is extensively dissociated. Such a mechanism does not explain why hydroxide is a good leaving group, for it is strongly held by platinum.[5] Instead, it appears that there must be little breaking of the strong platinum–hydroxide bond in the transition state. This would probably lead to an intermediate of octahedral platinum coordination. The unusual lability of hydroxide would then result from the ease with which it moved from the equatorial position in the square-planar reactant to the axial position in the octahedral intermediate. This in turn might result from the nonstereospecific σ bonding between hydroxide and platinum suggested by Basolo and Pearson (see ref 2, p 384).

Acknowledgment.—The authors wish to thank Professor Fred Basolo for the gift of the platinum(0) compound.

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CONTRIBUTION NO. 2381 FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF CALIFORNIA, LOS ANGELES, CALIFORNIA 90024

Coordination of Palladium by Azo and Related Functional Groups

BY A. L. BALCH AND D. PETRIDIS

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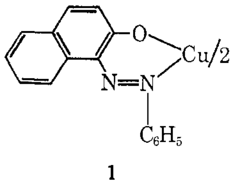
The preparation and physical properties of the simple azo complexes *trans*-$(RN=NR)_2PdX_2$ (R = CH_3, C_6H_5; X = Cl, Br) are reported. Infrared and nmr spectral observations indicate that each azo group is coordinated to palladium through a single nitrogen lone pair. Similar complexes of azoxybenzene could not be prepared, but it is possible to deprotonate azoxybenzene to form dichlorobis[2-(phenylazoxy)phenyl]dipalladium(II), 6. The dimer is readily cleaved by organic bases to give monomeric species. The preparation and properties of $(C_6H_5NO)_2PdCl_2$ are reported.

Introduction

Despite the fact that bonding between azo groups and transition metal ions is implicated in a large number of complexes, especially complexes of azo dyes, these are relatively few examples of compounds which involve ligands that are coordinated to a metal solely by means of an azo function. The largest group of simple azo complexes involves Cu(I); these generally have the constitution $(RN=NR)Cu_2Cl_2$.[1–3] In fact formation of a red cuprous chloride complex appears to be a qualitative test for the presence of the azo function. Platinum complexes of an azo compound which is constrained into the *cis* configuration[4] and of phenyldiimide (C_6H_5NNH)[5] have recently been reported. In the latter case it is interesting to note that coordination has stabilized a species whose existence otherwise is quite transitory.[6] Palladium and silver complexes of benzocinnoline[7] and a titanium complex of azobenzene[8] have also been described.

Although it has been suggested[9,10] that the metal–azo bond may involve an electronic structure analogous to that encountered in metal–olefin complexes, the few physical studies that have been conducted on azo complexes have indicated that a nitrogen lone pair rather than the π bond is the σ-donor site.[4,11–13] An X-ray crystallographic study[11] of $(CH_3N=NCH_3)Cu_2Cl_2$ has demonstrated that the azo function binds two copper ions through the two nitrogen lone pairs; the azomethane molecule maintains a *trans* configuration with little change in geometry from the free molecule. Similarily, X-ray studies of the two copper chelates **1**[12] and **2**[13] show that the metal is coordinated to a single nitrogen.



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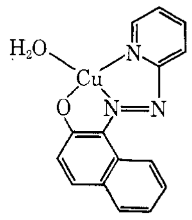

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Although olefinic coordination had been suggested for the product obtained from treating platinum tetrachloride with azobenzene in acetic acid, the compound has been recently shown to be a hexachloroplatinate(IV) salt of protonated azobenzene.[14]

Since the simplest azo molecule, diimide (HN=NH), is, especially in the complexed state, a likely intermediate in the biological fixation of molecular nitrogen, we have undertaken studies to elucidate the nature of

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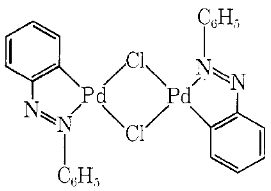
metal–azo bonding. This report is concerned with the synthesis and physical properties of complexes of palladium with azobenzene and azomethane. Previous studies[15,16] of the reaction of palladium salts with azobenzene have been concerned with the preparation of the unusual bright red complex **3**. In addition to azo complexes we have also investigated palladium complexes of two oxidation products of azobenzene, azoxybenzene and nitrosobenzene. It should also be noted that the nitroso group (in monomeric form) is isoelectronic with the azo group. There appear to be no substantiated reports of complexation of transition metals by azoxy groups. The donor properties of aromatic nitroso compounds have recently been reviewed.[17]



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Experimental Section

Preparation of Compounds.—*trans*-Dichlorobis(benzonitrile)-palladium(II) was prepared as reported.[18] Dibromobis(benzonitrile)palladium(II) was prepared similarily starting from palladium(II) bromide. Nitrosobenzene was sublimed prior to use.

Dichlorobis(azobenzene)palladium(II).—A solution containing 1.0 g of dichlorobis(benzonitrile)palladium(II) in 10 ml of dichloromethane was added to a solution of 2.0 g of azobenzene in 30 ml of dichloromethane. After standing for 24 hr the crystals which had deposited were collected by filtration. Purification was effected by Soxhlet extraction into dichloromethane; orange crystals (1.0 g) were obtained; mp 217–218° dec. *Anal.* Calcd for $C_{24}H_{20}N_4Cl_2Pd$: C, 53.21; H, 3.72; N, 10.34. Found: C, 53.35; H, 3.77; N, 10.52.

