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Silver(I) Complexes of Dichloromethane and 1,2-Dichloroethane

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Abstract: The complexes $[Ag(CH_2Cl_2)(OTeF_5)]_2$ (**1**), $[Ag(1,2\text{-}C_2H_4Cl_2)(OTeF_5)]_2$ (**2**), $Ag_2(CH_2Cl_2)_4Pd(OTeF_5)_4$ (**3**), and $Ag_2(1,2\text{-}C_2H_4Cl_2)_4Pd(OTeF_5)_4$ (**4**) have been prepared and studied by solution conductimetry, by tensimetric titrations with dichloromethane vapor, and by IR, Raman, liquid and solid ^{13}C NMR, and ^{35}Cl NQR spectroscopy. In addition, the structures of compounds **2**, **3**, and **4** have been determined by single-crystal X-ray diffraction methods: **2**, orthorhombic, *Pbca*, $a = 13.371$ (5) Å, $b = 8.192$ (2) Å, $c = 32.720$ (9) Å, $Z = 4$, $T = -120$ °C, $R = 0.052$; **3**, triclinic, $P\bar{1}$, $a = 8.923$ (2) Å, $b = 9.953$ (3) Å, $c = 9.985$ (2) Å, $\alpha = 114.23$ (2)°, $\beta = 100.54$ (2)°, $\gamma = 91.42$ (2)°, $Z = 1$, $T = -130$ °C, $R = 0.041$; **4**, triclinic, $P\bar{1}$, $a = 9.571$ (2) Å, $b = 10.314$ (3) Å, $c = 10.399$ (2) Å, $\alpha = 106.37$ (2)°, $\beta = 91.98$ (2)°, $\gamma = 112.21$ (2)°, $Z = 1$, $T = -127$ °C, $R = 0.025$. These compounds provide the first unambiguous evidence that simple chlorinated hydrocarbons can coordinate to metal ions. The Ag–Cl distances span the ranges 2.626 (3)–3.000 (3) Å (**2**), 2.775 (2)–2.882 (2) Å (**3**), and 2.645 (1)–2.928 (1) Å (**4**) and are all much shorter than the sum of van der Waals radii for silver and chlorine, 3.45 ± 0.05 Å. Dichloromethane and 1,2-dichloroethane coordinate to the Ag(I) ions in bidentate fashion, forming four- (**3**) and five-membered chelate rings (**2**, **4**). In addition, a chlorine atom in **2** bridges two Ag(I) ions. The Ag(I) ions are coordinated to two (**2**), three (**2**), or four (**3**, **4**) chlorine atoms from dichloromethane or 1,2-dichloroethane molecules. Bond distances and angles for the coordinated chlorocarbon molecules are not significantly different than for the corresponding noncoordinated molecules. Solid-state spectroscopic data, including $\nu(CCl)$ stretching frequencies, ^{13}C NMR chemical shifts, and ^{35}Cl NQR frequencies, show the effects of coordination on the spectra of the parent solvent molecules, criteria that can be used to demonstrate chlorocarbon coordination in the absence of a crystal structure. Tensimetric titrations of AgX solids with dichloromethane vapor show the order of formation of a 1:1 $AgX{\cdot}CH_2Cl_2$ complex is $X^- = OTeF_5^-$ ($P_{1/2} = 4$ (1) Torr) > $^1/_2Pd(OTeF_5)_4^{2-}$ ($P_{1/2} = 14$ (1) Torr) > SbF_6^- ($P_{1/2} = 22$ (1) Torr) ≫ Cl^- (AgCl showed no evidence of complex formation with dichloromethane). The unsolvated compounds $AgOTeF_5$ and $Ag_2Pd(OTeF_5)_4$ are weak electrolytes in dichloromethane and 1,2-dichloroethane, suggesting that small amounts of $Ag(CH_2Cl_2)_n^+$ and $Ag(1,2\text{-}C_2H_4Cl_2)_n^+$ may be produced. The compound $AgOTeF_5$, while stable indefinitely dissolved in dichloromethane, 1,2-dichloroethane, 1,1,2-trichloroethane, and 1,1,2,2-tetrachloroethane, rapidly forms AgCl and other organic products when dissolved in trichloromethane, tetrachloromethane, 1,1-dichloroethane, *trans*-1,2-dichlorocyclohexane, 1-chloro-2,2,2-trifluoroethane, and 1-chlorobutane.

One of the key concepts of homogeneous catalysis by metal complexes is that reactants are brought together in close proximity, and generally activated, by coordination to "vacant" coordination sites on the metal center. Enhancing the degree of "coordinative unsaturation" is thought to be synonymous with enhancing the activity of the catalyst.[4] However, except for those cases where steric hindrance prevents the coordination of a full complement of ligands to a metal ion, achieving genuine coordinative unsaturation *in solution* is an extremely difficult if not impossible task.[5] Part of the challenge is that most ligands L in a potentially unsaturated complex ML_{n-1} are quite versatile at filling the vacant site—either by bridging two or more metal ions or by coordinating another atom of the ligand to the metal ion. In the former case, dinuclear or oligonuclear complexes that are coordinatively saturated are formed, while in the latter case, the ligand becomes bidentate and chelated complexes that are coordinatively saturated are formed.[6] An even more vexing part of the challenge is the presence of the solvent, which is a potential ligand (even if a weak one) and is present at concentrations of 10 M or greater. Thus, even when carefully designed ligands that cannot readily bridge two metal ions or cannot be bidentate are used, solvated coordination sites, not vacant sites, may be the closest chemists can get to "coordinative unsaturation".

In the context described above, the activity of a catalyst would be inversely related to the strength of the metal–solvent bonds. There are few, if any, commonly used polar solvents that are more weakly basic than dichloromethane and 1,2-dichloroethane. Indeed, dichloromethane is frequently referred to as a "noncoordinating solvent",[7] and 1,2-dichloroethane was assumed to be noncoordinating in Gutmann's classic study of solvent donor numbers.[8] In this paper we report the synthesis and characterization of four new silver(I) complexes containing coordinated dichloromethane and 1,2-dichloroethane molecules.[9] Our results include the structures of three of the complexes, which represent the first precise structural results for metal complexes with simple chlorocarbon ligands. The structural results allow a meaningful analysis of spectroscopic data to be made and prove that chlorocarbons exhibit many of the tendencies of more traditional ligands. For example, our results show that chlorocarbons with more than one chlorine atom can function as polydentate ligands, that a chlorocarbon chlorine atom can bridge two metal ions, and that chlorocarbon chlorine atoms can be the predominant ligand type in the coordination sphere of a metal ion.

The nascent field of halocarbon coordination chemistry has brought together inorganic chemists, organometallic chemists, and biochemists.[10] (For our purposes, a halocarbon is defined as a mono- or polyhalogenated aliphatic or aromatic hydrocarbon—it

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(4) Parshall, G. W. *Homogeneous Catalysis*; Wiley-Interscience: New York, 1980; p 17.

(5) In the context of this discussion, the term "metal ion" includes zero-valent metal atoms in soluble complexes.

(6) *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergammon: Oxford, 1987; Vol. 2.

(7) This terminology has been used in many papers. Two recent examples are: (a) Bond, A. M.; Ellis, S. R.; Hollenkamp, A. F. *J. Am. Chem. Soc.* **1988**, *110*, 5293. (b) Siedle, A. R.; Newmark, R. A.; Korba, G. A.; Pignolet, L. H.; Boyle, P. D. *Inorg. Chem.* **1988**, *27*, 1593.

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(9) Some of these results have been published in two preliminary reports: (a) Colsman, M. R.; Noirot, M. D.; Miller, M. M.; Anderson, O. P.; Strauss, S. H. *J. Am. Chem. Soc.* **1988**, *110*, 6886. (b) Newbound, T. D.; Colsman, M. R.; Miller, M. M.; Wulfsberg, G. P.; Anderson, O. P.; Strauss, S. H. *J. Am. Chem. Soc.* **1989**, *111*, 3762.

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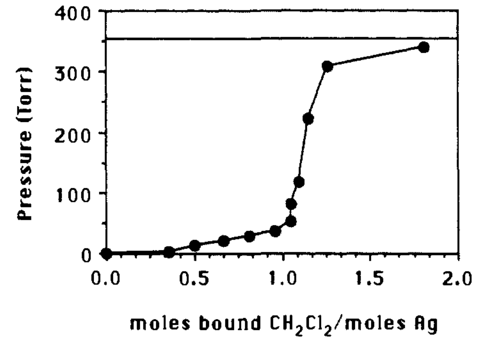

Figure 1. Tensimetric titration of $Ag_2Pd(OTeF_5)_4$ with dichloromethane. The pressure in the apparatus is due to dichloromethane vapor only. The straight horizontal line at 353.3 Torr represents the vapor pressure of dichloromethane at 20.0 °C.

contains no other heteroatoms.) Besides serving as the best model for "coordinative unsaturation" in condensed phases, halocarbon coordination will allow synthetic chemists to study the binding of other weakly basic ligands to metal ions and the activation of the halocarbons toward substitution reactions. In addition, halocarbon coordination will allow organometallic chemists to study the postulate that M–XR bonds form prior to oxidative addition of alky and aryl halides to some metal complexes[11] and biochemists to study the postulate that a Fe–F–C linkage causes the inhibition of the enzyme aconitase by fluorocitrate.[12] Despite the difficulty in isolating and completely characterizing $L_nM(RCl)_m$ complexes, this paper and other recent reports in the literature[13-16] continue to foster the expectation that halocarbons, which have ligand strengths far weaker than other main group alkyls such as amines, phosphines, ethers, and sulfides, will be found to have a rich and varied coordination chemistry.

Results

Preparation and Stability of 1–4. The four new chlorocarbon solvated silver(I) complexes are $[Ag(CH_2Cl_2)(OTeF_5)]_2$ (**1**), $[Ag(1,2\text{-}C_2H_4Cl_2)(OTeF_5)]_2$ (**2**), $Ag_2(CH_2Cl_2)_4Pd(OTeF_5)_4$ (**3**), and $Ag_2(1,2\text{-}C_2H_4Cl_2)_4Pd(OTeF_5)_4$ (**4**). The solvent-free compounds $AgOTeF_5$ and $Ag_2Pd(OTeF_5)_4$ can be prepared by removing all traces of dichloromethane solvent from **1** or **3**, respectively.

$$\mathrm{AgF} + \mathrm{HOTeF_5} \xrightarrow[3\ \mathrm{h},\ 25\ ^\circ\mathrm{C}]{\mathrm{CH_2Cl_2}} \underset{\mathbf{1}}{[\mathrm{Ag(CH_2Cl_2)(OTeF_5)}]_2} + \mathrm{HF} \tag{1}$$

$$\underset{\mathbf{1}}{[\mathrm{Ag(CH_2Cl_2)(OTeF_5)}]_2} \underset{\mathrm{vacuum}}{\overset{\mathrm{CH_2Cl_2}}{\rightleftharpoons}} \mathrm{AgOTeF_5} \tag{2}$$

$$4\mathrm{AgOTeF_5} + \mathrm{PdCl_2} \xrightarrow[24\ \mathrm{h,\ reflux}]{\mathrm{CH_2Cl_2}} 2\mathrm{AgCl} + \underset{\mathbf{3}}{\mathrm{Ag_2(CH_2Cl_2)_4Pd(OTeF_5)_4}} \tag{3}$$

$$\underset{\mathbf{3}}{\mathrm{Ag_2(CH_2Cl_2)_4Pd(OTeF_5)_4}} \underset{\mathrm{vacuum}}{\overset{\mathrm{CH_2Cl_2}}{\rightleftharpoons}} \mathrm{Ag_2Pd(OTeF_5)_4} \tag{4}$$

Table I. Equivalent Conductances (22 °C) in Dichloromethane and 1,2-Dichloroethane[a]

compd	concn, M	10^3 × equivalent conductance, Ω^{-1} cm^{-1} M^{-1} CH$_2$Cl$_2$	10^3 × equivalent conductance, Ω^{-1} cm^{-1} M^{-1} 1,2-C$_2$H$_4$Cl$_2$
$AgOTeF_5$	0.0101	0.14	0.52
$Ag_2Pd(OTeF_5)_4$	0.0100	2.9	14.4
$N(n\text{-}Bu)_4^+ClO_4^-$	0.0100	13.8	
$N(n\text{-}Bu)_4^+OTeF_5^-$	0.0100	14.8	15.2
$(N(n\text{-}Bu)_4^+)_2Pd(OTeF_5)_4^{2-}$	0.0100	15.6	16.4

[a] The specific conductance of both pure solvents was ≤3 × 10^{-7} Ω^{-1} cm^{-1}.

Table II. ^{13}C NMR Spectral Data[a]

compd	liquid state: neat solvent	liquid state: satd soln	solid state: MAS	solid state: CP–MAS	$\Delta\delta$[b]
CH_2Cl_2	54.1				
1	54.1		58.0, 56.4	58.0	3.9
3	54.1	54.2[c]	57.4, 55.8	57.6	3.5
$1,2\text{-}C_2H_4Cl_2$	43.9				
2	43.9		50.0, 48.5	50.0	6.1
4	43.9	45.0[d]	48.9, 47.4	48.9	5.0

[a] ppm from external Me_4Si; solid-state values are ±0.2 ppm. [b] The difference in ppm between the chemical shift for the resonance observed in the solid-state MAS experiment and the chemical shift for the neat liquid solvent. [c] $[Ag_2Pd(OTeF_5)_4]$ = 0.35 M. [d] $[Ag_2Pd(OTeF_5)_4]$ = 0.66 M.

Despite the stoichiometric simplicity of eqs 1 and 2, AgF did not react with neat $HOTeF_5$ (mp 39 °C[17]) in the absence of dichloromethane to form HF and $AgOTeF_5$. The presence of excess $PdCl_2$ in the synthesis of **3** (eq 3) had no effect on the products; no $Pd(OTeF_5)_2$ was produced. Furthermore, the reaction shown in eq 3 proceeded to completion more rapidly when a trace (~1%) of 1,2-dichloroethane was added to the reaction mixture; however, *complete* removal of 1,2-dichloroethane by evacuation (as in eq 4) proved difficult. Poor yields of **4** were obtained when neat 1,2-dichloroethane was substituted for dichloromethane in eq 3.

Equations 2 and 4 were found to be reversible, i.e., the solid compounds $AgOTeF_5$ and $Ag_2Pd(OTeF_5)_4$ readily absorbed dichloromethane vapor. Tensimetric titrations of $AgOTeF_5$, $Ag_2Pd(OTeF_5)_4$, $AgSbF_6$, and AgCl with dichloromethane vapor in a grease-free and O-ring-free apparatus showed moderate to strong binding of this chlorocarbon solvent to the first three solids, but no observable binding to AgCl. A titration curve for $Ag_2Pd(OTeF_5)_4$ is shown in Figure 1. We define $P_{1/2}$ as the pressure of dichloromethane necessary to bind one dichloromethane molecule to half of the Ag(I) ions in the sample. The strongest binding of dichloromethane was to $AgOTeF_5$ ($P_{1/2}$ = 4 (1) Torr), followed by $Ag_2Pd(OTeF_5)_4$ ($P_{1/2}$ = 14 (1) Torr) and $AgSbF_6$ ($P_{1/2}$ = 22 (1) Torr). Even at 353.3 Torr, which is the vapor pressure of dichloromethane at 20.0 °C, none of the dichloromethane in the titration apparatus was bound to AgCl.

