maximum error likely to arise from this assumption (4.0 cc?) cannot affect the calculated value of the electric moment by more than approximately 0.02 D. The electric moments were then evaluated from the difference between the total and induced polarizations in the usual manner[7] (Table I).

TABLE I
DIELECTRIC POLARIZATION DATA IN BENZENE AT 30.0°

10^3f_2	ϵ	d	P_2
Tris(acetylacetonato)chromium(III), $P_E + P_A = 133$, $\mu = 0.00$ D.			
0.000	2.2627	0.86823	(133)
3.106	2.2731	0.87219	129.8
4.691	2.2784	0.87421	129.7
5.031	2.2811	0.87467	134.1
6.852	2.2899	0.87693	139.1
Bis(acetyacetonato)mono(3-chloroacetylacetonato)-chromium(III), $P_E + P_A = 131$, $\mu = 1.73$ D.			
0.000	2.2627	0.86823	(191)
2.135	2.2791	0.87156	197.5
3.738	2.2895	0.87423	187.9
4.232	2.2923	0.87463	188.2
Mono(acetylacetonato)bis(3-chloroacetylacetonato)-chromium(III), $P_E + P_A = 128$, $\mu = 1.65$ D.			
0.000	2.2627	0.86823	(182)
8.677	2.2684	0.86992	180.6
15.511	2.2724	0.87116	181.7
26.119	2.2898	0.87308	182.8
Tris(3-chloroacetylacetonato)chromium(III), $P_E + P_A = 126$			
0.000	2.2627	0.86823	(126)
10.978	2.2655	0.87064	126.5
21.881	2.2687	0.87280	131.0
33.629	2.2698	0.87523	121.7
Bis(acetylacetonato)mono(3-nitroacetylacetonato)-chromium(III), $P_E + P_A = 141$, $\mu = 3.99$ D.			
0.000	2.2627	0.86823	(462)
0.9015	2.2845	0.86970	442.6
1.418	2.2987	0.87054	460.1
2.015	2.3147	0.87148	465.2
2.731	2.3361	0.87263	479.5
Mono(acetylacetonato)bis(3-nitroacetylacetonato)-chromium(III), $P_E + P_A = 150$, $\mu = 3.97$ D.			
0.000	2.2627	0.86823	(466)
0.9682	2.2779	0.87019	473.1
1.492	2.3008	0.8711	467.9
1.969	2.3130	0.87205	466.9
Tris(3-nitroacetylacetonato)chromium(III), $P_E + P_A = 158$, $\mu = 0.00$ D.			
0.000	2.2627	0.86823	(158.2)
1.664	2.2698	0.87205	158.0
1.899	2.2703	0.87261	158.7
2.131	2.2718	0.87314	157.9

The value of the moment of the mononitrated chelate, 3.99 D., is much closer to the value observed when the nitro group is bonded to aromatic (or unsaturated) carbon atoms than to those for aliphatic carbon atoms. This is compatible with the hypothesis of aromatic or pseudo-aromatic character of the chelate rings. In the case of the monochlorinated chelate, however, the value found, 1.73 D., is intermediate between the values for the aliphatic and aromatic cases. This might suggest that a substituent capable of withdrawing electron density *via* conjugation can elicit a greater back π-bonding response from the metal ion that can a substituent which is electron donating *via* conjugative interaction. This highly speculative suggestion should be tested with a wider variety of substituted chelates.

The values of the moments of both pairs of mono- and disubstituted chelates are identical, within experimental error. This would be predicted on the basis of vector addition of the C–X (X = Cl or NO_2) moments and, hence, indicates that no significant interaction occurs across chelate rings between either two chloro or nitro groups. A more sensitive test of cross-chelate ring interaction would be to observe whether there would be any significant deviation from vector additivity in a disubstituted chelate having one electron-releasing (say Cl) and one electron-withdrawing (say NO_2) group.

Experimental Section

Materials.—The substituted chromium acetylacetonates were prepared and purified by Professor J. P. Collman. These were used without further treatment.

Measurements and Calculations.—The procedure used in this study has been previously described.[9] The measurements are summarized in Table I where the dielectric constants, ϵ, and the densities, d, of benzene solutions containing mole fraction f_2 of the substance indicated are given as well as the calculated value of the molar polarization, $P_E + P_A$, the sum of the electronic and atomic polarizations, which are calculated by linear extrapolation of the P_2 values between the unsubstituted and trisubstituted chelates. The dipole moment, μ, is calculated in the usual way.

Acknowledgment.—The authors gratefully acknowledge the generosity of Professor James P. Collman in making samples of the chromium chelates available to us.

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[9] R. K. Keswani and H. Freiser, *J. Am. Chem. Soc.*, **71**, 218 (1949).

