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Studies on Complexes of Arylazooximes. II. Some Rhodium(III) and Palladium(II) Chelates

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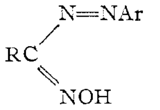
Syntheses of several tris(arylazooximato)rhodium(III) complexes are described. They can be separated into stable *cis* and *trans* isomers by chromatography on alumina. Unusually high yields of the *cis* form are observed in some cases. The isomers were identified by their pmr spectra. Arylazooximes react with potassium tetrachloropalladate(II) to form chlorine-bridged dinuclear complexes. A few reactions of these compounds are described. The dipole moment of a typical palladium(II) complex was found to be too high for a symmetrical *trans* structure. Infrared data imply the presence of five-membered chelate rings in both rhodium(III) and palladium(II) complexes. A well-defined electronic band is observed for these complexes in the visible region. This is assigned to a metal perturbed ligand transition. The unusual "bis" chelates of palladium and platinum are briefly introduced.

Introduction

Arylazooximes (1) are obtained by nitrosation of



1, R = H, alkyl, or aryl
Ar = aryl

aldehyde arylhydrazones.[1] The structure and stereochemistry of the tris chelates of cobalt(III) given by this class of ligands were described in part I[2] of this series. We have now investigated the rhodium(III) chelates and the results are reported in this paper. It was our intention to see if the change in the size of the central atom in going from cobalt(III) to rhodium(III) has any appreciable effect on the observed stereochemical pattern. Pmr, the major tool used in this study, is ideally suited for stereochemical identification of the species involved. The tris(arylazooximato)rhodium(III) complexes add to the small list[3] of known neutral tris chelates of rhodium(III) derived from bidenate ligands.

Azobenzene is known to react with $PdCl_2$ and K_2PtCl_4 to give rise to interesting chlorine-bridged dinuclear chelates.[4] Arylazooximes have, apart from the oxime function, an azo group linked to an aromatic ring. Their reactions with K_2PdCl_4 and K_2PtCl_4 were investigated. The structure and properties of some of the products are discussed in the present paper in the light of physical and chemical data.

Experimental Section

Preparation of Compounds.—The synthesis of arylazooximes was described before.[1,2] **Tris(arylazooximato)rhodium(III)** was prepared by adding an aqueous solution of rhodium nitrate trihydrate to a solution of the arylazooxime in ethanol. Details for a representative example, *viz.*, tris(phenylazoacetaldoximato)rhodium(III), are as follows. To a solution of 730 mg (0.039 mol) of phenylazoacetaldoxime in 95% ethanol (30 ml) was added 500 mg (0.013 mol) of $Rh(NO_3)_3 \cdot 3H_2O$ dissolved in 10 ml of water. The mixture which immediately turned deep red was heated to reflux. After 15 min, the pH of the solution was adjusted to ~4 by addition of sodium bicarbonate. The process was repeated after another 15 min. At the end of 1 hr, the solution was cooled, followed by addition of 100 ml of water. The precipitate was collected and washed with 5% ammonia solution (to remove any unreacted ligand) several times. After a final wash with water, the residue was dried and then extracted with chloroform. Removal of chloroform from the extract left 700 mg of the crude chelate which was directly subjected to chromatography.

Separation into Isomers.—The above product was put on a column of Fisher alumina (80–200 mesh; 50 g) and was eluted with benzene. From the first band which moved rapidly, 275 mg of the essentially pure *trans* complex was obtained by evaporation of benzene. Recrystallization was carried out from a dichloromethane–hexane mixture.

After removal of the *trans* complex, the eluent was changed to a benzene–chloroform (7:3) mixture. A second band which had already formed near the top of the column during elution with benzene now moved rapidly and was washed out completely from the column. By removal of solvent, 250 mg of the *cis* complex was isolated. The recrystallization medium was the same as for the *trans* chelate. A dark brown material still remained adsorbed at the top of the column. This was not investigated any further.

Two representative preparations of chlorine-bridged palladium(II) chelates are given.

