Coordination of *Ortho*-Chlorines in Copper(I) and Silver(I) 2,6-Di- and 2,4,6-Trichlorophenolates

Crystal Structure of (2,4,6-Trichlorophenolato-O,Cl)bis(triphenylphosphine)silver(I)*

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The crystal structure of $(Ph_3P)_2AgOC_6H_2Cl_3$ (**I**) is reported along with the syntheses and ^{35}Cl and ^{63}Cu NQR spectra of **I** and several related silver(I) and copper(I) 2,6-di- and 2,4,6-trichlorophenolates containing phosphines, phosphites, and pyridine as co-ligands. **I** crystallizes in space group $P2_1/c$ with $a = 16.692(4)$ Å, $b = 17.942(4)$ Å, $c = 12.857(3)$ Å, $\beta = 97.60(1)°$, $V = 3816.68$ Å^3, and $Z = 4$. The final $R(F) = 0.0475$ and $R(W) = 0.0396$. Ag is coordinated in a trigonal planar geometry by the P atoms of the two triphenylphosphine ligands and the O atom of the chlorophenolate; Ag is then capped by one *ortho*-chlorine of the trichlorophenolate ligand at a distance of 3.160(2) Å. In the ^{35}Cl NQR spectrum of this compound the two *ortho*-chlorines of the trichlorophenolate ligand have a large frequency difference of 1.500 MHz, indicating that one *ortho*-chlorine is coordinated to the silver; ^{35}Cl NQR spectra of related complexes are also presented and discussed. The ^{35}Cl NQR frequency differences of coordinated and non-coordinated *ortho*-chlorines in metal chlorophenolates correlate well with the metal-chlorine distances but not with the metal-chlorine-carbon bond angles. A different correlation is found for the silver complexes of dichloroalkanes; possible reasons for this are discussed.

Key words: Nuclear quadrupole resonance, Chlorophenolates, Crystal structure, Chlorocarbons as ligands, Silver(I) complexes.

Introduction

Inorganic chemists have generally assumed that the unshared electron pairs found on halogen atoms in halocarbons cannot be donated to metal atoms, so that chlorocarbons can safely be used as inert solvents in inorganic and organometallic reactions. But in recent years a number of complexes of simple and chelating halocarbons (especially 2,4,6-trichlorophenolate ions [1–10] with several metal ions (especially Ag^+, [11–13] have been synthesized and characterized by X-ray crystallography; these have been reviewed by Kulawiec and Crabtree [14]. However, no work has been done on silver complexes of the 2,4,6-trichlorophenolate ion; this work is intended to fill that gap.

Although crystallographic results are usually thought of as definitive, observed secondary [15] metal-organohalogen distances range from some which are virtually as short as a single metal-inorganic halogen bond (the sum of the covalent radii of Ag and Cl = 2.51 Å) [16] continuously upwards to others which may be about as long as the sum of the difficult-to-determine sum of the van der Waals radii (3.40–3.50 Å for Cl and Ag) [13]. Hence inorganic chemists

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working in this area desire to supplement the X-ray crystallographic evidence for metal-organohalogen secondary bonding with data from other physical methods. Of these, only halogen NQR (nuclear quadrupole resonance) spectroscopy seems sensitive enough to the small changes occurring at the coordinated chlorocarbon to give reliable results [12].

In this paper we report the syntheses and NQR spectra of some copper(I) and silver(I) chlorophenolates of organophosphines and related co-ligands. We also report the crystal and molecular structure of the complex (2,4,6-trichlorophenolato-O,Cl)bis(triphenylphosphine)silver(I).

Experimental

^{35,37}Cl NQR spectra were obtained on a Decca superregenerative spectrometer using Zeeman modulation at 77 K, 195 K, and 273 K; for room-temperature searches for ^{63,65}Cu signals in the frequency range 16–35 MHz, a Wilks NQR-1 A spectrometer was also employed.

Simple chlorophenolates of silver have long been known [17], but are insoluble and amorphous; these are probably polymeric, as was found in the crystal structure of some silver(I) 2,4,5-trichlorophenolate which crystallized [18] amidst mainly amorphous material. We unsuccessfully attempted to grow crystalline silver(I) 2,4,6-trichlorophenolate by modifying the precipitation procedure of Hunter [19] to one of homogeneous precipitation. Hence to break up the polymeric structures and synthesize discrete molecular silver and copper(I) chlorophenolates, triphenylphosphine (Ph_3P) and other phosphines, phosphites, and pyridine were included in the syntheses as co-ligands.

Two procedures were used to synthesize these compounds: (1) the amorphous silver(I) 2,4,6-trichlorophenolate of Hunter [19] was stirred with an ethereal solution of one or two moles of the ligand; (2) the phenol, the phosphine, and the metal oxide were heated in refluxing toluene until the metal oxide had dissolved:

$$M_2O + 2\,HOC_6H_2Cl_2X + 4\,Ph_3P \rightarrow 2(Ph_3P)_2MOC_6H_2Cl_2X + H_2O.$$

With most ligands solid complexes could only be isolated which contained one mole of ligand per silver ion. Elemental analyses (C, H, N or P, Cl) were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.; these have been deposited [20]. The chlorine analyses of these products were sometimes somewhat off, perhaps due to their instability; in such cases we confirmed the ligand: chlorophenolate ratio by integration of ^{1}H NMR spectra obtained on a Bruker AC-200 high resolution NMR spectrometer with a broad band probe.

The title compound, (2,4,6-trichlorophenolato-O,Cl)bis(triphenylphosphine)silver(I), was prepared by stirring silver(I) oxide (2.32 g, 10 mmol), 2,4,6-trichlorophenol (4.34 g, 22 mmol), and triphenylphosphine (11.54 g, 44 mmol) in 75 mL refluxing toluene in an aluminum-foil covered round bottomed flask under an argon atmosphere for 2 hr. Residual Ag_2O was filtered off; then petroleum ether was added to the clear solution, which was cooled to give white crystals of the product (14.56 g, 88% yield, m.p. 174–77°). It was recrystallized from hot 1:1 toluene/THF; cooling the solution gradually gave large colorless crystals, one of which was selected for the crystal structure determination.

The X-ray diffraction intensity data were collected on a four-circle diffractometer with Mo-K_α radiation and graphite monochromator, using the $\omega/2\theta$ scan technique, Scan 2θ up to 45°. Systematic absences found are $0k0$, $k = 2n$ and $h0l$, $l = 2n$. The space group is C_{2h}^5-$P2_1/c$. Experimental conditions and crystallographic data are shown in Table 1. The direct method (SHELXS-86) [21] was used to determine the structure. From the Fourier synthesis the coordinates of all atoms could then be located. The structure parameters were refined by means of the full-matrix least-squares method (SHELX-76) [22]. The positions of the hydrogen atoms were taken from the difference Fourier map and were refined by least-square cycles. The final R-value is reduced to 0.0396.