Infrared absorptions (cm^{-1}, in KBr) were observed at 3050 w, 1578 m, 1569 m, 1486 m, 1468 sh, 1458 m, 1441 m, 1375 w, 1296 w, 1283 w, 1203 m, 1192 w, 1160 w, 1156 w, 1156 w, 1140 m, 1085 w, 1060 w, 1024 m, 990 m, 960 w, 943 s, 912 w, 836 s, 821 s, 759 s, 689 s, 677 s, 663 s, 576 m.

Dibromobis(azobenzene)palladium(II).—This complex was obtained from dibromobis(benzonitrile)palladium(II) by the procedure used for dichlorobis(azobenzene)palladium(II). Orange crystals were produced; mp 217° dec. *Anal.* Calcd for $C_{24}H_{20}N_4Br_2Pd$: C, 45.70; H, 3.19; Pd, 16.86. Found: C, 45.93; H, 3.04; Pd, 17.12.

Infrared absorptions (cm^{-1}, in KBr) were observed at 3050 w, 1580 m, 1569 sh, 1487 m, 1469 sh, 1460 m, 1441 m, 1309 w, 1293 w, 1203 w, 1193 w, 1170 w, 1157 w, 1150 w, 1141 m, 1087 w, 1060 w, 1015 m, 994 m, 961 w, 945 s, 913 w, 833 m, 755 s, 687 s, 675 s, 662 s, 618 w, 575 m.

Dichlorobis(azomethane)palladium(II).—Azomethane was generated by adding a solution of 5.4 g (40 mmol) of *sym*-dimethylhydrazine dihydrochloride and 4.4 g (80 mmol) of potassium hydroxide in 30 ml of water to a stirred suspension of 12 g of mercuric oxide in 30 ml of water and then warming it to 60°. The azomethane vapor was led through a drying tube containing sodium hydroxide and Dryrite into a solution of 1.85 g (5 mmol) of dichlorobis(benzonitrile)palladium(II) in 20 ml of dichloromethane. The latter solution was immersed in a Dry Ice bath. Upon reaction, the solution slowly lightened in color from red-brown to yellow. Heptane (10 ml) was added to the yellow solution and the dichloromethane was evaporated. The resulting yellow powder which precipitated was collected. Recrystallization was effected by dissolving the powder in a minimum of dichloromethane, filtering, and cooling in Dry Ice. The fine yellow needles that formed were collected, washed with pentane, and vacuum dried; mp 149–150° dec. The yield was about 50%. *Anal.* Calcd for $C_4H_{12}N_4Cl_2Pd$: C, 16.37; H, 4.12; N, 19.09. Found: C, 16.72; H, 4.35; N, 19.16.

Infrared absorptions (cm^{-1}, in KBr) were observed at 3005 w. 2980 w, 2960 sh, 2920 w, 2895 sh, 1597 s, 1420 s, 1365 s, 1196 sh, 1186 m, 1035 w, 1013 m, 943 m, 600 m.

Dibromobis(azomethane)palladium(II).—This complex was obtained using the procedure developed for the chloro analog but with dibromobis(benzonitrile)palladium(II) as starting material. Fine yellow crystalline flakes were obtained; mp 155° dec. *Anal.* Calcd for $C_4H_{12}N_4Br_2Pd$: C, 12.56; H, 3.16; Pd, 27.82. Found: C, 12.76; H, 3.01; Pd, 27.73.

Infrared absorptions (cm^{-1}, in KBr) were observed at 3005 w, 2980 w, 2920 w, 2900 w, 1598 s, 1420 s, 1368 s, 1353 sh, 1185 m, 1014 m, 1006 sh, 944 m, 602 m.

Dichloro(azomethane)palladium(II).—The following procedure was found to give a homogeneous precipitate of $(CH_3N{=}NCH_3)_xPdCl_2$ with the lowest value of x that has been obtained. Analysis indicates that for this sample x is about 1.07. A filtered solution of 0.6 g of dichlorobis(azomethane)palladium(II) in 60 ml of 1:2 v/v dichloromethane–heptane was allowed to boil until the bulk of the dichloromethane was removed. The resulting yellow slurry was heated under reflux for 2 hr. The product was collected by filtration of the hot solution, washed with six 15-ml portions of boiling dichloromethane, and vacuum dried. The complex decomposes between 201 and 204°. *Anal.* Calcd for $C_2H_6N_2PdCl_2$: C, 10.20; H, 2.57; N, 11.90; Pd, 45.20. Found: C, 11.00; H, 2.63; N, 12.61; Pd, 44.38.

Infrared absorptions (cm^{-1}, in KBr) were observed at 3000 sh, 2980 w, 2908 m, 1599 m, 1434 m, 1380 s, 1187 w, 1140 w, 1003 m, 944 w, 600 w.

