105.9 (2)
O(1)–C(1)	1.441 (8)	S(2)–P(1)–O(2)	116.2 (2)
O(2)–C(2)	1.422 (9)	O(1)–P(1)–O(2)	94.8 (3)
O(3)–C(3)	1.406 (11)	S(3)–P(2)–S(4)	116.3 (1)
O(4)–C(4)	1.244 (12)	S(3)–P(2)–O(3)	108.3 (3)
ring C(11)–C(16)		S(4)–P(2)–O(3)	115.8 (3)
		S(3)–P(2)–O(4)	100.8 (4)
mean C–C	1.380 (10)[a]	S(4)–P(2)–O(4)	118.9 (4)
mean C–C–C	120.0 (6)	O(3)–P(2)–O(4)	93.6 (5)
ring C(21)–C(26)		P(1)–O(1)–C(1)	121.2 (5)
		P(1)–O(2)–C(2)	120.2 (5)
mean C–C	1.382 (10)	P(2)–O(3)–C(3)	120.0 (6)
mean C–C–C	120.0 (7)	P(2)–O(4)–C(4)	132.4 (11)
		Te–C(11)–C(12)	117.5 (4)
		Te–C(11)–C(16)	121.6 (4)
		Te–C(21)–C(22)	116.9 (4)
		Te–C(21)–C(26)	121.0 (4)

[a] Esd's on mean values have been calculated with the use of the Scatter formula $\sigma = [\sum(d_i - \bar{d})^2/(N - 1)]^{1/2}$, where d_i is the ith and $\bar{d}$ is the mean of N equal measurements.

adopting square-pyramidal geometry are $[p\text{-PhOC}_6\text{H}_4\text{TeCl}_4]^-$,[9] $[\text{MeTeI}_4]^-$,[10] and $(p\text{-PhOC}_6\text{H}_4\text{TeCl}_3)_2$.[13] It is generally assumed that the square-pyramidal structure arises because the sixth position of an octahedral arrangement about tellurium is occupied by a lone pair of electrons. However, in these compounds this position also provides the site of secondary bond interactions. Thus the tellurium atom is apparently involved in a secondary bond interaction with the Br(1) atom of an adjacent molecule $(1 - x, -y, 1 - z)$, which links the two molecules base to base into a loosely held dimer. The C(1)–Te···Br(1)′ angle is 159.4 (2)°, and the Te···Br(1)′ distance is 3.810 (1) Å, which is significantly less than the sum of the van der Waals radii of 4.15 Å.[20] The observed range for Te···Br secondary interactions in other organotellurium bromides is 3.564–3.930 Å.[7,8,11,21] The secondary interaction results in a slight lengthening of the Te–Br(1) bond (2.677 (1) Å) as compared to the Te–Br(2) bond (2.616 (1) Å). The two Te–Br distances are longer than the Te–Br(terminal) distances (2.527 (3) and 2.509 (3) Å) but shorter than Te–Br(bridging) distances (2.992 (3) and 2.940 (3) Å) in dimeric $p\text{-EtOC}_6\text{H}_4\text{TeBr}_3$.[5] The sum of the single covalent bond radii of tellurium and bromine is 2.51 Å.[20] The unusually long Te–Br distances in 1 could be a reflection of the strong trans influence of the two sulfur atoms of the dithiophosphate ligand as has been suggested for Te(II) thiourea complexes. In $\text{PhTe(tu)}_2\text{Cl}$ and *cis*-$\text{Te(tu)}_2\text{X}_2$ (tu = thiourea; X = Cl, Br),[22,23] it was claimed that the Te–X bonds are longer than normal because they are trans to Te–S bonds. The Te–Br distances 1 are similar to the axial Te–Br bond distances in trigonal-bipyramidal 1-thia-4-telluracyclohexane 4,4-dibromide, $\text{C}_4\text{H}_8\text{STeBr}_2$ (2.689 (2) and 2.657 (2) Å),[8] as well as in 2-biphenyltellurium tribromide, $\text{C}_{12}\text{H}_8\text{TeBr}_3$ (2.675 (1) and 2.647 (1) Å).[11]