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Complexes of Trichlorostannate(II) with Group Ib Metals

BY J. A. DILTS AND M. P. JOHNSON

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There has been a considerable interest recently in the formation of metal complexes containing the $SnCl_3^-$ species as a ligand.[1] The majority of these complexes has involved second- and third-row transition metal ions with d^6 and d^8 electronic configurations. Of the

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[1] (a) R. D. Cramer, E. L. Jenner, R. V. Lindsey, Jr., and U. G. Stolberg, *J. Am. Chem. Soc.*, **85**, 1691 (1963); (b) A. C. Davies, G. Wilkinson, and J. F. Young, *ibid.*, **85**, 1692 (1963); (c) R. C. Taylor, J. F. Young, and G. Wilkinson, *Inorg. Chem.*, **5**, 20 (1966).

post-transition metals, Cu, Ag, and Au, Malatesta and co-workers[2] have reported gold(0)–gold(I) compounds formulated as $Au_5((C_6H_5)_3P)_4SnCl_3$ and $Au_3(SnI_3)((C_6H_5)_3P)_2$ which are postulated to contain Au–Au as well as Au–Sn bonds. Glockling and Hooton[3] have reported the preparation of Cu, Ag, and Au complexes containing the $(C_6H_5)_3Ge^-$ group, but simple compounds with heavier group IVa elements and Ib metals have not been reported.

In an attempt to extend studies[4] on the basicity of $SnCl_3^-$ and to examine the effect of the electron-withdrawing powers of Lewis acids on $SnCl_3$ vibrational frequencies, we have prepared the compounds $[(C_6H_5)_3P]_3MSnCl_3$ (M = Cu, Ag, Au). One of the more interesting features of this series is the isolation of a four-coordinate gold(I) complex.

Experimental Section

$((C_6H_5)_3P)_3CuCl$ and $((C_6H_5)_3P)_3AgCl$ were prepared by the method of Cariati and Naldini.[5] $(C_6H_5)_3PAuCl$ was prepared according to Levi-Malvano.[6] The melting points of these compounds correspond to those reported in the literature.

Copper(I) Tris(triphenylphosphine)trichlorostannate(II).—An acetone solution (50 ml) containing 0.70 g of triphenylphosphine (2.6 mmoles) and 1.0 g of stannous chloride dihydrate (4.5 mmoles) was added to a solution of 2.29 g of tris(triphenylphosphine)copper(I) chloride (3 mmoles) in 25 ml of methylene chloride. The mixture was stirred at room temperature for 1 hr after which the methylene chloride was slowly removed under vacuum. White crystals precipitated and were collected and dried under vacuum; mp 156°, 79% yield. *Anal.* Calcd for $C_{54}H_{45}P_3CuSnCl_3$: C, 60.30; H, 4.22; Cl, 9.89; Cu, 5.91; Sn, 11.04. Found: C, 58.61, 58.53; H, 4.15, 4.05; Cl, 9.66; Cu, 5.47; Sn, 10.32.

Silver(I) Tris(triphenylphosphine)trichlorostannate(II).—Tris(triphenylphosphine) silver chloride, 2.95 g (3.17 mmoles), in 80 ml of acetone was mixed with 0.89 g of $SnCl_2 \cdot 2H_2O$ (3.96 mmoles) in 10 ml of acetone (a complete solution is not obtained unless a large excess of stannous chloride is used). The mixture was quickly filtered. Needlelike crystals appeared on standing; mp 194–196°, 60% yield. *Anal.* Calcd for $C_{54}H_{45}P_3AgSnCl_3$: C, 57.92; H, 4.05; Cl, 9.50; Ag, 9.63; Sn, 10.60. Found: C, 58.00, 57.82; H, 4.15, 3.96; Cl, 9.34; Ag, 7.11; Sn, 10.19.

Gold(I) Tris(triphenylphosphine)trichlorostannate(II).—Triphenylphosphine gold(I) chloride (2 g, 4.04 mmoles) and 1.36 g of $SnCl_2 \cdot 2H_2O$ (6 mmoles) were mixed in 100 ml of acetone. The solution was filtered and 2.1 g of triphenylphosphine (8 mmoles) in 10 ml of acetone was added. White crystals slowly formed. A second crop of the material can be obtained by adding the solid from the first filtration to enough acetone to effect complete solution, followed by addition of triphenylphosphine until the light yellow color is discharged; mp 193–195°, 66% yield. *Anal.* Calcd for $C_{54}H_{45}P_3AuSnCl_3$: C, 53.64; H, 3.75; Cl, 8.80; Au, 16.31; Sn, 9.82. Found: C, 53.37, 53.75; H, 3.91, 3.86; Cl, 8.71; Au, 15.03; Sn, 9.06.

