on the stability of the five-coördinate species. It is interesting that a five-coördinate complex Co-(NO)[S$_2$CN(CH$_3$)$_2$]$_2$[11] is known which is isoelectronic (around the Co atom) with the five-coördinate inter-

(11) P. R. H. Alderman, P. G. Owston, and J. M. Rowe, *J. Chem. Soc.*, 668 (1962).

mediate required in the substitution reactions of [Co-(en)$_2$NO$_2$X]$^+$.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF TENNESSEE, KNOXVILLE, TENNESSEE, AND THE DIVISION OF SCIENCE AND MATHEMATICS, HARPUR COLLEGE, BINGHAMTON, NEW YORK

Amides as Ligands. I. Metallic Complexes of N,N-Dimethylacetamide[1]

BY WILLIAM E. BULL, STANLEY K. MADAN,[2] AND JOSEPH E. WILLIS[3]

The preparation of 26 metallic complexes of 14 different metals of N,N-dimethylacetamide (DMA) is reported. The complexes have been characterized by their melting points, infrared spectra in the 2–15 μ region, electrical conductance in DMA, and magnetic moments. The infrared spectra suggest that coördination through the oxygen of DMA is occurring for all the metals investigated. In most instances, the complexes contain fewer moles of DMA than the maximum coördination number of the metal, indicating coördination by halide ion and/or water.

Introduction

The fact that amides can act as donor molecules is illustrated by the complexes of urea, thiourea, and dithioöxamide which have been known for many years and by the recent studies on dimethylformamide (DMF). A patent[4] recently has described the preparation of complexes of metal halide salts (atomic numbers 26–29) with variously substituted amides. Addition compounds of DMF have been described by several authors. Moeller and Galasyn[5] have prepared complexes of several rare earth metal iodides of the composition LnI$_3$·8DMF (Ln represents a rare earth metal ion). Moeller, Galasyn, and Xavier[6] also have isolated rare earth metal acetates with DMF of solvation. Ehrlich and Siebert[7] report the isolation of the following titanium chloride compounds: TiCl$_2$·2DMF, TiCl$_3$·2DMF, and TiCl$_4$·2DMF. Archambault and Rivert[8] also report the preparation of TiCl$_4$·2DMF as well as TiCl$_4$·2HCONH$_2$.

On the basis of spectral data, Dunn and Buffagni[9] have postulated the existence in DMA and DMF of MCl$_{4-n}$X$_n$ species where X is DMA or DMF. These workers also report the isolation of complexes of the types MCl$_2$(DMF)$_2$ and [M(DMF)$_6$](ClO$_4$)$_2$ for M = Mn, Co, and Ni.

Recently, Rollinson and White[10] have reported the

(1) Presented at the Southwest-Southeast Regional Meeting of the American Chemical Society, New Orleans, La., December, 1961.
(2) National Science Foundation Research Participant at The University of Tennessee, 1961.
(3) National Science Foundation Undergraduate Research Participant at The University of Tennessee, 1960–1961.
(4) British Patent 774,956, May 15, 1957.
(5) T. Moeller and V. Galasyn, *J. Inorg. and Nucl. Chem.*, **12**, 259 (1960).
(6) T. Moeller, V. Galasyn, and J. Xavier, *ibid.*, **15**, 259 (1960).
(7) D. Ehrlich and W. Siebert, *Z. anorg. allgem. Chem.*, **303**, 96 (1960).
(8) J. Archambault and R. Rivert, *Can. J. Chem.*, **36**, 1461 (1958).
(9) T. Dunn and S. Buffagni, *Nature*, **188**, 937 (1960); *J. Chem. Soc.*, 5105 (1961).
(10) C. L. Rollinson and R. C. White, *Inorg. Chem.*, **1**, 281 (1962).

preparation of a number of chromium(III) complexes of various amides.

