bipyridine exhibits no increase in rate in such media,[10a] it is reasonable to assume with Shu and Rorabacher[35] that the behavior of this ligand is complicated by steric factors. We conclude that in alcohol-water mixtures the composition of the inner sphere, the steric requirements of the ligand, and the structure of the solvent all play a significant role.

Registry No. Ni, 7440-02-0; water, 7732-18-5; methanol, 67-56-1; ethylene glycol, 107-21-1; acetonitrile, 75-05-8; pyridine, 110-86-1; bipyridine, 366-18-7; terpyridine, 1148-79-4; phenanthroline, 66-71-7; dimethyl sulfoxide, 75-18-3.

Contribution from the Department of Inorganic and Physical Chemistry,
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Ambidentate Coordination of Isonitrosoacetylacetone Imines in Their Nickel(II) and Palladium(II) Complexes[1]

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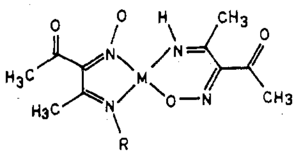
Nickel(II) and palladium(II) complexes of the types Ni(R–IAI)(IAI′), Pd(IAI)(IAI′), and $Pd(R\text{–}IAI)_2$, where IAI and IAI′ represent isonitrosoacetylacetone imine and R–IAI represents its *N*-alkyl derivative, have been prepared. The molar conductance, molecular weight, magnetic moment, and ir, pmr, and electronic spectra of these complexes have been studied. It is suggested that the isonitroso group of R–IAI coordinates through the nitrogen and that of IAI′ through the oxygen in Ni(R–IAI)(IAI′). In $Pd(R\text{–}IAI)_2$ the isonitroso groups of both ligands coordinate through nitrogen while Pd(IAI)(IAI′) has a structure similar to that of Ni(R–IAI)(IAI′). The amine-exchange reactions of nickel(II) and palladium(II) complexes are discussed and compared on the basis of their structures.

Introduction

Isonitrosoacetylacetone imine (HIAI, 4-imino-2,3-pentanedione 3-oxime) is expected to behave as a versatile ambidentate ligand as it has four donor atoms of which only two can bond to a single metal ion. Bis(isonitrosoacetylacetone imino)metal(II) (metal = Ni or Pd) has been prepared by different methods[2] and different structures have been assigned to these complexes.[2-4] The present paper deals with the preparation and structural characterization of a series of nickel(II) and palladium(II) complexes with isonitrosoacetylacetone imine and its *N*-alkyl derivatives. When the present work on nickel(II) complexes was completed, Lacey, *et al.*,[5] proposed structure Ia for bis(isonitrosoacetylacetone imino)nickel(II). In this structure, IAI represents isonitrosoacetylacetone imine with an N-coordinated isonitroso group and IAI′ that with an O-coordinated isonitroso group.



I

Ia, M = Ni, R = H
b, M = Ni, R = alkyl group
c, M = Pd, R = H

Experimental Section

Materials Used. Isonitrosoacetylacetone was prepared by the method of Wolff, *et al.*,[6] and crystallized from cyclohexane. Bis(isonitrosoacetylacetone imino)nickel(II) was prepared by the procedure described by Taylor and Ewbank[2a] and crystallized from a 1:1 mixture of chloroform and ethanol. Except benzylamine, *n*-propylamine, and ethylenediamine, all other amines were aqueous solutions. Palladium chloride was obtained from Arora-Mathey Ltd., Calcutta. Chloroform, benzene, and acetone were Analar grade reagents.

Method and Apparatus. Molecular weights of the complexes were determined in benzene by the freezing point method. Conductivity measurements were carried out in acetone using a Siemen's conductivity bridge. The magnetic susceptibilities of the nickel(II) complexes were determined at room temperature by the Gouy method using $Hg[Co(NCS)_4]$ as a calibrant. Infrared spectra of the complexes in Nujol mull and in chloroform were recorded on a Carl-Zeiss UR-10 spectrophotometer fitted with LiF, NaCl, and KBr prisms. The electronic spectra of the complexes in chloroform solution were recorded on a Unicam 700 A recording spectrophotometer. The proton magnetic resonance spectra of the complexes in $CDCl_3$ were recorded on a Varian HA-100 spectrometer, using precalibrated paper and tetramethylsilane as the internal standard.