The facile, reversible loss of solvent from **1–4** made the handling of these compounds difficult. Details of the preparation of samples for IR, Raman, NMR, NQR, and X-ray diffraction experiments are given in the Experimental Section. Unlike **1–4**, precise amounts of the solvent-free compounds $AgOTeF_5$ and $Ag_2Pd(OTeF_5)_4$ could be measured out by weighing samples on a balance in a glovebox under a purified nitrogen atmosphere. However, all six compounds were extremely hygroscopic, rapidly absorbing moisture from the air or from incompletely dried glassware or solvents.

Characterization of Halocarbon Solutions of 1–4. (a) Conductimetry. Equivalent conductances were measured for 0.0100 M dichloromethane and 1,2-dichloroethane solutions of $AgOTeF_5$, $N(n\text{-}Bu)_4^+OTeF_5^-$, $Ag_2Pd(OTeF_5)_4$, and $(N(n\text{-}Bu)_4^+)_2Pd(OTeF_5)_4^{2-}$. In addition, equivalent conductances were measured

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Table III. Details of the X-ray Diffraction Studies of **1–4**

compd	**1**	**2**	**3**	**4**
formula	$[Ag(CH_2Cl_2)OTeF_5]_2$	$[Ag(1,2\text{-}C_2H_4Cl_2)OTeF_5]_2$	$Ag_2(CH_2Cl_2)_4Pd(OTeF_5)_4$	$Ag_2(1,2\text{-}C_2H_4Cl_2)_4Pd(OTeF_5)_4$
molecular formula	$C_2H_4Ag_2Cl_4F_{10}O_2Te_2$	$C_4H_8Ag_2Cl_4F_{10}O_2Te_2$	$C_4H_8Ag_2Cl_8F_{20}O_4PdTe_4$	$C_8H_{16}Ag_2Cl_8F_{20}O_4PdTe_4$
formula wt, g mol^{-1}	862.78	890.84	1616.24	1672.36
space group		*Pbca*	$P\bar{1}$	$P\bar{1}$
unit cell dimensions				
a, Å	10.342 (6)	13.371 (5)	8.923 (2)	9.571 (2)
b, Å	16.131 (7)	8.192 (2)	9.953 (3)	10.314 (3)
c, Å	10.325 (5)	32.720 (9)	9.985 (2)	10.399 (2)
α, deg	90	90	114.23 (2)	106.37 (2)
β, deg	101.91 (4)	90	100.54 (2)	91.98 (2)
γ, deg	90	90	91.42 (2)	112.21 (2)
unit cell vol, Å^3	1685	3584	790.1	900.3
Z		4	1	1
calcd density, g cm^{-3}		3.30	3.40	3.08
cryst dimens, mm		0.40 × 0.40 × 0.55	0.30 × 0.38 × 0.47	0.20 × 0.16 × 0.40
data collection temp, °C	−80 (1)	−120 (1)	−130 (1)	−127 (1)
radiation (λ, Å)	Mo Kα (0.7107)	Mo Kα	Mo Kα	Mo Kα
monochromator	graphite	graphite	graphite	graphite
abs coeff, cm^{-1}		61.2	63.1	54.7
scan type	θ–2θ	θ–2θ	θ–2θ	θ–2θ
scan speed, deg min^{-1}	variable (2–30)	variable (2–30)	variable (2–30)	variable (2–30)
2θ range, deg		4–50	4–55	4–55
reflctns		h,k,l	$\pm h,-k,\pm l$	$\pm h,-k,\pm l$
total no. of reflcns measured		3764	3972	4546
no. of obsd reflcns, $\lvert F_o\rvert > 2.5\sigma(F_o)$		2709	3399	4001
data/param ratio		12.5	17.3	18.7
R		0.052	0.041	0.025
R_w		0.057	0.045	0.027
GOF		2.11	1.63	2.24
g (refined)		0.0005	0.0007	0.0001
slope of normal probability plot		1.48	1.41	1.84

for a 0.0100 M dichloromethane solution of $N(n\text{-}Bu)_4{}^+ClO_4{}^-$. These data are listed in Table I.

(b) ^{13}C NMR Spectroscopy. Solutions of $AgOTeF_5$ in dichloromethane or 1,2-dichloroethane exhibited only one ^{13}C NMR resonance from room temperature down to the freezing point of the solvent—separate resonances for free and coordinated chlorocarbon molecules were not observed. Carbon-13 NMR data for saturated dichloromethane and 1,2-dichloroethane solutions of $Ag_2Pd(OTeF_5)_4$ are listed in Table II. When this compound was dissolved in a 50:50 (mol:mol) mixture of dichloromethane and 1,2-dichloroethane ($[Ag_2Pd(OTeF_5)_4]$ = 0.65 M), the resonance for dichloromethane was not shifted relative to the free solvent values, while that for 1,2-dichloroethane *was* shifted by 0.9 ppm relative to the free solvent value (Figure 2).

(c) Solubility in CH_2Cl_2 and 1,2-$C_2H_4Cl_2$ and Reactions with Other Halocarbons. At 22 °C, saturated solutions of $AgOTeF_5$ and $Ag_2Pd(OTeF_5)_4$ in dichloromethane were found to be >2.5 and 0.35 M, respectively. In 1,2-dichloroethane, the solubilities were found to be >2.5 and 0.65 M, respectively. In contrast, the solubility of $AgClO_4$ in dichloromethane at 22 °C was found to be 0.0006 M, and that of $AgBF_4$ is reported to be ~0.01 M.[18] When care was taken to exclude moisture rigorously, dichloromethane and 1,2-dichloroethane solutions of $AgOTeF_5$ and $Ag_2Pd(OTeF_5)_4$ were stable indefinitely (i.e., no AgCl was formed). In addition, $AgOTeF_5$ dissolved in 1,1,2-trichloroethane and 1,1,2,2-tetrachloroethane without the formation of AgCl. However, $AgOTeF_5$ rapidly formed AgCl and organic products when dissolved in trichloromethane, tetrachloromethane, 1,1-dichloroethane, *trans*-1,2-dichlorocyclohexane, 1-chloro-2,2,2-trifluoroethane, and 1-chlorobutane. In the case of 1-chlorobutane, ^{13}C and ^{19}F NMR spectra revealed that the products were *n*-$BuOTeF_5$,[19] *s*-$BuOTeF_5$,[19] $HOTeF_5$,[20] and *trans*-2-butene. Neither $AgOTeF_5$ nor $Ag_2Pd(OTeF_5)_4$ dissolved to any extent in 1,1,2-trichlorotrifluoroethane (F-113). However, addition of $B(OTeF_5)_3$ to a mixture of $AgOTeF_5$ and F-113 caused some $AgOTeF_5$ to dissolve, presumably due to the following equilibrium:

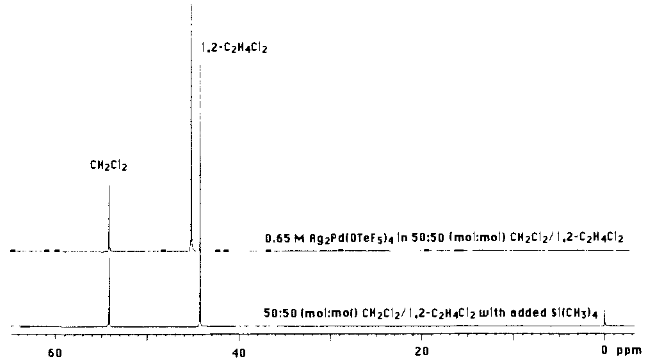

Figure 2. Liquid ^{13}C NMR spectra: 0.65 M $Ag_2Pd(OTeF_5)_4$ in 50:50 (mol:mol) CH_2Cl_2/1,2-$C_2H_4Cl_2$ (top trace) and 50:50 (mol:mol) CH_2Cl_2/1,2-$C_2H_4Cl_2$ with Me_4Si added (bottom trace).

$$AgOTeF_5(s) + B(OTeF_5)_3(soln) \rightleftharpoons Ag(F\text{-}113)_n{}^+B(OTeF_5)_4{}^-(soln)$$

Characterization of 1–4 as Solids. (a) X-ray Crystallography. Experimental parameters for the crystallographic studies are listed in Table III. Bond distances and angles for **2**, **3**, and **4** are listed in Tables IV and V. Drawings of **2**, **3**, and **4** are shown in Figure 3. Compound **2** (Figure 3) consists of dinuclear molecules, each with a Ag_2O_2 core and one bidentate 1,2-dichloroethane molecule per Ag(I) ion. The dimers are linked by intermolecular Ag–Cl and Ag–F bonds. Figure 4 shows that Ag1 is weakly bonded to F3 in one neighboring dimer (F3′) and F4 in another (F4″) besides being bonded to O1, O2, Cl1, and Cl2, while Ag2 is bonded to Cl3′ and weakly bonded to F2′ and F1″ besides being bonded to O1, O2, Cl3, and Cl4. The coordination spheres of six-coordinate Ag1, a distorted octahedron, and seven-coordinate Ag_2, a distorted pentagonal bipyramid, are shown in Figure 5. The five-membered $\overline{\text{Ag–Cl–C–C–Cl}}$ chelate rings adopt puckered conformations, as shown in Figure 6.

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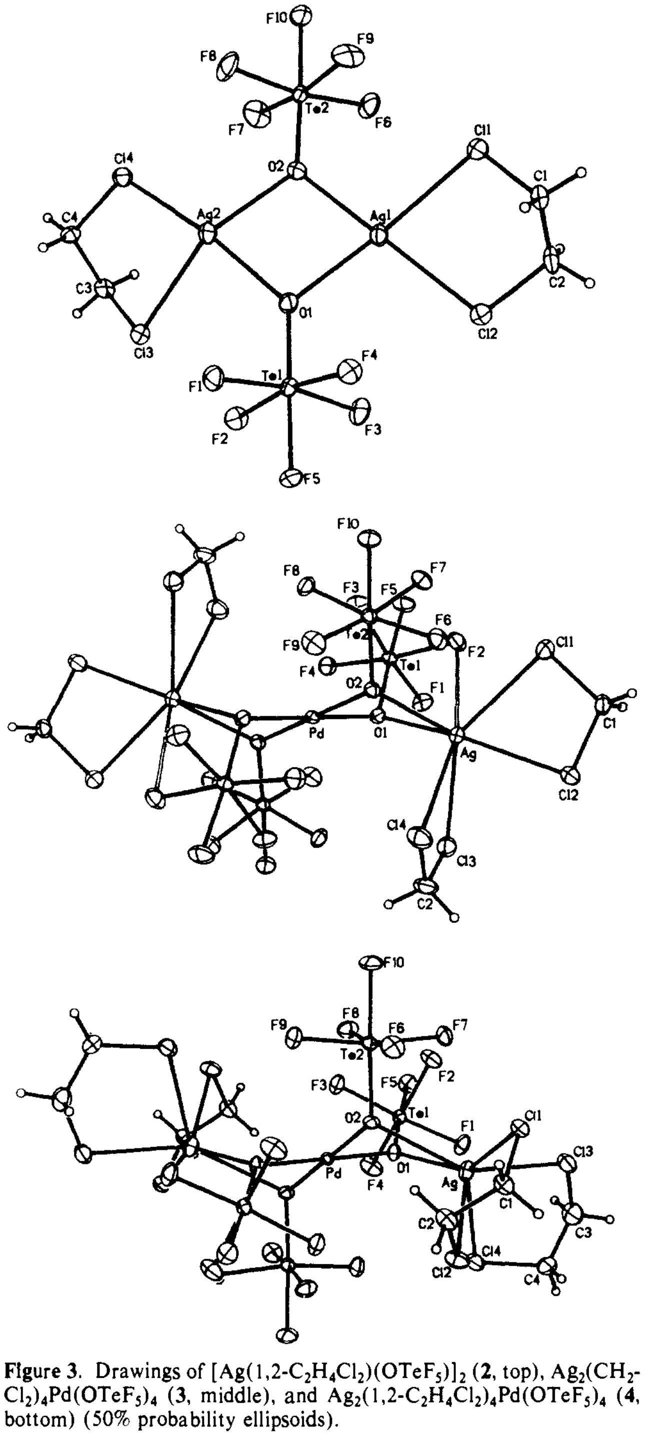

Figure 3. Drawings of $[Ag(1,2\text{-}C_2H_4Cl_2)(OTeF_5)]_2$ (**2**, top), $Ag_2(CH_2Cl_2)_4Pd(OTeF_5)_4$ (**3**, middle), and $Ag_2(1,2\text{-}C_2H_4Cl_2)_4Pd(OTeF_5)_4$ (**4**, bottom) (50% probability ellipsoids).

The structure of **1** could not be solved satisfactorily, since crystals of this compound were twinned. Cleavage of crystals did not resolve the twinning problem. However, in one of the crystals examined, one twin half was evidently dominant, and a model that refined to $R = 0.12$ (see Experimental Section) showed that this compound exhibits the same overall structure as **2**. The dimeric molecules of **1** have two $OTeF_5^-$ oxygen atoms bridging the two Ag(I) ions, one bidentate dichloromethane molecule per Ag(I) ion, and two weak intermolecular Ag–F bonds per Ag(I) ion, but they do not have any Ag–Cl···Ag′ bridges. While accurate bond distances and angles are not available for **1**, the crude model suggests that the size of the chelate rings formed by the different chlorocarbon ligands and the absence of Ag–Cl···Ag chlorine atom bridges in **1** are the only substantive differences between the two structures.

Table IV. Selected Bond Distances (Å) for **2**–**4**[a]

	2 $[Ag(1,2\text{-}C_2H_4Cl_2)\text{-}OTeF_5]_2$	**3** $Ag_2(CH_2Cl_2)_4\text{-}Pd(OTeF_5)_4$	**4** $Ag_2(1,2\text{-}C_2H_4Cl_2)_4\text{-}Pd(OTeF_5)_4$
Ag–Cl1	2.705 (3)[b]	2.775 (2)	2.840 (1)
Ag–Cl2	2.640 (3)[b]	2.811 (2)	2.655 (1)
Ag–Cl3	2.915 (3)[c]	2.859 (2)	2.645 (1)
Ag2–Cl3′	3.000 (3)		
Ag–Cl4	2.626 (3)[c]	2.882 (2)	2.928 (1)
Ag–O1	2.362 (7)[b]	2.532 (4)	2.372 (3)
Ag–O2	2.316 (7)[b]	2.404 (5)	2.777 (2)
Ag2–O1	2.308 (7)		
Ag2–O2	2.360 (7)		
Ag–F2		3.030 (4)	
Ag1–F3′	2.868 (7)		
Ag1–F4″	2.772 (6)		
Ag2–F1″	2.990 (7)		
Ag2–F2′	2.913 (7)		
C1–Cl1	1.79 (1)	1.770 (8)	1.791 (5)
C1–Cl2		1.762 (7)	
C2–Cl2	1.81 (1)		1.793 (3)
C2–Cl3		1.75 (1)	
C2–Cl4		1.76 (1)	
C3–Cl3	1.80 (1)		1.763 (4)
C4–Cl4	1.80 (1)		1.795 (5)
C1–C2	1.47 (2)		1.503 (5)
C3–C4	1.51 (2)		1.462 (8)
Pd–O1		2.014 (5)	2.006 (3)
Pd–O2		2.009 (4)	1.997 (2)
Te1–O1	1.792 (7)	1.825 (4)	1.827 (3)
Te2–O2	1.774 (7)	1.829 (5)	1.825 (2)
Te–F (av)	1.846 (22)	1.841 (15)	1.839 (9)

[a] Estimated standard deviations in the least significant digits are shown in parentheses. [b] Ag = Ag1. [c] Ag = Ag2.