The average Te–S bond distance of 2.679 (3) Å is considerably longer than that reported for $\text{Te}[\text{S}_2\text{P(OMe)}_2]_2$,[9] 2.440 (5) Å, and $\text{Te}[\text{S}_2\text{P(OEt}_2)_2]_2$,[5] 2.410 (1) Å (average). In $\text{Te}[\text{S}_2\text{COR}]_2$,[24-26] the average Te–S distances are 2.505 (1), 2.483 (12), and 2.488 (4) Å for methyl, ethyl, and isopropyl derivatives, respectively. This is probably the result of the different oxidation states and coordination numbers of the tellurium atom in the two types of systems, because similarly marked differences were noted for Te–S bonds in the dithiocarbamate derivatives of Te(II) and Te(IV), the average Te–S bond distance in $\text{Te}[\text{S}_2\text{CNEt}_2]_2$[27] and $\text{PhTe}[\text{S}_2\text{CNEt}_2]_3$[28] being 2.518 (4) and 2.743 (3) Å, respectively.

However, there are significant differences in the two Te–S distances and this difference is related to the two P–S distances. The shorter Te–S(1) bond (2.631 (3) Å) is associated with the longer P–S(1) bond (2.009 (3) Å) and is trans to the longer Te–Br(1) bond, while the longer Te–S(2) bond (2.728 (2) Å) is associated with the shorter P–S(2) bond (1.993 (4) Å) and is trans to the shorter Te–Br(2) bond. The range of P–S bond lengths is as expected for a dithiophosphate group in its bidentate mode. Thus, for example, in $\text{Ph}_2\text{Sn}[\text{S}_2\text{P(O-}i\text{-Pr)}_2]_2$,[29] the distances are 2.006 (2) and 1.990 (2) Å, and in $\text{Fe}[\text{S}_2\text{P(O-}i\text{-Pr)}_2]_3$,[30] the distances are 2.007 (3) and 1.998 (2) Å. All other bond distances and angles are as expected.

The Crystal Structure of $\text{Ph}_2\text{Te}[\text{S}_2\text{P(OMe)}_2]_2$ (7). This compound crystallizes in discrete molecular units (Figure 2), where the geometry about tellurium can be

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described as being based on a distorted saw horse structure or a trigonal bipyramid in which a long pair occupies a basal position. The dithiophosphate groups are monodentate with the bonding sulfur atoms occupying the axial positions. The S–Te–S angle is 171.8 (1)°. The carbon atoms of the two phenyl groups attached to tellurium occupy two of the basal positions, such that the C–Te–C angle is 98.5 (2)°. The STeC angles are close to 90° as is to be expected with the Te–C distances being typical of those found for other R_2TeX_2 types of compounds.[6,26]

The two Te–S distances of 2.619 (1) and 2.625 (2) Å are very similar to each other but are shorter, as is to be expected, than the distances found in 1, where the average distance in the bidentate linkage is 2.680 (3) Å. The two dithiophosphate ligands are positioned in such a way that the nonbonded sulfur atoms S(2) and S(4) approach the tellurium atom at distances of 3.383 (2) and 3.362 (2) Å, respectively. A comparison of these distances with Te···Cl secondary bond distances (3.4–3.7 Å)[7,9,13,15,31] relative to the van der Waals distances of 4.05 Å (between Te and S) and 4.00 Å (between Te and Cl) suggests that the Te···S interactions may be regarded as secondary interactions. If such is the case, then these sulfur atoms would apparently complete a distorted octahedral configuration about the tellurium atom, which has been found in the majority of organotellurium compounds.[8–11,13,15,31] Other Te···S contacts of a similar nature have been reported for $Te[S_2P(OMe)_2]_2$,[4] 3.306 (5) Å, (2-(phenylazo)phenyl-*C*,*N*′)-tellurium(II) dithiocarbamate ($(PhN_2C_6H_4)Te[S_2CNMe_2]$),[14] 3.225 (3) Å, $PhTe[S_2CNEt_2]_3$,[28] 3.228 (4) Å, and 1-thia-4-telluracyclohexane 4,4-dibromide ($C_4H_8STeBr_2$),[8] 3.588 (4) Å. However, the description of a distorted octahedral seems less appropriate when it is noted that the secondary bonded S atoms are considerably above and below the plane formed by the two carbon and tellurium atoms (i.e. C(11), C(21), and Te) by 1.59 (2) Å. Thus it may be more appropriate to describe the secondary bonds, if indeed they exist, as being formed in positions to avoid a stereochemically active lone pair. Further, the average bite angle of 66.8 (2)° is considerably less than that in the bidentate ligand of compound 1, 75.8 (1)°.