Preparation of the Complexes. (1) (*N*-Methylisonitrosoacetylacetone imino)(isonitrosoacetylacetone imino)nickel(II), Ni(Me-IAI)(IAI′). Methylamine (5 ml, 33% solution, ~0.05 mol) was added to a suspension of Ni(IAI)(IAI′) (2 g, ~0.0065 mol) in a mixture of 70 ml of alcohol and 50 ml of chloroform and refluxed over a water bath for 1 hr, when the suspension dissolved. The solution was cooled and filtered, and the filtrate was evaporated under vacuum to a small volume (10–15 ml), when crystals were obtained. The crystals were filtered off, washed with small amounts of alcohol, and recrystallized from alcohol; yield 83%.

(2) (*N*-Ethylisonitrosoacetylacetone imino)(isonitrosoacetylacetone imino)nickel(II), Ni(Et-IAI)(IAI′). Ethylamine (5 ml, 50% solution, ~0.05 mol) and Ni(IAI)(IAI′) (2 g, ~0.0065 mol) in a mixture of 70 ml of alcohol and 50 ml of chloroform were refluxed over a water bath for 5 hr. The rest of the procedure was the same as in section (1). The complex was recrystallized from alcohol; yield 72%.

(3) (*N*-*n*-Propylisonitrosoacetylacetone imino)(isonitrosoacetylacetone imino)nickel(II), Ni(*n*-Pr-IAI)(IAI′). *n*-Propylamine (5 ml, ~0.061 mol) and Ni(IAI)(IAI′) (2 g, ~0.0065 mol) in a

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(1) Part of the work dealing with nickel(II) complexes has been abstracted from the Ph.D. thesis of K. S. B., Indian Institute of Science, 1970.

(2) (a) T. W. J. Taylor and E. K. Ewbank, *J. Chem. Soc.*, 2818 (1926); (b) C. Djordjevic, J. Lewis, and R. S. Nyholm, *ibid.*, 4778 (1962).

(3) A. V. Ablov and V. N. Zubarev, *Russ. J. Inorg. Chem.*, 13, 1563 (1968).

(4) K. G. Das, D. N. Sen, and N. Thankarajan, *Tetrahedron Lett.*, 869 (1968).

(5) M. J. Lacey, C. G. Macdonald, J. S. Shannon, and P. J. Collins, *Aust. J. Chem.*, **23**, 2279 (1970).

(6) L. Wolff, P. Bock, G. Lorentz, and P. Trappe, *Justus Liebigs Ann. Chem.*, **325**, 134 (1902).

Table I. Colors, Melting Points, Molecular Weights, and Analytical Data of Nickel(II) and Palladium(II) Isonitrosoacetylacetone Imine Complexes

					Analytical data, %							
		Mp,	Mol wt		Calcd				Found			
Complexes	Color	°C	Calcd	Found	Ni	C	H	N	Ni	C	H	N
Ni(IAI)(IAI')	Red	246			18.76	38.36	4.47	17.90	18.80	38.51	4.63	17.58
Ni(Me–IAI)(IAI')	Brownish yellow	165	327	321	17.96	40.39	4.90	17.14	18.00	40.88	5.12	17.43
Ni(Et–IAI)(IAI')	Reddish brown	147	341	329	17.22	42.23	5.28	16.44	17.08	42.41	5.59	16.44
Ni(*n*-Pr–IAI)(IAI')	Yellow	134	355	337	16.54	43.96	5.64	15.79	16.48	43.62	6.10	15.62
Ni(*i*-Pr–IAI)(IAI')	Yellow	143	355	348	16.54	43.96	5.64	15.79	16.59	43.58	5.64	15.88
Ni(Bzl-IAI)(IAI')	Brownish yellow	178	389	392	14.54	50.63	4.97	13.90	14.65	50.76	5.20	14.19
Pd(IAI)(IAI')	Red	Dec				33.30	3.88	15.53		32.80	4.09	14.77
Pd(Me–IAI)$_2$	Yellow	261				37.12	4.64	14.43		37.90	5.26	15.18
Pd(Et–IAI)$_2$	Yellow	204	416	424		40.38	5.29	13.46		40.45	5.50	14.18
Pd(*n*-Pr–IAI)$_2$	Yellow	180	444	451		43.24	5.85	12.61		42.90	5.64	13.15

mixture of 70 ml of alcohol and 50 ml of chloroform were refluxed over a water bath for 3 hr. The rest of the procedure was the same as in section (1). The complex was recrystallized from alcohol; yield 90%.