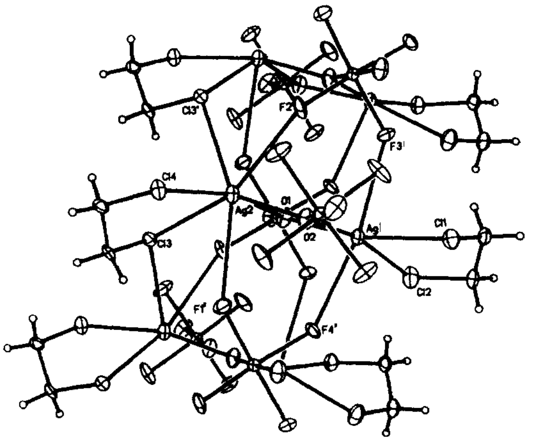

Figure 4. The chain structure of $[Ag(1,2\text{-}C_2H_4Cl_2)(OTeF_5)]_2$ (**2**), showing the intermolecular Ag–Cl and Ag–F bonds.

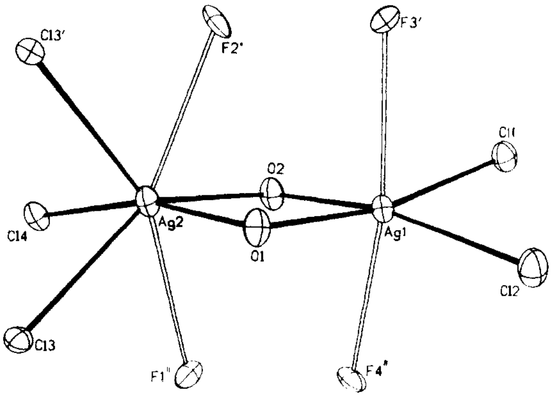

Figure 5. The coordination spheres for the Ag(I) ions in $[Ag(1,2\text{-}C_2H_4Cl_2)(OTeF_5)]_2$ (**2**).

The structures of **3** and **4** consist of discrete centrosymmetric trinuclear molecules with no intermolecular contacts involving the metal ions. In both structures, a $Pd(OTeF_5)_4^{2-}$ core containing a rigorously planar PdO_4 array bridges two $Ag(C_nH_{2n}Cl_2)_2^+$ moieties ($n = 1, 2$), forming butterfly (i.e., nonplanar) $AgPdO_2$

Table V. Selected Bond Angles (deg) for **2–4**[a]

	2 [Ag(1,2-$C_2H_4Cl_2$)-$OTeF_5$]$_2$	**3** $Ag_2(CH_2Cl_2)_4$-$Pd(OTeF_5)_4$	**4** Ag_2(1,2-$C_2H_4Cl_2$)$_4$-$Pd(OTeF_5)_4$
Cl1–Ag–Cl2	78.0 (1)[b]	62.1 (1)	74.8 (1)
Cl3–Ag–Cl4	75.9 (1)[c]	60.6 (1)	75.6 (1)
Cl3–Ag–Cl3′	88.3 (1)[c]		
Cl4–Ag–Cl3′	91.2 (1)[c]		
Cl1–Ag–Cl3		138.4 (1)	84.0 (1)
Cl1–Ag–Cl4		129.4 (1)	139.6 (1)
Cl2–Ag–Cl3		85.2 (1)	112.0 (1)
Cl2–Ag–Cl4		79.6 (1)	81.1 (1)
O1–Ag–O2	78.7 (2)[b]	67.0 (2)	63.8 (1)
O1–Ag2–O2	78.9 (2)		
O1–Ag–Cl1	167.8 (2)[b]	120.5 (1)	140.3 (1)
O1–Ag–Cl2	105.3 (2)[b]	159.4 (1)	118.9 (1)
O1–Ag–Cl3	92.6 (2)[c]	81.5 (1)	118.1 (1)
O1–Ag–Cl3′	98.0 (2)[c]		
O1–Ag–Cl4	165.1 (2)[c]	107.1 (1)	79.9 (1)
O2–Ag–Cl1	100.9 (2)[b]	101.7 (1)	81.0 (1)
O2–Ag–Cl2	166.0 (2)[b]	133.7 (1)	87.8 (1)
O2–Ag–Cl3	139.5 (2)[c]	119.8 (1)	151.0 (1)
O2–Ag–Cl3′	131.9 (2)[c]		
O2–Ag–Cl4	103.6 (2)[c]	80.9 (1)	130.3 (1)
F3′–Ag1–F4″	170.1 (2)		
F1″–Ag2–F2′	144.7 (2)		
F3′–Ag1–O1	89.4 (3)		
F3′–Ag1–O2	91.8 (3)		
F3′–Ag1–Cl1	78.5 (2)		
F3′–Ag1–Cl2	101.5 (2)		
F4″–Ag1–O1	81.3 (2)		
F4″–Ag1–O2	83.0 (3)		
F4″–Ag1–Cl1	110.8 (2)		
F4″–Ag1–Cl2	84.4 (2)		
F2–Ag–O1	81.7 (2)[d]	55.7 (1)	
F2–Ag–O2	71.4 (3)[d]	89.3 (1)	
F2–Ag–Cl1		66.4 (1)	
F2–Ag–Cl2		117.1 (1)	
F2–Ag–Cl3	146.9 (1)[d]	113.9 (1)	
F2–Ag–Cl3′	60.7 (2)[d]		
F2–Ag–Cl_4	113.1 (2)[d]	162.7 (1)	
F1″–Ag2–O1	84.2 (2)		
F1″–Ag2–O2	74.2 (3)		
F1″–Ag2–Cl3	65.6 (1)		
F1″–Ag2–Cl3′	153.9 (2)		
F1″–Ag2–Cl4	82.4 (1)		
Ag–Cl1–C1	97.2 (4)[b]	93.1 (2)	104.3 (1)
Ag–Cl2–C1		92.1 (2)	
Ag–Cl2–C2	105.0 (4)[b]		99.6 (2)
Ag–Cl3–C2		94.5 (3)	
Ag–Cl3–C3	98.9 (3)[c]		108.4 (2)
Ag2–Cl3–Ag2′	119.2 (1)		
Ag2′–Cl3–C3	106.3 (4)		
Ag–Cl4–C2		93.6 (3)	
Ag–Cl4–C4	107.8 (3)*c*		96.7 (1)
Cl1–C1–C2	111.3 (9)		111.6 (4)
Cl1–C1–Cl2		109.4 (3)	
Cl2–C2–C1	111.9 (8)		111.7 (3)
Cl3–C2–Cl4		111.3 (4)	
Cl3–C3–C4	111.6 (7)		114.4 (4)
Cl4–C4–C3	111.1 (8)		113.8 (4)
Ag1–O1–Ag2	101.2 (3)		
Ag1–O2–Ag2	101.0 (3)		
Ag–O1–Pd		95.4 (2)	102.3 (1)
Ag–O2–Pd		99.6 (2)	89.9 (1)
Ag–O1–Te1	125.9 (3)[b]	116.3 (2)	126.2 (1)
Ag–O2–Te2	129.6 (4)[b]	126.5 (2)	118.7 (1)
Ag2–O1–Te1	132.8 (4)		
Ag2–O2–Te2	128.6 (4)		
Pd–O1–Te1		122.2 (3)	127.1 (2)
Pd–O2–Te2		125.6 (2)	121.3 (2)
O1–Pd–O2		85.3 (2)	86.6 (1)
O–Te–F_{ax} (av)	178.7 (4)	177.3 (3)	177.6 (1)
O–Te–F_{eq} (av)	95.3 (8)	93.9 (6)	94.3 (3)
F_{ax}–Te–F_{eq} (av)	84.8 (8)	86.1 (6)	85.7 (3)
F_{eq}–Te–F_{eq} (av)	89.5 (10)	89.8 (6)	89.7 (3)

[a] Estimated standard deviations in the least significant digits are shown in parentheses. [b] Ag = Ag1. [c] Ag = Ag2. [d] Ag = Ag2; F2 = F2′.

four-membered rings. In both complexes, the Ag(I) ions are bonded to two teflate oxygen atoms and four chlorine atoms. In **3**, there is also a weak intramolecular Ag–F2 bond. The coordination spheres for the six-coordinate Ag(I) ion in **4**, a trigonal prism, and the seven-coordinate Ag(I) ion in **3**, a monocapped trigonal prism, are shown in Figure 7. The prism in **3** is formed by the O1, O2, Cl1 and Cl2, Cl3, Cl4 triangles, and F2 is closer to capping the O1···Cl1 edge than the O1, O2, Cl1 triangular face. The prism in **4** is formed by the O1, Cl3, Cl4 and O2, Cl1, Cl2 triangles. The five-membered $\overline{\mathrm{Ag{-}Cl{-}C{-}C{-}Cl}}$ chelate rings in **4** adopt puckered conformations similar to those in **2**, as shown in Figure 6. The four-membered $\overline{\mathrm{Ag{-}Cl{-}C{-}Cl}}$ chelate rings in **3** are nearly planar, as shown in Figure 6.

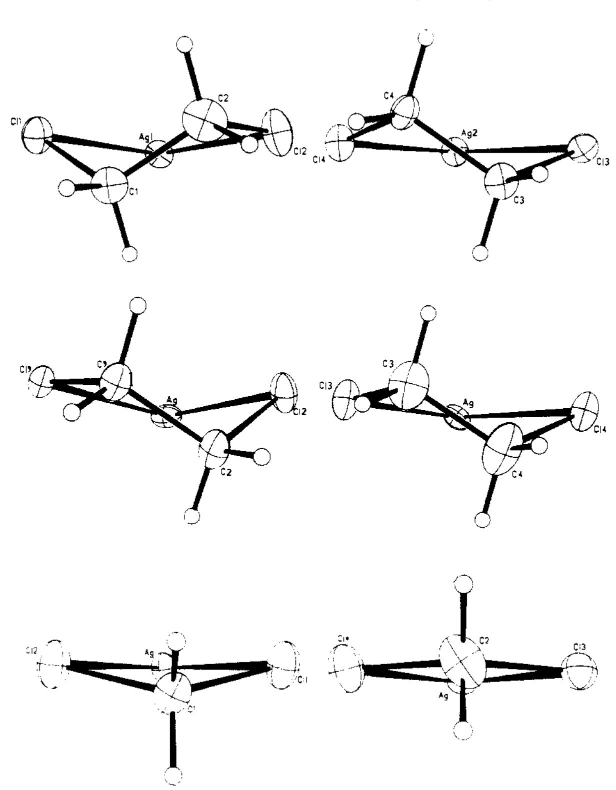

Figure 6. Conformations of the chelate rings in [Ag(1,2-$C_2H_4Cl_2$)($OTeF_5$)]$_2$ (**2**, top), Ag_2(1,2-$C_2H_4Cl_2$)$_4$$Pd(OTeF_5)_4$ (**4**, middle), and $Ag_2(CH_2Cl_2)_4Pd(OTeF_5)_4$ (**3**, bottom).

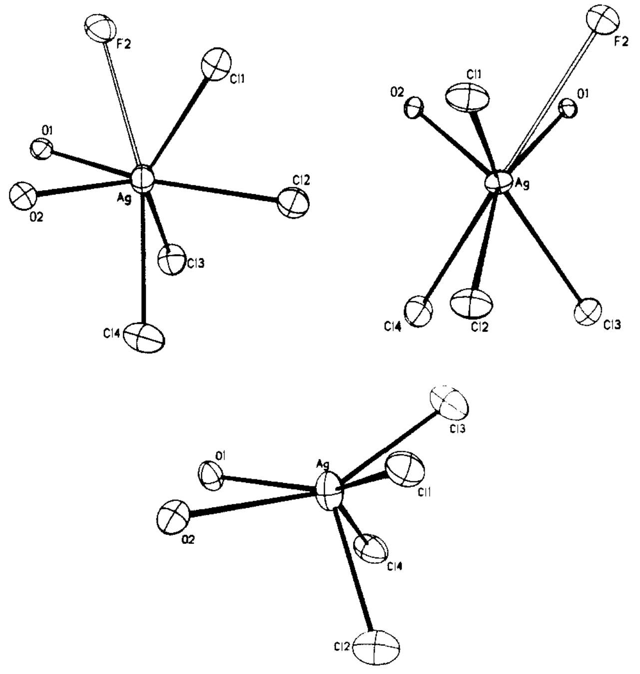

Figure 7. The coordination spheres for the Ag(I) ions in $Ag_2(CH_2Cl_2)_4Pd(OTeF_5)_4$ (**3**, top, two different views shown) and Ag_2(1,2-$C_2H_4Cl_2$)$_4$$Pd(OTeF_5)_4$ (**4**, bottom).

(b) Infrared and Raman Spectroscopy. Solid-state IR and Raman spectral data are collected in Table VI. Assignments of ν(TeO) and ν(TeF) bands follow from earlier publications about

Table VI. Solid-State Infrared and Raman Spectral Data[a]

	ν(TeO)				ν(MO)[b]							
	IR		Raman		IR		Raman		$\delta(CH_2)$[c]		ν(CCl)[c]	
compd	^{16}O	^{18}O	^{16}O	^{18}O	^{16}O	^{18}O	^{16}O	^{18}O	sym	asym	sym	asym
$AgOTeF_5$	806	770	794		449	426	439					
$Ag_2Pd(OTeF_5)_4$	764				534							
$(N(n\text{-}Bu)_4^+)_2Pd(OTeF_5)_4^{2-}$	802				487, 475							
CH_2Cl_2[d]										1261	707	743
CD_2Cl_2[d]										952	681	716
1	816, 783	776, 745	846	806	446	425	384	369		1260	*e*	738
1-d_4										951	*e*	*e*
3	777				517, 497					1258	*e*	725
3-d_8										949	*e*	*e*
1,2-$C_2H_4Cl_2$[d,f]									943	881	657	681
1,2-$C_2D_4Cl_2$[d,f]									766	746	616[g]	
2	825	785	843	800	390	372	372	356	945	877	*e*	*e*
2-d_8									767	737	600[g]	
4	774				516, 498				947	881	641[g]	*e*
4-d_{16}									*e*	739	601[g]	

[a] All data in cm^{-1}. [b] M = Ag and/or Pd. [c] From IR spectra. [d] Dispersed in Nujol. [e] Not observable due to the presence of strong ν(TeF) bands. [f] Gauche conformer only; see text for data for the anti conformer. [g] This ν(CCl) band may be $\nu(CCl)_{sym}$, $\nu(CCl)_{asym}$, or some other more complex normal mode: see text.