Results and Discussion

Crystal Structure

The positional parameters of the key heavy atoms are shown in Table 2; the key intramolecular distances and angles are listed in Table 3; further crystal structure data has been deposited [20]. Figure 1 shows the molecular structure; there are no intermolecular Ag–Cl contacts.

The two triphenylphosphine ligands present no unusual structural features. The Ag–P bond distances of 2.444 (1) and 2.451 (1) Å are slightly less than those

Table 1. Crystal structure of (2,4,6-Trichlorophenolato-O,Cl)bis(triphenylphosphine)silver(I), $C_{42}H_{32}AgCl_3OP_2$; experimental conditions for the structure determination and crystal structure data.

Formula	$C_{42}H_{32}AgCl_3OP_2$; $M = 828.90$
Crystal habitus	$(0.125 \times 0.32 \times 0.4)$ mm^3
Diffractometer	Stoe-Stadi 4
Wavelength/pm	71.069 (Mo-K_α)
Monochromator	Graphite (002)
Scan	$\omega/2\theta$
Absorption coefficient μ/m^{-1}	850
F (000)	1680
$(\sin\theta/\lambda)_{max}$/pm^{-1}	0.005385
Number of reflexions measured	6252
Independent reflexions	4998
Reflexions considered	4337
Number of free parameters	539
R(F)	0.0475
R_w(F)	0.0396
Lattice constants	
a/pm	1669.2 (4)
b/pm	1794.2 (4)
c/pm	1285.7 (3)
β/°	97.60 (1)
Volume/(pm$^3 \cdot 10^{-6}$)	3816.68
Space group	C_{2h}^5-P2$_1$/c
Per unit cell (Z)	4
ϱ_c/(Mg · m^{-3})	1.4442 (1) ($T = 297$ K)
Point positions: all atoms in 4e:	x, y, z; $x, 0.5-y, 0.5+z$; $\bar{x}, \bar{y}, \bar{z}$; $\bar{x}, 0.5+y, 0.5-z$

found for other four-coordinate (triphenylphosphine)$_2$-AgL_2 complexes, 2.47–2.48 Å [23]. The Ag–O distance, 2.235 (4) Å, is comparable to the sum of the covalent radii, 2.25 Å [16].

The chlorophenolate ligand itself is, as expected, essentially planar. The C–O distance of 1.288 (6) Å is comparable to those found in other chlorophenolate complexes (1.30–1.31 Å) [1–8] and in the hydrogen-bonded compounds of substituted amines with chlorophenols (1.30–1.31 Å) [24], and is intermediate between the bond lengths for phenolate anions (1.26 Å) [25] and *ortho*-chlorophenols and their ethers (1.36–1.38 Å) [26]. The M–O–C angle, 125.4°, is in the range found in the other metal chlorophenolates, 121.7–133.4°. The C–Cl distance of the coordinated *ortho*-chlorine atom (1.748 (6) Å) is slightly longer than the C–Cl distance of the non-coordinated *ortho*-chlorine atom (1.729 (6) Å), but is not significantly longer than the C–Cl distance of the *para*-chlorine atom (1.745 (7) Å).

The silver-chlorophenolate five-membered chelate ring **|Ag–O(1)–C(37)–C(38)–Cl(1)|** is not planar; the sum of the internal angles falls short of the ideal 540° by 17.9°. The angle O1–Ag1–Cl1, 64.5 (1)°, is more acute than the donor atom-metal-organohalogen atom angles found for any chelating organohalogen compound except the silver complex of dichloromethane [12]. The silver atom is the largest yet incorporated into chlorophenolate chelate rings; evidently it is too large for an ideal fit.

The coordination polyhedron around Ag is unusual. The three strong donor atoms, P1, P2, and O1, are coplanar with the silver atom, giving trigonal planar coordination about Ag which is capped with one *ortho*-organochlorine at an Ag–Cl distance, 3.160 (2) Å, which is substantially shorter than the sum of van der Waals radii, 3.40–3.50 Å. Normally, one would expect a fourth ligand (the organochlorine) to result in tetrahedral coordination about Ag, hence noncoplanarity of Ag, P1, P2, and O1. And it must be noted that the Ag–Cl distance is longer than that found in any other case of organochlorine to silver coordination [9]. Hence in the case of this crystal structure too, supplemental spectroscopic data would be useful to clarify the bonding (if any) to the nearby but irregularly-located chlorine.

NQR Spectra

The effect of the metal-organochlorine interaction on the ^{35}Cl NQR frequency of an organochlorine may involve a coordinate covalent donation of chlorine 3p valence electrons to a metal atom and/or an electrostatic polarization of chlorine atom core and valence orbitals by a metal ion and any other point charges present in an ionic lattice. An approximate Townes-Dailey treatment [27] of the covalent interaction shows that the ^{35}Cl NQR frequency of a coordinated chlorophenolate *ortho*-chlorine (Cl^2) should be lowered relative to that of the non-coordinated *ortho*-chlorine (Cl^6). This has been observed in practice in several crystallographically-characterized chlorophenolates of first-row transition metals [28, 29].

The 77 K ^{35}Cl NQR frequencies (in MHz), the signal-to-noise ratios, and the temperature dependence of each frequency for the compounds in this study are given in Table 4. The complexes with 1:1 co-ligand:silver (or copper) stoichiometry show almost no NQR frequencies below 34 MHz. Probably (although not certainly) this indicates the absence of organochlorine coordination, so no attempt was made to characterize these compounds crystallographically [30].

Table 2. Positions and thermal parameters of (2,4,6-Trichlorophenolato-O,Cl)bis(triphenylphosphine)silver(I), $C_{42}H_{32}AgCl_3OP_2$; the temperature factor is of the form:
$T = \exp -2\pi^2 (U_{11} h^2 a^{*2} + U_{22} k^2 b^{*2} + U_{33} l^2 c^{*2} + 2 U_{12} h k a^* b^* + 2 U_{13} h l a^* c^* + 2 U_{23} k l b^* c^*)$.
The U_{ij} are given in $(pm)^2$; U is isotropic mean for the hydrogen atoms.