Dichlorobis[2-(phenylazoxy)phenyl]dipalladium(II).—A solution of 1.5 g of lithium tetrachloropalladate in 30 ml of methanol was added to a solution containing 1.0 g of azoxybenzene in 30 ml of methanol. The mixture was refluxed for 2 days, during which a yellow solid formed. The precipitate (yield 1 g) was collected by filtration and washed with methanol. Purification was accomplished by Soxhlet extraction into dichloromethane. Golden needles were obtained; mp >320°. *Anal.* Calcd for $C_{24}H_{18}N_4O_2Cl_2Pd_2$: C, 42.51; H, 2.67; N, 8.26; Pd, 31.38; O, 4.72. Found: C, 42.72; H, 2.66; N, 7.95; Pd, 31.61; O, 4.50.

Infrared absorptions (cm^{-1}, in KBr) were observed at 3050 w, 1589 s, 1582 sh, 1558 m, 1469 s, 1445 m, 1433 s, 1425 s, 1321 s, 1303 s, 1204 w, 1145 w, 1125 w, 1086 m, 1066 w, 1044 m, 1020 m, 1000 w, 970 w, 915 w, 757 s, 749 s, 703 s, 700 s, 687 s, 662 w, 618 w, 611 w.

Tetrachlorobis[2-(phenylazoxy)phenyl]tripalladium(II).—A solution of 1.0 g of dichlorobis(benzonitrile)palladium(II) in 30 ml of tetrahydrofuran was added to a solution of 1.0 g of azoxybenzene in 30 ml of tetrahydrofuran. After standing for 3 days the dirty yellow solid which had formed was collected and washed with dichloromethane. Soxhlet extraction of the solid into dichloromethane resulted in the gradual formation of fine yellow needles in the hot extract. After cooling, the extract was filtered to collect the crystalline product. The product was subjected to a second extraction into dichloromethane. The yield was 0.5 g. The complex darkens on heating and blackens above 290°. The analytical data may reflect the presence of some dichlorobis[2-(phenylazoxy)phenyl]dipalladium(II). The solubility of the two species is so similar that a complete separation is probably impossible. *Anal.* Calcd for $C_{24}H_{18}N_4O_2Cl_4Pd_3$: C, 33.70; H, 2.12; N, 6.55; Pd, 37.31; O, 3.74. Found: C, 34.16; H, 2.22; N, 6.75; Pd, 36.90; O, 4.39.

Infrared absorptions (cm^{-1}, in KBr) were observed at 3050 w,

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1586 sh, 1583 m, 1559 m, 1470 s, 1446 m, 1434 s, 1424 s, 1320 s, 1301 s, 1166 w, 1155 w, 1144 w, 1135 w, 1088 m, 1068 w, 1041 m, 1019 m, 996 w, 966 w, 908 w, 766 m, 748 s, 710 m, 701 s, 698, 686 s, 662 m, 620 w, 612 w.

Chloro[2-(phenylazoxy)phenyl]triphenylphosphinepalladium(II).—A solution of 0.26 g (1.0 mmol) of triphenylphosphine in 10 ml of dichloromethane was added to a slurry of 0.34 g (0.50 mmol) of dichlorobis[2-(phenylazoxy)phenyl]dipalladium(II) in 20 ml of dichloromethane. The yellow solution was filtered, and the solvent was removed by means of a rotary evaporator. The solid was recrystallized from benzene–heptane to give yellow needles which were collected by filtration, washed with heptane, and vacuum dried at 80° for 12 hr. On heating the complex darkens above 200° and softens at 210°. *Anal.* Calcd for $C_{30}H_{24}N_2PPdClO$: C, 59.92; H, 4.02; N, 4.66; P, 5.15. Found: C, 60.36; H, 3.89; N, 4.36; P, 4.51.

Infrared absorptions (cm^{-1}, in KBr) were observed at 3050 w, 1575 m, 1550 sh, 1467 s, 1437 m, 1411 sh, 1318 m, 1298 m, 1245 w, 1175 w, 1150 w, 1120 sh, 1086 s, 1063 sh, 1036 w, 1020 w, 990 w, 955 w, 836 w, 826 w, 774 s, 749 s, 744 s, 718 s, 700 s, 688 sh, 680 s, 614 w.

Chloro[2-(phenylazoxy)phenyl]-*n*-propylaminepalladium(II).—This complex was obtained in a manner analogous to that devised for the triphenylphosphine complex. Yellow-orange needles were obtained: mp 187–189° dec. *Anal.* Calcd for $C_{15}H_{18}N_3OClPd$: C, 45.25; H, 4.56; N, 10.55. Found: C, 44.93; H, 4.45; N, 10.22.

Infrared absorptions in (cm^{-1}, KBr) were observed at 3320 w, 3261 w, 3040 w, 2946 w, 2918 sh, 2858 w, 1583 m, 1564 m, 1470 s, 1443 m, 1432 m, 1426 m, 1417 m, 1374 w, 1350 w, 1328 m, 1324 m, 1296 m, 1165 w, 1137 w, 1122 w, 1083 w, 1060 w, 1050 w, 1039 m, 1018 w, 958 w, 947 w, 840 w, 771 m, 757 s, 750 m, 717 m, 699 m, 685 w, 670 w, 618 w, 615 w.

