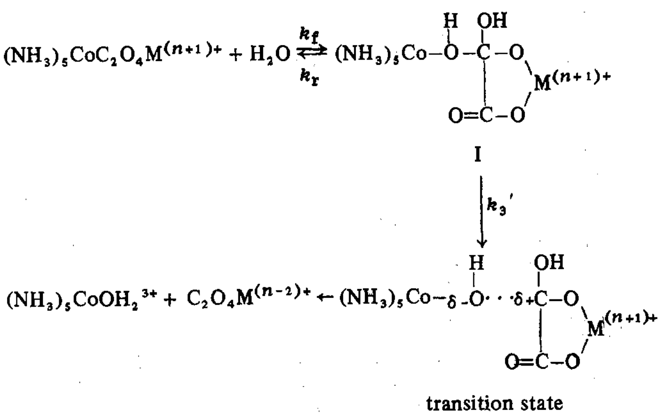
Scheme I



final products, respectively. k_f, k_r, and k_3' are expected to obey the Bronsted catalysis law ($k_i = G_iK_2^{\alpha_i}$). Positive catalytic effects of the metal ions are likely to be shown up in the hydration and dehydration steps.[10] The metal ions, on the other hand, would exert retarding influence on the acyl cleavage process (k_3') because of the unfavorable charge separation between the leaving groups in the transition state. These opposing effects of the metal ions on k_f/k_r and k_3' would have led to an inverse relationship between k_3 and K_2 (*i.e.*, the log k_3 *vs.* log K_2 plot will have a negative slope) in contrast to our observation. In fact it has been shown in the Co(II)-, Ni(II)-, Cu(II)-, and Zn(II)-catalyzed acid hydrolysis of ethyl glycinate[11] that the log $k_{(H_2O)}$ *vs.* log $K_{(ME^{2+})}$ plot ($k_{(H_2O)}$ and $K_{(ME^{2+})}$ are the rate and stability constants of the 1:1 metal-ester complex) is linear with negative slope. From the above considerations, it is reasonable to think that the metal ion promoted acyl cleavage mechanism probably does not operate in the k_3 path.

Alternatively, the metal ions in their binuclear complexes will polarize the carboxyl group bound to $(NH_3)_5Co^{3+}$, weaken the Co-O bond, and promote its heterolytic cleavage. According to this mechanism, the transition state for the k_3 path will be highly polar as the leaving groups are $(NH_3)_5Co^{3+}$ and $C_2O_4M^{(n-2)+}$. k_3 is, therefore, expected to increase with increasing charge, decreasing basicity, and increasing thermodynamic stabilities of $C_2O_4M^{(n-2)+}$ species. The observed log k_3 *vs.* log K_2 and log k_3 *vs.* $Z/(r_c + \alpha Z)$ correlations are in accord with these generalizations. Co-O bond fission, therefore, appears to be rate determining in the metal ion catalyzed path of aquation of oxalatopentaamminecobalt(III) complex. The activation enthalpies and entropies for the k_3 path agree, within experimental error, with the same for the k_0 and k_1 paths. As such it is not possible to make a reliable estimate of the energetic roles of the metal ions in the k_3 path of aquation of the oxalato complex.

Registry No. $[(NH_3)_5CoC_2O_4H](ClO_4)_2$, 15293-41-1; $(NH_3)_5CoC_2O_4^+$, 18443-73-7; Fe^{3+}, 20074-52-6; Al^{3+}, 22537-23-1; Ga^{3+}, 22537-33-3; In^{3+}, 22537-49-1; Mn^{2+}, 16397-91-4; Co^{2+}, 22541-53-3; Ni^{2+}, 14701-22-5; Cu^{2+}, 15158-11-9; Zn^{2+}, 23713-49-7.

Supplementary Material Available. A complete listing of the rate data will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-74-655.

---

[10] Y. Pocker and J. E. Meany, *J. Phys. Chem.*, 72, 655 (1968).

[11] J. E. Hix, Jr., and M. M. Jones, *Inorg. Chem.*, 5, 1863 (1966).

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Dinuclear Bridged d^8 Metal Complexes. I. Preparation and Structure of $[RhCl(CO)L]_2$ Compounds[1]

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The complex $[RhCl(CO)(C_2H_4)]_2$ provides a convenient starting material for the preparation of $[RhCl(CO)L]_2$ complexes where L = n-$C_3H_7OPF_2$, $P(OCH_3)_3$, $P(C_6H_5)_3$, $P[N(CH_3)_2]_3$, $P(CH_3)_2C_6H_5$, $P(CH_3)_3$, or $P(C_2H_5)_3$. Detailed infrared study has shown that the complex $[RhCl(CO)(C_2H_4)]_2$ exhibits two CO stretching frequencies and that the most probable structure is a double square plane ("cis" or "trans") with a bent configuration. Infrared and ^1H nmr data for the phosphine- or phosphite-substituted complexes suggest a similar structure but the planar configuration is not excluded. The ready displacement of ethylene from complexes $Rh_2Cl_2(CO)(C_2H_4)_3$ and $Rh_2Cl_2(CO)_3(C_2H_4)$ by triphenyl phosphine or tertiary phosphite provides also a convenient route to complexes $Rh_2Cl_2(CO)L_3$ and $Rh_2Cl_2(CO)_3L$, respectively.

Introduction

When a tertiary phosphine L is allowed to react with di-μ-chloro-tetracarbonyldirhodium with an L/Rh ratio of <2, an equilibrium mixture of mononuclear species $RhCl(CO)_{3-n}L_n$ (hereafter referred to as X_n) and dinuclear species $Rh_2Cl_2(CO)_{4-n}L_n$ (hereafter referred to as Y_n) is formed.[2] With careful control of the L/Rh ratio, infrared and mass spectroscopic evidence for complexes Y_1 (L/Rh = 1/2) has been obtained;[3,4] isolation in the solid state of these complexes at present has not been achieved. However stable complexes Y_2 (L/Rh = 1), originally thought to be mononuclear of type X_1,[5-8] have been isolated;[2-4,9,10] for

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[1] Preliminary communication: A. Maisonnat, P. Kalck, and R. Poilblanc, *C. R. Acad. Sci., Ser. C*, 276, 1263 (1973).

[2] R. Poilblanc and J. Gallay, *J. Organometal. Chem.*, 27, C53 (1971).

[3] J. Gallay, D. de Montauzon, and R. Poilblanc, *C. R. Acad. Sci., Ser. C*, 273, 988 (1971).

[4] J. Gallay, D. de Montauzon, and R. Poilblanc, *J. Organometal. Chem.*, 38, 179 (1972).