We report the preparation and partial characterization of 26 crystalline DMA complexes representing 14 different metals. The new compounds, perchlorates, nitrates, and halides, are listed in Table I, along with their respective compositions, melting points, colors, and perturbed carbonyl stretching frequencies.

Experimental and Results

All materials were of at least reagent grade. The N,N-dimethylacetamide was obtained from Eastman Kodak and was used in the preparations without further purification. The N,N-dimethylacetamide used in the conductance studies was purified as described by Schmulbach and Drago.[11]

Preparation of Complexes. (1) General.—Unless indicated elsewhere in the text, all complexes of N,N-dimethylacetamide reported here were prepared as follows. To an excess of DMA (b.p. 165.5°) was added the appropriate metal salt (hydrated or anhydrous according to availability). In most instances a very viscous solution resulted. Crystallization of the complex was accomplished either by removal of the excess DMA under vacuum (0.5 mm. for 48–60 hr.) or by the addition of anhydrous ether. In a number of cases the substances thus obtained were oily in appearance. By repeatedly washing with ether, the pure complexes finally were obtained. The fact that a large number of the compounds contain water indicates that water probably is more strongly coördinated than is DMA. All complexes were dried at room temperature under vacuum over P$_4$O$_{10}$. Analytical data for the new compounds are summarized in Table II.

(2) Chromium Complexes.—(a) Cr(ClO$_4$)$_3$·6DMA·H$_2$O was prepared by adding DMA to a concentrated aqueous solution of Cr(ClO$_4$)$_3$ which was prepared by treating excess Cr(OH)$_3$ with 71% HClO$_4$. Upon concentrating the solution containing DMA at room temperature under vacuum a green crystalline material separated. The crystalline material was washed with ether and dried under vacuum. (b) CrCl$_3$·3DMA was prepared

(11) C. D. Schmulbach and R. S. Drago, *J. Am. Chem. Soc.*, **82**, 4484 (1960).

Table I

DMA Complexes, Colors, Melting Points, and Infrared C=O Frequencies in cm.$^{-1}$

Compound	Color	M.p., °C.	C=O frequency,^{a,b} cm.$^{-1}$	Shift due to coordination, cm.$^{-1}$
DMA	...	...	1662	...
LiClO$_4$·DMA·2H$_2$O	White	133–135	1612	−50
Cr(ClO$_4$)$_3$·6DMA·H$_2$O	Green	66–68	1605	−57
CrCl$_3$·3DMA	Lilac	92–94	1610	−52
Mn(ClO$_4$)$_2$·4DMA	Light pink	73–75	1629	−44
MnCl$_2$·DMA·2H$_2$O	Pale yellow	dec.	1630	−32
MnBr$_2$·2DMA·4H$_2$O	Light yellow	dec.	1612	−50
FeCl$_2$·2DMA·2H$_2$O	Brown	98–100	1601	−61
FeCl$_3$·2DMA	Yellow	72–75	1612	−50
Co(ClO$_4$)$_2$·6DMA	Violet	70–72	1630	−32
CoCl$_2$·2DMA	Deep blue	125–127	1615, 1596	−47, −66
CoBr$_2$·2DMA	Deep blue	117–118	1615, 1597	−47, −65
NiCl$_2$·2DMA·6H$_2$O	Light green	84–86	1604	−58
NiBr$_2$·2DMA·3H$_2$O	Blue-green	82–84	1604	−58
Cu(ClO$_4$)$_2$·4DMA·H$_2$O	Blue	186–187	1590 (broad)	−72
ZnCl$_2$·2DMA	White	119–120	1620, 1603	−42, −59
ZnBr$_2$·2DMA	White	105–107	1620, 1599	−42, −63
ZnI$_2$·2DMA	White	112–114	1615, 1595	−47, −67
AgClO$_4$·DMA·H$_2$O	White	92 dec.	1628	−34
CdCl$_2$·DMA	White	dec.	1615	−47
CdBr$_2$·DMA	White	dec.	1612	−50
La(NO$_3$)$_3$·4DMA	White	92–93	1612	−50
HgCl$_2$·DMA	White	95–97	1615	−47
HgBr$_2$·DMA	White	82–84	1612	−50
PbI$_2$·DMA	Light yellow	120 dec.	1620	−42
Th(NO$_3$)$_4$·3DMA·3H$_2$O	White	127–128	1610	−52
Fe(ClO$_4$)$_3$·6DMA	Orange	112–114	1618	−44