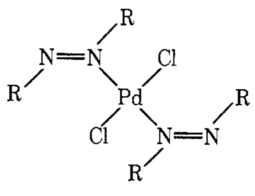
Dichlorobis(nitrosobenzene)palladium(II).—A solution of 0.65 g (6.0 mmol) of nitrosobenzene in 20 ml of dichloromethane was added to a solution of 1.15 g (3.0 mmol) of dichlorobis(benzonitrile)palladium(II) in 30 ml of dichloromethane. The brownish solid, which formed immediately, was collected by filtration and purified by Soxhlet extraction into dichloromethane. The product (0.9 g) was obtained as blue-black crystals; decomposition occurs above 205°. *Anal.* Calcd for $C_{12}H_{10}N_2O_2Cl_2Pd$: C, 36.81; H, 2.57; N, 7.15; Pd, 27.18. Found: C, 36.80; H, 2.44; N, 6.98; Pd, 27.35.

Infrared absorptions (cm^{-1}, in KBr) were observed at 3080 w, 3050 w, 1579 s, 1553 sh, 1496 s, 1451 m, 1432 s, 1340 w, 1318 m, 1300 m, 1190 s, 1172 s, 1120 s, 1085 sh, 1005 w, 990 m, 875 s, 833 m, 775 s, 682 s, 660 s, 622 s.

Physical Measurements.—Infrared spectra in the 4000–500-cm^{-1} region were recorded on a Perkin-Elmer 421 spectrometer. In the region 500–290 cm^{-1} a Beckman IR5A spectrometer was used to obtain infrared data. Raman spectra were recorded on a Cary 81 spectrometer. Electronic spectra were recorded on a Cary 14 spectrophotometer. Conductivities were measured with a Serfass conductivity bridge. A Varian A-60D spectrometer was utilized for nmr measurements.

Results and Discussion

Azo Complexes.—Benzonitrile is readily displaced from *trans*-$(C_6H_5CN)_2PdX_2$ (X = Cl or Br)[19] by azobenzene or azomethane to yield the corresponding *trans*-$(RN{=}NR)_2PdX_2$, **4**.[20] These complexes are stable to air and moisture and exhibit reasonable thermal stability. In nitromethane or dichloromethane solution, the complexes are nonelectrolytes. As described below, their other physical properties support and confirm formulation **4**.



4

Selected data from the vibrational spectra of these complexes are set out in Table I. Infrared spectra in the region 4000–500 cm^{-1} are recorded in the Experimental Section for identification purposes. The assignment of *trans* stereochemistry about palladium is based on the observation that in both $(C_6H_5N{=}NC_6H_5)_2PdCl_2$ and $(CH_3N{=}NCH_3)_2PdCl_2$ only one of the Pd–Cl stretching vibrations is infrared active while the other vibration is Raman active. Both of these bands are absent from the spectra of the respective bromo analogs. The N=N stretching vibration, which occurs at 1576 cm^{-1} in the Raman spectrum of *trans*-azomethane itself,[21] is shifted to higher energies by about 22 cm^{-1} in the palladium complexes and has become infrared active. The determination of the cause of this increase in frequency must await further study, but the observation of infrared activity for this band is consistent with the proposed structure **4**. The richness of the infrared spectra of the azobenzene complexes in the 1600–1300-cm^{-1} region renders the assignment of an N=N stretching vibration difficult. Azobenzene itself has absorptions at 1448 and 1477 cm^{-1}. The complexes, however, have three bands in this region; this is the most significant change in the entire 1600–1300-cm^{-1} region. The additional band is probably due to the N=N stretch gaining infrared activity. Similarily **3** exhibits three infrared absorp-

TABLE I
SELECTED VIBRATIONAL FREQUENCIES (CM^{-1}) AND THEIR ACTIVITIES[a]

Complex	$\nu_{N=N}$	ν_{M-X}
$(CH_3N{=}NCH_3)_2PdCl_2$	1597 (ir)[b] 1600 (ir)[c]	346 (ir), 306(R)
$(CH_3N{=}NCH_3)PdBr_2$	1599 (ir)[b] 1599 (ir)[c]	. . ., 220 (R)
$(CH_3N{=}NCH_3)PdCl_2$	1602 (ir)	351 (ir), 330(ir), 310 (R)
$(CH_3N{=}NCH_3)Cu_2Cl_2$	1530 (R)	310 (ir)
$(C_6H_5N{=}NC_6H_5)_2PdCl_2$	1486 (ir), 1460 (ir), 1441 (ir)[d]	337 (ir), 300 (R)
$(C_6H_5N{=}NC_6H_5)_2PdBr_2$	1487 (ir), 1460 (ir), 1442 (ir)[d]	. . ., 230 (R)

[a] Infrared data obtained from samples dispersed in a fluorocarbon or hydrocarbon mull; Raman data (R) obtained from finely powdered solid samples. [b] Very weakly Raman active. [c] Data obtained from dichloromethane solution. [d] One of these bands is probably due to the $\nu_{N=N}$ gaining infrared activity; see text.

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[19] In solution *trans*-$(C_6H_5CN)_2PdX_2$ appears to undergo extensive dissociation: D. Petridis, work in progress. Attempts at substituting azo compounds for benzonitrile in $(C_6H_5CN)_2PtCl_2$ have been unsuccessful.