The P—S bond lengths (2.045 (2) and 2.022 (3) Å) and P=S bond lengths (1.934 (2) and 1.928 (3) Å) are similar to those observed in $Ph_2Sn[S_2P(OEt)_2]_2$[29] in which the dithiophosphate groups show anisobidentate bonding. However, these distances are also virtually the same as those in the compounds where the dithiophosphate groups are monodentate, e.g. in $Ph_3Ge[S_2P(OMe)_2]$[33] (2.060 (2) and 1.923 (2) Å) and $Ph_3Sn[P(OEt)_2]$[34] (2.054 (1) and 1.93 (1) Å), and so the Te···S interactions appear to have little effect on P–S bond distances.

Vibrational Spectra. Characteristic features of the infrared and Raman spectra of compounds 1–11, excluding those associated with the well-known phenyl vibrations,[35] are displayed in Table VII.

The assignment of ν(POR) and $\nu(PO_2)$ in dithiophosphate compounds has been the subject of some controversy.[16] In a recent publication on germanium dithiophosphates, we discussed this in some detail and concluded that ν(POR) bands can be expected in the 1015–965 cm^{-1}

Table VII. Selected Infrared and Raman Bands (in cm^{-1}) in the Spectra of the Tellurium Dithiophosphates[a,b]

$RTeX_2[S_2P(OR')_2]_2$					$R_2Te[S_2P(OR')_2]_2$						
1	2	3	4	5	6	7	8	9	10	11	assignt
1048 sh	1044 s, b	1048 m	1049 sh	1049 w	1065 sh	1063 sh	1050 sh	1048 sh	1055 sh	1051 sh	ν(POR′,asym)
1008 vs	999 vs	1007 vs, b	1004 vs, b	1003 vs, b	1016 s, b	1014 vs, b	1014 vs, b	1020 vs, b	1027 vs, b	989 vs, b	ν(POR′,sym)
819 m	815 s	818 m	819 s, b	811 sh	810 s	805 m	822 m	818 sh	823 m		$\nu(PO_2$,asym)
785 vs, br	784 s	785 s	792 sh	778 m	787 s		790 s	785 s	770 m	770 m	$\nu(PO_2$,sym)
607 m	607 m	598 m	608 m	606 m	662 s	643 vs	649 s	643 s	643 s	641 s	$\nu(PS_2$,asym)
518 m	509 s	517 m	513 m	517 m	517 s	521 w	516 m	510 m	515 m	520 m	$\nu(PS_2$,sym)
293 w	282 w	288 w	300 vb	270 w	385 m	372 m	370 w	368 w	366 w	382 w	$\nu(TeS_2$,asym)
(294) [66]	(286) [49]	(288) [42]	(294) [100]	(270) [18]	(304) [60]	(287) [72]	(288) [100]	(304) [100]	(293) [82]	(304) [89]	$\nu(TeS_2$,sym)
209 w	203 w	196 w	250 sh, vb	196 w							$\nu(TeX_2$,asym)
(194) [87]	(203) [100]	(196) [100]	(253) [91]	(196) [100]							$\nu(TeX_2$,sym)

[a] Parentheses denote Raman active band; with square brackets denoting relative intensities below 400 cm^{-1}. [b] s = strong, m = medium, w = weak, sh = shoulder, b = broad, v = very.

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Table VIII. ^{1}H NMR Data for the Tellurium Dithiophosphates[a,b]

compd no.	$\delta(C_6H_4/C_6H_5)$	$^3J_{H-H}$	$\delta(CH_3OC_6H_4)$	$\delta(CH_3/CH_2CHOP)$	CH_3	$^3J_{HP}$	$^3J_{H-H}$
1	8.51 (d, 2 H)						
	6.92 (d, 2 H)	9	3.86 (s, 3 H)	3.47 (d, 6 H)		16	
2	8.41 (d, 2 H)						
	7.30 (d, 2 H)	9	3.80 (s, 3 H)	3.73 (dq, 4 H)	1.13 (t, 6 H)	12	8
3	8.45 (d, 2 H)						
	6.97 (d, 2 H)	9	3.86 (s, 3 H)	4.19 (dsep, 1 H)	1.08 (d, 12 H)	16	7
4	8.46 (d, 2 H)						
	7.09 (d, 2 H)	9	3.96 (s, 3 H)	3.85 (dq, 4 H)	1.36 (t, 6 H)	10	7
5	8.5, 7.3 (m, 5 H)			3.62 (dq, 4 H)	1.13 (t, 6 H)	10	7
6	7.75 (d, 4 H)						
	6.85 (d, 4 H)	9	3.80 (s, 6 H)	3.41 (d, 12 H)		15	
7	7.9, 7.4 (m, 10 H)			3.37 (d, 12 H)		15	
8	7.83 (d, 4 H)						
	6.94 (d, 4 H)	10	3.84 (s, 6 H)	3.81 (dq, 8 H)	1.16 (t, 12 H)	10	8
9	7.9, 7.4 (m, 10 H)			3.85 (dq, 8 H)	1.15 (t, 12 H)	12	8
10	7.75 (d, 4 H)	9	3.75 (s, 6 H)	4.43 (dsep, 4 H)	1.12 (d, 12 H)	12	6
	6.82 (d, 4 H)						
11	7.8, 7.3 (m, 10 H)			4.30 (dsep, 4 H)	1.09 (t, 12 H)	12	
				4.30 (dsep, 4 H)	1.09 (t, 12 H)	12	6