Di-μ-chloro-bis(phenylazobutyraldoximato)dipalladium(II) (5, **R** = n-C_3H_7; **Ar** = C_6H_5).—A 500-mg sample of the ligand was dissolved in 40 ml of 95% ethanol and to it was added a solution of 800 mg of potassium tetrachloropalladate(II) in 10 ml of water. The solution immediately turned violet and crystals started separating out. Recrystallization from 95% ethanol yielded 500 mg of the pure product. The chelates **di-μ-chloro-bis(phenylazoformaldoximato)dipalladium(II)** and **di-μ-chloro-bis(phenylazoacetaldoximato)dipalladium(II)** were prepared by similar procedures.

Di-μ-chloro-bis(phenylazobenzaldoximato)dipalladium(II) (5, **R** = **Ar** = C_6H_5).—To a solution of 200 mg of potassium tetrachloropalladate(II) in 10 ml of water was added, dropwise, a solution of 140 mg of phenylazobenzaldoxime in 20 ml of ethanol. The violet solid which separated was filtered, washed successively with water and ethanol, and finally dried. It was then washed with benzene until the filtrate, which was initially green, became colorless. The complex was then dried. The yield was 210 mg. The yield of the chlorine-bridged complex decreases if the reagents are mixed in the reverse way, *i.e.*, when K_2PdCl_4

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(1) E. Bamberger and W. Pemsel, *Ber.*, **36**, 85 (1903).

(2) K. C. Kalia and A. Chakravorty, *Inorg. Chem.*, **7**, 2016 (1968).

(3) B. Behera and A. Chakravorty, *J. Inorg. Nucl. Chem.*, **31**, 1791 (1969).

(4) (a) A. C. Cope and R. W. Siekman, *J. Am. Chem. Soc.*, **87**, 3273 (1965); (b) R. F. Heck, *ibid.*, **90**, 313 (1968).

TABLE I

CHARACTERIZATION OF RHODIUM(III) COMPOUNDS 2[a]

R	Ar	Isomer	Rel yield	Formula	Mp, °C[b]	% C Calcd	% C Found	% H Calcd	% H Found	% N Calcd	% N Found
H	*o*-$C_6H_4CH_3$	*cis*	1	$C_{24}H_{24}N_9O_3Rh$	175	48.90	48.76	4.10	4.74	21.39	21.72
		trans	3	$C_{24}H_{24}N_9O_3Rh$	252	48.90	48.43	4.10	3.70	21.39	21.63
CH_3	C_6H_5	*cis*	1	$C_{24}H_{24}N_9O_3Rh$	220	48.90	49.25	4.10	3.90	21.39	21.56
		trans	1	$C_{24}H_{24}N_9O_3Rh$	233	48.90	49.30	4.10	4.37	21.39	21.10
n-C_3H_7	C_6H_5	*cis*	1	$C_{30}H_{36}N_9O_3Rh$	106	53.50	53.64	5.35	5.82	18.72	18.67
		trans	1	$C_{30}H_{36}N_9O_3Rh$	126	53.50	54.06	5.35	5.82	18.72	18.90
p-$C_6H_4CH_3$	C_6H_5	*cis*	1	$C_{42}H_{36}N_9O_3Rh$	287	61.67	61.25	4.40	4.30	15.42	15.18
		trans	3	$C_{42}H_{36}N_9O_3Rh$	247	61.67	61.25	4.40	4.48	15.42	15.21

[a] Refers to structures in the text. [b] All melting points reported in this table are uncorrected.

TABLE II

CHARACTERIZATION OF PALLADIUM(II) COMPOUNDS 5[a]

R	Ar	Formula	Mp, °C[b]	% C Calcd	% C Found	% H Calcd	% H Found	% N Calcd	% N Found
H	C_6H_5	$C_{14}H_{12}N_6O_2Cl_2Pd_2$	>290	29.02	29.21	2.08	2.35	14.51	14.40
CH_3	C_6H_5	$C_{16}H_{16}N_6O_2Cl_2Pd_2$	265	31.66	32.15	2.64	2.69	13.80	13.97
n-C_3H_7	C_6H_5[c,d]	$C_{20}H_{24}N_6O_2Cl_2Pd_2$	150	36.14	36.35	3.83	3.80	12.66	12.52
C_6H_5	C_6H_5	$C_{26}H_{20}N_6O_2Cl_2Pd_2$	>280	42.64	42.76	2.73	2.97	11.48	11.42
p-$C_6H_4CH_3$	*p*-$C_6H_4CH_3$	$C_{30}H_{28}N_6O_2Cl_2Pd_2$	>280	45.69	45.52	3.55	3.46	10.66	10.70