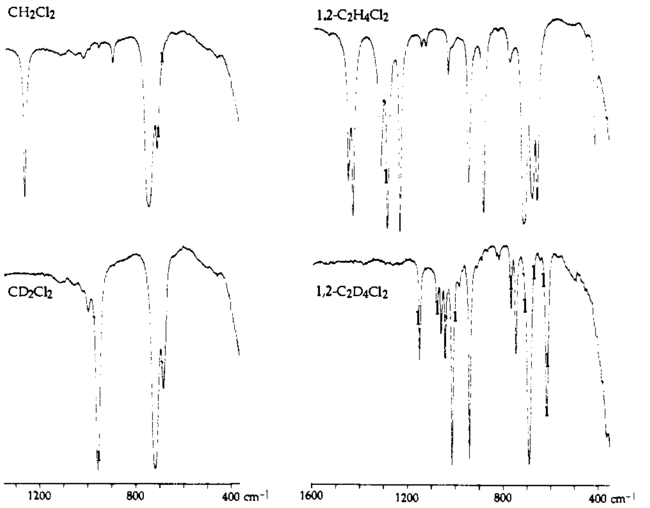

Figure 8. Nujol mull IR spectra of CH_2Cl_2, CD_2Cl_2, 1,2-$C_2H_4Cl_2$, and 1,2-$C_2D_4Cl_2$.

teflate compounds,[21] and ν(MO) (M = Ag, Pd) bands from $^{16}O/^{18}O$ isotopic substitution. We were especially interested in studying any shifts in the ν(CCl) bands of dichloromethane and 1,2-dichloroethane upon coordination to Ag(I). A reliable way of assigning these bands in our complexes was needed, since ν(CCl) bands for aliphatic chlorocarbons are generally found in the same spectral region (~800–600 cm^{-1} [22]) as the intense ν(TeO) and ν(TeF) bands of $OTeF_5^-$ complexes (~870–600 cm^{-1} [21]), and are sometimes obscured by them. For dichloromethane, the $\nu(CCl)_{asym}$ stretching normal mode is mixed with the $\delta(CH_2)$ rocking normal mode (both have B_2 symmetry);[23,24] a pair of bands that are predominantly $\delta(CH_2)$ and $\nu(CCl)_{asym}$ were found at 1262 and 743 cm^{-1}, respectively, for an IR spectrum of dichloromethane dispersed in Nujol. For dichloromethane-d_2, these bands were shifted to 952 and 716 cm^{-1}, demonstrating that deuterium substitution can be used to assign at least one of the two carbon–chlorine stretching bands in IR spectra of complexes containing coordinated dichloromethane.

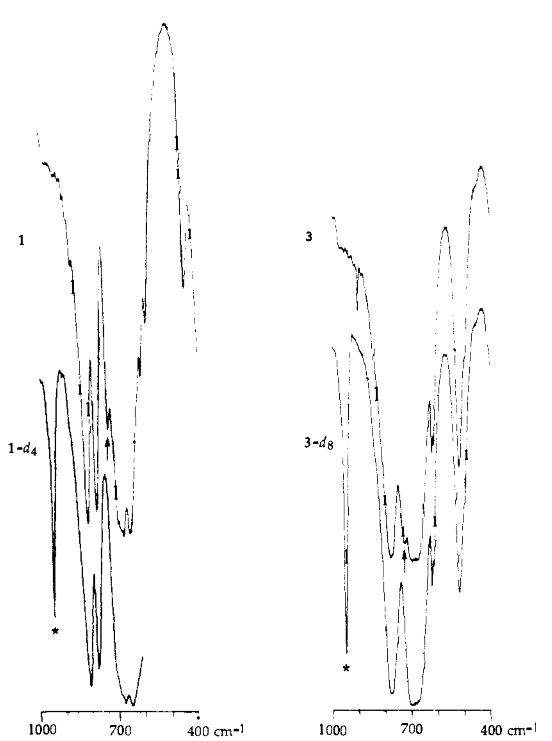

Figure 9. Nujol mull IR spectra of $[Ag(CH_2Cl_2)(OTeF_5)]_2$ (**1**), $[Ag(CD_2Cl_2)(OTeF_5)]_2$ (**1**-d_4), $Ag_2(CH_2Cl_2)_4Pd(OTeF_5)_4$ (**3**), and $Ag_2(CD_2Cl_2)_4Pd(OTeF_5)_4$ (**3**-d_8). The peaks marked with arrows are assigned as $\nu(CCl)_{asym}$. The peak marked with an asterisk in the two spectra of the deuterium isotopomers is assigned as $\delta(CD_2)$.

Nujol dispersion IR spectra of dichloromethane and dichloromethane-d_2 are shown in Figure 8. Nujol mull IR spectra of **1** and **3** exhibit bands at 738 and 723 cm^{-1}, respectively, that are assigned to ν(CCl), since they are absent from spectra of **1**-d_4 and **3**-d_8 (Figure 9). The ν(CCl) bands for the deuterium isotopomers have presumably shifted under the intense ν(TeF) band(s) at ~700 cm^{-1}.

A Nujol dispersion of 1,2-dichloroethane, which exists as a mixture of a C_{2h} anti conformer and a C_2 gauche conformer in the gas phase and in the liquid phase,[25] exhibited three IR bands at 709, 681, and 657 cm^{-1} (Figure 8). These have been assigned to $\nu(CCl)_{asym}$ for the anti conformer and to $\nu(CCl)_{sym}$ and $\nu(CCl)_{asym}$ for the gauche conformer, respectively;[26] they are absent

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[21] (a) Miller, P. K.; Abney, K. D.; Rappé, A. K.; Anderson, O. P.; Strauss, S. H. *Inorg. Chem.* **1988**, *27*, 2255. (b) Mayer, E.; Sladky, F. *Inorg. Chem.* **1975**, *14*, 589. (c) Burger, H. *Z. Anorg. Allg. Chem.* **1968**, *360*, 97.

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[25] (a) Mizushima, S.-I.; Shimanouchi, T.; Nakagawa, I.; Miyake, A. *J. Chem. Phys.* **1953**, *21*, 215. (b) Mizushima, S.-I.; Morino, Y.; Watanabe, I.; Simanouti, T.; Yamaguchi, S. *J. Chem. Phys.* **1949**, *17*, 591.

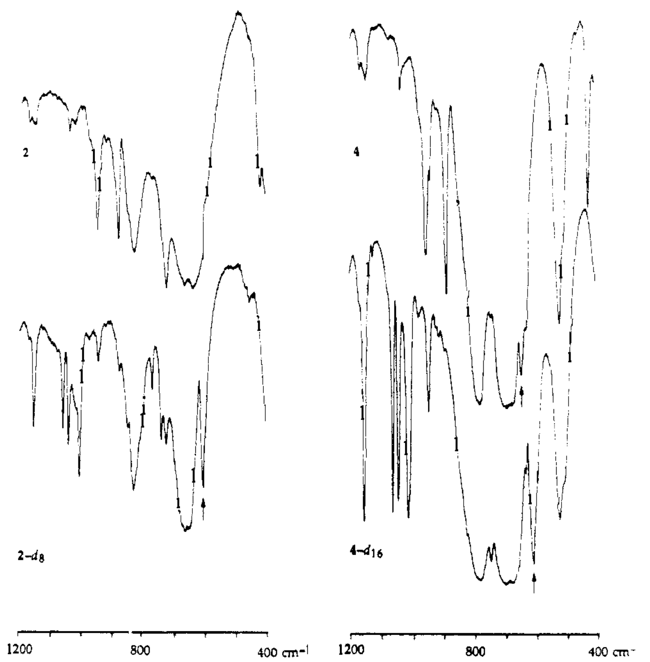

Figure 10. Nujol mull IR spectra of $[Ag(1,2\text{-}C_2H_4Cl_2)(OTeF_5)]_2$ (**2**), $[Ag(1,2\text{-}C_2D_4Cl_2)(OTeF_5)]_2$ (**2**-d_8), $Ag_2(1,2\text{-}C_2H_4Cl_2)_4Pd(OTeF_5)_4$ (**4**), and $Ag_2(1,2\text{-}C_2D_4Cl_2)_4Pd(OTeF_5)_4$ (**4**-d_{16}). The peaks marked with arrows are assigned as $\nu(CCl)_{asym}$.

from spectra of 1,2-dichloroethane-d_4 and are replaced by two bands at 692 and 616 cm^{-1} (Figure 8). It is not apparent why there are only two ν(CCl) bands in spectra of 1,2-dichloroethane-d_4, or whether the 616-cm^{-1} band of the gauche conformer of 1,2-dichloroethane-d_4 corresponds to $\nu(CCl)_{sym}$, $\nu(CCl)_{asym}$, or to some more complex normal mode of vibration. We will refer to the 616-cm^{-1} band of the gauche conformer of 1,2-dichloroethane-d_4 as simply ν(CCl).

In IR spectra of **2**-d_8 and **4**-d_{16}, only the band corresponding to the strong 616-cm^{-1} ν(CCl) band of the gauche conformer of free 1,2-dichloroethane-d_4 should be observed, since the conformation of the 1,2-dichloroethane ligands in these complexes is gauche, not anti. Due to the intense ν(TeF) bands, it was not possible to locate ν(CCl) bands in Nujol mull IR spectra of **2**: however, a band at 600 cm^{-1} was found in the IR spectrum of **2**-d_8 that was absent from the spectrum of **2**, and hence is assigned as ν(CCl). Similarly, a band at 641 cm^{-1} in the spectrum of **4** shifted to 600 cm^{-1} in the spectrum of **4**-d_{16}, and hence is also assigned as ν(CCl). These changes are shown in Figure 10.

(c) **^{13}C NMR Spectroscopy.** Solid-state ^{13}C NMR spectra were recorded for samples of **1**–**4** sealed in glass tubes with a drop of excess solvent added. In each case, two resonances were observed with use of magic angle spinning (MAS), as shown for **2** in Figure 11. When cross polarization–magic angle spinning (CP–MAS) was used, only the broader and more intense deshielded resonance was observed. In one experiment, the drop of 1,2-dichloroethane was omitted from a sample of **4**. In this case, two broad resonances were observed in the CP–MAS spectrum, one of which corresponded to the broad resonance in the MAS spectrum of a sample of **4** that contained the excess solvent. Chemical shift data for **1**–**4** are listed in Table II.

(d) **^{35}Cl NQR Spectroscopy.** Nuclear quadrupole resonance spectra were recorded for samples of **1**–**4** sealed in glass ampules with a drop of excess solvent added. We have previously reported 77 K spectra of **1**–**3**.[9] No NQR signals were observed for any of the compounds at ambient temperature or at 273 K. Additional measurements were made between 195 and 77 K so that line crossings and overlaps could be detected; for **1**–**3** each signal was observed at three or more temperatures over this range. Despite the large amount of **4** that was used (4.1 g), no signals above 77 K were detected; the two equal intensity signals observed at 77 K were unusually broad, so it is possible that they represent two sets of two overlapped signals. All of the NQR data for **1**–**4** are listed in Table VII.

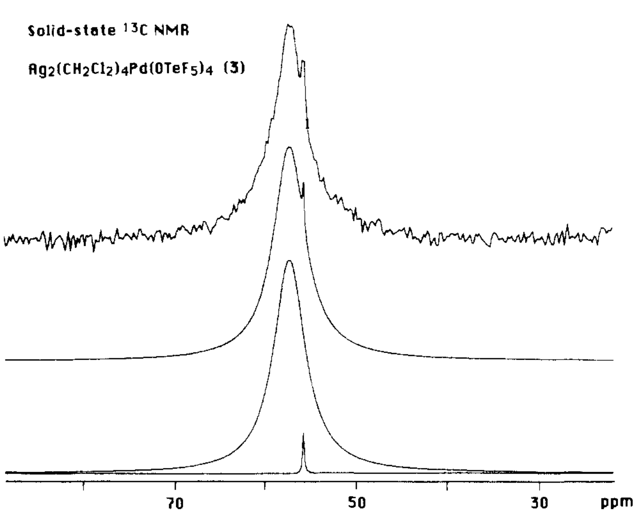

Figure 11. Solid-state ^{13}C NMR spectrum of $Ag_2(CH_2Cl_2)_4Pd(OTeF_5)_4$ (**3**). The top trace shows the experimental spectrum. The other traces are spectral simulations with Gaussian peaks.

Table VII. ^{35}Cl NQR Spectral Data[a]

compd	signal(s) at 77 K, MHz (S/N)	freq lowering,[b] MHz	temp coeff,[c] 10^{-4} K^{-1}
CH_2Cl_2[d]	35.991		−3.14
1	34.498 (36)[e]	1.493	−3.95
	34.230 (30)[e]	1.761	−3.81
3	35.483 (3)	0.508	−5.29
	34.827 (5)[f]	1.164	−2.61, −2.76
	34.640 (3)	1.351	−3.56
$C(O)(CH_2Cl)_2$[d]	35.943		−1.17
1,2-$C_2H_4Cl_2$[d]	34.361		
2	32.036 (6)	2.325	−1.34
	31.828 (11)[f]	2.533	−1.51, −1.67
	31.700 (5)	2.661	−0.89
4	33.608 (2)	0.753	*g*
	32.460 (2)	1.901	*g*

[a] All data from this work unless otherwise noted. [b] The frequency difference between the NQR signals for a ^{35}Cl atom in the complex and the ^{35}Cl atoms in the respective pure solvent. [c] The mean temperature coefficient of the ^{35}Cl NQR frequency $((1/\nu_{77K})(\Delta\nu/\Delta T))$. A negative value results from a frequency lowering as the temperature is raised. [d] Biryukov, I. P.; Voronkov, M. G.; Safin, I. A. *Tables of Nuclear Quadruple Resonance Frequencies*; Isreal Program for Scientific Translation: Jerusalem, 1969. Lucken, E. A. C. *Nuclear Quadrupole Coupling Constants*: Academic Press: London, 1969; pp 169–170. The temperature dependence of the NQR spectrum for 1,2-$C_2H_4Cl_2$ is anomalous (see text). [e] A ^{37}Cl signal at 1/1.2688 times the frequency of the ^{35}Cl signal was also observed. [f] Assigned to accidental overlap of two signals at 77 K; separate signals were observed at higher temperatures. [g] Spectra could not be observed for this compound at higher temperatures.

Discussion

Since halocarbons are very poor bases,[27] M–XR dative bonds have always been presumed to be weak and labile. Until recently, there were only a few published observations that suggested that simple halocarbons could form L_nM–XR complexes, although such adducts have long been proposed as reactive intermediates in many processes.[28] On the other hand, there are many examples in the

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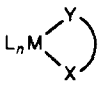
(26) Mizushima, S.-I. *Structure of Molecules and Internal Rotation*; Academic Press: New York, 1954; p 222.

(27) (a) Staley, R. H.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1975**, *97*, 5920 and references therein. (b) McMahon, T. B.; Heinis, T.; Nicol, G.; Hovey, J. K.; Kebarle, P. *J. Am. Chem. Soc.* **1988**, *110*, 7591 and references therein. (c) Smith, S. F.; Chandrasekhar, J.; Jorgensen, W. L. *J. Phys. Chem.* **1982**, *86*, 3308 and references therein.

(28) See, for example: Milder, S. J.; Gray, H. B.; Miskowski, V. M. *J. Am. Chem. Soc.* **1984**, *106*, 3764.

literature of molecular complexes such as I, in which the halogen atom is a substituent on a strong ligand such as an amine, a



I (Y = N, P, O, S; X = F, Cl, Br, I)

phosphine, a phenoxide, or a thiolate.[10] In these cases, the chelate effect assists, or perhaps forces, the coordination of the neutral halogen atom to the metal ion. There are also a number of salts in which M–X–C linkages have been observed,[10] such as calcium chloroacetate monohydrate,[29] silver(I) bromomethylsulfate,[30] and silver(I) 2,4,5-trichlorophenolate.[31] In these cases too, the formation of five-membered chelate rings does not allow the intrinsic tendency of halocarbon halogen atoms to coordinate to metal ions to be assessed.