(4) **(*N*-Isopropylisonitrosoacetylacetone imino)(isonitrosoacetylacetone imino)nickel(II), Ni(*i*-Pr–IAI)(IAI').** Isopropylamine (15 ml, 70% solution, ~0.15 mol) and Ni(IAI)(IAI') (2 g, ~0.0065 mol) in 80 ml of isopropyl alcohol were refluxed over a water bath for 10 hr. The rest of the procedure was the same as in section (1). The complex was recrystallized from petroleum ether (bp 40–50°); yield 63%.

(5) **(*N*-Benzylisonitrosoacetylacetone imino)(isonitrosoacetylacetone imino)nickel(II), Ni(B–IAI)(IAI').** Benzylamine (5 ml, ~0.046 mol) and Ni(IAI)(IAI') (2 g, ~0.0065 mol) in 80 ml of isopropyl alcohol were refluxed over a water bath for 3 hr. The rest of the procedure was as in section (1). The complex was recrystallized from alcohol containing a small amount of chloroform; yield 80%.

(6) **Bis(isonitrosoacetylacetone imino)palladium(II), Pd(IAI)(IAI').** Palladium chloride (0.17 g, ~0.001 mol), isonitrosoacetylacetone (0.3 g, ~0.002 mol), and liquor ammonia (0.5 ml, ~0.0078 mol) in 20 ml of methyl alcohol were stirred using a magnetic stirrer for 3 hr, when a red crystalline product was obtained. It was filtered off, washed thoroughly with methyl alcohol, and dried; yield 80%.

The complex was found to be identical with the one prepared by the method of Djordjevic, *et al.*,[2b] by comparison of their chemical analyses and ir spectra.

(7) **Bis(*N*-methylisonitrosoacetylacetone imino)palladium(II), Pd(Me–IAI)$_2$.** Palladium chloride (0.17 g, ~0.001 mol), isonitrosoacetylacetone (0.3 g, ~0.002 mol), and methylamine (0.25 ml, 33% solution, ~0.0025 mol) in 20 ml of methyl alcohol were stirred for 1 hr, when crystals separated. The crystals were filtered off and recrystallized from a 1:1 mixture of methyl alcohol and benzene; yield 54%.

(8) **Bis(*N*-ethylisonitrosoacetylacetone imino)palladium(II), Pd(Et–IAI)$_2$.** This was prepared by a procedure similar to that described in section (7) using ethylamine (0.4 ml, 50% solution, ~0.004 mol) instead of methylamine. The complex was recrystallized from methyl alcohol; yield 55%.

(9) **Bis(*N*-*n*-propylisonitrosoacetylacetone imino)palladium(II), Pd(*n*-Pr–IAI)$_2$.** This was prepared by a procedure similar to that in section (7) using *n*-propylamine (0.3 ml, ~0.0037 mol) instead of methylamine. The complex was recrystallized from methyl alcohol; yield 60%.

Reaction of Ni(IAI)(IAI') and Ni(R–IAI)(IAI') (R = CH_3, C_2H_5, *n*-C_3H_7, *i*-C_3H_7, or $C_6H_5CH_2$) with Ethylenediamine. To a solution of Ni(IAI)(IAI') or Ni(R–IAI)(IAI') (1 g) in a mixture of 30 ml of alcohol and 40 ml of chloroform, ethylenediamine (0.3 ml, ~0.0045 mol) was added and the solution was kept aside for about 4 hr. The orange-red precipitate which formed was filtered, washed with alcohol, and dried.