^{a} The assignment of this frequency to the carbonyl group is not intended to imply that the absorption is due only to the C=O bond. Undoubtedly there are significant contributions from the C—N bond. ^{b} For those compounds in which the analytical data indicate the presence of water, the infrared spectra have absorption in the 1600–1660 cm.$^{-1}$ region which surely includes in addition to the carbonyl amide absorption the deformation absorption bands of water. In a few cases these two bands can be resolved.

by adding filings of metallic chromium to a solution of DMA saturated with HCl. The resulting violet solution was filtered to remove excess metal, then concentrated at room temperature under vacuum. The crystalline material which separated was found to be very hydroscopic; thus all later handling of the material was carried out under anhydrous conditions.

(3) Cu(ClO$_4$)$_2$·4DMA·H$_2$O.—To 1.74 g. (0.02 mole) of DMA was added 3.72 g. (0.01 mole) of Cu(ClO$_4$)$_2$·6H$_2$O. The solution became a translucent blue mass of a pasty consistency. This mass of material was triturated with anhydrous ether and dried under vacuum to give the light blue complex.

(4) ZnCl$_2$·2DMA, ZnBr$_2$·2DMA, and ZnI$_2$·2DMA.—The addition of the zinc halide to DMA liberated sufficient energy to raise the temperature of the solution well above room temperature. Upon cooling, a white crystalline material separated. This white material for each of the zinc salts was washed with ether and dried under vacuum.

(5) La(NO$_3$)$_3$·4DMA.—Lanthanum nitrate was dissolved in DMA at an elevated temperature (100–110°). The excess salt was removed by filtration and upon cooling, colorless crystals separated from the filtrate. The product was triturated with ether and dried in a desiccator.

(6) Attempted Preparations with Other Metallic Salts.— Solid materials were obtained upon addition of ether or acetone to dimethylacetamide solutions or upon removal of DMA at reduced pressures from solutions containing CuCl$_2$, Zn(ClO$_4$)$_2$, MnBr$_2$, and AlCl$_3$. Analyses of the solid materials indicate a variable composition which depends upon the concentrations of the reactants and on the length of time the solutions were held at reduced pressures.

Analytical.—Perchlorate and nitrate analyses were obtained by the gravimetric determination of the nitron salt.[12] Halogen analyses were obtained by standard volumetric procedures[13]

using AgNO$_3$ as titrant and dichlorofluorescein as the absorption indicator, or by a commercial microanalytical laboratory. Metal analyses were obtained by specific methods as outlined in standard texts.[13] Carbon, hydrogen, and nitrogen analyses were performed by Weiler and Strauss Microanalytical Laboratory, Oxford, England. The analytical data of all compounds are summarized in Table II.

Infrared Spectra.—Infrared spectra in the 2–15 μ region were obtained on a Perkin–Elmer Model 21 recording spectrophotometer fitted with sodium chloride optics. The spectra of complexes were obtained by the KBr pellet technique. The absorption bands corresponding to the carbonyl stretching frequency are indicated in Table I.

Magnetic Measurements.—The magnetic susceptibility measurements were made on a Curie–Cheneveau balance constructed in this Laboratory. A 4884-gauss permanent magnet was used. Mohr's salt was used as the standard for calibration of the instrument. The magnetic moments as reported in Table III are corrected for diamagnetic contributions as outlined by Figgis and Lewis.[14] Duplicate measurements were within 0.04 Bohr magneton of each other.