In 1972 Dahl and co-workers published the disordered structure of $[CPh_3]^+[PtCl_5(CH_2Cl_2)]^-$.[32] These authors suggested that one of the chlorine atoms of the octahedral $PtCl_6$ array was a dichloromethane chlorine atom, but their results were not conclusive because of the disorder and "the questionable quality of the data due to crystal decomposition".[32] If their compound did contain a Pt–$ClCH_2Cl$ bond, it would have been the first isolated complex containing a coordinated halocarbon (i.e., a ligand possessing no heteroatoms other than halogens). A few years later, Beck and Schloter reported the synthesis of compounds formulated as $[Mo(Cp)(CO)_3(CH_2Cl_2)]^+[PF_6]^-$ and $[W(Cp)(CO)_3(CH_2Cl_2)]^+[PF_6]^-$ (Cp = C_5H_5).[13] Bands assigned to ν(CCl) in solid-state IR spectra were consistent with dichloromethane acting as a monodentate σ-donor in both complexes. No structural results or other spectroscopic data that corroborate the presence of the proposed Mo–$ClCH_2Cl$ and W–$ClCH_2Cl$ bonds have been published. In 1980 and 1981, Cotton and co-workers published structures of dichloro- and dibromomethane adducts of tetraamidodichromium(II) and tetraamidodimolybdenum(II) compounds, which revealed halogen atoms positioned at vacant sites along the axial extensions of the M–M quadruple bonds.[33] However, even the shortest M–XR distances observed, 3.354 (3) Å for Cr–$ClCH_2Cl$, 3.335 (4) Å for Cr–$BrCH_2Br$, 3.417 (6) Å for Mo–$ClCH_2Cl$, and 3.390 (3) Å for Mo–$BrCH_2Br$, are so long that they could be nonbonded or van der Waals contacts between the metal ion and the halogen atom. The authors stated that "The conclusion that *none* of the halogen atoms is engaged in significant bonding to the chromium atoms is entirely consistent with, but not necessarily required by, the interatomic distances."[33]

The first unambiguous example of an isolable halocarbon complex was published in 1982, when Crabtree and co-workers reported the synthesis and structure of $[IrH_2(PPh_3)_2(o\text{-}C_6H_4I_2)]^+[BF_4]^-$.[14a] The iodine atoms of the diiodobenzene ligand occupy two cis sites in the octahedral coordination sphere of the Ir(III) ion. Since that time, three groups have reported the structures of a number of iodocarbon complexes, including $[IrH_2(PPh_3)_2(MeI)_2]^+[SbF_6]^-$,[14b] $[Re(Cp)(NO)(PPh_3)(Me_3SiCH_2I)]^+[BF_4]^-$,[15b,c] $[Ru(Cp)(CO)(PPh_3)(p\text{-}CH_3C_6H_4I)]^+[PF_6]^-$,[14d] and $[Ru(Cp)(t\text{-}BuNC)(PPh_3)(MeI)]^+[PF_6]^-$.[16] Perhaps because of the apparent differences in bond strengths (M–IR > M–BrR > M–ClR[34]), similar complexes containing coordinated bromo- or chlorocarbons have not been isolated. Nevertheless, Gladysz and co-workers have reported compelling ^{13}C NMR evidence for the existence of the dichloromethane adducts $[Re(Cp)(NO)(PPh_3)(CH_2Cl_2)]^+$ and $[Re(C_5Me_5)(NO)(PPh_3)(CH_2Cl_2)]^+$ in solution at −85 °C.[15]

Dichloromethane and 1,2-Dichloroethane Coordination to Silver(I). (a) Structural Results. The structures of **2**, **3**, and **4** (Figure 3) leave little doubt that chlorocarbons can coordinate effectively to metal ions. The Ag–Cl bond distances span the ranges 2.626 (3)–3.000 (3) Å (**2**), 2.775 (2)–2.882 (2) Å (**3**), and 2.645 (1)–2.928 (1) Å (**4**). All of the Ag–Cl distances are significantly shorter than the sum of van der Waals radii for Ag and Cl atoms, 3.45 ± 0.05 Å.[35,36] Considering that the chlorine atom ligands do not bear a full negative charge, the Ag–Cl bonds to nonbridging chlorine atoms are quite short—they average 2.66 (4) Å in **2**, 2.83 (5) Å in **3**, and 2.8 (1) Å in **4**. These averages can be compared with Ag–Cl distances involving a terminal chloride ion, 2.512 (1) Å in Ag(diphos)Cl,[37] chloride ions that bridge Ag(I) and Pt(II) ions, 2.408 (8) and 2.724 (8) Å in $Ag_2Pt_2Cl_4(C_6F_5)_4$,[38] and an octahedral array of chloride ions, 2.77512 (5) Å in AgCl.[39]

The structures of **2**, **3**, and **4** show (a) that chlorocarbons with more than one chlorine atom can function as polydentate ligands, (b) that a chlorocarbon chlorine atom can bridge two metal ions (Cl3 in **2**), (c) that chlorocarbon chlorine atoms can be the predominant ligand type in the coordination sphere of a metal ion, and (d) that more than one dichloromethane or 1,2-dichloroethane molecule can coordinate to a metal ion if it is sufficiently unsaturated. These four observations demonstrate that chlorocarbon ligands can behave like more traditional ligands.

The five-membered chelate rings formed by 1,2-dichloroethane resemble those formed by ethylenediamine.[40] They adopt the normal puckered conformation, as shown in Figure 6, with Cl–Ag–Cl bite angles spanning the small range of 74.8 (1)–78.0 (1)° (see Table V). In **2**, each dimer contains one chelate ring of δ configuration and one of λ configuration. In **4**, both chelate rings for each Ag(I) ion adopt the same configuration. It is unlikely that this arises because of intramolecular repulsions of methylene groups since intramolecular C···C distances for the carbon atoms on different ligands are quite long (all four such distances are ~6 Å). The coordination of 1,2-dichloroethane to Ag1 in **2** is nearly symmetrical, i.e. the two Ag–Cl distances are similar (2.705 (3) Å for Ag1–Cl1 and 2.640 (3) Å for Ag1–Cl2. For Ag2 in **2**, the chelation is much less symmetric, with Ag–Cl distances of 2.914 (3) and 2.626 (3) Å. In this compound, the unsymmetric chelation to Ag2 might be attributable to the fact that Cl3 bridges two Ag(I) ions. However, unsymmetric chelation is also observed for the two chelate rings in **4**, each of which has a shorter Ag–Cl bond (2.655 (1) Å for Ag–Cl2 and 2.645 (1) Å for Ag–Cl3) and a longer Ag–Cl bond (2.840 (1) Å for Ag–Cl1 and 2.928 (1) Å for Ag–Cl4).

The chelate rings in **3** are nearly planar, as shown in Figure 6. The Cl–Ag–Cl bite angles, 62.1 (1) and 60.6 (1)°, are considerably smaller than those for the five-membered chelate rings in **2** and **4**. Both the planarity and the small bite angles are

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[34] The available data suggest that this trend is correct for the soft metal centers Ir(III),[14] Re(I),[15] and Ru(II).[16] However, for the hard metal center Li(I), gas-phase binding energies are Li^+–FR > Li^+–ClR ~ Li^+–IR.[27a]

[35] (a) Pauling, L. *The Nature of the Chemical Bond*; Cornell University Press: Ithaca, NY, 1960; p 257. (b) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

[36] Precise definitions or measurements of van der Waals radii are problematic, as they are for another elusive but highly important chemical quantity, electronegativity. Even for the halogens, Pauling's[35a] and Bondi's[35b] values differ by as much as 0.15 Å. The situation for metal ions is complicated by the fact that they are generally hidden from nonbonded contacts.[35b] Furthermore, the van der Waals radius of a metal ion, like its ionic radius, probably depends on the oxidation state, the coordination geometry, and the coordination number. This will necessarily lead to ambiguous conclusions about long M–XR distances, such as those in the dihalomethane adducts of tetraamidodichromium(II) complexes.[33] Nevertheless, there is no ambiguity about silver–chlorine bonding in **2**, **3**, and **4**, since the Ag–Cl distances are 0.5–0.9 Å less than 3.45 ± 0.05 Å.

[37] Barrow, M.; Burgi, H.-B.; Camalli, M.; Caruso, F.; Fischer, E.; Venanzi, L. M.; Zambonelli, L. *Inorg. Chem.* **1983**, *22*, 2356.

[38] Uson, R.; Fornies, J.; Menjon, B.; Cotton, F. A.; Falvello, L. R.; Tomas, M. *Inorg. Chem.* **1985**, *24*, 4651.

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[40] (a) Shriver, D. F.; Atkins, P. W.; Langford, C. H. *Inorganic Chemistry*; Oxford University Press: Oxford, 1990; p 202. (b) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Wiley-Interscience: New York, 1988; p 53. (c) Hawkins, C. J. *Absolute Configuration of Metal Complexes*; Wiley-Interscience: New York, 1971.

common features of four-membered chelate rings, such as those formed by carboxylates[41] and dithiocarbamates.[42] The chelation is nearly symmetric—in fact, all four Ag–Cl distances in **3** are within ~0.1 Å of one another. This is not necessarily a requirement of four-membered-chelate-ring formation; the compound $Hg(CH_3CO_2)_2(P(t\text{-}Bu)_3)$ contains asymmetrically bidentate acetate ligands.[43]

Unlike anionic ligands such as halide ions, alkoxides, thiolates, amides, phosphides, and carbanions, all of which commonly bridge two or more metal ions, neutral σ-donor ligands are rarely found to bridge metal ions. A few examples have been found for thioethers.[44] Another example was found in the salt $[Ag][BrCH_2SO_3]$, in which the bromine atom bridges two Ag(I) ions (Ag–Br = 2.970 (5) Å).[30] It is interesting, therefore, that Cl3 in **2** bridges two Ag(I) ions, especially considering that chlorocarbons are so weakly basic. For anionic ligands, it is frequently found that bond distances in M–L–M bridges are longer than terminal M–L bond distances involving the same atoms. The bridge bonds in **2**, Ag2–Cl3 and Ag2′–Cl3, which are 2.914 (3) and 3.000 (3) Å, respectively, are longer than the terminal Ag–Cl distances in that compound, 2.626 (3), 2.640 (3), and 2.705 (3) Å. However, Ag2–Cl3 is shorter than the terminal Ag–Cl4 bond in **4** (2.928 (1) Å). This is similar to what has been found for bridging thioethers—in some cases bridging $M\text{–}S(R)_2\text{–}M$ bonds are longer than terminal $M\text{–}SR_2$ bonds involving the same metal ions, while in most cases the bridge bonds are actually shorter.[44]

Whereas earlier studies that suggested or proved that halocarbons can coordinate to metal ions involved one or at most two M–XR bonds per metal ion,[13-16,32,33] our compounds each have several Ag–ClR bonds. The two unique Ag(I) ions in **2** have two (Ag1) and three (Ag2) bonds to 1,2-dichloroethane chlorine atoms, while each Ag(I) ion in **3** and **4** has four bonds to dichloromethane or 1,2-dichloroethane chlorine atoms. The presence of multiple Ag–ClR bonds in **2**, **3**, and **4** is probably related to the extremely weak basicity of the fluorine atoms of the teflate $(OTeF_5^-)$[45,46] and $Pd(OTeF_5)_4^{2-}$ anions; another likely factor is the expected increased stability of soft–soft Ag–Cl bonds relative to soft–hard Ag–F bonds. It is now a credible hypothesis that homoleptic $M(XR)_n^{m+}$ complex cations will be prepared and isolated, once more progress is made in the area of "least coordinating anions".[47]

The solid-state structures of $AgOTeF_5$ and $Ag_2Pd(OTeF_5)_4$ are not known, but it is likely that the Ag(I) ions in them are coordinated to several fluorine atoms and have coordination numbers of six or greater. Complexes **1–4**, which are formed by adding dichloromethane or 1,2-dichloroethane to these compounds, constitute a set of Lewis acid/base adducts in which chlorine atoms have displaced fluorine atoms from the coordination spheres of the Ag(I) ions. The fact that **4** contains two 1,2-dichloroethane ligands per Ag(I) ion while **2** only contains one is probably *not* related to the intrinsic Lewis acidities of the different Ag(I) ions: the tensimetric titrations reveal that the affinity of $AgOTeF_5$ for dichloromethane ($P_{1/2}$ = 4 (1) Torr) is greater than the affinity of $Ag_2Pd(OTeF_5)_4$ for dichloromethane ($P_{1/2}$ = 14 (1) Torr), yet it is the latter compound that forms the 2:1 complex.

The coordination spheres of Ag1 (donor atom set = $Cl_2F_2O_2$) and Ag2 (donor atom set = $Cl_3F_2O_2$) in **2** can be described as a distorted octahedron and a distorted pentagonal bipyramid, respectively (see Figure 5). For the distorted octahedron of Ag1, the Cl1–Ag1–Cl2, F3′–Ag1–F4″, and O1–Ag1–O2 angles are 78.0 (1), 170.1 (2), and 78.7 (2)°, respectively. For the distorted pentagonal bipyramid of Ag2, the Cl4 and O1 atoms occupy the axial positions with a Cl4–Ag2–O1 bond angle of 165.1 (2)°. The L–Ag2–L′ angles for the ligands in the pentagonal plane (ideal value = 72°) range from 60.7 (2)° (Cl3′–Ag2–F2′) to 88.3 (1)° (Cl3–Ag2–Cl3′).

The fluorine atoms are included in the donor atom sets for **2**, as shown in Figure 5, because the four intermolecular Ag–F bonds shown are shorter than the sum of van der Waals radii for these two atoms, 3.15 ± 0.08 Å.[35,36] The closest intramolecular Ag···F contacts are greater than 3.5 Å and so are clearly nonbonding. The Ag2–F distances (av 2.95 (1) Å) are slightly longer than the Ag1–F distances (av 2.82 (1) Å), probably as a consequence of the larger number of Ag2–Cl bonds (the individual Ag–F distances are listed in Table IV). These four Ag–F bonds are best classified as secondary bonding interactions.[48] They are longer than those in $AgSbF_6$ (2.62 Å)[49] and $[Ag_2(CH_2O)_6][Ag][AsF_6]_3$ (2.60 and 2.66 Å)[50] but are shorter than those in $[Ag(2,6\text{-lutidine})_2][BF_4]$ (3.01 Å).[51]

The intramolecular Ag–F2 distance in **3**, 3.030 (4) Å, is nearly as long as the sum of van der Waals radii for these two atoms, 3.15 ± 0.08 Å. It is obviously an extremely weak interaction and perhaps should not be included in the coordination sphere of the Ag(I) ion in this compound. We have chosen to include it in Figure 7, which shows two views of the coordination sphere of Ag in **3** (as well as the coordination sphere of Ag in **4**), so that its orientation with respect to the more strongly bound ligands can be seen. Ignoring F2 in **3**, the Ag(I) ions in both **3** and **4** have Cl_4O_2 donor atom sets and both exhibit trigonal prismatic coordination, which is a rare coordination geometry for transition-metal ions in general[52] and, to our knowledge, is unknown for Ag(I). For a d^{10} metal ion such as Ag(I), there cannot be an electronic bias favoring trigonal prismatic coordination over octahedral coordination. Furthermore, steric repulsions between the donor atoms favor octahedral coordination over trigonal prismatic coordination. While it is possible that the observed geometries are merely the result of packing forces, it is intriguing that the Ag(I) ions in both compounds adopt this geometry.