[20] These complexes have been prepared using the *trans*-azo isomers because of the ready availability of these compounds. Consequently we have formulated **4** as involving the *trans*-azo isomers, although both *cis*-azobenzene and *cis*-azomethane are known and isomerization could have occurred in forming **4**.

[21] G. Herzberg, "The Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., Princeton, N. J., 1964, p 359.

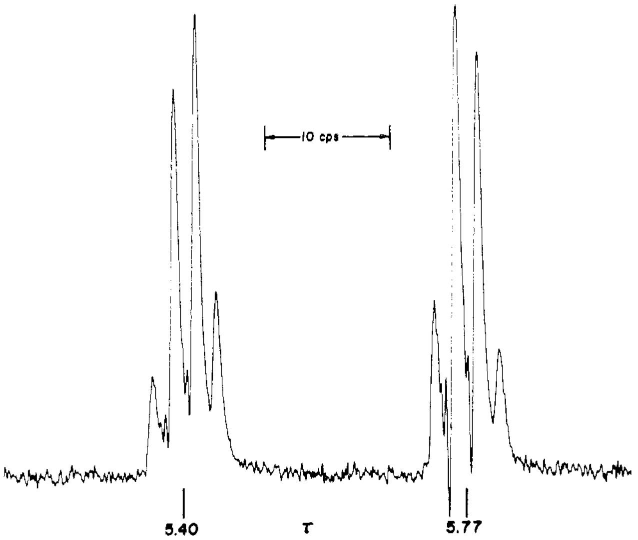

Figure 1.—Proton magnetic resonance spectrum of *trans*-dichlorobis(azomethane)palladium(II) in $CDCl_3$ at 60 Mc and 35°.

tions (at 1476, 1452, and 1439 cm^{-1}) in this region. In protonated azobenzene an infrared-active band at 1390 cm^{-1} has been assigned to the N=N stretch;[14] however, no infrared-active band has been observed in this region for the palladium complexes. In *trans*-azobenzene a Raman-active band at 1442 cm^{-1} has been assigned as the N=N stretching vibration.[22]

The strongest evidence in favor of coordination of palladium through a single nitrogen of each azo group in these compounds comes from the nmr spectra of the azomethane complexes. As shown in Figure 1, the nmr spectrum of $(CH_3N{=}NCH_3)_2PdCl_2$ in deuteriochloroform solution consists of two equally intense resonances located at τ 5.40 and 5.77. Each of these resonances is further split into a quartet. The magnitude of the splitting is the same, 1.7 cps, for both quartets. This pattern is what would be expected from **4** in which both azo ligands are in identical environments but in which the methyl groups within a single azomethane ligand are not equivalent by virtue of the palladium coordination to an individual nitrogen. The observation of coupling between the two methyl groups assures us that inequivalent methyl groups reside on the same azo ligand.[23] The nmr spectrum of $(CH_3N{=}NCH_3)_2PdBr_2$ in deuteriochloroform shows similar features but with less resolution. Two resonances of equal intensities are located at τ 5.44 and 5.72. Both resonances show evidence of further splitting of about 1.6 cps. In contrast to the coordinated situation, *trans*-azomethane is reported to exhibit a single resonance at τ 6.33 in carbon tetrachloride solution.[24] Because of the numerous similarities between the azomethane and the azobenzene complexes, we presume that similar bonding exists in the azobenzene complexes.

TABLE II
ELECTRONIC SPECTRA OF COMPLEXES IN DICHLOROMETHANE SOLUTION[a]

trans-$(CH_3N{=}NCH_3)_2PdCl_2$	26,000 (245), 33,100 (3840), 36,100 (5170)
trans-$(CH_3N{=}NCH_3)_2PdBr_2$	25,000 (292), 32,000 (3700), 39,800 (36,800)
trans-$(C_6H_5N{=}NC_6H_5)_2PdCl_2$	27,300 (8300), 31,800 (27,000)
trans-$(C_6H_5N{=}NC_6H_5)_2PdBr_2$	24,200 sh (5700), 25,600 sh (7400), 32,000 (31,000), 37,000 (24,000)
trans-$(C_5H_5N)_2PdCl_2$	25,600 (130), 30,600 (120), 43,000 (31,200)

[a] Positions are given in cm^{-1}; molar extinction coefficients are in parentheses.

Data concerning the electronic spectra of the new complexes are set out in Table II. The spectra are characterized by a number of charge-transfer absorptions which obscure most if not all of the d–d bands. The lowest energy bands in the azomethane complexes may, however, result from one or more of the d–d transitions. For comparison the spectrum of *trans*-$(py)_2PdCl_2$ has been measured. This latter complex exhibits two absorptions at 25,600 and 30,600 cm^{-1} whose intensities are compatible with assignments to d-d transitions. The first of these bands occurs at an energy comparable to the energy of the first transition in *trans*-$(CH_3N{=}NCH_3)_2PdCl_2$ (26,000 cm^{-1}). Assuming that similar transitions are involved in the pyridine and azomethane complexes (and by comparison with other palladium complexes an assignment as $d_{xy} \rightarrow d_{x^2-y^2}$ is most likely[25]), then it appears that these two ligands split the d orbitals by similar energies. In the azobenzene complexes the d–d transitions are completely buried. The spectra of these two complexes are similar to the spectrum of azobenzene itself, especially in the occurrence of a prominent band near 32,000 cm^{-1}. However, this similarity is probably coincidental, and a more germane comparison involves the complexes and protonated azobenzene. In this case the spectra are considerably different.[26] The chemical and physical behaviors of these complexes are not consistent with the presence of uncoordinated azobenzene in their solutions.