Atom	x/a	y/b	z/c	U_{11} (U)	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
$Ag^{(1)}$	0.1994 (0)	0.5287 (0)	0.2023 (0)	522 (2)	569 (3)	605 (3)	48 (2)	153 (2)	11 (3)
$P^{(1)}$	0.0946 (1)	0.6247 (1)	0.1851 (1)	524 (8)	490 (9)	552 (10)	39 (7)	110 (8)	−38 (8)
$P^{(2)}$	0.3153 (1)	0.5092 (1)	0.1066 (1)	487 (8)	554 (9)	568 (10)	32 (7)	144 (8)	−33 (8)
$Cl^{(1)}$	0.3087 (1)	0.5601 (1)	0.4178 (2)	1299 (15)	722 (11)	945 (15)	−199 (11)	−107 (13)	−52 (11)
$Cl^{(2)}$	0.1792 (1)	0.2858 (1)	0.3673 (2)	1285 (15)	653 (11)	1225 (17)	−130 (11)	240 (14)	−22 (12)
$Cl^{(3)}$	0.4532 (1)	0.3285 (1)	0.6303 (2)	1350 (17)	1839 (22)	837 (15)	930 (16)	65 (14)	36 (16)
$O^{(1)}$	0.1875 (2)	0.4467 (2)	0.3302 (3)	688 (25)	633 (26)	700 (30)	−43 (21)	91 (24)	103 (23)
$C^{(1)}$	0.0243 (3)	0.6206 (3)	0.2830 (4)	411 (29)	633 (37)	482 (36)	−4 (27)	55 (27)	−77 (36)
$C^{(2)}$	−0.0169 (3)	0.6845 (3)	0.3117 (5)	630 (36)	698 (42)	728 (46)	102 (32)	171 (35)	−142 (36)
$C^{(3)}$	−0.0712 (4)	0.6769 (4)	0.3853 (5)	755 (43)	948 (53)	821 (52)	− 4 (39)	310 (41)	−246 (44)
$C^{(4)}$	−0.0863 (3)	0.6058 (4)	0.4266 (5)	678 (42)	1099 (57)	641 (47)	−86 (41)	153 (37)	−121 (44)
$C^{(5)}$	−0.0455 (3)	0.5427 (4)	0.3954 (5)	636 (37)	961 (51)	610 (43)	−78 (37)	109 (34)	−27 (40)
$C^{(6)}$	0.0111 (3)	0.5500 (3)	0.3238 (4)	632 (35)	594 (39)	586 (40)	−67 (30)	63 (32)	36 (32)
$C^{(7)}$	0.0320 (3)	0.6200 (3)	0.0576 (4)	673 (36)	379 (31)	519 (31)	−51 (27)	52 (31)	−54 (29)
$C^{(8)}$	0.0722 (4)	0.6108 (3)	−0.0303 (5)	876 (45)	667 (42)	628 (45)	49 (34)	227 (39)	−86 (36)
$C^{(9)}$	0.0278 (4)	0.6071 (3)	−0.1316 (5)	1030 (53)	670 (44)	681 (50)	−12 (39)	53 (44)	−72 (39)
$C^{(10)}$	−0.0577 (4)	0.6117 (3)	−0.1422 (5)	969 (51)	454 (36)	749 (51)	−128 (35)	−30 (43)	9 (35)
$C^{(11)}$	−0.0964 (4)	0.6205 (3)	−0.0550 (5)	794 (45)	656 (42)	757 (50)	−154 (35)	−22 (41)	61 (40)
$C^{(12)}$	−0.0534 (3)	0.6252 (3)	0.0465 (5)	527 (35)	620 (38)	797 (48)	−66 (29)	52 (35)	22 (37)
$C^{(13)}$	0.1324 (3)	0.7217 (3)	0.1903 (5)	499 (31)	579 (38)	698 (44)	−31 (29)	152 (33)	−159 (36)
$C^{(14)}$	0.1133 (4)	0.7697 (3)	0.1067 (6)	1063 (50)	401 (35)	956 (56)	3 (35)	297 (45)	74 (38)
$C^{(15)}$	0.1529 (4)	0.8411 (4)	0.1166 (8)	1480 (83)	670 (58)	1222 (89)	83 (53)	447 (71)	231 (53)
$C^{(16)}$	0.2029 (5)	0.8647 (5)	0.2044 (8)	1096 (69)	1014 (71)	1403 (98)	72 (58)	398 (70)	−315 (69)
$C^{(17)}$	0.2171 (5)	0.8155 (6)	0.2824 (8)	728 (54)	1138 (71)	1321 (71)	−108 (54)	−50 (58)	−713 (69)
$C^{(18)}$	0.1838 (4)	0.7425 (4)	0.2797 (6)	750 (43)	723 (51)	917 (60)	49 (38)	67 (44)	−176 (43)
$C^{(19)}$	0.4033 (3)	0.4676 (3)	0.1850 (4)	557 (33)	688 (38)	472 (36)	67 (32)	118 (29)	−26 (36)
$C^{(20)}$	0.3931 (4)	0.4006 (4)	0.2337 (6)	753 (46)	797 (50)	655 (47)	89 (39)	239 (43)	−22 (47)
$C^{(21)}$	0.4592 (5)	0.3660 (4)	0.2926 (6)	1197 (60)	857 (55)	635 (50)	395 (54)	280 (48)	201 (44)
$C^{(22)}$	0.5333 (4)	0.4026 (5)	0.3024 (6)	684 (50)	1432 (82)	707 (58)	386 (52)	−2 (45)	−156 (56)
$C^{(23)}$	0.5463 (4)	0.4690 (4)	0.2566 (5)	982 (52)	1075 (58)	582 (47)	274 (49)	22 (42)	75 (45)
$C^{(24)}$	0.4789 (4)	0.5009 (4)	0.1976 (5)	681 (40)	874 (47)	607 (45)	38 (39)	83 (37)	−67 (39)
$C^{(25)}$	0.3058 (3)	0.4554 (3)	−0.0145 (4)	519 (31)	481 (34)	564 (38)	−62 (27)	144 (31)	9 (29)
$C^{(26)}$	0.3631 (4)	0.4050 (3)	−0.0382 (5)	686 (40)	648 (40)	656 (47)	23 (34)	123 (36)	−173 (36)
$C^{(27)}$	0.3546 (4)	0.3684 (4)	−0.1320 (6)	835 (50)	807 (51)	883 (58)	13 (41)	265 (46)	−177 (47)
$C^{(28)}$	0.2879 (5)	0.3810 (4)	−0.2045 (6)	1173 (61)	716 (49)	758 (56)	−230 (46)	373 (53)	−328 (44)
$C^{(29)}$	0.2308 (4)	0.4311 (5)	−0.1835 (6)	845 (52)	1056 (60)	641 (54)	−156 (50)	−76 (42)	−52 (47)
$C^{(30)}$	0.2388 (4)	0.4676 (4)	−0.0885 (6)	665 (42)	760 (47)	761 (50)	99 (35)	24 (39)	−146 (39)
$C^{(31)}$	0.3510 (3)	0.5990 (3)	0.0660 (5)	494 (31)	504 (34)	631 (41)	−17 (27)	151 (31)	−75 (31)
$C^{(32)}$	0.3962 (4)	0.6084 (3)	−0.0154 (5)	710 (39)	536 (40)	670 (44)	67 (32)	256 (35)	−14 (44)
$C^{(33)}$	0.4217 (4)	0.6778 (4)	−0.0431 (6)	794 (45)	648 (42)	837 (52)	−67 (36)	319 (40)	−17 (41)
$C^{(34)}$	0.4005 (5)	0.7391 (4)	0.0095 (8)	1182 (61)	574 (47)	1762 (94)	−187 (45)	804 (63)	−56 (56)
$C^{(35)}$	0.3566 (6)	0.7308 (4)	0.0900 (10)	1868 (94)	665 (60)	3005 (148)	−483 (64)	1714 (99)	−751 (77)
$C^{(36)}$	0.3312 (5)	0.6617 (4)	0.1180 (8)	1281 (68)	782 (51)	1736 (94)	−425 (49)	1074 (64)	−545 (59)
$C^{(37)}$	0.2462 (3)	0.4217 (3)	0.3960 (5)	716 (40)	615 (40)	503 (39)	12 (34)	255 (34)	21 (34)
$C^{(38)}$	0.3101 (4)	0.4650 (3)	0.4470 (5)	868 (42)	643 (39)	558 (42)	43 (37)	188 (36)	−9 (36)
$C^{(39)}$	0.3739 (4)	0.4380 (4)	0.5166 (5)	831 (48)	1022 (59)	525 (46)	99 (44)	50 (39)	−150 (46)
$C^{(40)}$	0.3753 (4)	0.3645 (5)	0.5405 (5)	965 (54)	1085 (62)	532 (46)	403 (48)	154 (41)	−35 (47)
$C^{(41)}$	0.3160 (5)	0.3169 (4)	0.4977 (6)	1152 (59)	673 (47)	732 (53)	359 (47)	357 (48)	107 (44)
$C^{(42)}$	0.2531 (4)	0.3458 (3)	0.4251 (5)	900 (45)	640 (42)	632 (45)	59 (37)	252 (39)	−37 (36)
$H^{(C2)}$	−0.0007 (28)	0.7256 (26)	0.2864 (40)	600					
$H^{(C3)}$	−0.1096 (25)	0.7195 (25)	0.3994 (37)	600					
$H^{(C4)}$	−0.1248 (26)	0.6007 (26)	0.4757 (38)	600					
$H^{(C5)}$	−0.0562 (27)	0.4949 (25)	0.4211 (39)	600					
$H^{(C6)}$	0.0521 (25)	0.5099 (24)	0.3040 (38)	600					
$H^{(C8)}$	0.1377 (25)	0.6020 (24)	−0.0219 (38)	600					
$H^{(C9)}$	0.0534 (29)	0.6035 (28)	−0.1837 (39)	600					
$H^{(C10)}$	−0.1048 (26)	0.6082 (25)	−0.2080 (38)	600					
$H^{(C11)}$	−0.1611 (26)	0.6236 (24)	−0.0670 (38)	600					
$H^{(C12)}$	−0.0864 (27)	0.6308 (27)	0.0976 (38)	600					
$H^{(C14)}$	0.0796 (26)	0.7572 (26)	0.0460 (38)	600					
$H^{(C15)}$	0.1351 (32)	0.8688 (29)	0.0654 (42)	600					