Electrolytic Conductance Measurements.—Conductances were measured with an Industrial Instruments Model RC-1 conductance bridge and a conventional cell previously calibrated with an aqueous solution of potassium chloride. All measurements were made at 25° in dimethylacetamide. The molar conductivities are listed in Table IV along with a proposed ionic nature.

Discussion

The structure of N,N-dimethylacetamide is best described as a resonance hybrid of the primary structures
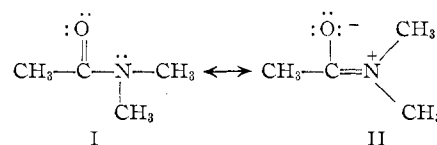
Since this molecule has two possible centers for coordination, either through the oxygen or through the nitrogen, one of our first considerations in this research was the position of coördination. Construction of typical compounds using good molecular models indicated appreciable steric interaction if coördination occurs through the nitrogen, especially for coördination numbers of six. Much less steric interaction is indicated by the models if coördination is through the oxygen.

The infrared spectra of the compounds show a considerable shift of the carbonyl group absorption to lower frequency, in some instances as much as 72 cm.$^{-1}$. The lowering of the absorption frequency of the carbonyl group indicates a decrease in the stretching force constant and favors coördination through the oxygen. Coördination to nitrogen, on the other hand, would increase the contribution of structure I to the ground state of the complexes and cause an increase in the carbonyl frequency, which is contrary to experimental evidence. Schmulbach and Drago[11] have likewise

(12) F. J. Welcher, "Organic Analytical Reagents," D. Van Nostrand and Co., Inc., New York, N. Y., 1947.

(13) I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," 3rd Ed., The Macmillan Co., New York, N. Y., 1952.

(14) B. N. Figgis and J. Lewis in J. Lewis and R. G. Wilkins, "Modern Coordination Chemistry," Interscience Publishers, Inc., New York, N. Y., 1960.

TABLE II

ANALYTICAL DATA OF DMA COMPLEXES

	Carbon		Hydrogen		Nitrogen		Other	
Compound	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
LiClO₄·DMA·2H₂O	20.00	19.29	6.08	6.22	6.50	6.63	ClO₄⁻¹ 43.30	43.01
Cr(ClO₄)₃·6DMA·H₂O	32.30	32.85	6.28	6.87	9.43	9.34	ClO₄⁻¹ 33.60	33.60
CrCl₃·3DMA	...	...	...	...	...	...	Cl⁻¹ 24.80	24.60
Mn(ClO₄)₂·4DMA	32.2	31.78	6.05	6.28	9.40	9.20	ClO₄⁻¹ 33.20	32.90
MnCl₂·DMA·H₂O	20.80	21.06	4.78	4.98	6.10	6.63	Cl⁻¹ 30.90	31.30
MnBr₂·2DMA·4H₂O	20.82	20.15	6.36	6.02	6.07	5.64	Br⁻¹ 34.70	34.40
Fe(ClO₄)₃·6DMA[a]	...	...	...	...	9.70	8.24	ClO₄⁻¹ 34.04	35.15
FeCl₃·2DMA·2H₂O	25.82	26.01	5.92	5.25	7.54	7.48	Fe 15.08	15.80
FeCl₃·2DMA	28.40	27.49	5.35	4.90	8.30	7.64	Cl⁻¹ 32.20	32.74
Co(ClO₄)₂·6DMA[a]	...	...	...	...	9.55	9.65	ClO₄⁻¹ 25.50	25.60
CoCl₂·2DMA	31.57	31.29	5.93	6.33	9.29	9.18	Cl⁻¹ 23.70	23.60
CoBr₂·2DMA	24.42	24.19	4.58	5.31	7.12	7.04	Br⁻¹ 40.07	40.04
NiCl₂·2DMA·6H₂O	23.28	23.78	7.30	7.58	6.83	7.49	Cl⁻¹ 17.25	17.92
NiBr₂·2DMA·3H₂O	21.42	21.42	5.36	5.10	6.25	5.57	Br⁻¹ 35.64	35.24
Cu(ClO₄)₂·4DMA·H₂O	30.52	30.25	6.04	6.81	8.93	9.17	ClO₄⁻¹ 31.68	31.52
ZnCl₂·2DMA	31.07	31.16	6.65	6.00	9.03	9.01	Cl⁻¹ 22.90	22.40
ZnBr₂·2DMA	24.00	24.23	4.50	4.49	7.00	7.84	Br⁻¹ 40.03	40.04
ZnI₂·2DMA	19.49	19.09	3.76	3.76	5.68	5.59	I⁻¹ 51.50	52.00
AgClO₄·DMA·H₂O	15.33	15.86	3.51	3.51	4.47	5.09	Ag 34.50	34.90
CdCl₂·DMA	17.72	18.11	3.73	3.48	5.37	5.76	Cl⁻¹ 26.05	25.80
CdBr₂·DMA	13.62	13.88	2.50	2.32	4.38	4.09	Br⁻¹ 44.40	43.90
La(NO₃)₃·4DMA	28.70	29.26	5.35	5.27	14.50	13.95	NO₃⁻¹ 27.70	28.90
HgCl₂·DMA	13.37	12.69	2.50	2.25	3.89	4.03	Hg 55.99	56.10
HgBr₂·DMA	10.71	10.88	2.02	2.57	3.12	2.72	Hg 44.82	45.15
PbI₂·DMA	8.75	9.04	1.81	1.68	2.55	1.95	PbI₂[b] 84.11	84.21
Th(NO₃)₄·3DMA·3H₂O	20.40	19.62	4.14	3.83	12.58	12.58	NO₃⁻¹ 31.20	31.40