The azo–palladium linkage in these complexes is rather easily broken. Treatment of $(CH_3N{=}NCH_3)_2PdCl_2$ with 2 equiv of pyridine or triphenylphosphine yields $(C_5H_5N)_2PdCl_2$ or $((C_6H_5)_3P)_2PdCl_2$, respectively. Prolonged heating of a solution or suspension of $(CH_3N{=}NCH_3)_2PdCl_2$ produces a pale yellow solid which is insoluble in solvents which are not themselves good Lewis bases toward palladium. Purification of this material is impossible due to its lack of solubility, but analytical data indicate that azomethane has been lost from the original complex to produce a material whose composition approaches $(CH_3N{=}NCH_3)PdCl_2$. The infrared spectrum of this powder is similar to that of $(CH_3N{=}NCH_3)_2PdCl_2$. The N=N stretching vibra-

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(22) R. Kübler, W. Lüttke, and S. Weckherlin, *Z. Elektrochem.*, **64**, 650 (1960).

(23) This argument in favor of a single N-Pd band is independent of whether the stereochemistry of the azo ligands is *cis* or *trans*. However, the simplicity of the spectrum virtually assures us that only a single isomer is present.

(24) R. F. Hutton and C. Steel, *J. Am. Chem. Soc*, **86**, 745 (1964).

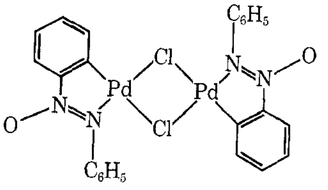
(25) W. R. Masson and H. B. Gray, *ibid.*, **90**, 5721 (1968).

(26) H. H. Jaffé, S. J. Yeh, and R. W. Gardner, *J. Mol. Spectry.*, **2**, 120 (1958).

tion remains infrared active and consequently a structure involving *trans*-azomethane bridging between two palladium atoms in identical environments is ruled out. Moreover the N=N stretch occurs at nearly the same frequency as found in $(CH_3N{=}NCH_3)_2PdCl_2$, whereas in a bridging situation in $(CH_3N{=}NCH_3)Cu_2Cl_2$ this band is observed at much lower frequencies. It is more likely that this yellow powder involves a chloro-bridged species. The lack of solubility suggests more extensive polymerization than simple dimer formation; numerous reasonable structures can be written for this material. Similarily $(CH_3N{=}NCH_3)_2PdBr_2$ loses azomethane to produce an azomethane complex with limited solubility.

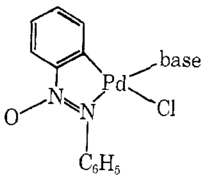
The ready conversion of $(C_6H_5N{=}NC_6H_5)_2PdCl_2$ into **3** has been observed. In an attempt to purify $(C_6H_5N{=}NC_6H_5)_2PdCl_2$ by Soxhlet extraction with tetrahydrofuran as solvent, the extract was found to contain only pure **3**. In fact it appears that the simple azobenzene complex is an intermediate in other preparative routes to **3**. Small amounts of $(C_6H_5N{=}NC_6H_5)_2PdCl_2$ have been observed to precipitate from methanolic solutions of $PdCl_4^{2-}$ and azobenzene during the early stages of the reaction developed by Heck[16] for the preparation of **3**.

Complexes Derived from Azoxybenzene.—The reaction of azoxybenzene with $(C_6H_5CN)_2PdCl_2$ in dichloromethane did not result in the displacement of the benzonitrile. Consequently the azoxy group must be classified as a poorer ligand toward palladium than the azo group. However refluxing a methanolic solution of $PdCl_4^{2-}$ and azoxybenzene produced a new substance whose physical properties and chemistry suggest that it is the chloro-bridged dimer **5**. The mode of preparation is similar to one used to make **3**, but the formation of **5** is considerably slower. The infrared spectrum of the complex closely resembles the infrared spectrum of free azoxybenzene itself. A related complex **6** was obtained from the reaction of azoxybenzene with $(C_6H_5CN)_2PdCl_2$ with tetrahydrofuran as solvent. Although the infrared spectrum of **6** is virtually identical with that of **5**, their visual appearances and thermal stabilities are different. Analytical data indicate that **6** contains an extra mole of $PdCl_2$; this extra $PdCl_2$ probably acts as a bridging group. Behavior of this sort, that is the observation of additional amounts of $PdCl_2$ in chloropalladium complexes, has been reported in several other cases.[27]