[a] Chemical shifts in ppm relative to internal Me_4Si recorded in CS_2; coupling constants in Hz. [b] Number of hydrogen atoms given in parentheses, s = singlet, d = doublet, t = triplet, q = quartet, sep = septet, m = multiplet.

region and $\nu(PO_2)$ bands in the 875–730 cm^{-1} region.[33] The bands associated with the dithiophosphate groups in the tellurium compounds **1**–**11** are readily assigned on the basis of this conclusion.

The assignments of the P–S vibrations in the free acids $HS_2P(OR)_2$ and their esters $R'S_2P(OR)_2$ clearly fall into two regions: 670–630 cm^{-1}, assignable to $\nu(PS_2$,asym) or $\nu(P{=}S)$, and 520–540 cm^{-1}, assignable to $\nu(PS_2$,sym) or $\nu(P{-}S)$.[36] The same is true where the dithiophosphate ligand is monodentate as in $Ph_2Ge[S_2P(OMe)_2]_2$.[33] However, it may not be diagnostic of the type of linkage as similar assignments have been reported when the ligand is bidentate as in $In[S_2P(OR)_2]_3$.[37] It is clear from Table VIII that in compounds **1**–**5**, where the dithiophosphate group is bidentate, $\nu(PS_2$,asym) occurs at significantly lower wavenumber than does the same vibration in compounds **6**–**11**, where the ligand is monodentate. This suggests that in the latter case the bond more closely resembles a P=S bond and the X-ray structures does show that the shortest P—S bond is in compound **7**.

The assignments of the Te–S stretching modes are consistent with those reported for some tellurium dithiocarbamates.[38] In compounds **6**–**11**, there are no other reasonable assignments possible to the peaks in the region and in compounds **1**–**5**, the Te–Br stretching modes can be selected by comparison with other aryltellurium(IV) halides.[39,40] In compounds **6**–**11** the two bands readily assignable to $\nu(TeS_2$,asym) and $\nu(TeS_2$sym) have average values of 372 and 297 cm^{-1}, respectively. The relatively large separation between the asymmetric and symmetric modes suggest that the STeS angle should be closer to 180° than 90°. In compound **7**, the STeS angle is actually 171.8 (1)°. By contrast, only one band, or possibly two bands split only very slightly, can be seen in the infrared and Raman spectra of compounds **1**–**5** at an average position of 287 cm^{-1}. The lower wavenumber and lack of separation suggest that in general the Te–S bonds should be weaker in compounds **1**–**5** and that the STeS angle should be closer to 90°. The STeS angle in compound **1** is in fact constrained to 75.8 (1)°, and the Te–S bonds are longer than those in compound **7**. It might be added that as far as the vibrational spectra are concerned, there is no evidence of secondary Te···S bonding. However, in these compounds at least, there is a distinction between bidentate and monodentate linkages.

As with the Te–S stretching vibrations, the Te–X (X = Cl, Br) vibrations show little splitting between the asymmetric and symmetric modes is to be expected with a BrTeBr angle in **1** of 93.3 (1)°. The value of ca. 200 cm^{-1} for ν(TeBr) compares well with that of other compounds containing a tellurium–bromine bond,[39,40] particularly in Ph_2TeBr_2.[39] Similarly, the TeCl stretches in Ph_2TeCl_2 are assigned in the 167–280 region. The appearance of the two peaks in the Raman spectrum at 253 and 294 cm^{-1} are such that it is possible that both $\nu(TeS_2$,sym) and $\nu(TeCl_2$,sym) occur at ca. 274 cm^{-1} and that they are in Fermi resonance. It is clear that the assignments of $\nu(TeX_2)$ are entirely consistent with relatively weak and hence longer Te–X bonds as is indicated by the crystal structure.