The infrared spectra of the compounds were obtained in Nujol mulls between polyethylene (200–500 cm^{-1}) and KBr (400–4000 cm^{-1}) on a Beckman IR 12.

The C and H analyses were done by Miss H. Beck of Northwestern University. Chloride analyses were by Alfred Bernhardt Mikroanalytisches Laboratorium, Mülheim (Ruhr), Germany, and metal analyses were done by Spectro Chemical Laboratories, Chicago, Ill.

Results and Discussion

From the analytical data it can be seen that the formulation $[(C_6H_5)_3P]_3MSnCl_3$ (M = Cu, Ag, Au) is reasonable for this series. Attempts were made to obtain molecular weight data for the compounds, but dissociation occurred in sulfolane and benzene. Similar behavior has been observed for analogous compounds.[7] The X-ray powder patterns (Table I) show the compounds to be isomorphous and presumably isostructural. This conclusion is consistent with the infrared spectra (Tables II and III). Based on these observations, the most probable structure is one containing a tin(II)–Ib metal–metal bond. The stereochemistry is probably best represented by a

TABLE I

X-RAY POWDER DATA[a]

$[(C_6H_5)_3P]_3CuSnCl_3$	$[(C_6H_5)_3P]_3AgSnCl_3$	$[(C_6H_5)_3P]_3AuSnCl_3$
10.4 s	10.5 s	10.5 s
9.3 s	9.4 s	9.4 s
8.0 w	8.0 m	7.9 w
7.4 m	7.4 m	7.4 m
6.3 m	6.3 w	6.2 w
...	...	
5.9 m	5.9 w	5.9 m
5.2 m	5.3 w	5.3 w
...	5.0 w	4.90 w
4.60 s	4.63 w	4.65 m
...	...	4.55 w
4.31 w	4.35 w	4.30 w
4.15 w	4.15 w	4.15 w
...	4.10 w	4.10 w
4.05 w	...	4.05 w
3.90 w	3.95 m	3.90 m
3.75 w	3.80 w	3.75 w
...	...	3.70 w
3.65 w	3.69 w	3.65 w
...	3.58 w	3.55 w
3.41 w	3.45 w	3.42 w
...	3.35 w	3.33 w
3.22 w	3.25 w	3.23 w
3.12 w	3.13 w	3.10 w
...	3.05 w	3.04 w
2.97 w	2.99 w	2.95 w
2.88 w	2.90 w	2.87 w
2.80 w	2.82 w	2.80 w
2.78 w	2.70 w	2.78 w
2.68 w	2.65 w	2.64 w
2.58 w	2.60 w	2.59 w
2.54 w	2.55 w	...
2.45 w	2.45 w	2.45 w
...	2.41 w	2.40 w
2.34 w	2.35 w	2.34 w
2.26 w	2.29 w	2.28 w
2.21 w	2.23 w	2.22 w

[a] These *d* values were obtained from a transparent scale made by N. P. Niles, Laguna Beach, Calif. Cu Kα radiation was used.

TABLE II

$SnCl_3$ STRETCHING FREQUENCIES

	ν_{sym}, cm^{-1}	ν_{asym}, cm^{-1}
$(C_6H_5)_4AsSnCl_3$[a]	288	252
$(C_6H_5)_4AsSnCl_3 \cdot BF_3$[a]	293	261
$((C_6H_5)_3P)_3CuSnCl_3$[b]	315	288
$((C_6H_5)_3P)_3AgSnCl_3$[b]	313	288
$((C_6H_5)_3P)_3AuSnCl_3$[b]	309	286
$((C_2H_5)_4N)_3Pt(SnCl_3)_5$[c]	335	(unresolved)

[a] M. P. Johnson, D. F. Shriver, and S. A. Shriver, *J. Am. Chem. Soc.*, **88**, 1588 (1966). [b] This work. [c] D. M. Adams and P. J. Chandler, *Chem. Ind.* (London), 269 (1965).

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[2] L. Malatesta, L. Naldini, G. Simonetta, and F. Cariati, "Proceedings of Bressanone Conference, 1965," Elsevier Publishing Corp., New York, N. Y., 1966.

[3] F. Glockling and K. A. Hooton, *J. Chem. Soc.*, 2658 (1962).

[4] M. P. Johnson, D. F. Shriver, and S. A. Shriver, *J. Am. Chem. Soc.*, **88**, 1588 (1966).

[5] (a) F. Cariati and L. Naldini, *Gazz. Chim. Ital.*, **95**, 3 (1965); (b) F. Cariati and L. Naldini, *ibid.*, **95**, 201 (1965).