[a] Refers to structures in the text. [b] All melting points reported in this table are uncorrected. [c] Pd analysis: calcd, 32.06%; found, 31.84%. [d] Osmometric molecular weight in benzene is 642 (calcd 664).

is slowly added to the ligand. The synthesis of **di-μ-chloro-bis(*p*-tolylazo-*p*-tolualdoximato)dipalladium(II)** follows a similar route.

Di-μ-bromo-bis(phenylazobutyraldoximato)dipalladium(II).—A 250-mg sample of the corresponding chloro complex (**5**, R = *n*-C_3H_7, Ar = C_6H_5) and 1 g of lithium bromide were dissolved in 200 ml of acetone. The solution was kept at room temperature for 1 hr. The solvent was then removed and the product was recrystallized from methanol after washing it with water. The yield was 100 mg. *Anal.* Calcd for $C_{20}H_{24}N_6O_2Br_2Pd_2$: C, 32.14; H, 3.21; N, 11.15; Pd, 28.27. Found: C, 32.46; H, 3.52; N, 10.92; Pd, 27.86. Palladium was estimated as dimethylglyoximate after decomposing the complex with aqua regia.

Chloro(anilino)phenylazobutyraldoximatopalladium(II).—To a solution of 500 mg of di-μ-chloro-bis(phenylazobutyraldoximato)dipalladium(II) in 100 ml of dichloromethane was added 200 mg of freshly distilled aniline. The solvent was removed completely on a rotary evaporator and 250 mg of the pure product was obtained by recrystallization of the residue from a dichloromethane–hexane mixture. *Anal.* Calcd for $C_{16}H_{19}N_4OClPd$: C, 45.17; H, 4.47; N, 13.18. Found: C, 44.81; H, 4.50; N, 13.58. Pmr spectrum (in hertz) in chloroform-*d:* CH_3, 99 (triplet); γ-CH_2, 174 (sextet); β-CH_2, 282 (triplet); NH_2, 528 (broad); aromatic protons, 700–800 (complex pattern).

Proton resonance measurements were done on a Varian HR-100 spectrometer. Tetramethylsilane was used as the internal standard and frequencies were measured by the side-band technique. **Electronic spectra** were measured on a Cary 14 recording spectrophotometer. **Infrared spectra** were taken on a Perkin-Elmer 521 recording spectrophotometer. **Dielectric constants** of solutions were determined on a Type DMO1 dipolemeter (Wissen-Schaftllich Technische Werkstatten, Gmbh, Germany) provided with cylindrical gold-plated condensers. Densities and dielectric constants were measured at 27° as a function of mole fraction of solute in the range 0.00054–0.00219 for complex **5** (R = *n*-C_3H_7; Ar = C_6H_5) in benzene. The total molar polarization was calculated by the usual procedure of G. Hedestrand.

Results and Discussion

Syntheses of Chelates.—To our knowledge, all complexes reported in this paper are new. Characterization of the complexes is shown in Tables I and II. Arylazooximes combine quite readily with rhodium(III) salts like chloride and nitrate to form tris chelates. The synthetic procedure described in this paper is similar to that used for the synthesis of tris(β-diketonato)rhodium(III).[5] The rhodium(III) chelates are red to black crystalline solids soluble in a variety of organic solvents giving red solutions. The chromatographic separation of these chelates into isomeric forms is quite straightforward. The *cis* isomer is much more strongly held on the alumina column than the *trans* form. This behavior is in keeping with the expected higher polarity of the *cis* isomer. The isomeric purity of the complexes was not lost by prolonged boiling in benzene.