[5] P. Uguagliati, G. Deganello, L. Busetto, and U. Belluco, *Inorg. Chem.*, 8, 1625 (1969).

$L = P(C_6H_5)_3$ and $As(C_6H_5)_3$ they have been prepared by another method.[11,12] It is also possible to isolate the dinuclear complex Y_3 ($L/Rh = 3/2$), $L = P(C_6H_5)_3$, but the preparation is tedious.[4] By this method, for $L/Rh \geqslant 2$, except for $L = PF_3$,[13] it is not possible to isolate Y_4 complexes, the products being the well-known mononuclear complexes X_2, $RhCl(CO)L_2$.[14,15] The Y_4 complexes have been prepared by different methods.[16-22]

Y_2 complexes undergo oxidative addition reactions over the two metallic centers with retention of the binuclear structure.[4,10,23] An initial study revealed that the reactivity of Y_2 complexes toward oxidative addition reactions is greater than that of corresponding X_2 complexes.[23] The importance of X_2 complexes in catalytic processes is well known,[20,24-26] and at the present time the corresponding activity of Y_2 complexes is under investigation.[23,27]

It was our aim to investigate the catalytic properties of these Y_2 complexes and now we report a simple synthetic procedure of a large range of these compounds.

Experimental Section

The $[RhCl(CO)(C_2H_4)]_2$ compound (I) was prepared as previously described[28] by mixing equimolecular quantities of $[RhCl(CO)_2]_2$[29] and $[RhCl(C_2H_4)_2]_2$.[30] This complex was recrystallized from a yellow toluene–hexane solution in yields of 80–90%.

All solvents were distilled and used under nitrogen atmosphere. Trimethyl phosphite and triphenylphosphine were purchased from the Fluka Co.; the tris(dimethylamino)phosphine was a gift from the Pierrefitte Co. The ligands $P(CH_3)_3$,[31] $P(C_2H_5)_3$,[31] $P(CH_3)_2C_6H_5$,[32] and $n\text{-}C_3H_7OPF_2$[33] were prepared by published methods. Rhodium trichloride trihydrate was purchased from the "Compagnie des Metaux Precieux."

Microanalyses were carried out by the "Service Central de Microanalyses du C.N.R.S." division of Montpellier. They are presented in Table I.

The infrared spectra were recorded with a Perkin-Elmer 225 grating infrared spectrometer either in hexadecane solutions or in cesium bromide pellets; in the carbonyl stretching region the spectra were calibrated by water vapor lines.

The Raman studies were performed on Coderg PH1 and T800 spectrometers.

The proton magnetic resonance spectra were recorded on a Varian Associates A-60A spectrometer. Dichloromethane was used as solvent and tetramethylsilane as internal standard.

Molecular weight measurements were determined in benzene using a Mechrolab osmometer.

Melting points were determined in air and were uncorrected.

Preparation of Complexes. The reactions are quantitative. The yields obtained after crystallization are shown.

$[RhCl(CO)P(C_2H_5)_3]_2$. A 0.510-g sample of I (1.31 mmol) was dissolved in 20 ml of toluene, and 0.385 ml of triethylphosphine (2.62 mmol) was added at room temperature. The solution became orange. Solvent was evaporated *in vacuo* and the orange oil was redissolved in ethanol. Crystals appeared at room temperature and crystallization was completed at −20°. The crystals were washed with pentane and dried *in vacuo*; 0.55 g of product was obtained (yield ≃ 75%).

$[RhCl(CO)P(CH_3)_3]_2$. A 0.500-g amount of I (1.28 mmol) was dissolved in 5 ml of toluene, and 0.259 ml of trimethylphosphine (2.56 mmol) was added at ambient conditions. The solution was stirred for a while. Fine orange crystals appeared and hexane was added to complete precipitation. Crystals were dried *in vacuo*, and the product was crystallized at −20° from a toluene–hexane solution. A 0.50-g quantity of orange crystals was obtained (yield ≃80%).

$[RhCl(CO)P(CH_3)_2C_6H_5]_2$. To 0.250 g of I (0.64 mmol) dissolved in 10 ml of toluene, 0.180 ml of dimethylphenylphosphine (1.28 mmol) was added at room temperature. The solution became brown. Hexane was added and the solution was cooled to −20°. Brown crystals were obtained, washed with hexane, and dried *in vacuo*. A 0.24-g quantity of product was obtained (yield ≃60%).

$[RhCl(CO)P(N(CH_3)_2)_3]_2$. This complex was similarly prepared. Brown crystals were obtained with a yield of ≃70%.

$[RhCl(CO)P(C_6H_5)_3]_2$. A 0.250-g sample of I (0.64 mmol) was dissolved in 10 ml of toluene, and a solution of 0.335 g of triphenylphosphine (1.28 mmol) in 5 ml of toluene was added. The solution was stirred at room temperature. Fine yellow crystals gradually appeared and were collected by filtration. The complex was washed three times with hexane and dried *in vacuo*. A 0.50-g quantity of product was obtained (yield ≃90%).

$[RhCl(P(OCH_3)_3)_2]_2$. A 0.328-g amount of $[RhCl(C_8H_{12})]_2$ (C_8H_{12} = 1,5-cyclooctadiene) prepared by the method of Chatt and Venanzi[34] was dissolved in 10 ml of dichloromethane, and 0.35 ml of trimethyl phosphite was added at room temperature. The solution immediately became yellow. The solvent was removed *in vacuo*, and the residue was recrystallized from a solution of toluene–hexane at −20°. Yellow needles were obtained (0.45 g, yield ≃90%). This preparation is similar to that of $[RhCl(P(OC_6H_5)_3)_2]_2$.[22]

$[RhCl(CO)P(OCH_3)_3]_2$. Method A. A solution of 0.212 g of $[RhCl(P(OCH_3)_3)_2]_2$ (0.274 mmol) in dichloromethane and a solution of 0.106 g of $[RhCl(CO)_2]_2$ (0.274 mmol) were mixed and stirred together. After 10 min the infrared spectrum showed the reaction to be complete. The solvent was removed *in vacuo*. Yellow needles were obtained from a toluene–hexane solution at −20°.

Method B. A 0.250-g sample of I (0.64 mmol) was dissolved in 10 ml of toluene, and 0.160 ml (1.28 mmol) of trimethyl phosphite was added at room temperature. Immediately the solution became pale yellow. Toluene was removed *in vacuo*, and the product was crystallized at −20° from a solution of hexane; 0.315 g of yellow crystals was obtained (yield ≃85%).