The bond angles at the chlorine atoms in **2**, **3**, and **4** span relatively small ranges, 97.2 (4)–107.8 (3)° for **2**, 92.1 (2)–94.5 (2)° for **3**, and 96.7 (1)–108.4 (2)° for **4**. The "optimum" Ag–Cl–C bond angle will not be known until a number of silver complexes of monodentate chlorocarbons have been structurally characterized. In one theoretical study, $[Li\text{–}Cl\text{–}CH_3]^+$ and $[Na\text{–}Cl\text{–}CH_3]^+$ bond angles were predicted to be 138 and 157°.[27c] In potassium tetrafluorophthalate, a C–F bond coordinates without being part of a chelate ring, and the K–F–C bond angle is 161 (1)°.[53] These values may not be relevant comparisons for complexes in which the M–XR bonds are expected to be largely covalent. A 1984 survey of the Cambridge Crystallographic Data Base revealed that the average M–X–C bond angle is ~100° for 39 structures with intermolecular M···X–C contacts (X = F, Cl, Br, I).[54] Since that time, four complexes containing monodentate iodocarbons have been reported. Their M–I–C angles are 106.9 (8)° (M = Ir(III); average of two values),[14b] 102.5 (5)° (M = Re(I)),[15d] 101.8 (2)° (M = Ru(II)),[14d] and 104.9 (7)° (M = Ru(II)).[16] One theoretical study of M–IR bonding predicted an angle of 100° for a $Pt\text{–}I\text{–}CH_3$ linkage,[55] while another used in-

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teratomic distances and angles from X-ray crystallographic data and did not allow the geometries to vary.[56]

(b) Solution Behavior. Despite the fact that Gladysz and coworkers reported separate ^{13}C NMR resonances for free and bound dichloromethane in −85 °C solutions of $[Re(Cp)(NO)(PPh_3)(CH_2Cl_2)]^+[BF_4]^-$ [15d] and $[Re(C_5Me_5)(NO)(PPh_3)(CH_2Cl_2)]^+[BF_4]^-$,[15c] we only observed one ^{13}C signal for $AgOTeF_5$ or $Ag_2Pd(OTeF_5)_4$ in dichloromethane or 1,2-dichloroethane, from room temperature down to the freezing point of the respective solvent (−95 °C for dichloromethane and −35 °C for 1,2-dichloroethane). The one observed signal, however, was shifted from the value for the pure solvent in each case. For example, the ^{13}C NMR spectrum of a 0.35 M solution of $Ag_2Pd(OTeF_5)_4$ in dichloromethane consisted of a single resonance at 54.2 ppm, whereas pure dichloromethane exhibits a single resonance at 54.1 ppm; the spectrum of a 0.66 M solution of $Ag_2Pd(OTeF_5)_4$ in 1,2-dichloroethane consisted of a single resonance at 45.0 ppm, whereas pure dichloromethane exhibits a single resonance at 43.9 ppm (Table II). These observations, as well as the high solubilities of $AgOTeF_5$ and $Ag_2Pd(OTeF_5)_4$ in dichloromethane and 1,2-dichloroethane (see above), strongly suggest that the Ag–Cl bonds observed in the structures of **1**–**4** are maintained to some extent in solution, with rapid exchange of free and bound chlorocarbons at all accessible temperatures.

Equivalent conductance data for $AgOTeF_5$ and $Ag_2Pd(OTeF_5)_4$ are listed in Table I, along with other relevant data. A study of the conductivity of tetraalkylammonium, tetraphenylarsonium, and bis(triphenylphosphine)iminium salts in dichloromethane demonstrated that they all behaved as weakly dissociated 1:1 electrolytes.[57] Thus, even $N(n\text{-}Bu)_4{}^+ClO_4{}^-$ exists largely as tight ion pairs in dichloromethane solution (our value for the equivalent conductance of a 0.0100 M dichloromethane solution of this salt, $13.8 \times 10^{-3}\ \Omega^{-1}\ cm^{-1}\ M^{-1}$, can be compared with the value we calculated using the simplest possible model for ion dissociation and the results reported in ref 57, $7.8 \times 10^{-3}\ \Omega^{-1}\ cm^{-1}\ M^{-1}$). Our data show that $AgOTeF_5$ is a much weaker electrolyte in these chlorocarbon solvents than $N(n\text{-}Bu)_4{}^+ClO_4{}^-$ or $N(n\text{-}Bu)_4{}^+OTeF_5{}^-$, but that some small amount of free $OTeF_5{}^-$ and the homoleptic cationic complexes $Ag(CH_2Cl_2)_n{}^+$ and $Ag(1,2\text{-}C_2H_4Cl_2)_n{}^+$ may exist (other interpretations are possible, such as dissociation to free $OTeF_5{}^-$ and dinuclear $Ag_2(OTeF_5)(solv)_n{}^+$). The concentrations of free ions must be very small, however, since IR spectra of chlorocarbon solutions of $AgOTeF_5$ do not show bands attributable to free $OTeF_5{}^-$.

The equivalent conductance data show that a higher concentration of ions was produced in 0.0100 M solutions of $AgOTeF_5$ or $Ag_2Pd(OTeF_5)_4$ in 1,2-dichloroethane than in 0.0100 M solutions of these compounds in dichloromethane. These results require that specific solvation (i.e., coordination) must be stronger with 1,2-dichloroethane than with dichloromethane, since the equivalent conductances of $N(n\text{-}Bu)_4{}^+OTeF_5{}^-$ (or of $(N(n\text{-}Bu)_4{}^+)_2Pd(OTeF_5)_4{}^{2-}$) in the two solvents are barely distinguishable (the dielectric constants for dichloromethane and 1,2-dichloroethane at 20 °C are 9.08 and 10.65, respectively[58]). The conclusion that 1,2-dichloroethane is a stronger ligand than dichloromethane is sensible, since five-membered chelate rings are generally more stable than four-membered chelate rings, and is corroborated by the ^{13}C NMR experiment shown in Figure 2: a 0.65 M solution of $Ag_2Pd(OTeF_5)_4$ in an equimolar mixture of dichloromethane and 1,2-dichloroethane exhibited a ^{13}C NMR resonance for each solvent, but only the resonance assigned to 1,2-dichloroethane was shifted from the free solvent value.

Since the conductance data demonstrate that dissociation into free ions is limited, the bulk of the dissolved species are tight ion pairs or molecular complexes. It is easy to envision similar or identical solid-state and solution structures for **3** and **4**, but the solid-state structure of **2** cannot be maintained in solution, since the network of intermolecular Ag–Cl and Ag–F bonds is almost certainly broken in solution. A reasonable possibility is that each Ag(I) ion in $AgOTeF_5$ coordinates to two dichloromethane or 1,2-dichloroethane molecules in solution, and possesses a coordination geometry in solution that is similar to the coordination geometries exhibited in the solid state by the Ag(I) ions in **3** and **4**.

Effects of Coordination on the Chlorocarbon. There are two main reasons to compare the structures and spectral properties of free and bound dichloromethane and 1,2-dichloroethane. First, it may eventually be possible to use spectral shifts alone to demonstrate reliably the coordination of a chlorocarbon (i.e., in the absence of a crystal structure). Since this is the first study in which structural and more than one type of spectroscopic results are reported, we can begin to catalog spectral features that are indicative of chlorocarbon coordination. The second reason is to understand what effect metal ion coordination has on the reactivity of chlorocarbons. In view of the facts that chlorocarbons (i) oxidatively add to many low-valent metal ions[11] and (ii) undergo Ag(I) assisted nucleophilic substitution,[59] it is important to know whether C–Cl bonds are appreciably lengthened and/or weakened upon coordination of chlorocarbons to metal ions.

(a) Structural Results. The structures of the bound chlorocarbon ligands in **2**, **3**, and **4** are not significantly perturbed from the structures of the free molecules. In solid 1,2-dichloroethane at −140 °C, which exists as the anti conformer, the C–Cl and C–C bond distances and the Cl–C–C bond angle are 1.80 (2) Å, 1.49 (4) Å, and 105.5 (5)°, respectively.[60] Only the Cl–C–C bond angle is distinguishable from the values found for bound 1,2-dichloroethane in **2** and **4**, which vary from 111 to 114° (see Tables IV and V). A better comparison for our complexes would be a 1,2-dichloroethane solvate with a gauche conformation; one such example (data obtained at −160 °C) has an average C–Cl bond distance, a C–C bond distance, and an average Cl–C–C bond angle of 1.798 (5) Å, 1.467 (5) Å, and 112.6 (4)°, respectively.[61] This solvate has a Cl–C–C–Cl torsional angle of 61.6°, while in our complexes this angle takes the following values: 67.9° for the Cl1 ligand in **2**, 70.0° for the Cl3 ligand in **2**, 65.0° for the Cl1 ligand in **4**, and 66.4° for the Cl3 ligand in **4**. The increase in the Cl–C–C–Cl torsional angle in the complexes relative to the solvate is minor: the change of 4–8° may allow the ligand to achieve a more optimal Cl–Ag–Cl bite angle. Similarly, the two bidentate dichloromethane ligands in **3** are essentially unperturbed from the gas-phase structure (C–Cl = 1.7724 (5) Å, Cl–C–Cl = 111.78 (2)°[62]) or solid-state structure (C–Cl = 1.77 (1) Å, Cl–C–Cl = 112 (1)°, data obtained at −120 °C[63]) of free dichloromethane. The foregoing results are in harmony with crystallographic studies of coordinated iodocarbons, which have all showed that C–I bonds are not significantly lengthened upon coordination to Ir(III),[14a,b] Re(I),[15b,e] or Ru(II).[14d,16]

(b) Spectroscopic Results. The above results notwithstanding, spectroscopic measurements might be more sensitive probes of subtle changes in C–Cl bonding upon coordination than X-ray crystallography. In this section of the paper, we will show that certain IR, ^{13}C NMR, and ^{35}Cl NQR spectral features are different for the chlorocarbon ligands in **1**–**4** than for the respective free chlorocarbons. The conclusion that the spectral shifts are caused by coordination to Ag(I) must remain tentative, however, at least for the IR and ^{13}C shifts, which are relatively small. We do not yet know if dichloromethane solvates that are definitely not coordinated to metal ions would also experience small shifts in ν(CCl) bands and in solid-state ^{13}C chemical shifts. In ongoing work, we will examine a number of structurally characterized

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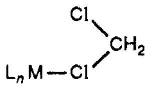
Table VIII. Comparison of Spectral Data for Dichloromethane Complexes[a]

compd	$\delta(^{13}C)$, ppm	$\nu(CCl)$,[b] cm^{-1}
CH_2Cl_2	54.1[c]	743, 707
$[Ag(CH_2Cl_2)(OTeF_5)]_2$ (**1**)	58.0[d]	738
$Ag_2(CH_2Cl_2)_4Pd(OTeF_5)_4$ (**3**)	57.6[d]	725
$[Re(C_5H_5)(NO)(PPh_3)(CH_2Cl_2)]^+[BF_4]^-$[e]	78.3[f]	
$[Re(C_5Me_5)(NO)(PPh_3)(CH_2Cl_2)]^+[BF_4]^-$[g]	75.8[f]	
$[Mo(C_5H_5)(CO)_3(CH_2Cl_2)]^+[PF_6]^-$[h]		757, 629
$[W(C_5H_5)(CO)_3(CH_2Cl_2)]^+[PF_6]^-$[h]		760, 616

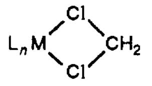
[a] Data from this work unless otherwise noted. [b] From IR spectra of Nujol mulls (except for CH_2Cl_2, which was dispersed in Nujol) at 296 K. [c] From liquid-state NMR spectrum at 296 K. [d] From solid-state NMR spectra at 296 K. [e] Reference 15d. [f] From liquid-state NMR spectra at 188 K. [g] Reference 15c. [h] Reference 13.

compounds that crystallize with one or more molecules of dichloromethane of solvation to directly address this issue.

(i) **IR Spectroscopy.** The carbon–chlorine stretching vibrations of bound dichloromethane, for example, would depend on whether it was monodentate (II) or bidendate (III). By analogy to the behavior of monodentate vs bidentate carboxylates and dithiocarbamates,[64] monodentate coordination should produce two



II



III

$\nu(CCl)$ bands, one higher in energy than $\nu(CCl)_{asym}$ for free dichloromethane (743 cm^{-1}) and one lower in energy than $\nu(CCl)_{sym}$ for free dichloromethane (707 cm^{-1}); bidentate coordination should also produce two bands, but in this case they will be between $\nu(CCl)_{asym}$ and $\nu(CCl)_{sym}$ for free dichloromethane. The dichloromethane ligands in $[M(Cp)(CO)_3(CH_2Cl_2)]^+[PF_6]^-$ (M = Mo, W) are believed to be monodentate based on IR $\nu(CCl)$ data (see Table VIII). The dichloromethane ligands in **1** and **3** are known to be bidentate, but only $\nu(CCl)_{asym}$ has been positively assigned due to the very intense $\nu(TeF)$ bands in the region around 700 cm^{-1} (see Figure 9 and Table VI). Nevertheless, the bands we have assigned are 5 cm^{-1} (**1**) and 18 cm^{-1} (**3**) lower than $\nu(CCl)_{asym}$ for free dichloromethane.

Even though $\nu(CCl)_{asym}$ shifts to a greater extent in **3** than in **1**, we hesitate to conclude that coordination of dichloromethane is stronger in **3** than in **1**. Considering the weak binding of the *second* equivalent of dichloromethane to each Ag(I) ion in $Ag_2Pd(OTeF_5)_4$ (see Figure 1), it is possible that a Nujol mull IR sample of **3** loses some dichloromethane during sample preparation and is composed of predominantly 1:1 instead of 2:1 complexes. Recall that solid-state ^{13}C NMR spectra showed the presence of at least one new species other than **4** when a sample of **4** was sealed in a glass tube *without excess solvent present.* The addition of excess chlorocarbon is obviously not possible for IR samples if small shifts in $\nu(CCl)$ are to be observed. Unfortunately, our tensimetric titration data cannot be used to order the relative strengths of the Ag–Cl bonds in question—the differences between $P_{1/2}$ for dichloromethane binding to $AgOTeF_5$ and to $Ag_2Pd(OTeF_5)_4$ could arise from differences in the strengths of Ag–Cl bonds and/or the strengths of the Ag–F bonds they replace.

IR spectra of **2** and **4** show a shift of 16 cm^{-1} to lower energy of a $\nu(CCl)$ band. Metal complexes of 1,2-disubstituted ethane ligands such as $H_2NCH_2CH_2NH_2$, $^-SCH_2CH_2S^-$, and $CH_3SCH_2CH_2SCH_3$ have been studied by IR spectroscopy, but no definite assignments of C–E stretching frequencies are available (E = NH_2, S^-, or SCH_3).[64] Keeping in mind the caveat mentioned at the beginning of this section, we conclude that $\nu(CCl)$ bands do show a measureable shift upon coordination of dichloromethane and 1,2-dichloroethane to metal ions, even for relatively weak bidentate coordination. Infrared spectroscopy can apparently be used to detect this mode of coordination and, in the case of dichloromethane, can distinguish it from monodentate coordination.