The chlorine-bridged palladium(II) compounds are formed by an extremely facile reaction between K_2PdCl_4 and arylazooximes. The dinuclear nature of these chelates is established from analytical data and from the molecular weight determination on one compound (Table II). These violet to black solids produce violet solutions in, *e.g.*, benzene and chloroform. Complexes with R = aryl are very sparingly soluble. For a given aryl group, the following increasing order of solubility is observed: aryl $\ll$ H $<$ CH_3 $<$ *n*-C_3H_7 (these groups refer to R).

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(5) R. C. Fay and T. S. Piper, *J. Am. Chem. Soc.*, **84**, 2303 (1962).

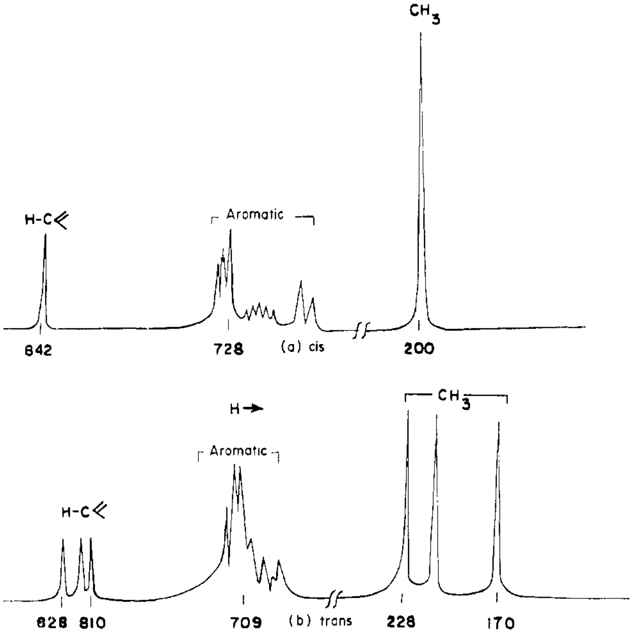
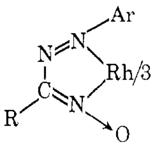


Figure 1.—Pmr spectra of isomeric tris(*o*-tolylazoformaldoximato)rhodium(III) in $CDCl_3$. Numerical figures refer to chemical shifts from tetramethylsilane at 100 MHz.

Structure and Stereochemistry of Rhodium(III) Chelates.—On the basis of the shift of ν_{N-O} from 1000–1050 cm^{-1} in the free ligand to 1220–1350 cm^{-1} in complexes, it was suggested that tris(arylazooximato)-cobalt(III) probably has five-membered chelate rings.[2] The rhodium(III) chelates behave similarly (*vide infra*) and accordingly ring structure **2** will be used in further discussions.



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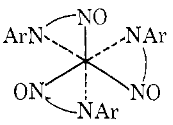

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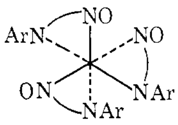

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Structures **3** and **4** represent possible *cis* and *trans* isomers, respectively, of chelate **2**. Nuclear resonance is a well-established tool[2,3,5,6] for characterization of such isomers. The representative pmr data for a few isomeric pairs are shown in Figure 1 and Table III. Clearly *cis–trans* isomerism is involved. Thus, tris-(*o*-tolylazoformaldoximato)rhodium(III) (mp 175°; less easily eluted isomer) shows a sharp single line for the HC=N proton; the same is true of the methyl protons (Figure 1a). The isomeric complex (mp 252°) shows three signals for each of the above groups (Figure 1b). Hence the former isomer has an effective threefold axis of symmetry and is *cis*, while the latter having all three chelate rings symmetrically distinct is *trans*.