^{1}H NMR Spectra. The details of the ^{1}H NMR spectra for compounds **1**–**11** are summarized in Table VIII. The relative peak heights and splitting patterns are entirely consistent with the stoichiometry of the groups attached to tellurium and the two solid-state structures. Thus, in the ^{1}H NMR spectrum of **1**, the C_6H_4 ring protons are seen as a pair of doublets, each of intensity corresponding to 2 H, centered at 8.51 and 6.92 ppm with ^2J(HH) = 9 Hz. The methoxy (phenyl) group is seen as a singlet, of intensity corresponding to 3 H, at 3.86 ppm while the methoxy (phosphorus) groups are seen as doublets, of intensity equivalent to 6 H, with ^3J(HP) = 16 Hz. Compounds **2**–**4** show similar features, with similar chemical shifts, for the $CH_3OC_6H_4$– groups, and the features associated with the $(C_2H_5O)_2P$ and $(i\text{-}C_3H_7O)_2P$ groups of the dithiophosphate groups are exactly as expected for simple first-order spectra, as they are in compound **5**. Thus, the ^{1}H NMR spectra of compounds **1**–**5** are at least consistent with the assumption that they have the same basic structure in solution as compound **1** has in the solid state.

The ^{1}H NMR spectrum of **7** shows a similar multiplet as in **5** typical of a phenyl group. Similarly, the methoxy (phosphorus) groups are seen as doublets at 3.37 ppm, corresponding to an intensity of 12 H, with ^3J(PH) = 15

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Hz. The spectrum is therefore consistent with the solid-state structure. The ^{1}H NMR spectra of **6** to **11** recorded immediately after dissolution are equally well seen to be consistent with the presence of the two dithiophosphate groups and hence consistent with the solid-state structure of **7**. However, while the ^{1}H NMR spectra of **1**–**5** show no change when re-recorded after some time, the spectra of **6**–**11**, each show the appearance of an additional set of peaks of the same multiplicity and relative heights of the original set. Thus, **6**–**11** undergo isomerism in solution while **1**–**5** do not.

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Registry No. 1, 106799-90-0; 2, 106799-91-1; 3, 106799-92-2; 4, 106799-93-3; 5, 106799-94-4; 6, 106820-90-0; 7, 106820-91-1; 8, 106820-92-2; 9, 106820-93-3; 10, 106820-94-4; 11, 106820-95-5; *O,O'*-dimethyl dithiophosphate, 756-80-9; (*p*-methoxyphenyl)tellurium tribromide, 36309-69-0; diphenyltellurium dichloride, 1206-36-6.

Supplementary Material Available: Unit cell packing diagrams, tables of anisotropic thermal parameters for non-hydrogen atoms, and tables of final fractional coordinates and thermal parameters for hydrogen atoms (7 pages); tables of observed and calculated structure factors (30 pages). Ordering information is given on any current masthead page.

Structural and Bonding Features of the Methoxymethylidyne Ligand in Cluster Complexes. X-ray Crystal Structures of $Co_3(\mu_3\text{-}COCH_3)(CO)_9$ and $Fe_3(\mu_3\text{-}COCH_3)(\mu\text{-}CO)_2(CO)_6(\eta\text{-}C_5H_5)$