Table 2. (Continued).

Atom	x/a	y/b	z/c	U_{11} (U)	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
$H^{(C16)}$	0.2416 (25)	0.9202 (26)	0.2069 (39)	600					
$H^{(C17)}$	0.2434 (31)	0.8207 (32)	0.3339 (43)	600					
$H^{(C18)}$	0.1996 (28)	0.7061 (26)	0.3307 (38)	600					
$H^{(C20)}$	0.3481 (26)	0.3774 (27)	0.2209 (43)	600					
$H^{(C21)}$	0.4500 (28)	0.3202 (25)	0.3207 (40)	600					
$H^{(C22)}$	0.5720 (27)	0.3782 (27)	0.3322 (42)	600					
$H^{(C23)}$	0.5891 (28)	0.4944 (28)	0.2712 (46)	600					
$H^{(C24)}$	0.4893 (26)	0.5319 (24)	0.1665 (38)	600					
$H^{(C26)}$	0.4156 (25)	0.3946 (24)	0.0146 (38)	600					
$H^{(C27)}$	0.3985 (25)	0.3332 (24)	−0.1481 (38)	600					
$H^{(C28)}$	0.2840 (28)	0.3548 (26)	−0.2672 (38)	600					
$H^{(C29)}$	0.1873 (26)	0.4389 (28)	−0.2262 (40)	600					
$H^{(C30)}$	0.2021 (27)	0.4980 (26)	−0.0741 (41)	600					
$H^{(C32)}$	0.4113 (26)	0.5665 (25)	−0.0557 (37)	600					
$H^{(C33)}$	0.4533 (25)	0.6808 (25)	−0.1076 (37)	600					
$H^{(C34)}$	0.4174 (26)	0.7884 (25)	−0.0140 (38)	600					
$H^{(C35)}$	0.3432 (34)	0.7654 (27)	0.1140 (43)	600					
$H^{(C36)}$	0.3024 (28)	0.6577 (28)	0.1660 (39)	600					
$H^{(C39)}$	0.4187 (25)	0.4737 (24)	0.5585 (38)	600					
$H^{(C41)}$	0.3164 (26)	0.2624 (24)	0.5114 (38)	600					