$[RhCl(CO)(n\text{-}C_3H_7OPF_2)]_2$. To 0.346 g of I (0.89 mmol) dissolved in 15 ml of toluene, 0.228 ml (1.78 mmol) of $n\text{-}C_3H_7OPF_2$ was added. After removal of the solvent *in vacuo*, hexane was added to the dark yellow oil and the solution was cooled at −20°; 0.38 g of red crystals was obtained (yield ≃75%).

$[RhCl(n\text{-}C_3H_7OPF_2)_2]_2$. A 0.294-g sample of $[RhCl(C_8H_{12})]_2$[34] (0.598 mmol) was dissolved in toluene, and 0.294 ml of $n\text{-}C_3H_7OPF_2$ was added at room temperature. Solvent was removed *in vacuo* and the orange oil was dissolved in hexane. By cooling at −20° the orange oil was separated from the hexane–cyclooctadiene phase.

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(6) G. Deganello, P. Uguagliati, B. Crociani, and U. Belluco, *J. Chem. Soc. A*, 2726 (1969).

(7) U. Uguagliati, A. Palazzi, G. Deganello, and U. Belluco, *Inorg. Chem.*, **9**, 724 (1970).

(8) L. Busetto, G. Carturan, A. Palazzi, and U. Belluco, *J. Chem. Soc. A*, 474 (1970).

(9) D. F. Steele and T. A. Stephenson, *Inorg. Nucl. Chem. Lett.*, **7**, 877 (1971).

(10) D. F. Steele and T. A. Stephenson, *J. Chem. Soc., Dalton Trans.*, 2161 (1972).

(11) F. Faraone, C. Ferrara, and E. Rotondo, *J. Organometal. Chem.*, **33**, 221 (1971).

(12) D. M. Barlex, M. J. Hacker, and R. D. W. Kemmitt, *J. Organometal. Chem.*, **43**, 425 (1972).

(13) J. F. Nixon and J. R. Swain, *J. Chem. Soc., Dalton Trans.*, 1044 (1972).

(14) L. Vallarino, *J. Chem. Soc.*, 2287 (1957).

(15) W. Hieber, H. Heusinger, and O. Vohler, *Chem. Ber.*, **90**, 2425 (1957).

(16) D. A. Clement and J. F. Nixon, *J. Chem. Soc., Dalton Trans.*, 2553 (1972).

(17) D. A. Clement, J. F. Nixon, and M. D. Sexton, *Chem. Commun.*, 1509 (1969).

(18) M. A. Bennett and D. J. Patmore, *Chem. Commun.*, 1510 (1969); *Inorg. Chem.*, **10**, 2387 (1971).

(19) M. A. Bennett and P. A. Longstaff, *Chem. Ind. (London)*, 846 (1965).

(20) J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc. A*, 1711 (1966).

(21) R. D. W. Kemmitt, D. I. Nichols, and R. J. Peacock, *J. Chem. Soc. A*, 1898 (1968).

(22) L. M. Haines, *Inorg. Chem.*, **9**, 1517 (1970).

(23) M. Doyle and R. Poilblanc, submitted for publication.

(24) J. M. Davidson, *MTP (Med. Tech. Publ. Co.) Int. Rev. Sci.: Inorg. Chem., Ser. One*, **6**, 347 (1972).

(25) A. J. Deeming, *MTP (Med. Tech. Publ. Co.) Int. Rev. Sci.: Inorg. Chem., Ser. One*, **9**, 117 (1972).

(26) C. A. Tolman, *Transition Metal Hydrides*, **1**, 271 (1971).

(27) See for instance J. P. Scholten and H. J. van der Ploeg, *J. Polym. Sci., Polym. Chem. Ed.*, **10**, 3067 (1972).

(28) J. Powell and B. L. Shaw, *J. Chem. Soc. A*, 211 (1968).

(29) J. A. Mc Cleverty and G. Wilkinson, *Inorg. Syn.*, **8**, 211 (1966).

(30) R. D. Cramer, *Inorg. Chem.*, **1**, 722 (1962).

(31) F. G. Mann and A. F. Wells, *J. Chem. Soc.*, 702 (1938).

(32) P. R. Bloomfield and K. Parvin, *Chem. Ind. (London)*, **541** (1959).

(33) R. Schmutzler, *Chem. Ber.*, **96**, 2435 (1963).

(34) J. Chatt and L. M. Venanzi, *J. Chem. Soc.*, 4735 (1957).

[$1,5\text{-}C_8H_{12}Rh_2Cl_2(CO)_2$]. A solution of 0.417 g of [$RhCl(C_8H_{12})]_2$[34] (0.846 mmol) in toluene and a solution of 0.329 g of [$RhCl(CO)_2]_2$ (0.846 mmol) in toluene were mixed and stirred together for 15 min. The solution was concentrated *in vacuo* and hexane was added. Orange crystals were obtained at −20° (0.63 g, yield ≃85%).

[$Rh_2Cl_2(CO)(P(C_6H_5)_3)_3$]. A 0.05-g sample of [$RhCl(CO)_2]_2$ (0.128 mmol) and 0.150 g of [$RhCl(C_2H_4)_2]_2$ (0.386 mmol) were dissolved in 25 ml of toluene, and a solution of 0.404 g of triphenylphosphine (1.54 mmol) in 5 ml of toluene was added. The solution was stirred at room temperature for 4 hr. Fine pale yellow crystals were collected, washed with hexane, and dried *in vacuo*. A 0.53-g quantity of product was obtained (yield ≃95%).

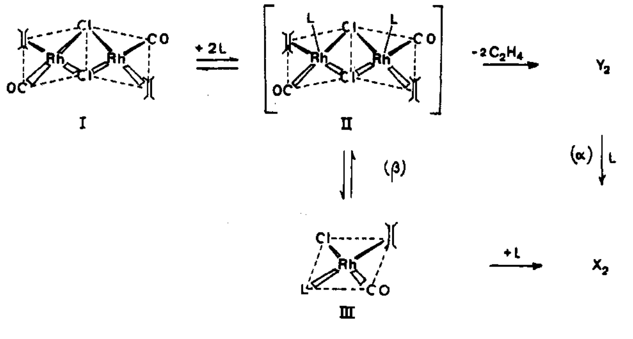
Results and Discussion

General Considerations. Addition of a tertiary phosphine or phosphite L to a toluene solution of the complex [$RhCl(CO)(C_2H_4)]_2$ (I) with the ratio L/Rh = 1 leads to rapid substitution of ethylene with formation of the single product [$RhCl(CO)L]_2$ in high yield. If this ratio is not respected, the formation of by-products is observed. The ease of substitution of ethylene molecules is well known; for example 1,5-cyclooctadiene displaces all ethylene molecules from [$RhCl(C_2H_4)_2]_2$ to give [$RhCl(C_8H_{12})]_2$.[30]

A series of dinuclear complexes of type Y_2 has been synthesized and characterized by molecular weight measurements, elemental analysis (see Table I), and infrared and proton magnetic resonance spectroscopy (see Table II).