[a] The explosive nature of these two substances hampered the carbon and hydrogen analysis.   [b] This analysis was obtained by placing the PbI₂·DMA complex in water, then collecting the PbI₂ by filtration, drying at room temperature over P₄O₁₀, and then weighing.

TABLE III

MAGNETIC PROPERTIES OF SOME DMA COMPLEXES (300°K.)

Compound	$\chi_M \times 10^6$	Diamag. cor. $\times 10^6$	$\chi_M' \times 10^6$	$\mu_{eff},$[a] B.M.
Cu(ClO₄)₂·4DMA·H₂O	705	313	1,018	1.57
NiCl₂·2DMA·6H₂O	3,745	249	3,994	3.11
NiBr·2DMA·3H₂O	2,708	233	2,941	2.67
CoCl₂·2DMA	9,075	171	9,246	4.73
CoBr₂·2DMA	8,964	204	9,168	4.71
MnBr₂·2DMA·4H₂O	14,130	256	14,386	5.90

[a] The magnetic moment, μ_{eff}, was estimated from the relationship, $\mu_{eff} = 2.84\sqrt{\chi_M'T}$, which assumes a Curie–Weiss constant of zero.

concluded that the iodine–DMA addition compound is bonded through the oxygen. Similar arguments have been forwarded for coördination through oxygen in ligands containing the M–O group where M = S P, As, or N.[15]

It should be noted that the carbonyl band in a few instances appears as a doublet in the complexes. For the cobalt halide and zinc halide complexes, two absorption maxima appear which are separated by about 20 cm.⁻¹. Splitting of the P → O band of phosphine oxide complexes has been observed for the same metal salts.[15b] As pointed out by Cotton, this splitting could be caused by several things such as (1) coupling of two M → O vibrations *via* the metal atom to which

(15) (a) J. Selbin, W. E. Bull, and L. H. Holmes, *J. Inorg. Nucl. Chem.*, **16**, 219 (1961); (b) F. A. Cotton, R. D. Barnes, and E. Bannister, *J. Chem. Soc.*, 2199 (1960); (c) S. Horner and S. Y. Tyree, Jr., *Inorg. Chem.*, **1**, 122 (1962); (d) J. V. Quagliano, T. Fujita, G. Franz, D. J. Phillips, J. A. Walmsby, and S. Y. Tyree, Jr., *J. Am. Chem. Soc.*, **83**, 3770 (1961).