(ii) **^{13}C NMR Spectroscopy.** Coordination of iodocarbons to metal ions deshields the α-carbon atom by 12–27 ppm (the spectra were generally recorded with dichloromethane-d_2 solutions of the complexes).[14-16] While there are fewer data for coordinated chlorocarbons, the same trend has been observed.[15c-e] For example, the α-carbon atom of free chloroethane is deshielded by 30.0 ppm in $[Re(Cp)(NO)(PPh_3)(EtCl)]^+[BF_4]^-$.[15e] Our results for **1**–**4**, listed in Table II, show that coordination of chlorocarbons to Ag(I) also deshields the α-carbon atom, but only by 3–6 ppm. Since we could not detect separate resonances for free and bound dichloromethane or 1,2-dichloroethane in solution, even at low temperatures, we measured the deshielding ($\Delta\delta$) for solid samples. Whereas $\Delta\delta$ is 24.3 and 21.8 ppm for $[Re(Cp)(NO)(PPh_3)(CH_2Cl_2)]^+[BF_4]^-$ and $[Re(C_5Me_5)(NO)(PPh_3)(CH_2Cl_2)]^+[BF_4]^-$, respectively, $\Delta\delta$ is only 3.9 and 3.5 ppm for **1** and **3**, respectively (see Table VIII). The differences in chemical shifts are consistent with kinetic data in that free and bound dichloromethane exchanged very rapidly in solutions of **1** and **3**, while the exchange of free dichloromethane with bound dichloromethane-d_2 in $[Re(Cp)(NO)(PPh_3)(CD_2Cl_2)]^+[BF_4]^-$ was incomplete after 2 h at -40 °C.[15d] While the mechanisms of solvent exchange may not prove to be dissociative for both the Re(I) complexes and the Ag(I) complexes, the chemical shift and exchange rate data taken together suggest much stronger M–ClR bonding in the Re(I) complexes than in our Ag(I) complexes, which may be due to the fact that the Re(I) complexes are cationic while the Ag(I) complexes are neutral.

Even though there are two or more crystallographically unique carbon atoms in **2**, **3**, and **4**, we only observed a single ^{13}C resonance in CP–MAS spectra of these compounds. The resonances are broad, as shown in Figure 11, at least in part because dipolar coupling between spin $^1/_2$ nuclei and quadrupolar nuclei such as ^{35}Cl and ^{37}Cl is not in general averaged to zero by MAS.[65] The broad resonances may mask two or more separate resonances. We believe that the small, relatively sharp resonance observed in each of the MAS spectra of **1**–**4** but absent from the CP–MAS spectra represents a mobile phase of the excess solvent added to each sample (see Figure 11). These resonances are sharp because rapid tumbling averages the quadrupolar interactions to zero. Rapid tumbling also averages C–H dipolar coupling to zero, which explains why the mobile-phase ^{13}C resonances do not cross-polarize. Their chemical shifts are deshielded from the bulk solvent value because these mobile phases are probably saturated solutions of **1**–**4**, not pure solvent.

(iii) **^{35}Cl NQR Spectroscopy.** This spectroscopic technique is a very sensitive probe of M–ClR bonding. It can distinguish between chlorine atoms that are bonded to metal ions and those that are not,[66] and it has been used to characterize metal complexes of the 2,6-dichlorophenolate ion and related ligands, which can form five-membered chelate rings containing M–Cl–C linkages.[31,66c,d,f] For example, the compound $Ag(2,4,6\text{-}C_6H_2Cl_3O)(PPh_3)_2$ contains a weak Ag–Cl bond of 3.160 (2) Å between the Ag(I) ion and one of the two ortho chlorine atoms.[67] At 77 K, the ^{35}Cl NQR frequency of the coordinated ortho chlorine atom was 1.500 MHz lower than the frequency of the noncoordinated ortho chlorine atom.[67] Shifts of this magnitude and greater were

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observed for **1**–**4** (see Table VII).

The NQR frequency of a spin $^3/_2$ nucleus such as ^{35}Cl is given by

$$\nu = (1/2h)(e^2Qq_{zz})(1 + \eta^2/3)^{1/2}$$

in which e^2Qq_{zz}, the quadrupole coupling constant of the nucleus, is a measure of the deviation of its electronic environment from spherical symmetry.[68] According to the widely used Townes–Dailey approximation, the quadrupole coupling constant for a chlorine atom in a molecule is principally due to imbalance in the populations N_x, N_y, and N_z of the valence 3*p* orbitals

$$e^2Qq_{zz} = (e^2Qq_{\text{atom}})(((N_x + N_y)/2) - N_z)$$

where e^2Qq_{atom} is the quadrupole coupling constant for a gaseous chlorine atom with an imbalance of 1 electron, 109.746 MHz.[69] In a saturated chlorocarbon, $N_x = N_y = 2$, but N_z is determined by the nature of the C–Cl σ bond. If a second bond is formed between the chlorine atom and a metal ion, N_y falls below 2, and the quadrupole coupling constant and NQR frequency are less than the values for the free chlorocarbon.

The simple treatment is the basis for using NQR to detect the weak coordination of chlorocarbons to metal ions: the quadrupole coupling constant and NQR frequency are very sensitive to small changes in electron populations. Implicit in this treatment is the assumption that the asymmetry parameter, η, does not change significantly when a chlorocarbon chlorine atom forms a bond to a metal ion. η, which can vary from 0 to 1, measures the deviation of the electronic environment from axial symmetry and can be expressed as[70]

$$\eta = (3/2)(N_x - N_y)/(N_z - ((N_x + N_y)/2))$$

Measurements of η for crystalline halophenols in which one halogen atom is engaged in hydrogen bonding, a type of secondary bonding, show it to be generally less than 0.16;[71] for $\eta = 0.16$, the term $(1 + \eta^2/3)^{1/2}$ would raise the NQR frequency, ν, by less than 0.5%.

For **2** and **3**, each crystallographically unique chlorine atom gave rise to a discrete NQR signal, although not necessarily at 77 K. The observation of only two signals at all temperatures for **1** suggests that this compound contains two unique chlorine atoms. Unfortunately, signals for **4** were very weak at 77 K and not observable at higher temperatures. Nevertheless, the two equally intense signals for **4** were unusually broad, so it is possible that they represent two sets of two overlapping signals. The range of NQR frequencies for **1**–**4** could be due to differences in Ag–Cl bonding or to differences in the local environment of the chlorine atoms (the crystal field effect). Weiss studied the crystal field effect for a series of chlorinated benzenes and found that, for 95% of the compounds, the range of frequencies for chemically equivalent chlorine atoms was 0.5 MHz or less.[72] In the discussion that follows, different NQR frequencies are assumed to reflect differences in silver–chlorine bonding interactions. Alternative explanations, such as a substantial value of η or larger crystal field effects than have been observed for chlorobenzenes, cannot be tested until a larger variety of metal complexes containing coordinated chlorocarbons have been prepared and studied.

The NQR data suggest that the AgOTeF$_5$ moiety in **2** bonds to 1,2-dichloroethane more strongly than does the Ag$_2$Pd(OTeF$_5$)$_4$ moiety in **4**, since all NQR frequency lowerings are greater in **2** than in **4**. This trend is not clearly seen in the structural results for **2** and **4**, however. While both compounds exhibit a range of Ag–Cl distances, the shorter and presumably stronger Ag–Cl distances in **2** (2.626 (3) and 2.640 (3) Å) and in **4** (2.645 (1) and 2.655 (1) Å) are nearly the same. One of the two strongly bound chlorine atoms in **2** must have a frequency lowering of 2.533 MHz or greater, while the strongly bound chlorine atoms in **4** have frequency lowerings no greater than 1.901 MHz. The NQR data for **1** and **3** follow the same trend: the greatest frequency lowering for **3** (1.351 MHz) is smaller than the smallest frequency lowering for **1** (1.493 MHz), but the differences are not as dramatic in this case. Solid-state ^{13}C NMR data (Table II) also suggest that the AgOTeF$_5$ moiety in **1** and **2** interacts more strongly with its respective chlorocarbons than does the Ag$_2$Pd(OTeF$_5$)$_4$ moiety in **3** and **4**: $\Delta\delta$ for **1** is greater than $\Delta\delta$ for **3**, while $\Delta\delta$ for **2** is greater than $\Delta\delta$ for **4**. It is possible that the Ag(I) ions in **2** (Ag1 and Ag2) interact more strongly with their chlorine atoms than the Ag(I) ions in **4**, *even at a constant Ag–Cl distance*. The O$_2$Cl$_2$F$_2$ and O$_2$Cl$_3$F$_2$ coordination spheres of Ag1 and Ag2, respectively, may render Ag(I) ions more acidic and/or more polarizing than the O$_2$Cl$_4$ coordination spheres in **4**. Alternatively, the differences in NQR frequencies for **2** and **4** may be a function of differences in Ag–Cl–C bond angles. The angles Ag1–Cl2–C2 (105.0 (4)°) and Ag2–Cl4–C4 (107.8 (3)°) in **2** are larger by 5–10° than the angles Ag–Cl2–C2 (99.6 (2)°) and Ag–Cl4–C2 (96.7 (1)°) in **4**. However, the angular dependence of NQR frequencies is expected to be small in cases of weak, secondary bonding.[73]

The 77 K data for **3** seem to underscore our incomplete understanding of the factors that affect NQR frequencies for this type of compound: the four Ag–Cl bond distances vary by only 0.11 Å and the four Ag–Cl–C bond angles vary by only 2.4°, yet the NQR frequency lowerings range from 0.508 to 1.351 MHz. However, the signal that corresponds to the 0.508 MHz frequency lowering has an usually large temperature effect when compared with the temperature effect observed for dichloromethane. The variable-temperature data for **3** reveal that the frequency lowerings at 146 K, approximately the temperature at which the X-ray diffraction data were collected, vary over a smaller range of values, from 1.11 MHz (for the 35.483-MHz signal at 77 K) to 1.57 MHz (for the 34.640-MHz signal at 77 K). In previous work, it was observed that secondary M–Cl bonding in metal chlorophenolate complexes *reduced* the temperature effect of the ^{35}Cl NQR frequencies for strongly metal-bound chlorine atoms.[66c,d,f,67] The significance of the *enhanced* temperature effects for most of the signals for **1**, **2**, and **3**, relative to the free chlorocarbon, is not clear at this time. The temperature effect for 1,2-dichloroethane is not included in Table VII because its ^{35}Cl NQR frequency exhibits an anomalous temperature dependence.[74] This compound undergoes an order–disorder phase transition at about 150 K, which has been studied by X-ray crystallography.[60,75]

Our variable-temperature data suggested a phase transition for **1** at about 170 K. It is possible that the high-temperature phase is disordered. This could explain our inability to solve the structure of this compound. We were not able to obtain X-ray diffraction data for **1** below 190 K because crystals of this compound cracked at lower temperatures, probably as a result of the phase transition.

Finally, we consider the unique chlorine atom in **2** (Cl3), which bridges two Ag(I) ions at distances of 2.915 (3) and 3.000 (3) Å. The ^{35}Cl NQR frequency lowering for this atom is not substantially different than for the three more tightly bound chlorine atoms in **2**. A number of factors might produce similar frequency lowerings. It may be that two weak Ag–Cl bonds at >2.9 Å has nearly the same effect on the quantity $(N_x + N_y)/2 - N_z$ as does one stronger Ag–Cl bond at ≤2.7 Å. Alternatively, it may be that η is smaller for Cl3 than for the other three chlorine atoms, since

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with similar bonds to two Ag(I) ions, it would have nearly equal N_x and N_y values.

Comparison of $OTeF_5^-$, $Pd(OTeF_5)_4^{2-}$, $B(OTeF_5)_4^-$, ClO_4^-, and SbF_6^-. In the present study as well as in previous reports, we have shown that $OTeF_5^-$ (teflate) renders metal ions open to coordination by weak solvent molecules such as chlorocarbons and arenes.[76] The unique structural properties of teflate distinguish it from oxyanions such as ClO_4^-, FSO_3^-, and $CF_3SO_3^-$, as well as from fluoroanions such as BF_4^-, PF_6^-, and SbF_6^-. With only one reasonably strong donor atom, teflate cannot form insoluble lattices with three-dimensional extended bridging, as can perchlorate and sulfonates. Alternatively, since teflate's negative charge is concentrated on the oxygen atom,[46] its fluorine atoms are probably weaker donors than the fluorine atoms of fluoroanions. Furthermore, since teflate forms relatively strong M–O bonds, a $M(OTeF_5)_n$ or $M_2(OTeF_5)_{2n}$ fragment is probably more molecular than a $M(SbF_6)_n$ or $M_2(SbF_6)_{2n}$ fragment.

These ideas are borne out not only by solubility data but also by our tensimetric titration results, which show that $AgOTeF_5$ has a higher affinity for dichloromethane than $AgSbF_6$ ($P_{1/2}$ values are 4 (1) and 22 (1) Torr, respectively). Since $OTeF_5^-$ and SbF_6^- are isostructural, the difference must be due to the relative strengths of Ag–F bonds in the two solids (X-ray powder diffraction results have shown that $CsOTeF_5$[77] and $CsSbF_6$[78] have the same unit cell parameters to within experimental error).

The $Pd(OTeF_5)_4^{2-}$ and $B(OTeF_5)_4^-$ anions represent two different extensions of our approach to producing "coordinative unsaturation". The former anion still allows molecular complexes to be formed. It may also allow a higher concentration of completely solvated metal ions to be produced (recall that a much higher concentration of ions was produced in 0.0100 M solutions of $Ag_2Pd(OTeF_5)_4$ in either dichloromethane or 1,2-dichloroethane than in 0.0100 M solutions of $AgOTeF_5$ (see Table I)). Presumably, the $B(OTeF_5)_4^-$ anion is too sterically congested to allow M–O–B bridges to be formed: the only salt of it to be structurally characterized contained weak M–F–Te bridges.[76b] The fluorine atoms of this anion must bear much less negative charge than the fluorine atoms of conventional fluoroanions. The low but detectable solubility of $AgB(OTeF_5)_4$ in 1,1,2-trichlorotrifluoroethane stands in contrast to the complete insolubility of $AgOTeF_5$ and $Ag_2Pd(OTeF_5)_4$ in this solvent.

Summary and Conclusions. The chlorocarbons dichloromethane and 1,2-dichloroethane can coordinate in bidentate fashion to metal ions. Chlorocarbon chlorine atoms can bridge two metal ions and can serve as the predominant ligand type in the coordination sphere of a metal ion. Three spectroscopic criteria have been verified for detecting coordinated chlorocarbons. However, compared with the clear crystallographic evidence for coordination, the spectral shifts for **1**–**4** are subtle. Considering the spectral shifts that have been reported for $[M(Cp)(CO)_3(CH_2Cl_2)]^+[PF_6]^-$ (M = Mo, W) and $[Re(Cp)(NO)(PPh_3)(CH_2Cl_2)]^+[BF_4]^-$, the IR and NMR shifts for **1**–**4** by themselves would *not* have been compelling evidence for chlorocarbon coordination. Finally, we suggest that X-ray crystallography alone may not always provide unequivocal evidence for the bonding of extremely weak donors. As bond distances approach the van der Waals limit, which is difficult to assign unequivocally in most cases, spectroscopic criteria will have to be used to help establish when a metal ion and a potential ligand are bonded and when they are not.