TABLE III

PROTON RESONANCE FREQUENCIES[a] OF TRIS(ARYLAZOOXIMATO)RHODIUM(III)

R	Ar	Isomer	Group	Chem shift,[b,c] Hz
H	*o*-$C_6H_4CH_3$	*cis*	H	842
			o-$C_6H_4\mathit{CH_3}$	200
H	*o*-$C_6H_4CH_3$	*trans*	H	810, 818, 828
			o-$C_6H_4\mathit{CH_3}$	170, 209, 228
CH_3	C_6H_5	*cis*	CH_3	229
CH_3	C_6H_5	*trans*	CH_3	206, 219, 247
n-C_3H_7	C_6H_5	*cis*	$\mathit{CH_3}CH_2CH_2$	77[d]
			$CH_3\mathit{CH_2}CH_2$	150[e]
			$CH_3CH_2\mathit{CH_2}$	260[d]
n-C_3H_7	C_6H_5	*trans*	$\mathit{CH_3}CH_2CH_2$	70 (2),[d] 109 (1)[d]
			$CH_3\mathit{CH_2}CH_2$	144 (2),[e] 187 (1)[e]
			$CH_3CH_2\mathit{CH_2}$	258,[d] 263,[d] 295[d]
p-$C_6H_4CH_3$	C_6H_5	*cis*	*p*-$C_6H_4\mathit{CH_3}$	248
p-$C_6H_4CH_3$	C_6H_5	*trans*	*p*-$C_6H_4\mathit{CH_3}$	240, 242, 245

[a] Aromatic protons give signals in the region 670–850 Hz and are not tabulated. [b] From tetramethylsilane at 100 MHz in $CDCl_3$. [c] Unless otherwise indicated, the tabulated frequencies of each group represent bands (or multiplets) of equal intensity. [d] Center of a triplet ($J \backsimeq 7.5$ Hz). [e] Center of a sextet ($J \backsimeq$ 7.5 Hz).

The isomerism of the rhodium(III) chelates is in striking contrast with the exclusive *trans* structure of the cobalt(III) complexes.[2] No parallel of this observation is known[7,8] to the present authors in bidentate chelate chemistry. It was argued[2] that overcrowding of substituents (Ar and O in **3**) on one face of the octahedron is responsible for the nonexistence of the *cis* form in the cobalt(III) chelates. Similar observations were made in several other cases.[6] On the basis of formulation 2, both *cis* (**3**) and *trans* (**4**) isomers of tris(arylazooximato)rhodium(III) have three substituents projecting from the corners of each face of the octahedron. In the *cis* form three aryl groups project from one of the faces while in the *trans* isomer at least one of the substituents on each face is an oxygen atom. This may conceivably lead to a critical balance of steric factors. The octahedral covalent radii[9] of cobalt(III) and rhodium(III) are 1.22 and 1.32 Å, respectively. A rough calculation on this basis shows a ∽10% increase in the facial area in going from the cobalt(III) to the rhodium(III) chelate. This may ease the steric situation calling the *cis* form of the latter complex into existence.

However, factors other than steric, are undoubtedly involved in determining the relative population of *cis* and *trans* isomers. Statistically, the equilibrium concentration of the *trans* form should be thrice that of the *cis* isomer. In the case of tris(β-diketonato)-rhodium(III),[5] the ratio of yields (*cis*/*trans*) is found to be somewhat less than $^1/_3$. The behavior of the arylazooxime complexes is most remarkable.[10,11] In

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(6) (a) A. Chakravorty and R. H. Holm, *Inorg. Chem.*, **3**, 1521 (1964); (b) A. Chakravorty and K. C. Kalia, *ibid.*, **6**, 690 (1967); (c) A. Chakravorty and B. Behera, *ibid.*, **6**, 1812 (1967); (d) F. Röhrscheid, R. E. Ernst, and R. H. Holm, *ibid.*, **6**, 1315 (1967); (e) A. Chakravorty, B. Behera, and P. S. Zacharias, *Inorg. Chim. Acta*, **2**, 85 (1968); (f) K. C. Kalia and A. Chakravorty, *ibid.*, **2**, 154 (1968).