TABLE IV

ELECTROLYTIC CONDUCTANCES OF DMA COMPLEXES IN DMA

Compound	Concn., mmoles l.⁻¹	$\Lambda_m,$ ohm⁻¹ cm.² mole⁻¹	Ionic nature[a]
CH₃CON(CH₃)₂ ~ DMA			
[Cr(DMA)₆](ClO₄)₃·H₂O	2.00	229	1:3
[Cr(DMA)₃Cl₃]	3.00	23	..
[Mn(DMA)₄](ClO₄)₂	3.00	141	1:2
MnCl₂·DMA·2H₂O	3.00	24	..
[Fe(DMA)₄Cl₂][FeCl₄]	3.60	41	1:1
FeCl₃·2DMA·2H₂O	3.00	50	..
[Co(DMA)₆](ClO₄)₂	3.00	179	1:2
[Co(DMA)₂Cl₂]	3.00	3.6	0
[Co(DMA)₂Br₂]	3.00	12.7	0
NiCl₂·2DMA·6H₂O	3.00	22	..
NiBr₂·2DMA·3H₂O	3.00	52	..
[Cu(DMA)₄](ClO₄)₂·H₂O	2.20	168	1:2
[Zn(DMA)₂Cl₂]	3.00	1.5	0
[Zn(DMA)₂Br₂]	3.00	2.2	0
[Zn(DMA)₂I₂]	3.00	9.3	0
CdCl₂·DMA	3.00	18.6	..
CdBr₂·DMA	3.00	20.2	..
[La(DMA)₄(NO₃)₂]NO₃	3.00	53	1:1
HgCl₂·DMA	3.00	0.77	0
HgBr₂·DMA	3.00	1.2	0
PbI₂·DMA	3.00	17.9	..
Th(NO₃)₄·3DMA·3H₂O	3.00	52	..
[Fe(DMA)₆](ClO₄)₃	3.00	214	1:3

[a] The ionic nature is based on 1:3 complexes exhibiting molar conductances in DMA at 25° in the range 200–250, 1:2 complexes in the range 130–180, 1:1 complexes in the range 85 downward, and non-electrolytes exhibiting molar conductances below 15.

both are coördinated, tending to produce or actually producing separate symmetric or asymmetric stretching modes, or (2) the existence of non-equivalent ligands

in the crystal which would differ in the vibrational frequencies.

The infrared spectra of the two nitrate compounds contain strong absorptions in the 1040–1010 cm.$^{-1}$ and the 1320–1280 cm.$^{-1}$ range characteristic of coordinated nitrates. The $La(NO_3)_3 \cdot 4DMA$ material exhibits bands at 1027 and 1303 cm.$^{-1}$ as well as absorption bands characteristic of ionic nitrate.[16]

The magnetic moments for all the complexes studied are close to the expected values except for $Cu(ClO_4)_2 \cdot 4DMA \cdot H_2O$. The value of 1.57 for the magnetic moment of a Cu(II) complex is somewhat low if the compound is monomeric. Apparently there is some spin–spin coupling occurring which results in the antiferromagnetism.[14] The magnetic moments of the cobalt, nickel, and manganese complexes correspond to the spin-free values.

All of the perchlorate salts were found to be strong electrolytes in dimethylacetamide. The molar conductances of the halide-containing complexes vary from 0.77 for $HgCl_2 \cdot DMA$ to 52 for $NiBr_2 \cdot 2DMA \cdot 3H_2O$. These conductance data indicate that halide coördination persists even at the dilutions used for these

(16) B. M. Gatehouse, S. E. Livingston, and R. S. Nyholm, *J. Chem. Soc.*, 4222 (1957).

measurements. It is apparent in the cobalt series and the zinc series that replacement of the halide from the coördination sphere is most pronounced with the iodide followed by bromide and then chloride. The omission of brackets in some of the compounds listed in Table IV indicates considerable doubt as to the correct formulation of several possible structures for these materials.