Experimental Section

Inert Atmosphere. None of the new compounds appeared to be oxygen sensitive, but all were extremely moisture sensitive. Therefore, all preparations and physical measurements were carried out with rigorous exclusion of air and water. Schlenk, glovebox, and high-vacuum techniques were employed, with purified nitrogen or argon used when an inert atmosphere was required.[79]

Reagents and Solvents. These were reagent grade or better. The following compounds were used as received: $PdCl_2$ (Aesar), $AgPF_6$ (Aesar), $AgSbF_6$ (Aesar), $AgClO_4$ (Alfa), and AgF (Cerac). The following compounds were prepared following literature procedures: $HOTeF_5$,[17,80] $B(OTeF_5)_3$,[17,81] and $N(n\text{-}Bu)_4{}^+OTeF_5^-$.[80] The salt $N(n\text{-}Bu)_4{}^+ClO_4^-$ was prepared from $N(n\text{-}Bu)_4{}^+OH^-$ (Aldrich) and aqueous $HClO_4$ (Mallinckrodt) and dried by successive recrystallizations from ethyl acetate. The following chlorinated solvents (Aldrich, unless otherwise noted) were dried by distillation from P_2O_5 and/or 4Å molecular sieves: CH_2Cl_2, CD_2Cl_2 (Merck), $CHCl_3$, CCl_4, 1,2-$C_2H_4Cl_2$, 1,2-$C_2D_4Cl_2$ (Merck), 1,1-$C_2H_4Cl_2$, 1,1,2-$C_2H_3Cl_3$, CH_2ClCF_3 (Fluka), 1,1,2-$C_2Cl_3F_3$, 1,1,2,2-$C_2H_2Cl_4$, *trans*-1,2-$C_6H_{10}Cl_2$, and *n*-C_4H_9Cl. The samples of solvents used for conductimetry (CH_2Cl_2 and 1,2-$C_2H_4Cl_2$) and tensimetric titration experiments (CH_2Cl_2) were more rigorously dried by subsequent treatment with $AgOTeF_5$ (see below), which, because of its extremely hygroscopic nature, removed any remaining traces of water. After vacuum distillation, these samples were treated briefly with CaH_2 to remove any $HOTeF_5$ that might have formed.

Preparation of Compounds. $AgOTeF_5$. This compound was prepared by using an earlier procedure.[76a] In that earlier paper, the vacuum-dried product was incorrectly formulated as $AgOTeF_5(CH_2Cl_2)$. While a fresh sample of $AgOTeF_5$ isolated in crystalline form from dichloromethane solution does have this composition, exposure of the solvated complex to vacuum for 4 h completely removes the bound dichloromethane. The vapor pressure of dichloromethane above a solid sample of $AgOTeF_5$ that has $^1/_2$ mol of bound dichloromethane per 1 mol of Ag is 4 ± 1 Torr.

$Ag_2Pd(OTeF_5)_4$. Anhydrous $PdCl_2$ (1.24 g, 7.00 mmol) and $AgOTeF_5$ (6.15 g, 17.7 mmol) were combined with dichloromethane (50 mL). The mixture was stirred and heated to reflux for 26 h, during which time an amber solution and light grey precipitate formed. Filtration, concentration, and cooling (−20 °C) of the amber solution resulted in large dark amber crystals (5.21 g, 73% based on $AgOTeF_5$; see eq 3). The light brown solvent-free compound was obtained by exposure of these crystals to dynamic vacuum for 24 h. The vapor pressure of dichloromethane above a solid sample of $Ag_2Pd(OTeF_5)_4$ that has $^1/_2$ mol of bound dichloromethane per 1 mol of Ag is 14 ± 1 Torr. ^{19}F NMR: δ_A −34.4, δ_B −37.4, J_{AB} = 180 Hz.

$[Ag(CH_2Cl_2)(OTeF_5)]_2$ (1), 1-d_4, $[Ag(1,2\text{-}C_2H_4Cl_2)(OTeF_5)]_2$ (2), 2-d_8, $Ag_2(CH_2Cl_2)_4Pd(OTeF_5)_4$ (3), 3-d_8, $Ag_2(1,2\text{-}C_2H_4Cl_2)_4Pd(OTeF_5)_4$ (4), and 4-d_{16}. Samples of $AgOTeF_5$ or $Ag_2Pd(OTeF_5)_4$ were dissolved in a minimum amount of dichloromethane, dichloromethane-d_2, 1,2-dichloroethane, or 1,2-dichloroethane-d_4. Slow evaporation of the solution or placement of the solution in a −20 °C freezer resulted in large platelets, some of which were suitable for X-ray diffraction experiments. The crystalline solids were isolated by decanting away the saturated solution. Exposure of the crystalline solids to vacuum or to the nitrogen atmosphere in the glovebox (~1 atm) caused them to effloresce.

$(N(n\text{-}Bu)_4{}^+)_2Pd(OTeF_5)_4^{2-}$. Anhydrous $PdCl_2$ (0.33 g, 1.9 mmol), $AgOTeF_5$ (1.3 g, 3.8 mmol), and $N(n\text{-}Bu)_4{}^+OTeF_5^-$ (1.8 g, 3.8 mmol) were combined with 1,2-dichloroethane (20 mL). The mixture was stirred and heated to reflux for 4 h, during which time an amber solution and white precipitate formed. Filtration, concentration, and cooling (−20 °C) of the amber solution yielded 2.1 g (73%) of the brown crystalline product (mp 126 °C). Anal. Calcd for $C_{32}H_{72}F_{20}N_2O_4PdTe_4$: C, 24.87; H, 4.69; N, 1.81. Found: C, 25.32; H, 4.86; N, 1.78. ^{19}F NMR: δ_A −29.3, δ_B −37.8, J_{AB} = 180 Hz.

Physical Measurements. Conductimetry. With use of dichloromethane and 1,2-dichloroethane that were specially purified (see above), duplicate 5-mL samples of 0.0100 M solutions of the compounds listed in Table I were prepared in a nitrogen-filled glovebox. Portions of these solutions were transferred via pipet to an inverted Yellow Springs Instruments (YSI) 3403 conductivity cell (cell volume ≈ 1 mL; cell constant = 1.29 cm^{-1}). The conductance of each of the pure solvents and the solutions was measured with use of YSI Model 31 conductivity bridge. The conductance of both of the pure solvents was $\leq 3 \times 10^{-7}\ \Omega^{-1}\ cm^{-1}$, the lowest conductance measurable with this apparatus.

Tensimetric Titrations. Since dichloromethane is absorbed by stopcock grease and by most O-ring materials, the titration apparatus consisted of a 30 mm × 170 mm glass tube equipped with a 4 mm Kontes Teflon

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valve. The tube had a sidearm connected to a 800 mm length of 2 mm i.d. glass tubing, which extended down into a flask filled with mercury. The apparatus was connected to a high-vacuum line by means of an O-ring joint, but when the Teflon valve was closed, the contents of the apparatus were only exposed to Teflon, mercury, and glass. Weighed samples of $AgOTeF_5$, $Ag_2Pd(OTeF_5)_4$, and $AgSbF_6$ were dissolved in a minimum amount of dichloromethane that had been specially purified (see above). The solutions were quantitatively transfered to the apparatus with Schlenk and syringe techniques.[79] Dichloromethane was removed under vacuum and the resulting powders were dried under vacuum (~ 10^{-5} Torr) for at least 24 h. In the case of AgCl, a weighed amount of solid was transferred to the apparatus with use of a funnel.

For each of the four solids, successive additions of known amounts of dichloromethane were added to the titration apparatus by freezing the sample to −196 °C and allowing the chlorocarbon to condense. The sample tube was warmed to 20.0 ± 0.2 °C and the equilibrium pressure was measured (generally several hours elapsed before equilibrium was established. The number of moles of dichloromethane bound to silver(I) was determined by subtracting the number of moles of dichloromethane in the gas phase at equilibrium from the total number of moles of dichloromethane added.

Spectroscopic Methods. Samples for IR spectroscopy were Nujol mulls between KBr windows. Spectra were recorded at room temperature on a Perkin-Elmer 983 spectrometer. Peak positions are ±1 cm^{-1}. Samples for Raman spectroscopy were crystalline solids sealed in glass capillaries. Spectra were recorded at room temperature on a Spex 1403 spectrometer (514.5-nm excitation). Peak positions are also ±1 cm^{-1}.

Samples for liquid ^{13}C and ^{19}F NMR spectroscopy were dichloromethane or 1,2-dichloroethane solutions in 5-mm glass tubes. The spectrometers, a Bruker SY-200, SY-270, or WP-300, were tuned with separate samples of pure dichloromethane-d_2 or 1,2-dichloroethane-d_4. Chemical shifts (δ scale) are relative to external Me_4Si (^{13}C) or $CFCl_3$ (^{19}F). All ^{19}F NMR spectra were AB_4X patterns shielded relative to $CFCl_3$ ($X = {}^{125}Te$, $I = {}^1/_2$ 7% natural abundance).

Samples of **1**–**4** for solid ^{13}C NMR spectroscopy were crystalline solids loaded into 8-mm glass tubes. The sample size was typically 1.0 g. After a drop of dichloromethane (samples of **1** and **3**) or 1,2-dichloroethane (samples of **2** and **4**) was added to each sample, it was frozen to −196 °C and sealed under vacuum. In one experiment, the drop of 1,2-dichloroethane was not added to a sample of **4**. Spectra were recorded on a modified Nicolet NT-200 spectrometer operating at a ^{13}C frequency of 50.3 MHz, using a home-built cross-polarization–magic angle spinning (CP-MAS) unit which included the probe. The spinner system, a modified version of Gay's,[82] spun the sample tubes at 2 kHz. The CP contact time was 2 ms, the acquisition time was 52 ms, the repetition time was 2 s, the full spectral width was 10 kHz, and the number of data points collected was 2048. Single-pulse spectra were acquired with a 180–90–τ–90 pulse sequence to suppress baseline artifacts,[83] with $\tau = 50$ μs. Chemical shifts are relative to external Me_4Si, with C_6Me_6 as a secondary standard (δ = 17.4, 132.2 ppm), and are accurate to ±0.2 ppm.

Samples for ^{35}Cl NQR spectroscopy were crystalline solids loaded into 2-mL glass ampules (sample sizes shown in parenthesis): **1** (2.5 g), **2** (3.2 g), **3** (0.9 g), **4** (4.1 g). After a drop of dichloromethane (samples of **1** and **3**) or 1,2-dichloroethane (samples of **2** and 4) was added to each sample, it was frozen to −196 °C and sealed under vacuum. Spectra were recorded on a Decca NQR spectrometer with Zeeman modulation. The sample compartment was cooled with liquid nitrogen or with various low-temperature slush baths. The accuracy of the reported frequencies is ±0.012 MHz.

Crystallographic Studies. A Nicolet *R*3*m* diffractometer equipped with a LT-1 variable-temperature accessory was used. Crystals of **1** and **2** were examined under mineral oil to prevent hydration and efflorescence. A crystal embedded in Dow-Corning silicone grease at the end of a glass fiber was quickly placed in the cold nitrogen stream of the LT-1 unit. Crystals of **3** and 4 appeared to degrade when in contact with mineral oil, Paratone, or Dow-Corning silicone grease; therefore, another method of mounting these crystals was devised. An apparatus was constructed that allowed the examination and manipulation of crystals while they remained at −20 °C or colder under an atmosphere of dried argon. It consisted of a heavy 15 cm diameter glass plate with a moat around its edge filled with mineral oil. An inverted Petri dish with a 2-cm hole in its center was the lid of the apparatus (the edge of the Petri dish fit into the moat of the heavy glass plate). The Petri dish was equipped with an argon inlet tube. The apparatus was positioned on top of an aluminum cylinder (5 cm diameter × 10 cm high), which was cooled to −20 °C or below by immersion in a shallow Dewar flask filled with an appropriate coolant. After the apparatus was cooled and flushed with argon, crystals were loaded through the 2-cm hole, which was otherwise kept covered with a small glass disk sitting on top of a Viton O-ring. When a suitable crystal was found, it was embedded in Halocarbon 25-5S grease at the end of a glass fiber and quickly placed in the cold nitrogen stream of the LT-1 unit.

Crystals of **1** were found to be twinned. Cleavage was not capable of resolving the twinning problem. The diffraction pattern was always indexable in terms of a *C*-centered monoclinic cell with the unit cell parameters given in Table III. In one of the crystals examined, one twin half was evidently dominant, since intensity data from that crystal yielded an apparent solution in *C*2/*c*. Placement of atoms only at positions corresponding to the dominant image from that data set resulted in the structural model described earlier; that model refined (anisotropic thermal parameters on Ag and Te) to $R = 0.12$. Many bonds were unusual in length, and residual peaks (up to 4 e $Å^{-3}$) could not be interpreted as resulting from chemically reasonable disorder. No further attempts were made to improve the model. A data set from another crystal (significant differences in intensities existed, despite identical cell parameters) yielded $R = 0.20$ for the same model, and residual peaks were much more pronounced. Despite the uncertainty introduced by the twinning, the basic structure described seems confirmed by these results.

For **2**, **3**, and **4**, centering of 25 reflections allowed least-squares calculation[84] of the cell constants given in Table III. Other experimental parameters are also listed in Table III. The intensities of control reflections (600, 040, 004 for **2**; 100, 010, 001 for **3**; 100, 010, 001 for **4**) monitored every 97 reflections showed no significant trend during the course of the data collections. Empirical absorption corrections, based on intensity profiles for 16 reflections over a range of setting angles (ψ) for the diffraction vector, were applied to the observed data. The transmission factors ranged from 0.054 to 0.086 for **2**, from 0.055 to 0.116 for **3**, and from 0.520 to 0.706 for **4**. Lorentz and polarization corrections were applied to the data.

The structures were solved by interpretation of the Patterson map.[84] The refinements involved anisotropic thermal parameters for all nonhydrogen atoms. Hydrogen atoms were included in calculated positions (C–H = 0.96 Å, $U(H) = 1.2U_{iso}(C)$). Neutral atom scattering factors (including anomalous scattering) were taken from ref 85. The weighted least-squares refinements converged (weights calculated as $(\sigma^2(F) + |g|F_o^2)^{-1})$, with the average shift/esd <0.004 for **2**, <0.0005 for **3**, and <0.019 for **4** over the last three refinement cycles. In the final difference Fourier maps, the maximum and minimum electron densities were 1.95 and −1.17 e $Å^{-3}$ for **2**, 1.29 and −2.40 e $Å^{-3}$ for **3**, and 1.02 and −0.74 e $Å^{-3}$ for **4**. Analysis of variance as a function of Bragg angle, magnitude of F_o, reflection indices, etc., showed no significant trends.

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Supplementary Material Available: Complete tables of bond distances and angles, anisotropic thermal parameters, and hydrogen atom coordinates and thermal parameters for **2**–**4** (22 pages); table of observed and calculated structure factors for **2**–**4** (60 pages). Ordering information is given on any current masthead page.

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