The compound was identified as *N,N'*-ethylenebis(isonitrosoacetylacetone imino)nickel(II), Ni(EIAI), by chemical analysis and by comparison of its ir spectrum with that of an authentic sample prepared by direct nitrosation of *N,N'*-ethylenebis(acetylacetone imino)nickel(II), as well as by direct condensation of isonitrosoacetylacetone with ethylenediamine in the presence of nickel acetate.[7]

Amine-Exchange Reactions of Pd(IAI)(IAI'). (a) **With Methylamine.** Methylamine (3 ml, 33% solution, ~0.03 mol) and Pd(IAI)(IAI') (0.17 g, ~0.0005 mol) in 50 ml of a 1:1 mixture of methyl alcohol and chloroform were refluxed on a water bath for 1 hr. The solution was then filtered and concentrated by passing dry air when crystals separated. The crystals were filtered off and recrystallized from a 1:1 mixture of methyl alcohol and benzene; yield 70%.

The compound was identical with Pd(Me–IAI)$_2$ obtained by direct reaction described in section (7), as shown by the comparison of their ir spectra and melting points.

(b) **With Ethylamine.** A procedure similar to that in section (a) was employed using ethylamine (5 ml, 50% solution, ~0.05 mol) instead of methylamine and the contents was refluxed for 3 hr. The complex was recrystallized from methyl alcohol; yield 62%.

This compound was found to be identical with Pd(Et–IAI)$_2$ obtained by direct reaction in section (8), as shown by the comparison of their ir spectra and melting points.

(c) **With *n*-Propylamine.** A procedure similar to that in section (a) was employed using *n*-propylamine (2 ml, ~0.025 mol) instead of methylamine. The contents was refluxed for 5 hr. The complex was recrystallized from methyl alcohol; yield 18%.

This compound was found to be identical with Pd(*n*-Pr–IAI)$_2$ obtained by direct reaction in section (9), as shown by the comparison of their ir spectra and melting points.

Some General Properties of the Complexes. All the complexes are crystalline, stable in the atmosphere, and insoluble in water. Except Ni(IAI)(IAI') and Pd(IAI)(IAI'), all the complexes have good solubility in common organic solvents. While Ni(IAI)(IAI') is only sparingly soluble in organic solvents, Pd(IAI)(IAI') is almost insoluble. The colors and melting points of these complexes are listed in Table I.

Analyses. Nickel(II) in the complexes was analyzed gravimetrically as nickel dimethylglyoximate after decomposing the complexes in a mixture of sulfuric, nitric, and perchloric acids. Carbon, hydrogen, and nitrogen were determined by microanalytical methods. The analytical data are given in Table I.

Results and Discussion

The molar conductances (in the range 1.5×10^{-2} to 2.9×10^{-1} ohm^{-1} cm^2 mol^{-1}) of all the complexes except Pd(IAI)(IAI') in acetone (10^{-3} *M*) show them to be nonelectrolytes. The conductivity of Pd(IAI)(IAI') could not be determined due to its low solubility. Molecular weights of the complexes (Table I) in benzene indicate their monomeric nature. The molecular weights of Ni(IAI)(IAI'), Pd(IAI)(IAI') and Pd(Me-IAI)$_2$ could not be determined because of their insufficient solubility in benzene.

Structure of Ni(R-IAI)(IAI'). All the nickel(II) complexes are diamagnetic indicating their square-planar stereochemistry. The electronic spectra of Ni(R-IAI)(IAI') in chloroform in the region 40,000–8000 cm^{-1} are very similar to that of Ni(IAI)(IAI') (Table II) indicating their close structural similarity.

The ir spectra of Ni(R-IAI)(IAI') in the solid state and in chloroform are also closely similar to those of Ni(IAI)(IAI') (Table III). The bands occurring around 1695 and 1672 cm^{-1} in the solution spectra of Ni(R-IAI)(IAI') can be assigned to two noncoordinated carbonyl groups. The corresponding bands of Ni(IAI)(IAI') occur at 1697 and 1672 cm^{-1},

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(7) K. S. Bose and C. C. Patel, *J. Inorg. Nucl. Chem.*, **33**, 2947 (1971).