5

Like its probable analog **3**, **5** is cleaved without loss of the organic ligand by Lewis bases to give new species of probable structure **7**. Species of this sort have been isolated with triphenylphosphine or *n*-propylamine as the base. The infrared spectra of these new complexes appear as a superposition of the spectrum of the base component on the spectrum of the original dimer **5**. In addition terminal Pd–Cl vibrations are observed in the infrared and Raman spectra of the triphenylphosphine complex at 330 cm^{-1} and the spectra of the *n*-propylamine complex at 358 cm^{-1}. Although structures **5** and **7** have been drawn with Pd–N bonds, the structures may be drawn with palladium bonding to the azoxy oxygen. The latter would also involve a geometrically favorable five-membered chelate ring. Thorough examination of the rich infrared spectra of these complexes has not uncovered any features that differentiate between Pd–N and Pd–O bonding. However in general palladium prefers nitrogen over oxygen donors, and we believe that the structures as drawn are more likely.



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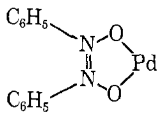
Nitrosobenzene Complex.—Treatment of *trans*-$(C_6H_5CN)_2PdCl_2$ or $PdCl_4^{2-}$ with nitrosobenzene produces the very slightly soluble $(C_6H_5NO)_2PdCl_2$. Unlike the other complexes described herein, which are yellow or orange, this complex is obtained as blue-black crystals with a metallic luster.

The nitroso group could bond palladium in a variety of ways. Coordination could involve donation of the lone pairs on oxygen or nitrogen or could involve olefinic-like coordination. In addition, nitrosobenzene could bond palladium in its dimeric form to give a bidentate chelate with coordination through the oxygen atoms as in **8**. Unfortunately the limited spectroscopic data available do not allow a choice to be made among these possibilities. If the two chlorine atoms could be shown to be *trans*, the coordination of nitrosobenzene as dimer **8** could be eliminated as a possibility. Unfortunately the stereochemistry about palladium has not been unambiguously determined. It has proven impossible to obtain a Raman spectrum of this complex. A Pd–Cl stretching frequency is observed at 344 cm^{-1} in the infrared spectrum. However this band is very broad and slightly asymmetric, and it could consist of two superimposed absorptions. Since the assignment of group frequencies to the nitroso moiety in free



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[27] H. Reinheimer, H. Dietl, J. Moffat, D. Wolff, and P. M. Maitlis, *J. Am. Chem. Soc.*, **90**, 5321 (1968), and references therein.

nitrosobenzene is in doubt because of the dimer–monomer equilibrium and because of possible conjugation effects,[28] examination of other regions of the infrared spectrum of the complex does not aid in ascertaining the mode of coordination.

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[28] K. Nakamoto and R. E. Rundle, *J. Am. Chem. Soc.*, **78**, 1113 (1956).

Contribution from the Department of Chemistry,
The University of Texas at Austin, Austin, Texas 78712

Deprotonation of 2-Aminoethanethiol Complexes of Nickel(II) and Palladium(II)

By George W. Watt, John F. Knifton, and C. V. Senoff

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The complexes $M(SC_2H_4NH_2)_2$ (M = Ni, Pd) are not deprotonated by anhydrous liquid ammonia at −33.5° but undergo successive deprotonation upon treatment with 1 and 2 molar equiv of amide ion in ammonia. The reprotonation and methylation of the resulting species are described and interpreted in relation to infrared spectral data.

Deprotonation of ethylenediamine complexes of several transitional metal ions has been reported from this laboratory;[1] these studies have recently been extended to glycine, alanine,[2] *o*-aminophenolato, and *o*-aminothiophenolato complexes.[3] We report here the results of an investigation of the deprotonation of 2-aminoethanethiolato complexes of nickel(II) and palladium(II) in liquid ammonia.

Experimental Section

Materials and Methods.—All chemicals were reagent grade and used without further purification with the exception of methyl iodide, which was dried over P_4O_{10} and fractionally distilled prior to use. 2-Aminoethanethiol hydrochloride[4] was kindly donated by Evans Chemetics, Inc., Houston, Texas. The reactions in liquid ammonia were carried out as previously described.[5] All hygroscopic samples were handled in a drybox filled with helium which was maintained free of oxygen by continuous exposure to liquid Na–K alloy. Only standard methods of analysis were employed.

Infrared spectra were recorded as Nujol or halocarbon mulls between NaCl or CsI disks with Beckman IR-7 (4000–600 cm^{-1}) and Beckman IR-11 (600–200 cm^{-1}) spectrophotometers.

X-Ray diffraction data were obtained using Cu Kα radiation (Ni filter) at 35 kV and 15 mA. Exposure times were 8–12 hr; relative intensities were estimated visually. The data are listed immediately following analytical data.

$Ni(SC_2H_4NH_2)_2$ and $Pd(SC_2H_4NH_2)_2$ were prepared as described by Jicha and Busch.[6] *Anal.* Calcd for $Ni(SC_2H_4NH_2)_2$: C, 22.77; H, 5.73; Ni, 27.83. Found: C, 23.32; H, 5.98; Ni, 28.2. X-Ray diffraction data: 6.25 (0.9), 5.14 (0.6), 4.83 (0.5), 3.72 (0.9), 2.95 (0.4), 2.70 (0.7), 2.68 (0.6), 1.95 (0.3). Calcd for $Pd(SC_2H_4NH_2)_2$: C, 18.78; H, 4.68; Pd, 41.13. Found: C, 18.38; H, 4.67; Pd, 40.7. X-Ray diffraction data: 6.34 (1.0), 5.18 (0.6), 4.90 (0.5), 3.74 (0.9), 3.16 (0.4), 2.96 (0.5), 2.70 (0.3), 2.10 (0.1).