(7) Tris(β-diketonato) metal(III)[5] (metal = Rh or Co) complexes exist in isomeric forms for both elements. Tris(triazene 1-oxide) chelates,[3,6e] on the other hand, exist only in the *trans* form. A pertinent observation in this context is that $CrCl_3 \cdot 3py$ (py = pyridine) apparently exists only in the *trans* form, while the corresponding Rh(III) and Ir(III) complexes are known both as *cis* and *trans* isomers.[8] We note that the octahedral radius of Cr(III) is expected to be higher than that of Co(III). Hence if size is the determining factor, $CoCl_3 \cdot 3py$ is also expected to exist in only the *trans* form.

(8) R. J. H. Clark and C. S. Williams, *Inorg. Chem.*, **4**, 350 (1965).

(9) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 249.

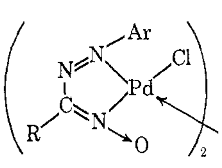
(10) Another authentic example of the "anomalous" population of the *cis* structure is provided by tris(β-thioketonato)metal(III)[11] (metal = Co, V) which exists exclusively in the *cis* form.

(11) R. H. Holm, D. H. Gerlach, J. G. Gordon, II, and M. G. McNamee, *J. Am. Chem. Soc.*, **90**, 4184 (1968).

two cases (Table I) the yields[12] of the *cis* and *trans* isomers are nearly equal. For a given complex, the yield ratio was reproducible from preparation to preparation. Whether these unusually high yields of the *cis* isomer are due to its thermodynamic stability[13] or whether they are attributable to kinetic factors operative during synthesis remains to be investigated.

The infrared spectra (KBr disk, 700–3200 cm^{-1}) of *cis* and *trans* isomers of given chelates are essentially identical except for very minor differences in frequencies and number of bands. The vibrational spectra of analogous *trans* chelates of rhodium(III) and cobalt(III) are superposable on each other but for slight frequency shifts.

Chlorine-Bridged Palladium(II) Chelates.—The N–O stretch in these chelates appears in the region 1200–1300 cm^{-1}. Five-membered chelate rings are suggested on this basis. Complexes **5** add to the very small list of known halogen-bridged palladium(II) chelates[4,14,15] (*e.g.*, **6**[4] and **7**[14]) derived from bidentate nitrogenous ligands. In fact **5** is unique in that bonding to carbon is not involved. The alternative structure **8** having a Pd–C bond is a distinct possibility in view of structure **6** which is well established for the azobenzene chelate. However, this possibility is ruled out by the following observations. (1) The reaction of arylazooximes with K_2PdCl_4 is very fast whereas the reaction of $PdCl_2$ with azobenzene is very slow.[4] (2) There is a large shift of ν_{N-O} (on complex formation) which we have already noted. (3) The oxime proton and ν_{N-O} are absent, respectively, in pmr and ir spectra of the chelates; these features are clearly observable in the corresponding ligands.



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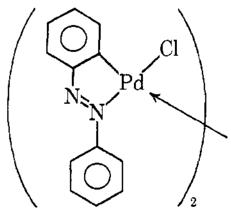

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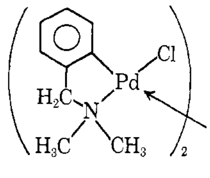

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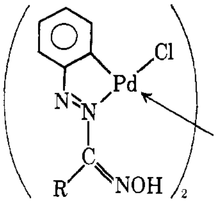

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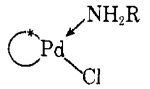
Since the bidentate ligand is unsymmetrical, *cis* and *trans* structures can be written for **5** (the same is true of **6** and **7**). Only one type of crystalline solid can however be isolated in each case. Chromatography of **5** (R = n-C_3H_7, Ar = C_6H_5) on a column of alumina failed to shown the presence of more than one separable species. Room-temperature pmr spectra showed single multiplets for each group (CH_3, triplet at 112 Hz; γ-CH_2, sextet at 181 Hz; β-CH_2, triplet at 291 Hz). These observations suggest the existence of only one particular isomeric species or of a mixture of isomers with identical chemical shifts or of a rapidly (by pmr criterion) interconverting mixture of isomers with different chemical shifts. Assuming that a single species is involved, it will be traditional to suggest a *trans* structure. For example, complex **6** is usually given[4b] a *trans* formulation apparently without any experimental evidence.