Table II. Electronic Spectral Bands of Nickel(II) and Palladium(II) Isonitrosoacetylacetone Imine Complexes

	Absorption max, cm^{-1}(ϵ, l. mol^{-1} cm^{-1})			
Ni(IAI)(IAI′)	36,000 (2.31×10^4)	33,900 sh	28,600 (1.73×10^4)	22,200 sh
Ni(Me-IAI)(IAI′)	35,600 (2.32×10^4)	33,300 sh	28,600 (1.73×10^4)	22,700 sh
Ni(Et-IAI)(IAI′)	35,600 (2.45×10^4)	33,300 sh	28,600 (1.85×10^4)	23,300 sh
Ni(*n*-Pr-IAI)(IAI′)	35,700 (2.46×10^4)	33,300 sh	28,600 (1.93×10^4)	22,700 sh
Ni(*i*-Pr-IAI)(IAI′)	36,000 (2.56×10^4)	33,600 sh	28,600 (1.93×10^4)	22,700 sh
Ni(Bzl-IAI)(IAI′)	35,700 (2.23×10^4)	33,300 sh	28,400 (1.94×10^4)	27,300 sh
Pd(IAI)(IAI′)	38,800	32,900	28,300	
Pd(Me-IAI)$_2$	38,800 (3.56×10^4)	32,700 (1.30×10^4)	24,500 (0.51×10^4)	
Pd(Et-IAI)$_2$	38,800 (3.76×10^4)	32,700 (1.41×10^4)	24,500 (0.52×10^4)	
Pd(*n*-Pr-IAI)$_2$	38,800 (3.80×10^4)	32,500 (1.43×10^4)	24,500 (0.55×10^4)	

Table III. Important Infrared Bands of Nickel(II) and Palladium(II) Isonitrosoacetylacetone Imine Complexes

	C=O str, cm^{-1}		N–H str, cm^{-1}		N–O(N coordinated) str in mull, cm^{-1}
Complexes	In mull	In $CHCl_3$	In mull	In $CHCl_3$	
Ni(IAI)(IAI′)	1680	1697	3258	3365	1210
	1650	1672	3230 sh	3225	
Ni(Me-IAI)(IAI′)	1690	1696	3165	3190	1195
	1662	1671			
Ni(Et-IAI)(IAI′)	1692	1695	3155	3190	1195
	1660	1673			
Ni(*n*-Pr-IAI)(IAI′)	1700	1695	3190	3190	1195
	1665	1673			
Ni(*i*-Pr-IAI)(IAI′)	1695	1695	3250	3190	1190
	1675	1672			
Ni(Bzl-IAI)(IAI′)	1690	1696	3180	3195	1185
	1660	1675			
Pd(IAI)(IAI′)	1684		3250		1217
	1655		3200 sh		
Pd(Me-IAI)$_2$	1674	1676			1206
Pd(Et-IAI)$_2$	1692	1672			1198
Pd(*n*-Pr-IAI)$_2$	1700	1670			1198

Table IV. Proton Magnetic Resonance Signals (in τ, ppm) of Nickel(II) and Palladium(II) Isonitrosoacetylacetone Imine Complexes with Their Assignments[a]

Complexes	C–CH_3 of isonitrosoacetylacetone imine moiety				N–R			N–H	
Ni(IAI)(IAI′)	7.62	7.54 d (*J* = 1.2 Hz)	7.48	7.45 d (*J* = 1.3 Hz)				1.10	2.48
Ni(Me-IAI)(IAI′)	7.66	7.62		7.47	6.87 (CH_3)			1.13	
Ni(Et-IAI)(IAI′)	7.66	7.62		7.46	6.46 q (CH_2)	8.74 t (CH_3)		1.10	
Ni(*n*-Pr-IAI)(IAI′)	7.66	7.62		7.46	6.54 t (CH_2)	8.31 s (CH_2)	8.96 t (CH_3)	1.13	
Pd(Et-IAI)$_2$	7.58	7.66			6.11 q (CH_2)	8.84 t (CH_3)			
Pd(*n*-Pr-IAI)$_2$	7.60	7.68			6.22 t (CH_2)	8.49 s (CH_2)	8.96 t (CH_3)		

[a] Key: d, doublet; t, triplet; q, quartet; s, sextet.

respectively. Although the spectrum of Ni(IAI)(IAI′) in chloroform shows two N-H stretching frequencies at 3365 and 3225 cm^{-1}, Ni(R-IAI)(IAI′) shows only one band around 3190 cm^{-1}. The disappearance of the 3365-cm^{-1} band can be attributed to the replacement of one of the N-H hydrogens of Ni(IAI)(IAI′) by an alkyl group.