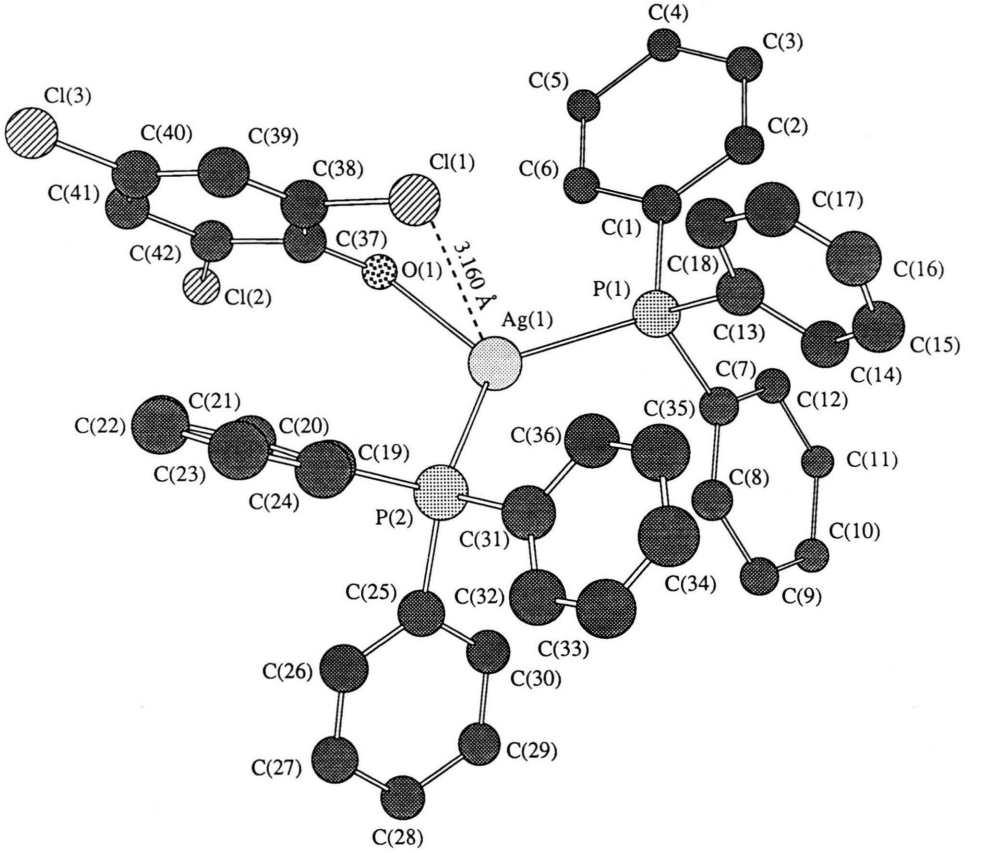

Fig. 1. Chem3D drawing of molecular structure of $(Ph_3P)_2AgOPhCl_3$ with atom numbers. Hydrogen atoms are omitted for clarity.

Table 3a. Crystal structure of (2,4,6-Trichlorophenolato-O,Cl)bis(triphenylphosphine)silver(I), $C_{42}H_{32}AgCl_3OP_2$; Intramolecular distance (d/pm).

Atoms	Length/pm	Atoms	Length/pm	Atoms	Length/pm	Atoms	Length/pm
$Ag^{(1)}-P^{(1)}$	244.4 (1)	$C^{(3)}-C^{(4)}$	141.5 (8)	$C^{(18)}-C^{(13)}$	139.1 (8)	$C^{(33)}-C^{(34)}$	136.3 (9)
$Ag^{(1)}-P^{(2)}$	245.1 (1)	$C^{(4)}-C^{(5)}$	140.6 (8)	$C^{(19)}-C^{(20)}$	137.6 (8)	$C^{(34)}-C^{(35)}$	135.2 (12)
$Ag^{(1)}-O^{(1)}$	223.5 (4)	$C^{(5)}-C^{(6)}$	140.9 (7)	$C^{(20)}-C^{(21)}$	139.8 (9)	$C^{(35)}-C^{(36)}$	137.4 (11)
$Ag^{(1)}-Cl^{(1)}$	316.0 (2)	$C^{(6)}-C^{(1)}$	140.0 (7)	$C^{(21)}-C^{(22)}$	139.1 (10)	$C^{(36)}-C^{(31)}$	137.2 (8)
$P^{(1)}-C^{(1)}$	183.3 (5)	$C^{(7)}-C^{(8)}$	139.9 (7)	$C^{(22)}-C^{(23)}$	135.8 (10)	$C^{(37)}-C^{(38)}$	141.0 (7)
$P^{(1)}-C^{(7)}$	182.6 (5)	$C^{(8)}-C^{(9)}$	141.3 (8)	$C^{(23)}-C^{(24)}$	139.5 (8)	$C^{(38)}-C^{(39)}$	138.5 (8)
$P^{(1)}-C^{(13)}$	184.8 (5)	$C^{(9)}-C^{(10)}$	141.8 (8)	$C^{(24)}-C^{(19)}$	138.5 (7)	$C^{(39)}-C^{(40)}$	135.3 (9)
$P^{(2)}-C^{(19)}$	182.8 (5)	$C^{(10)}-C^{(11)}$	137.5 (8)	$C^{(25)}-C^{(26)}$	138.0 (7)	$C^{(40)}-C^{(41)}$	136.6 (9)
$P^{(2)}-C^{(25)}$	182.0 (5)	$C^{(11)}-C^{(12)}$	140.6 (8)	$C^{(26)}-C^{(27)}$	136.4 (9)	$C^{(41)}-C^{(42)}$	140.8 (9)
$P^{(2)}-C^{(31)}$	181.6 (5)	$C^{(12)}-C^{(7)}$	141.7 (7)	$C^{(27)}-C^{(28)}$	137.3 (9)	$C^{(42)}-C^{(37)}$	141.3 (7)
$O^{(1)}-C^{(37)}$	128.8 (6)	$C^{(13)}-C^{(14)}$	138.2 (8)	$C^{(28)}-C^{(29)}$	136.4 (10)	$P^{(1)}-P^{(2)}$	445.7
$Cl^{(1)}-C^{(38)}$	174.8 (6)	$C^{(14)}-C^{(15)}$	144.0 (10)	$C^{(29)}-C^{(30)}$	137.6 (9)	$P^{(1)}-O^{(1)}$	391.3
$Cl^{(2)}-C^{(42)}$	172.9 (6)	$C^{(15)}-C^{(16)}$	137.9 (12)	$C^{(30)}-C^{(25)}$	138.7 (8)	$P^{(1)}-Cl^{(1)}$	449.8
$Cl^{(3)}-C^{(40)}$	174.5 (7)	$C^{(16)}-C^{(17)}$	133.3 (12)	$C^{(31)}-C^{(32)}$	137.9 (7)	$Cl^{(1)}-C^{(24)}$	439.8
$C^{(1)}-C^{(2)}$	141.1 (7)	$C^{(17)}-C^{(18)}$	142.2 (11)	$C^{(32)}-C^{(33)}$	137.7 (8)		
$C^{(2)}-C^{(3)}$	140.1 (8)						

Table 3b. Crystal structure of (2,4,6-Trichlorophenolato-O,Cl)bis(triphenylphosphine)silver(I), $C_{42}H_{32}AgCl_3OP_2$; Intramolecular angles (°).