The dipole moment of the *trans* isomer may be expected to be very low. In benzene solution **5** (R = n-C_3H_7; Ar = C_6H_5)[16] has a total molar polarization of 461 cm^3 (at 27°). The dark color of the solutions precluded reliable determination of refractive indices. However use of atomic refraction data[17] leads to a dipole moment[18] of $\sim$4 D. If the complex has a *trans* configuration at all, the latter must be highly distorted. It is tempting to suggest a *cis* structure (possibility of a *cis* $\rightleftharpoons$ *trans* equilibrium cannot be eliminated) for the chelate in solution.

Complex **5** undergoes the usual bridge replacement or bridge splitting reactions of chlorine-bridged palladium(II) chelates. Thus aliphatic or aromatic amines[19] split the bridge instantaneously producing the monoamine derivative **9** which can, in principle, exist in two isomeric forms. Evidences we have, at present, indicate that in practice only one isomer (configuration not known) is obtained. Lithium bromide in acetone[20] converts **5** into the corresponding bromine-bridged derivative. Triphenylphosphine appears to split the bridge in a reversible way. This and several other reactions of the bridge will be described in detail later.



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Electronic Spectra of Chelates 2 and 5.—Electronic spectral data for rhodium(III) chelates are shown in Table IV. Two intense bands at $\sim$20,000 and $\sim$32,000 cm^{-1} are observed in general. For a given chelate type, the lower energy band is systematically more intense in the *cis* than in the *trans* isomer. Further, it is generally shifted slightly to higher frequencies in the *cis* isomer.

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[12] The approximate ratios of yields reported in Table I refer to crude complexes obtained by complete evaporation of solvents immediately after chromatographic separations. Although for analytical purposes, the crude samples were further recrystallized, pmr data showed them to be essentially pure isomers.

[13] Because of higher symmetry, entropywise the *cis* isomer is less favored than the *trans* isomer. On the basis of the simplest model $\Delta S(cis \rightarrow trans)$ is $R \ln 3 = 2.18$ eu. Higher thermodynamic stability of the *cis* form implies higher bond energies.

[14] A. C. Cope and E. C. Freidrich, *J. Am. Chem. Soc.*, **90**, 909 (1968).

[15] T. Yukawa and S. Tsutsumi, *Inorg. Chem.*, **7**, 1458 (1968).

[16] The repeated use of this particular chelate in the various studies is because of its good solubility.

[17] N. Bauer, K. Fajans, and S. Z. Lewin in "Technique of Organic Chemistry," Vol. I, Part II, A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1960, p 1171.

[18] Atom polarization was assumed to be 20% of electronic polarization.

[19] J. Chatt and L. M. Venanzi, *J. Chem. Soc.*, 2445 (1957).

[20] M. S. Lupin, J. Powell, and B. L. Shaw, *ibid.*, *A*, 1410 (1966).

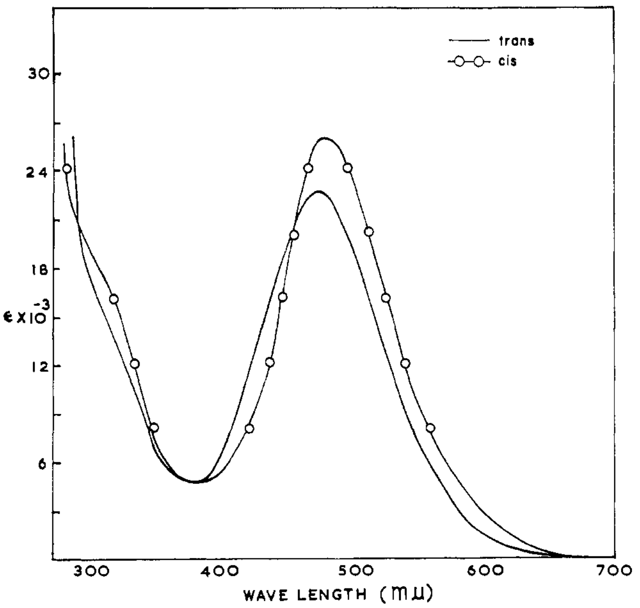


Figure 2.—Electronic spectra of isomeric tris(phenylazoacetaldoximato)rhodium(III) in benzene.