By the above method, complexes Y_2 for a range in basicity of L from L = $n\text{-}C_3H_7OPF_2$ to L = $P(C_2H_5)_3$ have been obtained with equal facility, and it is reasonable to assume that from a purely electronic consideration any complex Y_2 with L having a basicity in this range may be prepared. The steric properties of L, however, play an important role in the reaction. For example, with the bulky phosphine L = $P(C_6H_{11})_3$ the mononuclear complex $RhCl(CO)[P(C_6H_{11})_3]_2$[35] (type X_2) is formed preferentially with only a small quantity of Y_2; approximately 50% of starting material may be recovered from the reaction. This observation may be discussed and rationalized on the ground of Scheme I.

Scheme I. Possible Paths Leading to X_2 Complexes[a]



[a] Proposed structure for II is one of the most probable.

For ligands of low steric requirements rapid formation of II with subsequent loss of ethylene to form Y_2 seems a reasonable mechanism. Bulky groups, however, would be expected to retard to some extent formation of II and hence the resultant large concentration of free ligand in solution could react with Y_2 and/or III to form X_2 (path α and/or β). Thus it is possible to attribute the observed distribution of products (X_2 and Y_2) either to the using up of ligand for the path α or to a kinetic competition between the paths α and β. Furthermore it is plausible that with bulky ligand L attack on the sterically hindered Y_2 is inhibited and path β is favored.

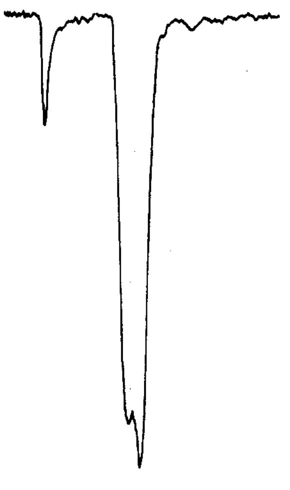


Figure 1. Infrared spectrum of [$RhCl(CO)C_2H_4]_2$ in hexadecane.

Thus it appears that tertiary phosphines of various basicities but of low steric hindrance give exclusively the desired complex [$RhCl(CO)L]_2$.

Infrared Study of [$RhCl(CO)_2]_2$-[$RhClL_2]_2$ Mixtures. Powell and Shaw[28] reported the complex of type Y_2 [$RhCl(CO)C_2H_4]_2$ to exhibit one carbonyl stretching mode at 2010 cm^{-1} in benzene solution. [We suggest the following convention: Y_0 = [$RhCl(CO)_2]_2$; $Y_n^L = Rh_2Cl_2(CO)_{4-n}L_n$ even in the case L = C_2H_4.] A reexamination of the carbonyl stretching region of this complex in hexadecane solution shows three frequencies (Figure 1). It is suggested that these absorptions arise from an equilibrium mixture of the dinuclear complexes $Y_1^{C_2H_4}$, $Y_2^{C_2H_4}$, and $Y_3^{C_2H_4}$, the concentration of $Y_2^{C_2H_4}$ being greatest. A series of spectra obtained in toluene-hexadecane solution from progressive addition of $Y_4^{C_2H_4}$ to Y_0 is shown in Figure 2 and may be interpreted as (i) high concentration of $Y_1^{C_2H_4}$ (2090, 2027, 2020 cm^{-1}) [all known Y_1 complexes have three CO frequencies of respective intensities vs, vs, s[4]] with a small amount of Y_0 and $Y_2^{C_2H_4}$, (ii) high concentration of $Y_2^{C_2H_4}$ (2027, 2020 cm^{-1}) with small amount of $Y_1^{C_2H_4}$ and $Y_3^{C_2H_4}$, and (iii) high concentration of $Y_3^{C_2H_4}$ (2020 cm^{-1}) with small concentration of $Y_2^{C_2H_4}$ and hence $Y_4^{C_2H_4}$. (See Figure 2.)

Evidence for the above interpretation is obtained by repeating progressive addition of Y_4^L to Y_0. Thus for L = $P(OCH_3)_3$ the ν(CO) frequencies of the species formed are not coincident as for L = C_2H_4. The frequencies obtained are $Y_1^{P(OCH_3)_3}$ (2089, 2028, 2021 cm^{-1}), $Y_2^{P(OCH_3)_3}$ (2020, 2014 cm^{-1}), and $Y_3^{P(OCH_3)_3}$ (2014 cm^{-1}). Also when L = $n\text{-}C_3H_7OPF_2$ the assigned frequencies are Y_1 (2093, 2042, 2027 cm^{-1}), Y_2 (2045, 2034 cm^{-1}), and Y_3 (2033 cm^{-1}). (See Figure 3.)

Nixon and Swain[13] have presented mass spectroscopic evidence for the presence of Y_1 and Y_3 as well as the expected Y_2 from a mixture of equal quantities of Y_0 and Y_4 where L = PF_3. The ν(CO) region of the infrared spectrum shows three bands at 2100, 2055, and 2032 cm^{-1}; one resonance only was assigned to $Y_2^{PF_3}$.[13] In the light of the previous experiments we think that the assignments of frequencies should be $Y_1^{PF_3}$ (2100, 2055, 2032 cm^{-1}), $Y_2^{PF_3}$ (2055, 2032 cm^{-1}), and $Y_3^{PF_3}$ (2055 cm^{-1}).

Structure of the [$RhCl(CO)C_2H_4]_2$ Complex. X-Ray studies have shown that the complexes Y_0 and Y_4 (L =

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[35] W. Strohmeier, W. Rehder-Stirnweiss, and G. Reischig, *J. Organometal. Chem.*, 27, 393 (1971).