Behavior of $Ni(SC_2H_4NH_2)_2$ and $Pd(SC_2H_4NH_2)_2$ toward Liquid Ammonia at −33.5°.—Samples (0.50 g) of bis(2-aminoethanethiolato)nickel(II) and of bis(2-aminoethanethiolato)palladium(II) were suspended in liquid ammonia (*ca.* 25 ml) at −33.5° and stirred for 2 hr. The ammonia was then filtered off under reduced pressure and the remaining solids collected. The infrared spectra and X-ray diffraction data for these solids were identical with those of the starting materials.

$K[Ni(SC_2H_4NH)(SC_2H_4NH_2)]$.—Bis(2-aminoethanethiolato)nickel(II) (4.75 g) was suspended in liquid ammonia (*ca.* 45 ml) at −33.5° and 1 molar equiv of KNH_2 in liquid ammonia (20 ml) was added slowly at −33.5°. After 3–4 hr, the reddish brown precipitate was washed with ammonia (10 ml) and dried *in vacuo* overnight. *Anal.* Calcd for $K[Ni(SC_2H_4NH)(SC_2H_4NH_2)]$: C, 19.29; H, 4.45. Found: C, 20.08; H, 4.82. X-Ray diffraction data: 9.40 (0.4), 8.67 (0.6), 8.15 (1.0), 6.25 (0.4), 3.72 (0.5).

$K_2[Ni(SC_2H_4NH)_2]$.—Bis(2-aminoethanethiolato)nickel(II) (2.14 g) was suspended in liquid ammonia (*ca.* 40 ml) at −33.5°, titrated with 2 molar equiv of KNH_2, and thereafter treated as described above. *Anal.* Calcd for $K_2[Ni(SC_2H_4NH)_2]$: C, 16.73; H, 3.51. Found: C, 16.55; H, 3.99. X-Ray diffraction data: 8.62 (1.0), 8.11 (0.3), 4.55 (0.4), 4.37 (0.4), 3.77 (0.2).

$K[Pd(SC_2H_4NH)(SC_2H_4NH_2)]$.—Similarly, bis(2-aminoethanethiolato)palladium(II) (2.89 g) was suspended in liquid ammonia (40 ml) at −33.5° and 1 molar equiv of KNH_2 in liquid ammonia (20 ml) was added slowly; the product was isolated as described above. *Anal.* Calcd for $K[Pd(SC_2H_4NH)(SC_2H_4NH_2)]$: C, 16.7; H, 3.71. Found: C, 15.95; H, 4.39. X-Ray diffraction data: 9.11 (0.9), 6.36 (1.0), 5.20 (0.2), 4.77 (0.2), 4.23 (0.4), 3.76 (0.7).

$K_2[Pd(SC_2H_4NH)_2]$.—In a similar manner, bis(2-aminoethanethiolato)palladium(II) was treated with 2 molar equiv of KNH_2 in liquid ammonia at −33.5°. *Anal.* Calcd for $K_2[Pd(SC_2H_4NH)_2]$: C, 14.35; H, 3.01. Found: C, 14.10; H, 3.05. X-Ray diffraction data: 9.01 (0.9), 7.10 (0.2), 5.57 (1.0), 4.73 (0.3), 4.49 (0.3), 3.39 (0.2), 3.24 (0.4).

Reaction of $K[M(SC_2H_4NH)(SC_2H_4NH_2)]$ and $K_2[M(SC_2H_4NH)_2]$ with Water.—Samples (0.50 g) of the singly and doubly deprotonated nickel(II) and palladium(II) complexes were each added to water (25 ml) and stirred for 8 hr. The products from these reactions were collected by filtration and thoroughly washed with water and ethanol. X-Ray diffraction and infrared spectral data for these materials showed them to be $Ni(SC_2H_4NH_2)_2$ and $Pd(SC_2H_4NH_2)_2$, respectively.

Reaction of $K[Pd(SC_2H_4NH)(SC_2H_4NH_2)]$ with Methyl Iodide.

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[1] G. W. Watt and D. G. Upchurch, Advances in Chemistry Series, No. 62, American Chemical Society, Washington, D. C., 1966, pp 253–271.

[2] G. W. Watt and J. F. Knifton, *Inorg. Chem.*, **6**, 1010 (1967).

[3] G. W. Watt and J. F. Knifton, *ibid.*, **7**, 1443 (1968).

[4] To conform to earlier usage the $NH_2C_2H_4S^-$ ligand is abbreviated as bme, and bme-H denotes a deprotonated bme ligand.

[5] G. W. Watt and P. W. Alexander, *Inorg. Chem.*, **7**, 537 (1968), and references therein.

[6] D. C. Jicha and D. H. Busch, *J. Am. Chem. Soc.*, **1**, 872 (1962).