In agreement with the above observations, the pmr spectra of Ni(R-IAI)(IAI′) in $CDCl_3$ show only one N-H proton signal around τ 1.10 (Table IV). Ni(IAI)(IAI′), on the other hand, gives two N-H proton signals at τ 1.10 and 2.48. Although four methyl resonances excluding those due to the *N*-alkyl group are expected for Ni(R-IAI)(IAI′), only three signals are observed. The integrated intensity shows that the signal around τ 7.46 is due to two methyl resonances. The merging of the two methyl signals may be due to small changes in electron shielding brought about by the introduction of the alkyl group.

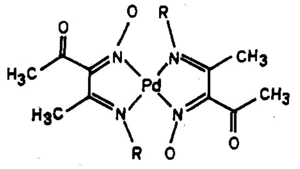
The above data suggest that the structure (Ib) of Ni(R-IAI)(IAI′) is closely similar to that of Ni(IAI)(IAI′). As in Ni(EIAI)[3,7] and Pd(R-IAI)$_2$ (*vide infra*), which are formed by the amine-exchange reaction of Ni(IAI)(IAI′) and Pd(IAI)(IAI′), respectively, the ligands are suggested to coordinate through the isonitroso nitrogen; the *N*-alkyl-substituted isonitrosoacetylacetone imine in Ni(R-IAI)(IAI′) is expected to coordinate through the isonitroso nitrogen.

Structure of Bis(isonitrosoacetylacetone imino)palladium(II). The ir spectrum (Table III) of Pd(IAI)(IAI′) in the solid state is closely similar to that of Ni(IAI)(IAI′), suggesting that the mode of coordination of the ligand in both the complexes is the same. As in the case of the nickel(II) complex, structure Ic can be assigned to the palladium complex.

Structure of Pd(R-IAI)$_2$. On reaction of Pd(IAI)(IAI′) with primary monoalkylamines, the N-H stretching frequency disappears from the resulting Pd(R-IAI)$_2$ complex. This shows that both imine groups present in Pd(IAI)(IAI′) have undergone an amine-exchange reaction. This is in contrast to the behavior of Ni(IAI)(IAI′), where only IAI undergoes amine exchange with the monoalkylamines to form Ni(R-IAI)(IAI′). There are also significant changes in the ir spectra of Pd(R-IAI)$_2$ compared to that of Pd(IAI)(IAI′), suggesting that certain changes occur in the mode of coordination of the ligands on reaction of Pd(IAI)(IAI′) with monoalkylamines.

In the pmr spectra of Pd(R-IAI)$_2$ (R = Et or *n*-Pr), only two sets of methyl resonances due to the ligands, excluding those due to the *N*-alkyl groups, are present. This suggests a symmetrical structure for Pd(R-IAI)$_2$. Further, in the ir spectra of Pd(R-IAI)$_2$, only one carbonyl band is present in the range 1672-1700 cm^{-1}. The band is much more intense than either of the two carbonyl bands of Pd(IAI)(IAI′). This further supports that both ligands in Pd(R-IAI)$_2$ have the same mode of coordination.

The mode of coordination of R-IAI in Pd(R-IAI)$_2$ is expected to be similar to that of IAI in Pd(IAI)(IAI′) as shown by the presence of a strong band around 1200 cm^{-1} which has been assigned to the N-coordinated isonitroso group of Pd(IAI)(IAI′). It is also in agreement with the X-ray structural data of complexes of oxime ligands, which show that the oxime (isonitroso) group invariably coordinates through nitrogen rather than oxygen.[8-11] The structure of Pd(R-IAI)$_2$ can, therefore, be represented as II.

