coupling constant of 77.8 Mc/sec—do not significantly change this expectation; the expected value is lowered to 30.7 Mc/sec.

For the bridging chlorine atoms the unique symmetry axis is normal to the molecular plane and the coupling constant along this axis should be the same as that of the chlorine nuclei in ICl_4^- in *this same* direction, +22.3 Mc/sec. The resonance should then appear near 11.2 Mc/sec for the Cl^{35} atoms; the observation of the resonance at 13.7 Mc/sec shows that the postulated contributing structures provide a fairly reasonable approximation to the molecular structure.

A refinement of this description is possible now that quadrupole coupling data are available for all of the nuclei in the molecule. The procedures devised by Townes and Dailey[7] yield the electric field gradient q at the nucleus of interest as a sum of contributions by the valence p electrons only

$$q = q_0[N_z - {}^1/_2(N_x + N_y)]$$

where N_t is the electron population of the valence p_t orbital and eq_0Q/h is the known contribution of one p electron to the coupling constant. The z axis is the unique principal axis for the field gradient tensor at the nucleus of interest, and it lies along the I–Cl bond for each terminal Cl atom but perpendicular to the molecular plane for the bridging Cl atoms and the iodine atoms.

Substitution of $eqQ/h = -68.34$ Mc/sec (mean of observed), $eq_0Q/h = +109.74$ Mc/sec,[7] and $N_x = N_y = 2$ electrons in the expression given above yields a value of $N_z = 1.38$ for the number of electrons in the bonding orbitals of each terminal Cl atom. This is a gain of 0.38 electron at each terminal Cl atom over the electron population of this orbital in the unbonded atom.

For the bridging chlorine atoms in the ideal, square configuration—to which the molecule approximates rather closely—the in-plane p_x and p_y orbitals are completely equivalent so that $N_x = N_y$; the p_z orbital contains a lone pair so $N_z = 2$. With $eqQ/h = +27.48$ Mc/sec, the total electron population of the two planar p orbitals is $N_x + N_y = 3.50$ electrons. Since the unbonded Cl atom has 3 electrons in these orbitals, this represents a gain of 0.5 electron at each bridging Cl atom.

The iodine atoms are equivalent[3] and for these also, $N_x = N_y$ and $N_z = 2$. The observed coupling constant of +2989 Mc/sec and the value[1] +2640 Mc/sec for eq_0Q/h yield $N_x + N_y = 1.74$ electrons, *i.e.*, a loss of 1.26 electrons at each iodine atom.

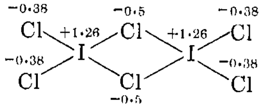
The total electron population in the molecular orbitals which are formed by combinations of the valence p atomic orbitals is thus given by the nqr data as

$$(4 \times 1.38)_{Cl} + (2 \times 3.50)_{Cl} + (2 \times 1.74)_I = 16.0 \text{ electrons}$$

These same atomic orbitals in the unbonded atoms contain

$$(4 \times 1)_{Cl} + (2 \times 3)_{Cl} + (2 \times 3)_I = 16 \text{ electrons}$$

The exact agreement is, of course, fortuitous, and, as soon as refinements are introduced, the bonding electron population calculated from the nqr data will fall below the quoted total; for example, the use of sp hybrid orbitals instead of the pure p orbitals considered for the terminal chlorine atoms would reduce the total bonding population by about 0.4 electron if the usual assumption of 15% s character for the Cl orbitals were used. For our present, qualitative purpose, the approximation of using p orbitals suffices to yield estimates of the formal charges at each atom



These values show that considerable transfer of charge from the iodine to the chlorine atoms occurs.