Table IV

Frequencies (ν, cm^{-1}) and Extinction Coefficients (ϵ, l. mol^{-1} cm^{-1}) of Electronic Bands of Rhodium(III) Compounds **2**[a] in Benzene

R	Ar	Isomer	ν (ϵ)
H	o-$C_6H_4CH_3$	*cis*	21,700 (18,700), 31,200 sh[b] (11,200)
H	o-$C_6H_4CH_3$	*trans*	21,700 (18,000), 31,200 sh (11,800)
CH_3	C_6H_3	*cis*	20,800 (26,000), 32,300 sh (17,600)
CH_3	C_6H_5	*trans*	21,000 (22,600), 31,200 sh (13,200)
n-C_3H_7	C_6H_5	*cis*	20,800 (27,300), 34,200 (20,700)
n-C_3H_7	C_6H_5	*trans*	21,000 (22,700), 32,300 sh (15,300)
p-$C_6H_4CH_3$	C_6H_5	*cis*	19,400 (20,300), 31,700 (56,100)
p-$C_6H_4CH_3$	C_6H_5	*trans*	19,800 (17,800), 32,800 (64,000)

[a] Refers to structures in the text. [b] sh, shoulder.

A typical case is illustrated in Figure 2. The ∽20,000-cm^{-1} band also seems to be common with the Co(III) chelates[2] and the Pd(II) chelates (Table V). It probably represents an allowed (since intensities are so high) transition which is centered primarily on the ligand.

Table V

Frequencies (ν, cm^{-1}) and Extinction Coefficients (ϵ, l. mol^{-1} cm^{-1}) of Electronic Bands of Palladium(II) Compounds **5**[a] in Benzene

R	Ar	ν (ϵ)
H	C_6H_5	19,600 (7000), 27,000 sh[b] (5300), 31,300 (8800)
CH_3	C_6H_5	18,700 (10,200), 27,000 sh (12,300), 30,300 sh (14,900)
n-C_3H_7	C_6H_5[c,d]	18,500 (10,500), 27,000 sh (12,500), 30,300 sh (14,700)

[a] Refer to structures in the text. [b] sh, shoulder. [c] Bromo analog has the following absorption data: 19,000 (10,900), 24,400 sh (6300), 27,800 sh (10,500). [d] Chloro(anilino)phenylazobutyraldoximatopalladium(II) absorbs at 19,400 (6200), 25,000 sh (2500), 30,300 sh (8400), 31,900 sh (11,700).

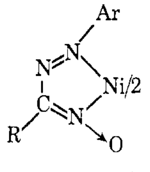
Halogen-Free Complexes of Palladium and Platinum.—By treating **5** with the corresponding ligand (in the ratio 1:2) in the presence of suspended sodium carbonate in benzene, a halogen-free crystalline solid can be isolated.[21] On the basis of analytical data, this contains 2 mol of arylazooxime anion per mole of palladium. K_2PtCl_4 does not immediately react with arylazooximes in aqueous ethanol. However, a slow reaction does take place leading to a black crystalline product, which again analyzes as a "bis" complex. No halogen-bridged platinum chelates have been isolated.

These "bis" chelates have unusual electronic (several bands in the energy range 17,000–7000 cm^{-1}) and pmr spectra. There is little doubt that they are different from what a simple "bis" formulation would suggest.[22,23] Further, on the basis of ir evidence, the platinum and palladium chelates of a given ligand are structurally distinct. Details of these unusually interesting compounds will be presented shortly.

Acknowledgment.—Thanks are due to Dr. S. N. Bhat for providing help in measurement of dielectric constants.

[21] With arylazooximes having R = aryl, some "bis" complex is always formed during synthesis of the halogen-bridged material (**5**).

[22] Several bis complexes of nickel(II) are described in the literature.[23] Presumably they have the structure[23]



[23] L. Malatesta and R. Pizzoti, *Gazz. Chim. Ital.*, **76**, 141 (1946).