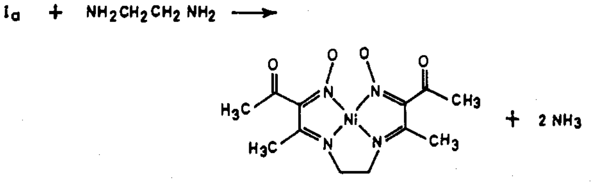


II

Pd(R-IAI)$_2$

A surprising feature is the close similarity of the electronic spectra of Pd(IAI)(IAI′) and Pd(R-IAI)$_2$ in chloroform solution (Table II), although the ligand coordination in the former is different from that of the latter in the solid state. This probably indicates that, in chloroform, Pd(IAI)(IAI′) has a structure similar to that of Pd(R-IAI)$_2$.

Amine-Exchange Reactions of the Complexes. A large excess of the amine is used in the preparation of Ni(R-IAI)(IAI′) from Ni(IAI)(IAI′) so as to facilitate the reaction. Qualitatively, steric interaction seems to influence the reaction, as the amine-exchange reactions of Ni(IAI)(IAI′) with isopropylamine and benzylamine were comparatively difficult. Both of these amines are expected to provide more steric hindrance than the other amines used. To test whether both N-H groups in Ni(IAI)(IAI′) can be replaced, its reactions with methylamine and *n*-propylamine were carried out in the presence of a large excess of the amine (double that used in the given preparations) and the reaction mixture was refluxed for about 16 hr. Even under such conditions, only one of the groups gets substituted. But with ethylenediamine both imine groups present in Ni(IAI)(IAI′) as well as in Ni(R-IAI)(IAI′) undergo amine exchange (eq 1) at room temperature to form *N,N′*-ethylenebis(isonitrosoacetylacetone imino)nickel(II), Ni(EIAI). However, unlike the case for Ni(IAI)(IAI′), attempts to cause a Pd(IAI)(IAI′)-ethylenediamine reaction have not succeeded.



(1)

In contrast to Ni(IAI)(IAI′), both ligands in Pd(IAI)(IAI′) undergo amine exchange with monoalkylamines, giving rise to Pd(R-IAI)$_2$. The reaction, further, involves a rearrangement in the coordination of one of the ligands.

Pd(R-IAI)$_2$ can be prepared by the direct reaction of palladium chloride with isonitrosoacetylacetone in the presence of the corresponding alkylamine. Attempts to prepare the corresponding nickel(II) complexes by a similar procedure have not succeeded.

The nonreactivity of IAI′ in Ni(IAI)(IAI′) toward monoalkylamines could be due to the difference in the electronic configurations of IAI′ and IAI. But the failure to prepare Ni(R-IAI)$_2$ by direct reaction of nickel(II) acetate with isonitrosoacetylacetone and alkylamine cannot, however, be accounted for by the above explanation.

Steric hindrance appears to be a more plausible reason for the failure to prepare Ni(R-IAI)$_2$. Ni(R-IAI)$_2$ with a structure similar to that of Pd(R-IAI)$_2$ is expected to be unstable due to the steric interference between the projecting >N-O and >N-R groups in cis positions. Steric hindrance is expected to be less significant in the case of palladium(II) complexes because of the larger ionic size of palladium(II) than that of nickel(II), thus facilitating the preparation of Pd(R-IAI)$_2$. The same factor can also account for the nonreactivity of IAI′ in Ni(IAI)(IAI′) toward alkylamines.

Registry No. Ni(IAI)(IAI′), 35996-07-7; Ni(Me-IAI)(IAI′), 35996-08-8; Ni(Et-IAI)(IAI′), 35996-09-9; Ni(*n*-Pr-IAI)(IAI′), 35996-16-8; Ni(*i*-Pr-IAI)(IAI′), 35996-15-7; Ni(Bzl-IAI)(IAI′), 35996-14-6; Pd(IAI)(IAI′), 35996-13-5; Pd(Me-IAI)$_2$, 35996-12-4; Pd(Et-IAI)$_2$, 35996-11-3; Pd(*n*-Pr-IAI)$_2$, 35996-10-2.

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