Table I. Analytical and Physical Data

Compd	% calcd						% found								Mol wt	
	C	H	P	Cl	N	F	C	H	P	Cl	N	F	Color	Mp, °C	Calcd	Found
$Rh_2Cl_2(CO)_2[P(C_2H_5)_3]_2$	29.55	5.31	10.88	12.46			29.41	5.34	11.25	12.57			Orange	71	569	589
$Rh_2Cl_2(CO)_2[P(CH_3)_3]_2$	19.81	3.75	12.77	14.62			19.92	3.96	13.35	14.45			Dark orange	123 dec	485	481
$Rh_2Cl_2(CO)_2[P(CH_3)_2C_6H_5]_2$	35.49	3.65	10.17	11.64			34.77	3.81	10.35	11.62			Brown	84	609	610
$Rh_2Cl_2(CO)_2[P(N(CH_3)_2)_3]_2$	25.51	5.50	9.39	10.75	12.75		24.97	5.71	9.72	10.93	12.66		Brown	154	659	631
$Rh_2Cl_2(CO)_2[P(C_6H_5)_3]_2$	53.23	3.53	7.22	8.27			53.37	3.67	7.44	8.47			Yellow	216 dec	857	860[a]
$Rh_2Cl_2(CO)_2[P(OCH_3)_3]_2$	16.54	3.13	10.66	12.20			16.89	3.09	11.12	12.07			Yellow	63	581	573
$Rh_2Cl_2(CO)_2[n\text{-}C_3H_7OPF_2]_2$	16.32	2.40	10.52	12.04		12.91	16.59	2.53	10.55	11.76		13.53	Red	29	595	589
$Rh_2Cl_2(CO)[P(C_6H_5)_3]_3$	60.51	4.16	8.51	6.49			61.22	4.62	8.50	6.26			Yellow	178 dec	1092	a
$Rh_2Cl_2[P(OCH_3)_3]_4$	18.64	4.70	16.02	9.17			19.78	4.63	16.22	9.19			Yellow	205 dec	773	a
$Rh_2Cl_2(CO)_2(C_8H_{12})$	27.24	2.75		16.08			27.73	2.72		16.05			Orange	219 dec	441	434
$Rh_2Cl_2[n\text{-}C_3H_7OPF_2]_4$	18.27	3.58	15.70	8.99		19.26	19.12	3.72	15.93	7.87		19.60	Orange	Oil	789	797

[a] Low solubility or decomposition of products has prevented good measurements.

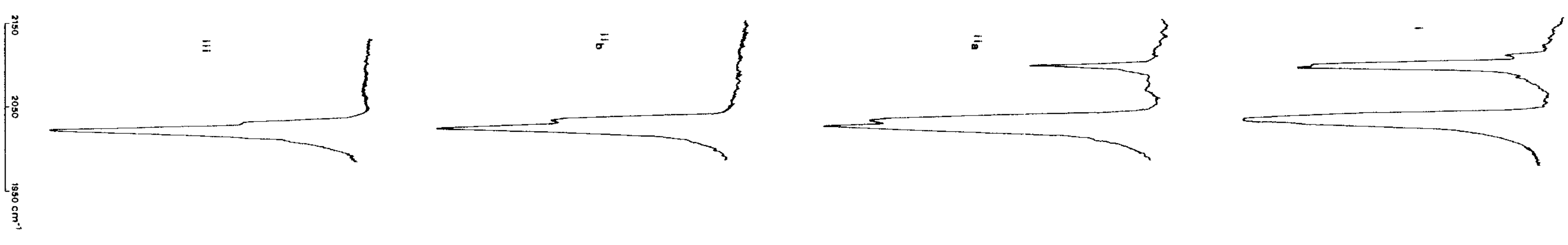


Figure 2. Infrared spectra in toluene–hexadecane of $[RhCl(C_2H_4)_2]_2$ (Y_4)–$[RhCl(CO)_2]_2$ (Y_0) mixtures: (i) $[Y_4]/[Y_0] = 1/3$; (ii$_a$) $[Y_4]/[Y_0] = 4/5$; (ii$_b$) $[Y_4]/[Y_0] = 6/5$; (iii) $[Y_4]/[Y_0] = 3$.

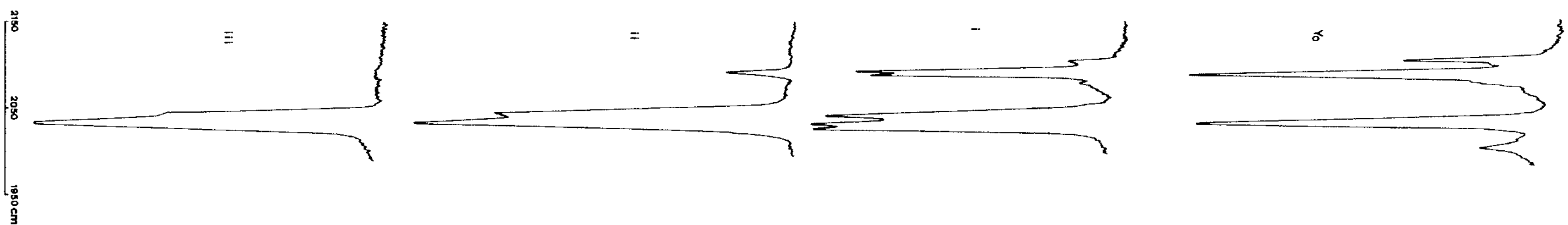


Figure 3. Infrared spectra in toluene–hexadecane of $[RhCl(n\text{-}C_3H_7OPF_2)_2]_2$ (Y_4)–$[RhCl(CO)_2]_2$ (Y_0) mixtures: (i) $[Y_4]/[Y_0] = 1/3$; (ii) $[Y_4]/[Y_0] = 1$; (iii) $[Y_4]/[Y_0] = 3$.

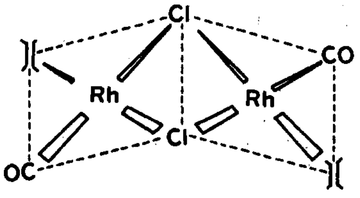
Table II. Carbonyl Stretching Frequencies and Nmr Data