Atoms	Angle/°	Atoms	Angle/°	Atoms	Angle/°	Atoms	Angle/°
$P^{(1)}-Ag^{(1)}-P^{(2)}$	131.1 (1)	$Ag^{(1)}-O^{(1)}-C^{(37)}$	125.4 (3)	$P^{(1)}-C^{(13)}-C^{(14)}$	121.1 (5)	$C^{(25)}-C^{(26)}-C^{(27)}$	121.2 (6)
$P^{(1)}-Ag^{(1)}-O^{(1)}$	113.4 (4)	$P^{(1)}-C^{(1)}-C^{(2)}$	121.7 (4)	$P^{(1)}-C^{(13)}-C^{(18)}$	116.9 (5)	$C^{(26)}-C^{(27)}-C^{(28)}$	120.0 (7)
$P^{(1)}-Ag^{(1)}-Cl^{(1)}$	106.1 (11)	$P^{(1)}-C^{(1)}-C^{(6)}$	116.2 (4)	$C^{(14)}-C^{(13)}-C^{(18)}$	121.4 (7)	$C^{(27)}-C^{(28)}-C^{(29)}$	120.0 (7)
$P^{(2)}-Ag^{(1)}-O^{(1)}$	115.4 (1)	$C^{(2)}-C^{(1)}-C^{(6)}$	122.1 (5)	$C^{(13)}-C^{(14)}-C^{(15)}$	115.4 (7)	$C^{(28)}-C^{(29)}-C^{(30)}$	120.0 (7)
$P^{(2)}-Ag^{(1)}-Cl^{(1)}$	93.6 (1)	$C^{(1)}-C^{(2)}-C^{(3)}$	118.5 (6)	$C^{(14)}-C^{(15)}-C^{(16)}$	124.6 (8)	$C^{(29)}-C^{(30)}-C^{(25)}$	120.6 (6)
$O^{(1)}-Ag^{(1)}-Cl^{(1)}$	64.5 (1)	$C^{(2)}-C^{(3)}-C^{(4)}$	120.3 (6)	$C^{(15)}-C^{(16)}-C^{(17)}$	116.1 (9)	$P^{(2)}-C^{(31)}-C^{(32)}$	124.0 (4)
$Ag^{(1)}-P^{(1)}-C^{(1)}$	115.2 (2)	$C^{(3)}-C^{(4)}-C^{(5)}$	120.1 (6)	$C^{(16)}-C^{(17)}-C^{(18)}$	124.2 (8)	$P^{(2)}-C^{(31)}-C^{(36)}$	118.6 (5)
$Ag^{(1)}-P^{(1)}-C^{(7)}$	111.5 (2)	$C^{(4)}-C^{(5)}-C^{(6)}$	120.2 (6)	$C^{(17)}-C^{(18)}-C^{(13)}$	117.7 (7)	$C^{(32)}-C^{(31)}-C^{(36)}$	117.4 (6)
$Ag^{(1)}-P^{(1)}-C^{(13)}$	115.1 (2)	$C^{(5)}-C^{(6)}-C^{(1)}$	118.7 (5)	$P^{(2)}-C^{(19)}-C^{(20)}$	118.0 (5)	$C^{(31)}-C^{(32)}-C^{(33)}$	121.8 (6)
$C^{(1)}-P^{(1)}-C^{(7)}$	105.8 (2)	$P^{(1)}-C^{(7)}-C^{(8)}$	116.9 (4)	$P^{(2)}-C^{(19)}-C^{(24)}$	122.7 (7)	$C^{(32)}-C^{(33)}-C^{(34)}$	119.5 (6)
$C^{(7)}-P^{(1)}-C^{(13)}$	105.0 (3)	$P^{(1)}-C^{(7)}-C^{(12)}$	122.5 (5)	$C^{(20)}-C^{(19)}-C^{(24)}$	119.3 (6)	$C^{(33)}-C^{(34)}-C^{(35)}$	119.5 (7)
$C^{(7)}-P^{(1)}-C^{(13)}$	103.2 (3)	$C^{(8)}-C^{(7)}-C^{(12)}$	120.6 (5)	$C^{(19)}-C^{(20)}-C^{(21)}$	119.8 (6)	$C^{(34)}-C^{(35)}-C^{(36)}$	121.2 (7)
$Ag^{(1)}-P^{(2)}-C^{(19)}$	114.3 (2)	$C^{(7)}-C^{(8)}-C^{(9)}$	120.1 (6)	$C^{(20)}-C^{(21)}-C^{(22)}$	117.9 (7)	$C^{(35)}-C^{(36)}-C^{(31)}$	120.7 (7)
$Ag^{(1)}-P^{(2)}-C^{(25)}$	121.3 (2)	$C^{(8)}-C^{(9)}-C^{(10)}$	119.0 (6)	$C^{(21)}-C^{(22)}-C^{(23)}$	124.5 (7)	$O^{(1)}-C^{(37)}-C^{(38)}$	125.2 (6)
$Ag^{(1)}-P^{(2)}-C^{(31)}$	109.2 (2)	$C^{(9)}-C^{(10)}-C^{(11)}$	120.3 (6)	$C^{(22)}-C^{(23)}-C^{(24)}$	115.5 (7)	$O^{(1)}-C^{(37)}-C^{(42)}$	122.6 (6)
$C^{(19)}-P^{(2)}-C^{(25)}$	103.2 (2)	$C^{(10)}-C^{(11)}-C^{(12)}$	121.8 (6)	$C^{(23)}-C^{(24)}-C^{(19)}$	122.9 (6)	$C^{(38)}-C^{(27)}-C^{(42)}$	112.2 (6)
$C^{(19)}-P^{(2)}-C^{(31)}$	104.5 (3)	$C^{(11)}-C^{(12)}-C^{(7)}$	118.2 (6)	$P^{(2)}-C^{(25)}-C^{(26)}$	123.5 (4)	$C^{(37)}-C^{(38)}-C^{(39)}$	125.3 (6)
$C^{(25)}-P^{(2)}-C^{(31)}$	102.7 (2)	$C^{(41)}-C^{(42)}-C^{(37)}$	123.9 (6)	$P^{(2)}-C^{(25)}-C^{(30)}$	118.3 (4)	$C^{(38)}-C^{(39)}-C^{(40)}$	118.4 (7)
$Cl^{(1)}-C^{(38)}-C^{(37)}$	116.8 (5)	$Cl^{(1)}-C^{(38)}-C^{(39)}$	117.9 (5)	$C^{(26)}-C^{(25)}-C^{(30)}$	118.1 (6)	$C^{(39)}-C^{(40)}-C^{(41)}$	121.9 (7)
$Cl^{(2)}-C^{(24)}-C^{(41)}$	118.9 (5)	$Cl^{(2)}-C^{(42)}-C^{(37)}$	117.2 (5)	$C^{(13)}-C^{(40)}-C^{(41)}$	118.2 (6)	$C^{(40)}-C^{(41)}-C^{(42)}$	118.3 (6)
$Cl^{(3)}-C^{(40)}-C^{(38)}$	119.9 (7)	$C^{(38)}-Cl^{(1)}-Ag^{(1)}$	90.2 (2)				

The NQR spectra of the bis(triphenylphosphine)-copper(I) and silver(I) 2,6-dichlorophenolates ($OPhCl_2$) show the pattern previously found by us in the analogous cobalt(II), nickel(II), copper(II), and zinc(II) complexes [2, 28, 29]: half the *ortho*-chlorine frequencies are relative high, comparable to those found in the parent chlorophenol, while the other half are shifted to unusually low frequencies. This suggests the presence of the O,Cl-chelated chlorophenolate ring. The 2:1 complexes of the 2,4,6-trichlorophenolate ion ($OPhCl_3^-$) show one-third of their ^{35}Cl NQR frequencies as low (below 34 MHz); in these spectra the NQR signals of *para*-chlorines are in the same frequency range as (but usually slightly higher than) those of the non-coordinated *ortho*-chlorines [28, 29]. In the NQR spectrum of the 1:1 complex Ph_3P-$CuOPhCl_3 \cdot C_7H_8$, one of six frequencies is at a very low value, 33.465 MHz, suggesting coordination involving half of the chlorophenolate groups.