$IAlCl_6$

An X-ray study of this material[5] revealed a structure containing distinct ICl_2^+, with I–Cl bonds of length 2.26 and 2.29 A and ClICl angle of 96.7°, and approximately tetrahedral $AlCl_4^-$ ions. The nqr data, Table II, are in accord with this structure. The Cl^{35} resonances near 39 Mc/sec are compatible with the ICl_2^+ structure[1] while those near 11.4 Mc/sec are reasonably assigned to the Cl^{35} nuclei of $AlCl_4^-$. The only reported observation for this ion is that by Segal and Barnes[8] for $GaAlCl_4$; the mean of four resonances was 10.6 Mc/sec. An additional check with a salt known from X-ray studies to contain the $AlCl_4^-$ ion seemed desirable, and $Na^+AlCl_4^-$ [9] was prepared by fusing equimolar quantities of dried NaCl and $AlCl_3$ together in an evacuated tube. It gave, at 24°, four resonances at 11.583, 11.385, 11.272, and 11.009 Mc/sec, which are assigned to the four Cl^{35} nuclei of $AlCl_4^-$; the mean value is 11.312 Mc/sec.

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[8] S. L. Segal and R. G. Barnes, USAEC Report IS-520, 1962.

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CONTRIBUTION FROM THE ISTITUTO DI CHIMICA GENERALE ED INORGANICA DELL'UNIVERSITÀ DI MILANO, MILAN, ITALY

Tris(π-allyl)iridium(III)

BY P. CHINI AND S. MARTINENGO

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Wilke and co-workers[1] have recently reported on tris(π-allyl)cobalt and Powell and Shaw[2] on tris(π-allyl)rhodium, while the analogous tris(π-allyl)iridium has not yet been reported. We have now obtained this compound, in yield of about 20%, by the reaction of $Ir(acac)_3$ or $IrCl_3$ with allylmagnesium chloride in THF.

Tris(π-allyl)iridium(III) is a white crystalline sub-

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stance that sublimes easily at 50° (15 mm). In the solid state, it is stable in air at room temperature and it begins to decompose at about 65° without melting. The nmr spectrum is very similar to the one reported for tris(π-allyl)rhodium and is consistent with two sets of π-allyl groups in the ratio 1:2. The mass spectrum shows the presence of parent peaks corresponding to the expected masses 316 and 314.

The compound reacts readily with carbon monoxide, giving air-unstable substances which slowly transform to $[Ir(CO)_3]_4$.

Experimental Section

A 1 *M* solution of C_3H_5MgCl (0.02 mole) in THF was added to a benzene solution (20 ml) of $Ir(acac)_3$[3] (1 g or 0.002 mole). The yellow solution became orange immediately.

The reaction mixture was then warmed at 50° for 10 hr, the excess of Grignard reagent was decomposed with carbon dioxide, and, after evaporation of the solvents under vacuum, the mixture was extracted with *n*-hexane. Then the crude product, obtained by evaporation, was sublimed: it gave white crystals of camphoraceous odor (0.125 g or 20% yield). *Anal.* Calcd for $C_9H_{15}Ir$: C, 34.27; H, 4.79; Ir, 60.94. Found: C, 34.04; H, 4.46; Ir, 59.8.

The mass spectrum was recorded on an LKB 9000A spectrometer at electron accelerating voltage of 70 v.

The nmr spectrum was recorded on a Perkin-Elmer R10 spectrometer at 60 Mc in CCl_4 solution, using TMS as internal standard. The set of peaks of intensity 1 consists of signals at 4.9 ppm (τ_1, multiplet), at 7.26 ppm (τ_2, doublet), and at 7.45 ppm (τ_3, doublet) with $J_{12} \sim 8.6$ cps and $J_{13} = 11.1$ cps.

The set of peaks of intensity 2 gives τ_1 at 6.6 ppm (multiplet), τ_2 at 7.24 ppm (doublet), and τ_3 at 8.4 ppm (doublet) with $J_{12} = 6.8$ cps and $J_{13} = 9.5$ cps.

The infrared spectrum was recorded on a Perkin-Elmer 621 spectrophotometer in CCl_4 solution. In the C–H stretching region there are bands at 3051 (s), 2992 (s), 2912 (m), and 2905 (w) cm^{-1}, in the corresponding bending region there are bands at 1472 (s), 1456 (s), and 1385 (m) cm^{-1}.