Compd	$\nu(CO)$, cm^{-1}		Ppm[c] (TMS)		J_{PCH}, Hz	J_{POCH} or J_{PNCH}, Hz	J_{RhPCH}, Hz
	Hexadecane	CsBr	CH_3	Other			
$Rh_2Cl_2(CO)_2[P(C_2H_5)_3]_2$[a]	1989 sh 1982 sh 1975 vs	1977 sh 1964 vs					
$Rh_2Cl_2(CO)_2[P(CH_3)_3]_2$	1992 sh 1978 vs	1982 s 1969 vs	−1.70 dd		11.2		1.6
$Rh_2Cl_2(CO)_2[P(CH_3)_2C_6H_5]_2$	1993 sh 1981 vs	1986 vs 1972 vs	−1.77 dd	C_6H_5 −7.43	10.6		1.7
$Rh_2Cl_2(CO)_2[P(N(CH_3)_2)_3]_2$	1991 sh 1978 vs	1971 sh 1962 vs		NCH_3 −2.74 d		10.2	
$Rh_2Cl_2(CO)_2[P(C_6H_5)_3]_2$		1979 vs					
$Rh_2Cl_2(CO)_2[P(OCH_3)_3]_2$	2020 sh 2012 vs	2005 s 1997 vs		OCH_3 −3.81 d		12.7	
$Rh_2Cl_2(CO)_2[n\text{-}C_3H_7OPF_2]_2$	2044 s 2035 vs		−1.01 t	OCH_2 −4.35 dt CH_2 −1.80 tq		9.3 ($J_{HCCH} = 6.35$)	
$Rh_2Cl_2(CO)_2(C_2H_4)_2$	2023 s 2014 vs	} 1995 br		C_2H_4 −3.93			
$Rh_2Cl_2(CO)[P(C_6H_5)_3]_3$		1977 vs					
$Rh_2Cl_2[P(OCH_3)_3]_4$				OCH_3[d] −3.70 t		12.0[e]	
$Rh_2Cl_2[n\text{-}OC_3H_7PF_2]_4$			−0.98 t	OCH_2 −4.29 tt CH_2 −1.77 tq		9.4[e] ($J_{HCCH} = 6.2$)	
$Rh_2Cl_2(CO)_2(C_8H_{12})$	2087 vs 2018 vs			CH −4.4 CH_2 −2.5, −1.8			
$Rh_2Cl_2(CO)_3(C_2H_4)$	2092 vs[b] 2027 vs 2020 s						
$Rh_2Cl_2(CO)_3(n\text{-}C_3H_7OPF_2)$	2093 vs[b] 2042 vs 2027 s						
$Rh_2Cl_2(CO)_3[P(OCH_3)_3]$	2089 vs[b] 2028 vs 2021 s						
$Rh_2Cl_2(CO)_3[P(C_6H_5)_3]$	2086 vs[b] 2017 vs 2004 s						
$Rh_2Cl_2CO(C_2H_4)_3$	2020 s[b]						
$Rh_2Cl_2CO(n\text{-}C_3H_7OPF_2)_3$	2033 s[b]						
$Rh_2Cl_2(CO)[P(OCH_3)_3]_3$	2014 s[b]						

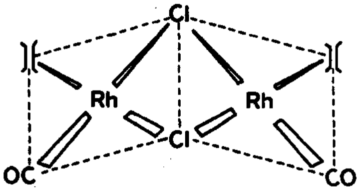
[a] Second-order nmr spectrum. [b] Hexadecane–toluene solutions (70:30). [c] Abbreviations: d, doublet; dd, double doublet; t, triplet, dt, double triplet; tt, triple triplet; tq, triple quadruplet. [d] Benzene solution. [e] Apparent coupling constant.

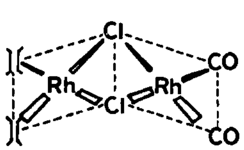
C_2H_4) have a double square-planar structure,[36,37] the two planes being bent about the Cl–Cl axis. In the case of Y_0 the $RhCl_2Rh$ bridge is bent with an angle of 124°.[36] The symmetry group of these molecules is C_{2v}, and for Y_0 this structure is maintained in solution, the three $\nu(CO)$ frequencies predicted from group theory for such a structure being observed.

If we assume the complex $Y_2^{C_2H_4}$ has a "*bent*" structure similar to Y_0 and $Y_4^{C_2H_4}$, two $\nu(CO)$ absorptions are predicted for structures Ia–Ic.



Ia





Ib Ic

Moreover the most simple interpretation of the infrared data is to assign the two observed bands to the symmetric and antisymmetric modes of a single isomer. In this assumption the 9-cm^{-1} splitting between the two modes is inconsistent with isomer Ic. In such an isomer, the neighboring CO groups would give a stronger interaction as exemplified by the complexes [(azobenzene)$_2$Rh^{III}Cl$_2$Rh^{I}(CO)$_2$][38] and [(1,5-cyclooctadiene)Rh^{I}Cl$_2$Rh^{I}(CO)$_2$] in which splittings of about 70 cm^{-1} are observed.

The above result depends on the accuracy of the assignment of the infrared bands to symmetric and antisymmetric modes.

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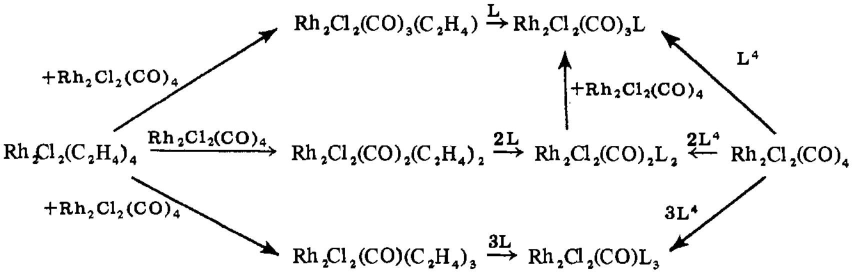
(36) L. F. Dahl, C. Martell, and D. J. Wampler, *J. Amer. Chem. Soc.*, **83**, 1761 (1961).

(37) K. Klanderman and L. F. Dahl quoted by W. E. Oberhansli and L. F. Dahl, *J. Organometal. Chem.*, **3**, 43 (1965).

(38) M. I. Bruce, B. L. Goodall, M. Z. Iqbal, and F. G. A. Stone, *Chem. Commun.*, 661 (1971).

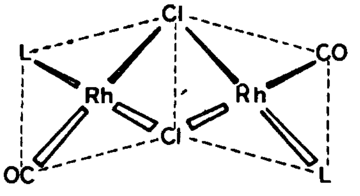
Scheme II. Preparation of $Y_n^{PPh_3}$ Complexes ($L = PPh_3$)



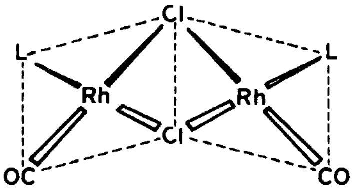
As the Cotton-Kraihanzel parameters[39] have been obtained[40] for Y_0 (Figure 4) it is possible, by transferring the relevant parameters from Y_0 to Y_2, to evaluate the following splittings: (i) from $k_t = 0.057$, $\nu_1 - \nu_2 = 7$ cm^{-1} for Ia; (ii) from $k_c = 0.078$, $\nu_1 - \nu_2 = 10$ cm^{-1} for Ib; (iii) from $k_g = 0.541$, $\nu_1 - \nu_2 = 66$ cm^{-1} for Ic.