[6] M. Levi-Malvano, *Atti. Accad. Lincei.*, **17**, 847 (1908).

[7] R. S. Nyholm, *J. Chem. Soc.*, 1257 (1952).

TABLE III

SPECTRA AT 400–4000 CM^{-1}

$((C_6H_5)_3P_3CuSnCl_3$	$((C_6H_5)_3P)_3AgSnCl_3$	$((C_6H_5)_3P)_3AuSnCl_3$
445 m	443 m	445 m
494 s	489 s	491 s
502 s	501 s	502 s
516 s	515 s	515 s
619 w	618 w	...
660 m, sh	668 m, sh	670 m, sh
695 s	695 s	695 s
725 m	724 m	722 m
745 s	745 s	745 s
755 m, sh	755 m, sh	755 m, sh
850 m	847 m	850 w
998 m	1000 m	995 m
1015 w	1025 w	1025 w
1090 m	1090 m	1092 m
1160 w	1162 w	1155 w
1180 w	1185 w	1170 w
1223 w	1226 w	1221 w
1311 w	1312 w	1309 w
1722 w	1721 w	1720 m

distorted tetrahedron. While four-coordinate complexes of copper and silver are common, the corresponding compounds of Au(I) are rarer. It is interesting to note that Glockling and Hooton[3] were unable to prepare $[(C_6H_5)_3P]_3AuGe(C_6H_5)_3$, although the copper and silver complexes were isolated. The occurrence of maximum coordination in these systems is probably due to d_π–d_π bonding between the central metal and the phosphorus and tin which prevents a buildup of electron density on the metal.

From the infrared data given in Table II it can be seen that the $SnCl_3$ stretching frequencies increase upon coordination to a Lewis acid. For a series of Pt(II) complexes, Parshall[8] reported that a doublet in the infrared spectra at 330 cm^{-1} is characteristic of σ-bonded $SnCl_3$. In our compounds two $SnCl_3$ vibrations are observed at *ca.* 290 and 310 cm^{-1}. By analogy with $SnCl_3^-$ and $SnCl_3BF_3^-$, these bands have been assigned to the symmetric and asymmetric stretching modes of $SnCl_3$. The appearance of two bands is consistent with the local C_{3v} symmetry about the tin atom.

Johnson and Shriver[9] have shown that there is a correlation between the $SnCl_3$ stretching frequencies and the oxidation state of a given acid in mononuclear compounds. As shown in Table II the frequencies for complexes containing a metal in the +1 oxidation state occur between the values for free $SnCl_3^-$ and the Pt(II) complexes of $SnCl_3$.

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[9] M. P. Johnson and D. F. Shriver, unpublished results.

Correspondence

The Ambiguity of Mechanistic Interpretations of Rate Laws: Alternate Mechanisms for the Vanadium(III)-Chromium(II) Reaction[1]

Sir:

Although some of the features of the mechanism of a reaction can be established from kinetic data, it is well known that such data are usually insufficient to derive a complete and unique mechanism. The mechanistic information contained in a rate law has been expressed in terms of the composition of the activated complex[2,3] or, alternately, in terms of the net activation process.[4] Beyond this, what is usually done is to propose various mechanisms *consistent* with the observed rate law and, with the aid of additional considerations, to choose the most "reasonable" mechanism.

In going from rate laws to mechanisms, two related questions may be raised. First, how is a complete set of mechanisms derived from an experimental rate law? Second, given a set of kinetically indistinguishable mechanisms, what classes of mechanistic ambiguities can be discerned? Neither of these questions has been treated systematically in the published literature.[5] However, Newton[6] has developed an elegant method, based on electrical analogs of reaction paths, to obtain a complete set of mechanisms consistent with a given rate law. Furthermore, Newton[6] has discussed, in a general manner, various levels of mechanistic ambiguities.

One type of mechanistic ambiguity, exemplified by the ammonia–cyanic acid reaction,[7] has been recognized for a long time. Since the rate law defines the composition of the activated complex but not the species from which it is generated, various mechanisms can be devised when the rate-determining step is preceded by rapid equilibria.[2,3,7] Such ambiguities can be circumvented, although not eliminated, by making use of the concept of net activation process.[4]

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[1] This work was supported by Grant GP-2001 from the National Science Foundation.

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[4] T. W. Newton and S. W. Rabideau, *J. Phys. Chem.*, **62**, 943 (1958).

[5] Some general comments about the mechanistic significance of rate laws can be found in ref 2.

[6] T. W. Newton, private communication.

[7] See, for example, I. Weil and J. C. Morris. *J. Am. Chem. Soc.*, **71**, 1664 (1949).