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Contribution from the Chemistry Department,
Brookhaven National Laboratory,
Upton, New York 11973

The Kinetics of Some Oxidation–Reduction Reactions Involving Silver(II)[1]

By D. H. Huchital,[2a] N. Sutin, and B. Warnqvist[2b]

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Although many oxidation–reduction reactions are catalyzed by silver ions,[3,4] rate constants for only very few silver(II) oxidations have been reported. Kirwin, *et al.*,[5,6] have studied the reaction between silver(I) and cobalt(III) as part of an investigation of the silver(I)-catalyzed oxidation of chromium(III) by cobalt(III). From their data they were able to estimate the rate constant for the silver(I)–cobalt(III) reaction.[6] We have studied the effect of silver(I) on the rate of oxidation of iron(II) by cobalt(III).[7] These studies afford another determination of the rate constant for the silver(I)–cobalt(III) reaction and, in addition, provide a check on the mechanism proposed by Kirwin, *et al.*, for the silver(I)-catalyzed oxidation of chromium(III) by cobalt(III). For the purpose of comparison with these systems we have also measured the rate of oxidation of cobalt(II), iron(II), manganese(II), and vanadium(IV) by silver(II).

Experimental Section

Materials.—Cobalt(II) perchlorate solutions were prepared by dissolving reagent grade cobalt carbonate in perchloric acid of the desired concentration. Solutions containing cobalt(III) were prepared by electrooxidation of the cobalt(II) solutions. About 30–40% yield of cobalt(III) was usually obtained after prolonged electrolysis at 0°. Iron(III) perchlorate was purified by recrystallization. Solutions of iron(II) were prepared by electroreduction of the iron(III) solutions. Silver(II) oxide was prepared according to the method described in the literature.[8] Solutions of silver(II) were prepared by dissolving the solid in 4 *M* perchloric acid at −15 to −20°. Most of the solid was reduced to the +1 oxidation state upon dissolution. Vanadium(IV) was prepared by electrolysis of a solution of vanadium pentoxide in perchloric acid using a platinum gauze cathode. Manganese(II) solutions were prepared by dissolution of manganese metal in 4 *M* perchloric acid. The other chemicals were used without further purification.

Analyses.—Solutions for the stopped-flow and equilibrium measurements were prepared with triple distilled water. The cobalt(II) and cobalt(III) solutions were analyzed spectrophotometrically (ϵ_{max}[cobalt(II)] = 4.84 at 509 mμ and ϵ_{max}[cobalt(III)] = 37.0 at 605 mμ). The concentration of cobalt(II) was also checked by titration with EDTA using methyl thymol blue as indicator. The concentration of silver(I) in the stock solutions was determined by the Volhard method. Silver(II) oxide was analyzed for silver[8] and its oxidizing power was checked by adding the solid to an excess of iron(II) and titrating the excess iron(II) as described below. Solutions of silver(II) were analyzed spectrophotometrically[5,9] (ϵ_{max}[silver(II)] = 140 at 470 mμ). The analyses were performed concurrently with stopped-flow runs. The concentrations of iron(II) and iron(III) in the stock solutions were determined by titration with standard cerium(IV) sulfate using ferroin as indicator. The iron(III) was reduced to iron(II) with a Jones reductor. The concentration of vanadium(IV) in the stock solution was determined by titration with permanganate at 80° and was checked spectro-

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[1] Research performed under the auspices of the U. S. Atomic Energy Commission.

[2] (a) Summer visitor; now at the Chemistry Department, Seton Hall University, South Orange, N. J. (b) Summer student from the Royal Institute of Technology, Stockholm.

[3] See, for example, reviews by (a) W. K. Wilmarth and A. Haim in "Peroxide Reaction Mechanisms," J. O. Edwards, Ed., Interscience Publishers, New York, N. Y., 1962, pp 194–200, and (b) J. A. McMillan, *Chem. Rev.*, **61**, 65 (1961).

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