The temperature dependence of the NQR spectra of the silver(I) and copper(I) chlorophenolates (indicated in brackets in Table 4) shows little variation, giving no

Table 4. ^{35}Cl NQR frequencies (MHz at 77 K) of group 11 chlorophenolates [a]

Compound ^{63}Cu	Cl^4	Cl^6	Cl^2	$\Delta\nu$ [b]
$(Ph_3P)_2CuOPhCl_2$		34.598 (3) [0.509]	(32.72) [c] [0.45]	1.88
		34.162 (3) [0.674]	32.548 (3) [0.451]	2.050
$(Ph_3P)_2AgOPhCl_2$		34.425 (8) [0.525]	(32.75) [c] [0.46]	1.675
$(Ph_3P)_2CuOPhCl_3$	35.447 (2) [0.767]	34.855 (2) [0.83]	33.188 (3) [0.401]	1.667
16.987 (2) [d]				
$(Ph_3P)_2AgOPhCl_3$	35.100 (9) [0.834]	35.039 (8) [0.693]	33.539 (9) [0.713]	1.500
$Ph_3PCuOPhCl_3 \cdot C_7H_8$	36.087 (3) [0.648]	35.563 (4) [0.646]	35.037 (2) [0.577]	
	35.631 (3) [0.764]	35.137 (2) [0.677]	33.465 (2) [0.544]	2.098
30.580 (3) [d, e]				
$Ph_3PAgOPhCl_3$	35.620 (5) [0.578]	34.730 (9) [0.955]	34.553 (4) [0.627]	
	35.197 (8) [0.689]	34.631 (4) [0.550]	34.104 (7) [0.795]	
α-$(PhO)_3PAgOPhCl_3$	35.200 (4) [0.604]	34.945 (3) [0.562]	34.280 (2) [0.466]	
β-$(PhO)_3PAgOPhCl_3$	35.900 (2) [0.512]	34.506 (2) [0.516]	34.432 (2) [0.487]	
$(MePh_2P)AgOPhCl_3$	35.450 (3) [0.925]	35.016 (2) [0.794]	(34.3) [c] [0.930]	
	35.367 (3) [1.131]	34.966 (2) [0.744]	not observed	
$(py)_{0.5}AgOPhCl_3$	35.180 (3) [0.580]	34.365 (3) [0.535]	33.356 (3) [0.261]	1.009
$(py)_{>1}AgOPhCl_3$	34.881 (6) [0.451]	34.148 (7) [0.681]	33.844 (7) [0.528]	

[a] Signal-to-noise ratios given in parentheses; temperature dependence of the frequencies (frequency at 77 K minus frequency at 273 K) given in brackets. In the case of closely-spaced Cl^4 and Cl^6 frequencies, the higher frequencies are arbitrarily listed under the Cl^4 column.
[b] Frequency shift in MHz at 77 K = frequency of highest Cl^6 – frequency of Cl^2, if the difference exceeds ca. 0.7 MHz.
[c] Not detected at 77 K (frequency extrapolated from higher temperature values).
[d] ^{63}Cu NQR frequency.
[e] Not detected at 77 K; frequency detected at 195 K instead.
f Not detected at 195 K or 273 K.

reason to suppose that intermolecular coordination of organochlorines is present. One unusual effect was the disappearance of certain signals at 77 K in some of these compounds. Presumably the chlorine relaxation times have become excessively long for detection with our superregenerative spectrometer in some of these compounds, but it could be that phase transitions occurred.

The NQR spectra of the copper(I) complexes were also searched for $^{63,65}Cu$ signals, since the Cu NQR frequencies empirically are found to fall in characteristic ranges depending on the coordination geometry about the copper(I) in phosphine and pyridine complexes: the more symmetrical tetrahedral coordination at copper results in low ^{63}Cu frequencies of 8–17 MHz [31, 32] while the less-symmetrical trigonal planar or linear coordination at copper results in higher ^{63}Cu frequencies of 26–38 MHz [32, 33].

In $(Ph_3P)_2CuOPhCl_3$ a weak signal was reproducibly detected at 16.987 MHz at 77 K and at 16.197 MHz at 195 K. Although the weakness of the signal allowed no confirmation by its identity by observation of the corresponding ^{65}Cu signal, the frequency is too low to be an organochlorine and too high to be an inorganic chlorine coordinated to copper(I) (i.e. $(Me_3P)_3CuCl$ at 9.16 MHz) [32]. The similarity of the organochlorine NQR spectrum of $(Ph_3P)_2CuOPhCl_3$ to that of $(Ph_3P)_2AgOPhCl_3$ suggests, but by no means proves, a similar structure. Although the Ag compound has a capped trigonal planar structure, the Cu NQR frequency of the Cu analogue falls at the upper end of the range usually found for tetrahedrally-coordinated Cu atoms. Such might be anticipated for a copper atom with four ligands, one of which is an exceptionally poor donor, or it might mean that the chlorophenolate containing the smaller Cu atom has a better ligand "bite angle" and is better able to approach tetrahedral coordination.

In the compound $Ph_3PCuOPhCl_3 \cdot C_7H_8$ the ^{63}Cu signal at 30.580 MHz (at 195 K) was strong enough to allow confirmatory observation of the corresponding ^{65}Cu signal at the predicted frequency of 28.312 MHz, at the lower end of the range usually found for low-symmetry three- or two-coordinate copper. The organochlorine spectrum of this compound requires the presence of another Cu signal, which was not detected.