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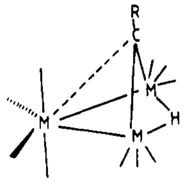
The methoxymethylidyne cluster complexes $Co_3(\mu_3\text{-}COCH_3)(CO)_9$ (**1**) and $Fe_3(\mu_3\text{-}COCH_3)(\mu\text{-}CO)_2(CO)_6(\eta\text{-}C_5H_5)$ (**2**) have been examined by X-ray diffraction. Complex **1** crystallizes in the triclinic space group $P\bar{1}$ (No. 2) with a = 8.0125 (6) Å, b = 8.3823 (4) Å, c = 12.3052 (7) Å, α = 93.011 (5)°, β = 102.025 (5), γ = 104.890 (5)°, V = 777.12 (9) Å^3, and D_{calcd} = 2.02 g cm^{-3} for Z = 2 and M_r 471.94. Data were collected for $1.5 \leqslant \theta \leqslant 30°$ with graphite-monochromated X-radiation (Mo Kα). The structure was refined to R = 0.026 (R_w = 0.035) for 3528 observed reflections [$I \geqslant 2.5\sigma(I)$]. The three Co–Co separations are identical within error [Co(1)–Co(2) = 2.478 (1), Co(1)–Co(3) = 2.478 (1), and Co(2)–Co(3) = 2.480 (1) Å], while there is a slight but significant asymmetry in the $Co_3(\mu_3\text{-}C)$ moiety [Co(1)–C(10) = 1.882 (2), Co(2)–C(10) = 1.912 (2), and Co(3)–C(10) = 1.906 (2) Å]. The plane of the μ_3-COCH$_3$ ligand is perpendicular to the Co(2)–Co(3) vector (angle between normal to plane and Co–Co = 0.63°), resulting in near idealized mirror symmetry for **1**. Complex **2** crystallizes in the monoclinic space group $P2_1/n$ (No. 14) with a = 9.336 (2) Å, b = 18.896 (2) Å, c = 9.936 (2) Å, β = 99.65 (2)°, V = 1728.0 (6) Å^3, and D_{calcd} = 1.92 g cm^{-3} for Z = 4 and M_r 499.7. Data were collected as above for $2 \leqslant \theta \leqslant 25°$ with the structure refined to R = 0.032 (R_w = 0.044) for 2131 observed [$I \geqslant 2.5\sigma(I)$] data. The triiron triangle [Fe(1)–Fe(2) = 2.582 (1), Fe(1)–Fe(3) = 2.547 (1), and Fe(2)–Fe(3) = 2.524 (1) Å] is capped by a slightly asymmetric μ_3-COCH$_3$ ligand [Fe(1)–C(9) = 1.905 (5), Fe(2)–C(9) = 1.935 (5), and Fe(3)–C(9) = 1.952 (5) Å]. The two μ-carbonyl ligands bridge to the unique iron atom, which also bears the cyclopentadienyl group, while both the other iron atoms are ligated to three terminal carbonyl groups. Although the cluster fragment "$Fe_3(\mu\text{-}CO)_2(CO)_6(\eta\text{-}C_5H_5)$" has pseudomirror symmetry, the orientation of the μ_3-COCH$_3$ ligand, approximately parallel to the Fe(1)–Fe(2) axis (angle between normal to plane and Fe–Fe = 90.39°) removes this symmetry element from **2**. Extended Hückel MO calculations on **1** and **2** show that the differing observed orientations of the COCH$_3$ group lie close in energy, with a small barrier to rotation or inversion. The bonding capabilities of the COCH$_3$ moiety have similarities to both CO and the alkylidyne ligand CR. Calculations on the model complexes $Fe_3(\mu\text{-}H)(\mu\text{-}CR)(CO)_{10}$ (R = H, OCH$_3$) allow a rationalization of the differing "semi-μ_3" interactions found in related osmium species and indicate that their divergent electrophilic behavior may be frontier orbital controlled.

Introduction

Since the initial report by Shriver et al.[1] on the methylation of the bridging carbonyl ligand in $[Fe_3(\mu\text{-}H)(\mu\text{-}CO)(CO)_{10}]^-$ resulting in the methoxymethylidyne complex $Fe_3(\mu\text{-}H)(\mu\text{-}CR)(CO)_{10}$ (**1a**, R = OCH$_3$), several other cluster species including the ruthenium[2] and osmium[3] analogues of **1a** have been prepared by similar routes. Polynuclear compounds containing the COCH$_3$ ligand bridging two, three, and four metal atoms are now known. Examples in the first class include $[Fe_2(\mu\text{-}COCH_3)(\mu\text{-}CO)(Ph_2PCH_2CH_2PPh_2)(\eta\text{-}C_5H_5)_2]^+$ (providing a rare example of synthesis by alkylation of a *neutral* carbonyl complex)[4] and the recently reported[5] FeMn(μ-COCH$_3$)(μ-



$M_3(\mu\text{-}H)(\mu\text{-}CR)(CO)_{10}$

(M = Fe; R = OCH$_3$ **1a**, R = H **1b**)
(M = Os; R = H **2a**, R = OCH$_3$ **2b**,
R = Ph **2c**, R = CH$_2$CHMe$_2$ **2d**)

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