It is of interest to note the similarities in the composition of the complexes of DMA with those of dimethyl sulfoxide (DMSO). The compositions of the cadmium, mercury, and lead halide compounds of DMA and DMSO are analogous, both ligands forming compounds in which the mole ratio of ligand to metal halide is 1:1. Likewise, the $FeCl_3 \cdot 2DMA$ is analogous to $FeCl_3 \cdot 2DMSO$. Of the anhydrous DMA compounds isolated only the cobalt halides differ in their composition when compared to the corresponding DMSO compounds.

Transition Metal Complexes of Secondary Phosphines. II. Complexes of Diethylphosphine and Ethylphenylphosphine with Palladium(II)[1]

By R. G. Hayter and F. S. Humiec

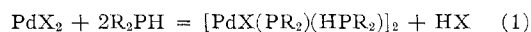Diethylphosphine and ethylphenylphosphine react with palladium halides and with $[PdCl_2(PR_3')]_2$ (R' = C_2H_5, C_6H_5) to give complexes of the type $[PdX_2L'L'']$ (X = halogen; L' = L'' = $(C_2H_5)_2PH$, $C_2H_5C_6H_5PH$, and L' = $(C_2H_5)_2PH$, L'' = PR_3', respectively). In the presence of a base, $[PdX_2L'L'']$ lose HX to give the phosphorus-bridged complexes *trans*-$[PdX(PR_2)L]_2$ (R₂ = $(C_2H_5)_2$, $C_2H_5C_6H_5$; L = $(C_2H_5)_2PH$, $C_2H_5C_6H_5PH$, or R₃'P), which react with chelate ligands to give $[Pd_2(PR_2)_2(chelate)_2]X_2$.

Introduction

A recent investigation of the reactions of diphenylphosphine with palladium halides under a variety of conditions yielded two series of binuclear complexes I (X = halogen, SCN; R = C_6H_5; L = $(C_6H_5)_2PH$ or a tertiary phosphine) and II (chelate = $(C_6H_5)_2PC_2H_4$-
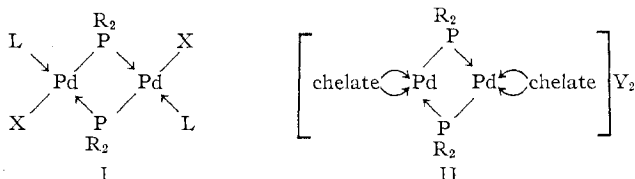
$P(C_6H_5)_2$, o-phenan; Y = Cl^-, ClO_4^-, $B(C_6H_5)_4^-$, etc.).[2,3] Since the stable Pd_2P_2 ring in these compounds was readily formed, we have investigated the conditions under which analogous compounds may be obtained with diethylphosphine and ethylphenylphosphine. No complexes of these ligands with palladium halides have been described previously although Issleib and Wenschuh[4] have reported that, unlike diphenylphosphine, dialkyl- and dicycloalkylphosphines do not displace acid in their reactions with palladium halides, *i.e.*, reactions such as (1) are not observed. We have con-

$$PdX_2 + 2R_2PH = [PdX(PR_2)(HPR_2)]_2 + HX \quad (1)$$

(1) Presented in part at the Seventh International Conference on Coordination Chemistry in Stockholm, June 24–29, 1962.

(2) Part I. R. G. Hayter, *J. Am. Chem. Soc.*, **84**, 3046 (1962).

(3) R. G. Hayter, *Nature*, **193**, 872 (1962).

(4) K. Issleib and E. Wenschuh, *Z. anorg. allgem. Chem.*, **305**, 15 (1960).