Conclusions

It is useful to plot the NQR criterion of secondary bonding strength, the ^{35}Cl NQR frequency difference, against the main crystallographic criterion, the metal-

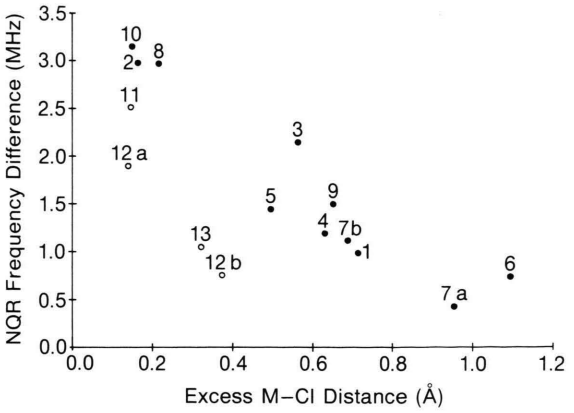

Fig. 2. Average NQR frequency difference $\nu(Cl^6)-\nu(Cl^2)$, in MHz, versus average excess M–Cl distance, in Å, for chlorophenolate and chloro-Schiff base complexes (closed circles) and silver-chloroalkane complexes (open circles). Excess M–Cl distance is defined as the observed metal-organochlorine distance minus the normal metal-terminal chlorine distance, 2.441 Å for Ni^{2+} [33], 2.414 Å for Co^{2+} [33], 2.354 Å for Cu^{2+} [33], 2.473 Å for Mo^{2+} [10], and 2.51 Å, the sum of covalent radii [16], for Ag^+. Crystallographic data for each point is from the reference with the same number as that point; NQR data is from refs. [12, 13, 27, 28], or data to be published from this laboratory.

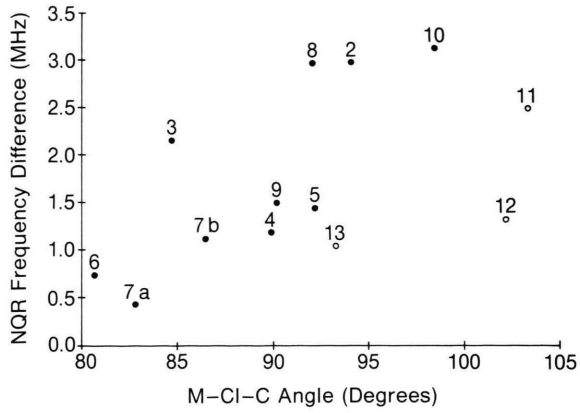

Fig. 3. Average NQR frequency difference $\nu(Cl^6)-\nu(Cl^2)$, in MHz, versus M–Cl–C bond angle, in degrees, for chlorophenolate complexes (closed circles) and silver-chloroalkane complexes (open circles). References and data point numbers are as in Figure 2.

chlorine bond distance. Meyer et al. [28] have noted previously that these measures correlate among cobalt(II) and copper(II) 2,4,6-trichlorophenolate complexes. To accommodate metals such as silver that are larger than the fourth-period *d*-block metal ions, in Figure 2 we replot the available ^{35}Cl NQR data [33] as a function of the average excess of the metal-chlorine distance over the normal bond distance for a terminal metal-inorganic chlorine bond [34]. $(Ph_3P)_2AgOPhCl_3$ fits in the middle of the range of the same correlation as the first-row transition-metal chlorophenolates [NQR frequency difference of Cl^6 and $Cl^2 = 3.394-2.959$ (excess distance) ± 0.353, $r = 0.938$], and is comparable in frequency difference to the well-characterized copper(II) chlorophenolates [1, 3–5, 29].

There appears to be little correlation of the NQR frequency difference with the C–Cl–M bond angle (Fig. 3; $r = 0.781$). In the Townes-Dailey theory for symmetrically bridging halogen atoms, the NQR frequency of the bridging halogen is strongly dependent on this angle, due to the varying hybridization of the halogen atom needed to form two strong bonds. But in the theory for secondary-bridging halogen atoms (in which the bond to the metal atom is much weaker) it is assumed that it is energetically unfavorable to hybridize the halogen just to form a very weak bond to a metal. Consequently the NQR frequency should have no dependence on the C–Cl–M bond angle, and this bond angle should be in the vicinity of 90°, as is observed empirically [14] and has been predicted from theoretical calculations [35]. Thus the NQR data suggest that, despite the closeness of approach of the chlorine and metal in some of these compounds, the bond remains secondary, and thus distinct in nature from the carbon-chlorine bond.

The silver(I) complexes of dichloroalkanes (open circles of Figure 2) exhibit a different correlation of ^{35}Cl NQR frequency shifts (measured from the free dichloroalkane) and excess Ag–Cl distances; $(Ph_3P)_2AgOC_6H_2Cl_3$ does not fit this correlation. We may cite several generic differences between these two types of metal-chlorocarbon complexes, any one (or more than one) of which may be responsible for these differences.

(1) Chlorophenolate and chloro-Schiff bases anions, and the co-ligands used with them (phosphines, amines) are stronger Lewis bases than are the neutral dichloroalkanes and the accompanying pentafluoro-oxotellurate anion [13]. Consequently the chlorophenolate complexes contain covalent metal-ligand bonds, while the bonding in the silver-dichloroalkane complexes is much more likely to be predominantly ionic. Hence the NQR frequencies of the latter complexes are more likely to be influenced by ionic lattice contributions, which may oppose the contributions made by the covalent bonds to chlorine [36].

(2) The chlorophenolate and chloro-Schiff base ligands, in contrast to the dichloroalkane ligands, are aromatic, with conjugation of the chlorine lone-pair electrons with those of the pi system of the ligand. Aromatic chlorines start with nonzero NQR asymmetry parameters, which may well be reduced to zero by coordination before being increased upon stronger coordination. This behavior would differ considerably from that of the dichloroalkanes, although if the asymmetry parameters in these complexes are all small as expected, this would have a small effect on the NQR frequencies.

(3) The correlation of Fig. 2 extrapolates to zero NQR frequency reduction [37] at an excess M–Cl distance of about 1.0 Å for the chlorophenolate complexes, i.e. an Ag–Cl distance of 3.5 Å, the normal sum of van der Waals radii of silver and chlorine. The correlation for dichloroalkane complexes extrapolates to zero NQR frequency difference much more rapidly. Given the likely high charge of silver in the dichloroalkane complexes, and given the high polarizability of Ag^+, it might be that its outer core and valence orbitals, hence radius, may contract quite significantly. Thus the van der Waals radius of Ag may be substantially smaller when the silver is positively charged than when it is closer to neutral in charge. Although it is presently not possible to determine which (if any) of these cause the two distinct correlations, new metal-halocarbon complexes of diverse types are being discovered rapidly enough that this soon should be possible.

Finally, we note that Fig. 2 suggests that there may be a maximum possible ^{35}Cl NQR frequency difference of about 3.5 MHz (i.e. a 10% frequency shift) in either metal chlorophenolates or silver chloroalkane complexes if and when the excess metal-chlorine bond distance falls to zero. Intuitively this would seem to suggest that perhaps there is some fairly modest upper limit to the degree of electron transfer possible from the chlorine to the metal while retaining a secondary bridging bond. In many cases in which synthetic chemists attempt to make complexes using stronger Lewis acids, complete transfer of the chlorine as Cl^- occurs instead to give a metal halide or, if the metal is reducing, Cl^+ is formally transferred to give oxidative addition of the chlorocarbon to the metal.

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