Finally the 9-cm^{-1} difference observed for $Y_2^{C_2H_4}$ is consistent with symmetric and antisymmetric modes. It does not allow differentiation between either structure Ia or Ib; also a mixture of structures Ia and Ib cannot be excluded.

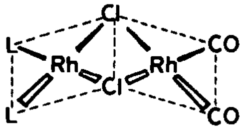
Structure of [RhCl(CO)L]$_2$ Complexes. All crystal structures of halogen-bridged dinuclear complexes of rhodium(I) have revealed a double square-planar structure; some are bent along the Cl-Cl line[36,37,41] (see also ref 42), while one is planar.[43] It is reasonable to assume therefore that the complexes Y_2 have also a double square-planar structure either with a bent (structures IVa-IVc) or with a planar configuration.



IVa



IVb



IVc

By the same argument as above isomer IVc, in both configurations, may be disregarded since the experimental difference between the CO stretching frequencies is small, lying in the range 8-15 cm^{-1} (see Table II), indicating one CO group attached per metal center. Additionally the nmr of $Y_2^{POMe_3}$ shows a simple doublet, whereas for the tetrasubstituted $Y_4^{POMe_3}$ complex fine structure is observed due to the cis phosphorus-phosphorus coupling of the $X_9AA'X'_9$ system;[44] likewise a doublet was observed for methyl resonances (see Table II), each line being further split into a doublet by the coupling ^{103}Rh-^{1}H when L = $P(CH_3)_3$ and $P(CH_3)_2C_6H_5$. Nixon and Swain have arrived at the same conclusion from the ^{19}F spectrum of complex $Y_2^{PF_3}$ in comparison with that of $Y_4^{PF_3}$, fine structure being observed for Y_4 but not for Y_2.[13] This indicates only one phosphorus atom coordinated per metal center.

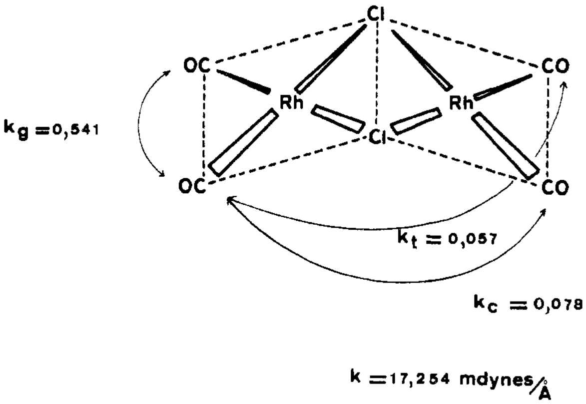


Figure 4. Interaction force constants in $[RhCl(CO)_2]_2$ (from ref 40).

A poor Raman spectrum of Y_2^L was obtained due to extensive decomposition of sample in the laser beam; however, in the best cases the presence of a weak broad band coincident with those in the infrared region and the absence of any band at higher frequency confirm that the two infrared frequencies are due to symmetric and antisymmetric modes of IVa and IVb isomers.

From the above considerations, isomers IVa and IVb in a bent configuration and IVb in a planar configuration are plausible. Specially, a mixture of isomers is probable in the case of $Y_2^{P(C_2H_5)_3}$. Concerning the planarity of these complexes, the absence of two methyl chemical shifts in the case of $[RhCl(CO)P(CH_3)_2C_6H_5]_2$ provides some evidence for a planar structure, since the methyl protons are equivalent for a planar dimer but inequivalent for a "folded" one. Nevertheless, rapid interconversion of a "folded" structure would average the two expected signals.

A General Method for Preparation of Y_n Complexes (n = 1-3). Complexes $Y_1^{PPh_3}$, $Y_2^{PPh_3}$, and $Y_3^{PPh_3}$ have been obtained by direct substitution of respectively one, two, and three carbonyl ligands from $[RhCl(CO)_2]_2$ by L.[4] Except for $Y_1^{PPh_3}$, decarbonylation is invariably slow and mixed products are usually obtained. Moreover by mixing $Y_2^{PPh_3}$ and Y_0 solutions, the complex $Y_1^{PPh_3}$ is obtained quantitatively in solution as demonstrated by the infrared spectrum which exhibits three CO stretching frequencies. The displacement of ethylene by triphenylphosphine or tertiary phosphite from the corresponding $Rh_2Cl_2(CO)_{4-n}(C_2H_4)_n$ complex rapidly affords complexes $Y_1^{PPh_3}$, $Y_2^{PPh_3}$, and $Y_3^{PPh_3}$ and is therefore proposed to be a more general method.

[39] F. A. Cotton and C. S. Kraihanzel, *J. Amer. Chem. Soc.*, **84**, 4432 (1962).

[40] B. F. G. Johnson, J. Lewis, P. W. Robinson, and J. R. Miller, *J. Chem. Soc. A*, 2693 (1969).

[41] J. Coetzer and G. Gafner, *Acta Crystallogr., Sect. B*, **26**, 985 (1970).

[42] R. J. Hoare and O. S. Mills, *J. Chem. Soc., Dalton Trans.*, 2141 (1972).

[43] J. R. Ibers and R. G. Snyder, *Acta Crystallogr.*, **15**, 923 (1962).

[44] R. K. Harris, *Can. J. Chem.*, **42**, 2275 (1964).

Scheme II summarizes the preparative routes for $Y_n^{PPh_3}$ complexes.

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Registry No. $Rh_2Cl_2(CO)_2[P(C_2H_5)_3]_2$, 41507-98-6; $Rh_2Cl_2(CO)_2[P(CH_3)_3]_2$, 49634-24-4; $Rh_2Cl_2(CO)_2[P(CH_3)_2C_6H_5]_2$, 36713-91-4; $Rh_2Cl_2(CO)_2[P(N(CH_3)_2)_3]_2$, 36713-92-5; $Rh_2Cl_2(CO)_2[P(C_6H_5)_3]_2$, 34676-63-6; $Rh_2Cl_2[P(OCH_3)_3]_4$, 49634-27-7; $Rh_2Cl_2(CO)_2[P(OCH_3)_3]_2$, 41612-78-6; $Rh_2Cl_2(CO)_2[n\text{-}C_3H_7OPF_2]_2$, 49634-30-2; $Rh_2Cl_2[n\text{-}C_3H_7OPF_2]_4$, 49634-31-3; $Rh_2Cl_2(CO)_2(C_8H_{12})$, 49855-72-3; $Rh_2Cl_2(CO)[P(C_6H_5)_3]_3$, 36713-93-6; $Rh_2Cl_2(CO)_3(C_2H_4)$, 49694-03-3; $Rh_2Cl_2(CO)_3[P(C_6H_5)_3]$, 34818-92-3; $Rh_2Cl_2(CO)_2(C_2H_4)_2$, 12306-60-4; $[RhCl(C_8H_{12})]_2$, 12092-47-6; $[RhCl(CO)_2]_2$, 14523-22-9; $n\text{-}C_3H_7OPF_2$, 3964-95-2; $[RhCl(C_2H_4)_2]_2$, 12081-16-2; $Rh_2Cl_2(CO)_3(n\text{-}C_3H_7OPF_2)$, 49634-34-6; $Rh_2Cl_2(CO)_3[P(OCH_3)_3]$, 49634-35-7; $Rh_2Cl_2(CO)(C_2H_4)_3$, 49634-54-0; $Rh_2Cl_2CO(n\text{-}C_3H_7OPF_2)_3$, 49634-36-8; $Rh_2Cl_2(CO)[P(OCH_3)_3]_3$, 49634-37-9.

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Cobalt-, Nickel-, Copper-, and Zinc(II) Nitrate and Nitrite Complexes of 1,2-Dimorpholinoethane and 1,2-Dipiperidinoethane[1]

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Received July 30, 1973

The ligands 1,2-dimorpholinoethane (EDM) and 1,2-dipiperidinoethane (EDP) have been shown to react with Co(II), Ni(II), Cu(II), and Zn(II) nitrites and nitrates to give complexes with the general formulation MLX_2 (L = EDM and EDP; X = NO_2 and NO_3). The complexes were characterized by elemental analysis, infrared, visible, and ultraviolet spectroscopy, solution and solid state magnetic susceptibilities, and conductivity measurements. The complexes have a six-coordinate, distorted octahedral geometry with two nitrogens from the EDM or EDP ligand and two bidentate oxygen coordinated NO_2^- or NO_3^- moieties making up the coordination sphere of the central metal atom. The stabilities, solubilities, and coordination geometry of these species are discussed in light of the base strengths and steric requirements of the EDM and EDP ligands.

Introduction

We have previously investigated the complexes formed by the interaction of 1,2-dimorpholinoethane (EDM) and 1,2-dipiperidinoethane (EDP) with divalent first-row transition-metal halides as well as with divalent palladium and platinum halides.[2] Both of these ligands coordinate as though they are tetra-N-substituted ethylenediamines. The EDM ligand has two ether linkages which are potential donor sites but have been shown not to take part in coordination.[3] Both of these ligands have been shown to be extremely sterically demanding due to the spatial requirements of the morpholine and piperidine rings.[3]

In light of these extreme steric requirements, it was of interest to investigate the interaction of these ligands with transition-metal salts containing bulky and/or ambidentate anions. The salts chosen for this study were the nitrates and nitrites of selected divalent first-row transition metals.

Both nitrate and nitrite can coordinate to a central transition-metal ion in several different ways. Nitrate can coordinate either as a monodentate or bidentate ligand bonding through one or two of the oxygens. Being a relatively weak ligand, it can also act as a noncoordinating anion. Nitrite being a much stronger ligand never acts as a noncoordinating or ionic ligand in coordination compounds. It can bond through the nitrogen to give the well-known nitro complexes or through one of the oxygens to give the less common nitrito species. It can also act as a bridging ligand bonding through the nitrogen and one of the oxygens.[4] A fourth mode of coordination is also known with the nitrite acting as a bidentate ligand coordinating through the two oxygens.[5]

Herein we report the preparation and characterization of the divalent cobalt, nickel, copper, and zinc nitrate and nitrite complexes of EDM and EDP.

Experimental Section

All reagents were commercially available and were used as obtained except for the following. Both of the ligands, EDM and EDP, were prepared according to the literature by the condensation of the appropriate amine with 1,2-dichloroethane in refluxing benzene.[6] EDM was recrystallized from absolute ethanol, mp 73–74° (lit. 73–74°), and confirmed by mass spectrum, parent = 200, and nmr.[7] EDP was purified by vacuum distillation through a 10-cm Vigreaux column at 55–57° at 10^{-3} mm of pressure and confirmed by mass spectrum, parent = 196, and nmr. Acetonitrile was distilled from CaH_2. Acetone was dried over anhydrous $MgSO_4$, and benzene was distilled over sodium prior to use.

Physical Measurements. Infrared spectra were recorded on a Beckman Instruments Model I.R.-10 recording spectrophotometer in the range 4000–600 cm^{-1} as KBr disks or Nujol mulls. Near-infrared, visible, and ultraviolet spectra were recorded on a Beckman Instruments Model DK-1 recording spectrophotometer in the range 40.0 to 4.0 kK with 1.0-cm matched quartz cells as methylene chloride or chloroform solutions. Conductivities were measured on an Industrial Instruments Model RC-16B-2 conductivity bridge. The conductivity cell was equipped with bright platinum electrodes and calibrated with a standard aqueous potassium chloride solution. Magnetic susceptibilities were determined in solution by the method of Evans on a Varian Associates Model T-60 spectrometer.[8] The sweep width was calibrated against the splitting of the methyl doublet of

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(1) A preliminary account of part of this work has appeared in A. L. Lott II, *J. Amer. Chem. Soc.*, 93, 5313 (1971).

(2) A. L. Lott II and P. G. Rasmussen, *J. Inorg. Nucl. Chem.*, 32, 101 (1970); A. L. Lott II and P. G. Rasmussen, *J. Amer. Chem. Soc.*, 91, 6502 (1969).

(3) W. R. Scheidt, J. C. Hanson, and P. G. Rasmussen, *Inorg. Chem.*, 8, 2398 (1969).

(4) J. Chatt, L. A. Duncanson, B. M. Gatehouse, J. Lewis, R. S. Nyholm, M. L. Tobe, P. F. Todd, and L. M. Venanzi, *J. Chem. Soc.*, 4073 (1959); K. Nakamoto, J. Fujita, and H. Murata, *J. Amer. Chem. Soc.*, 80, 4817 (1958).

(5) D. M. L. Goodgame and M. A. Hitchman, *Inorg. Chem.*, 4, 721 (1965).

(6) A. Gero, *J. Amer. Chem. Soc.*, 76, 5158 (1954).

(7) S. M. Ali, F. M. Brewer, J. Chadwick, and G. Garton, *J. Inorg. Nucl. Chem.*, 9, 124 (1959).

(8) D. F. Evans, *J. Chem. Soc.*, 2003 (1959).